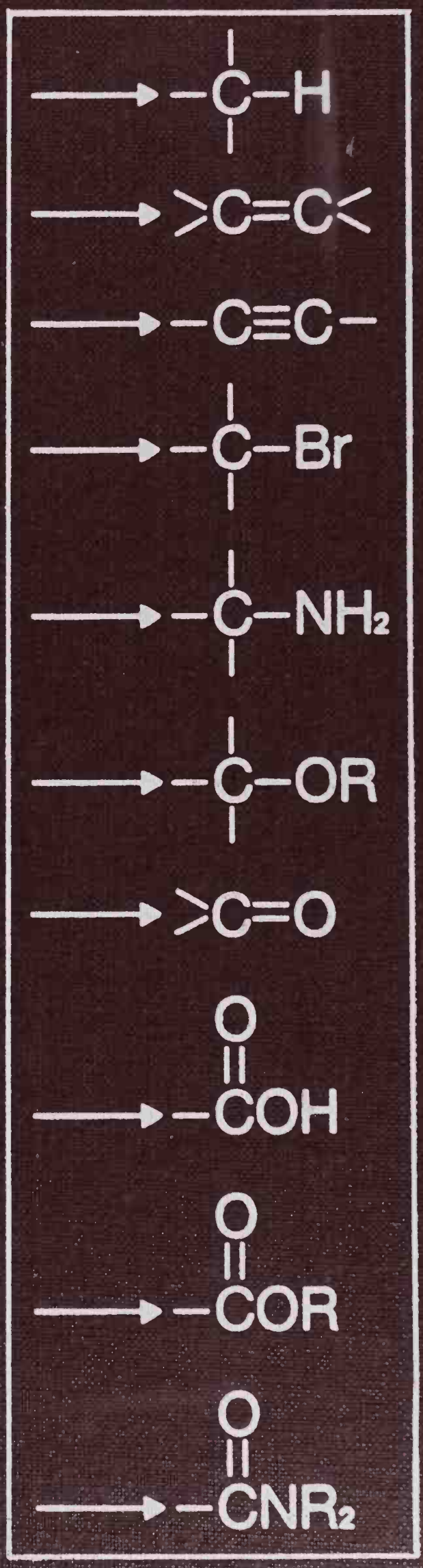
COMPREHENSIVE ORGANIC TRANSFORMATIONS

A GUIDE TO FUNCTIONAL GROUP PREPARATIONS

By Richard C. Larock

Foreword by H.C. Brown



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By
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To all the students, past, present, and future,
with whom I have had or will have the pleasure of working
on the development of new organic synthetic methodology.

FOREWORD

At one time organic chemists looked askance at those who elected to devote their research effort to the development of new, selective methods for achieving chemical transformations of organic compounds. Early practitioners in this area received many critical comments—it was felt that the proper objective of organic chemists was the synthesis of natural products, and that one should only develop a new method when such a method was required to overcome a hurdle in the synthetic procedure. But we persisted. Now there appears to be a general acceptance of the value of such research.

Now a new problem has appeared. We have brought forth so many new, highly selective synthetic methods that it is difficult for the chemist to know all of them and to select the method that would be most effective for the synthesis in hand. One approach is to publish monographs that review specialized areas. For example, my own field of borane reagents was reviewed 15 years ago (*Organic Syntheses via Boranes*, by H. C. Brown, Wiley, 1975). A more recent book of this sort is *Borane Reagents*, by A. Pelter, K. Smith, and H. C. Brown, Academic Press, 1988.

But such specialized books solve only part of the problem. In the present work, Richard C. Larock has set himself the goal of organizing the entire panoply of synthetic methods. But there are now so many methods that even brief descriptions of each procedure would have produced a work as large as the new Oxford English Dictionary (16 volumes, Oxford University Press, 1986). Instead, he adopted the unique solution of indicating the reagent and transformation, with pertinent references. This provides a concise summary that should be of enormous assistance to those searching for a selective reaction to achieve a desired transformation in the presence of difficult substituents. This problem is frequently faced today by those who undertake the involved syntheses that are often an important objective of current research.

One must admire Richard Larock's courage in undertaking this monumental task.

Herbert C. Brown
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PREFACE

Organic synthesis is one of the most rapidly developing areas of chemistry. Every day useful new reagents and reactions are reported worldwide in the chemical literature. It is increasingly difficult for the organic chemist to keep up with the latest in synthetic organic methodology without spending an inordinate amount of time reading a wide variety of chemical journals, including those whose focus is not strictly synthetic organic chemistry.

In recent years a variety of books and reviews have appeared to aid the organic chemist interested in synthetic methodology, but even the best of these have now ballooned to inconvenient multivolume sets whose cost is prohibitive to those just entering the field. The intent of the present volume is to provide a comprehensive, highly condensed, systematic collection of useful synthetic methodology that both the beginning student and the long-time practitioner of organic synthesis will find useful.

This book began in 1973 as a series of course handouts designed to cover the key reactions of the major organic functional groups. Like the aforementioned publications, this reference work has grown rapidly over the years to a major treatise covering a vast amount of synthetic organic methodology. It was felt that the synthetic organic community might find this compilation useful, so a serious effort has been made in the last two years to thoroughly update and organize this material for publication.

The author takes full responsibility (and credit?) for the choice of reactions and references. Obviously not every reaction or reference could be included. In choosing material for this text the author has observed the following guidelines. All reactions to be included should be general in scope or else so unique that the methodology will find real synthetic utility. Yields should generally be at least 50%. Reagents should be readily available or easily prepared and handled in the laboratory. As much as possible, similar transformations should appear together in as concise a format as possible. Significant limitations in methodology shall be noted. No effort has been made to cover the use of protecting groups since excellent reviews on this subject are already available. Likewise, heterocyclic chemistry has consciously been omitted, except where heterocycles have been employed to effect simple functional group manipulations. Multiple group transformations have been covered, although they present certain organizational problems. To those chemists whose contributions to synthetic organic chemistry may have been slighted or altogether ignored, I apologize. It would be appreciated if major errors or omissions be brought to the author's attention so that future printings or subsequent editions may be corrected.

All reactions have been systematically organized according to the functional group being synthesized, with no attempt to cover the less important functional groups. Within each section the methodology is subdivided into major processes, such as oxidation, reduction,

alkylation, etc. It is hoped that the reader will easily find the desired transformations by skimming the detailed Table of Contents, although an extensive Transformation Index is available in time of need.

Literature coverage is complete through 1987. Some 160 or more primary chemical journals and a number of books and reviews have been abstracted. Obscure journals not readily available to most synthetic organic chemists have been avoided. The names of authors have been omitted to save space. Original publications have not always been cited if they do not necessarily describe the best reaction conditions for running the reaction or purvey little of the scope of the reaction. References containing full experimental procedures, though they may be buried in an experimental section, have been favored over communications lacking such details. An attempt has been made to highlight reviews and significant publications. One immediately encounters problems in deciding where to draw the line on references. Initial reports of a useful new reaction have received complete coverage. However, the time soon comes when a truly significant reaction, such as the use of ester enolates in synthesis, appears routinely in publication after publication and no reviews have appeared. In such situations, the author has tended to include all new material and may not have had the time to omit the more inconsequential earlier references.

It is hoped that the reader finds this effort worthwhile and will not hesitate to make suggestions on ways this material may be improved.

Richard C. Larock
Ames, Iowa U.S.A.
May, 1988

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The preparation of a book of this magnitude requires the assistance of a number of people. The author is indebted to Iowa State University for providing the time and assistance necessary for the preparation of much of this book. The Department of Chemistry at the University of Hawaii at Manoa is gratefully acknowledged for having provided a visiting professorship which allowed the author to push this manuscript through to publication.

To those around me who have had to "endure" this book, your patience and perseverance are appreciated. To my students who have sometimes had to take a back seat to this project, I thank them for waiting. To those who volunteered to help in proofing the final text, I extend my gratitude.

I must also acknowledge a core of dedicated secretaries over the years who have continually updated this material for classroom use. Most important of these secretaries is Mrs. Nancy Qvale, who is responsible for the preparation of a major portion of this work and bore the burden of putting this manuscript in final form. Without her outstanding technical assistance and dedication, this book might never have materialized.

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LITERATURE ABBREVIATIONS

Acct Chem Res	*Accounts of Chemical Research*
Acta Chem Scand	*Acta Chemica Scandinavica*
Acta Chem Scand B	*Acta Chemica Scandinavica. Series B: Organic Chemistry and Biochemistry*
Adv Alicyclic Chem	*Advances in Alicyclic Chemistry*
Adv Carbohydr Chem	*Advances in Carbohydrate Chemistry*
Adv Catalysis	*Advances in Catalysis*
Adv Chem Ser	*Advances in Chemistry Series*
Adv Heterocyclic Chem	*Advances in Heterocyclic Chemistry*
Adv Org Chem	*Advances in Organic Chemistry: Methods and Results*
Adv Organometal Chem	*Advances in Organometallic Chemistry*
Adv Photochem	*Advances in Photochemistry*
Adv Phys Org Chem	*Advances in Physical Organic Chemistry*
Agric Biol Chem	*Agricultural and Biological Chemistry*
Anal Chem	*Analytical Chemistry*
Anal de Quim	*Anales de Quimica*
Angew	*Angewandte Chemie*
Angew Int	*Angewandte Chemie, International Edition in English*
Ann	*Justus Liebig's Annalen der Chemie*
Ann Chim	*Annales de Chimie*
Ann NY Acad Sci	*Annals of the New York Academy of Sciences*
Ann Rep Med Chem	*Annual Reports in Medicinal Chemistry*
Appl Microbiol	*Applied Microbiology*
Appl Microbiol Biotechnol	*Applied Microbiology and Biotechnology*
Arch Pharm	*Archiv der Pharmazie*
Arkiv Kemi	*Arkiv for Kemi*
Austral J Chem	*Australian Journal of Chemistry*
BCSJ	*Bulletin of the Chemical Society of Japan*
Ber	*Berichte der Deutschen Chemischen Gesellschaft*
Biochem	*Biochemistry*
Biochem Biophy Res Commun	*Biochemical and Biophysical Research Communications*
Biochem J	*Biochemical Journal*
Biochim Biophys Acta	*Biochimica et Biophysica Acta*
Bioorg Chem	*Bioorganic Chemistry*
BSCF	*Bulletin de la Societe Chimique de France*
Bull Acad Polon Sci, Ser Sci Chem	*Bulletin de l'Academie Polonaise des Sciences, Serie des Sciences Chimiques*
Bull Acad Sci USSR, Div Chem Sci	*Bulletin of the Academy of Sciences of the USSR. Division of Chemical Science*
Bull Korean Chem Soc	*Bulletin of the Korean Chemical Society*
Bull Soc Chim Belg	*Bulletin des Societes Chimiques Belges*
CA	*Chemical Abstracts*
Can J Chem	*Canadian Journal of Chemistry*
Cancer Lett	*Cancer Letters*

Carbohydr Res	*Carbohydrate Research*
Catal Rev	*Catalysis Reviews*
CC	*Journal of the Chemical Society: Chemical Communications*
Chem Eng News	*Chemical and Engineering News*
Chem in Britain	*Chemistry in Britain*
Chem Ind	*Chemistry and Industry*
Chem Listy	*Chemicke Listy*
Chem Pharm Bull	*Chemical and Pharmaceutical Bulletin*
Chem Phys Lipids	*Chemistry and Physics of Lipids*
Chem Rev	*Chemical Reviews*
Chem Scripta	*Chemica Scripta*
Chem Soc Rev	*Chemical Society Reviews*
Chem Weekb	*Chemisch Weekblad*
Chem Zeitung	*Chemiker Zeitung*
Chem Zentr	*Chemisches Zentralblatt*
CL	*Chemistry Letters*
Coll Czech Chem Commun	*Collection of Czechoslovak Chemical Communications*
Compt Rend	*Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences*
Compt Rend C	*Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Serie C: Sciences Chimiques*
Curr Sci	*Current Science*
Discuss Faraday Soc	*Discussions of the Faraday Society*
Fortschr Chem Forsch	*Fortschritte der Chemischen Forschung*
Fund Res Homogeneous Catal	*Fundamental Research in Homogeneous Catalysis*
Gazz Chim Ital	*Gazzetta Chimica Italiana*
Helv	*Helvetica Chimica Acta*
Ind Eng Chem	*Industrial and Engineering Chemistry*
Ind J Chem	*Indian Journal of Chemistry*
Ind J Chem B	*Indian Journal of Chemistry. Section B: Organic Chemistry and Medicinal Chemistry*
Inorg	*Inorganic Chemistry*
Int J Sulfur Chem	*International Journal of Sulfur Chemistry*
Intra-Science Chem Reports	*Intra-Science Chemistry Reports*
Israel J Chem	*Israel Journal of Chemistry*
Izv Akad Nauk SSSR, Ser Khim	*Izvestiia Akademii Nauk SSSR. Seriia Khimicheskaia*
J Am Oil Chem Soc	*Journal of the American Oil Chemists' Society*
J Antibiotics	*Journal of Antibiotics*
J Biol Chem	*Journal of Biological Chemistry*
J Catalysis	*Journal of Catalysis*
J Chem Ed	*Journal of Chemical Education*
J Chem Eng Data	*Journal of Chemical and Engineering Data*
J Chem Res (S)	*Journal of Chemical Research. Synopses*
J Fluorine Chem	*Journal of Fluorine Chemistry*
J Gen Chem USSR	*Journal of General Chemistry of the USSR*
J Heterocyclic Chem	*Journal of Heterocyclic Chemistry*
J Ind Chem Soc	*Journal of the Indian Chemical Society*

J Label Compds	*Journal of Labelled Compounds*
J Lipid Res	*Journal of Lipid Research*
J Med Chem	*Journal of Medicinal Chemistry*
J Mol Catal	*Journal of Molecular Catalysis*
J Nat Prod	*Journal of Natural Products*
J Pharm Sci	*Journal of Pharmaceutical Sciences*
J Photochem	*Journal of Photochemistry*
J Polym Sci, Polym Chem Ed	*Journal of Polymer Science: Polymer Chemistry Edition*
J Prakt Chem	*Journal für Praktische Chemie*
J Russ Phys Chem Soc	*Journal of the Russian Physical Chemical Society*
J Sci Ind Res B	*Journal of Scientific and Industrial Research. Part B: Physical Sciences*
J Vitaminol (Osaka)	*Journal of Vitaminology*
JACS	*Journal of the American Chemical Society*
JCS	*Journal of the Chemical Society*
JCS A	*Journal of the Chemical Society. Section A: Inorganic, Physical and Theoretical*
JCS B	*Journal of the Chemical Society. Section B: Physical Organic*
JCS C	*Journal of the Chemical Society. Section C: Organic*
JCS D	*Journal of the Chemical Society. Section D: Chemical Communications*
JCS Dalton	*Journal of the Chemical Society: Dalton Transactions*
JCS Japan	*Journal of the Chemical Society of Japan*
JCS Perkin I	*Journal of the Chemical Society: Perkin Transactions I*
JCS Perkin II	*Journal of the Chemical Society: Perkin Transactions II*
JOC	*Journal of Organic Chemistry*
JOC USSR	*Journal of Organic Chemistry of the USSR*
JOMC	*Journal of Organometallic Chemistry*
Methods Carbohydr Chem	*Methods in Carbohydrate Chemistry*
Monatsh	*Monatshefte für Chemie*
Natl Prod Repts	*Natural Product Reports*
Naturwiss	*Naturwissenschaften*
Newer Methods Prep Org Chem	*Newer Methods of Preparative Organic Chemistry*
Nouv J Chim	*Nouveau Journal de Chimie*
Org Mag Res	*Organic Magnetic Resonance*
Org Photochem	*Organic Photochemistry*
Org Prep Proc Int	*Organic Preparations and Procedures International*
Org Rxs	*Organic Reactions*
Org Syn	*Organic Syntheses*
Org Syn Coll Vol	*Organic Syntheses. Collective Volume*
Organomet	*Organometallics*
Organomet Chem Rev A	*Organometallic Chemistry Reviews. Section A: Subject Reviews*
Organomet Chem Syn	*Organometallics in Chemical Synthesis*
Phosphorus	*Phosphorus and the Heavier Group Va Elements*
Phosphorus and Sulfur	*Phosphorus and Sulfur and the Related Elements*
Photochem Photobiol	*Photochemistry and Photobiology*
Pol J Chem	*Polish Journal of Chemistry*
Polym J	*Polymer Journal*

Proc Acad Sci USSR, Chem Sec	*Proceedings of the Academy of Sciences of the USSR. Chemistry Section*
Proc Chem Soc	*Proceedings of the Chemical Society (London)*
Proc Ind Acad Sci A	*Proceedings — Indian Academy of Sciences. Section A, Part 1: Chemical Sciences*
Proc Natl Acad Sci USA	*Proceedings of the National Academy of Sciences of the United States of America*
Pure Appl Chem	*Pure and Applied Chemistry*
Quart Rev	*Quarterly Reviews — Chemical Society, London*
Rec Chem Prog	*Record of Chemical Progress*
Rec Trav Chim	*Recueil des Travaux Chimiques des Pays-Bas*
Recl J R Neth Chem Soc	*Recueil: Journal of the Royal Netherlands Chemical Society*
Rev Chem Intermed	*Reviews of Chemical Intermediates*
Rev Pure Appl Chem	*Reviews of Pure and Applied Chemistry*
Rocz	*Roczniki Chemii*
Russ Chem Rev	*Russian Chemical Reviews*
Soc Chem Ind	*Society of Chemical Industry, London Chemical Engineering Group, Proceedings*
Syn	*Synthesis*
Syn Commun	*Synthetic Communications*
Tetr	*Tetrahedron*
TL	*Tetrahedron Letters*
Topics Curr Chem	*Topics in Current Chemistry*
Topics Stereochem	*Topics in Stereochemistry*
Trans Faraday Soc	*Transactions of the Faraday Society*
Transition Met Chem	*Transition Metal Chemistry (New York)*
Z Chem	*Zeitschrift für Chemie*
Z Naturforsch B	*Zeitschrift für Naturforschung. Tiel B: Anorganische Chemie, Organische Chemie, Biochemie, Biophysik, Biologie*
Zh Obshch Khim	*Zhurnal Obshchei Khimii*

CHEMICAL ABBREVIATIONS

Ac	Acetyl
acac	acetylacetonate [$CH_3COCHCOCH_3$]
acaen	*N*, *N*′-bis(1-methyl-3-oxobutylidene)ethylenediamine
AIBN	2,2′-azobisisobutyronitrile [$Me_2C(CN)N{=}NC(CN)Me_2$]
Am	amyl
aq	aqueous
Ar	aryl
B◠	9-borabicyclo[3.3.1]nonyl
9-BBN	9-borabicyclo[3.3.1]nonane [HB◠]
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bipy	2,2′-bipyridyl
Bu	butyl
c	cyclo
cat	catalytic
COD	**cis**,**cis**-1,5-cyclooctadiene
Cp	Cyclopentadienyl
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBA	dibenzylideneacetone [$PhCH{=}CHCOCH{=}CHPh$]
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
diop	(2,3)-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	*N*, *N*-dimethylformamide
DMSO	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane [$Ph_2PCH_2CH_2PPh_2$]
E^+	electrophile
EDA	ethylenediamine [$H_2NCH_2CH_2NH_2$]
EDTA	ethylenediaminetetraacetate
Et	ethyl
fod	6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato [$CF_3CF_2CF_2COCHCOC(CH_3)_3$]
Fp	dicarbonyl(η^5-cyclopentadienyl)iron(I) [$Fe(CO)_2$(cyclopentadienyl)]
Het	heterocycle
HMPA = HMPT	hexamethylphosphoramide

i	iso
L	ligand
LDA	lithium diisopropylamide [$LiN(i\text{-}C_3H_7)_2$]
m	meta
Me	methyl
Mes	mesityl
mesal	*N*-methylsalicylaldimine
Ms	methanesulfonyl
n	normal
NBA	*N*-bromoacetamide
NBD	norbornadiene
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
Nuc	nucleophile
o	ortho
p	para
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PEG-400	poly(ethylene glycol)-400
Ph	phenyl
phen	1,10-phenanthroline
PPA	polyphosphoric acid
Pr	propyl
py	pyridine
R	an organic group
R_f	perfluoroalkyl
Salen	*N*,*N*′-ethylenebis(salicylideneiminato)
salophen	*o*-phenylenebis(salicylideneiminato)
sec	secondary
Sia	1,2-dimethylpropyl [$(CH_3)_2CHCHCH_3$]
S,**S**-chiraphos	(**S**,**S**)-2,3-bis(diphenylphosphino)butane [(**S**,**S**)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$]
t	tertiary
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine [$Me_2NCH_2CH_2NMe_2$]
Tol	tolyl
tolbinap	2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl
Ts	*p*-toluenesulfonyl

ALKANES AND ARENES

GENERAL REFERENCES

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1a (alkanes), G. Thieme, Stuttgart (1970)

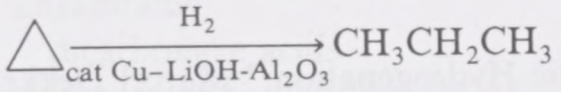
Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol IV/3 (cyclopropanes), G. Thieme, Stuttgart (1971)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol IV/4 (cyclobutanes), G. Thieme, Stuttgart (1971)

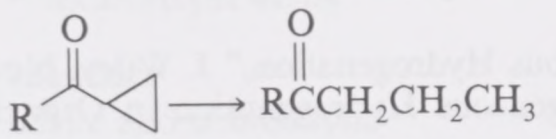
Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/2b (arenes), G. Thieme, Stuttgart–New York (1981)

1. REDUCTION

1. Cyclic Alkanes



JOC USSR *18* 585 (1982)



Li, NH_3

Acta Chem Scand *19* 1289 (1965)
JOC *31* 3794 (1966); *35* 374 (1970)
BSCF 4449 (1968)
TL 2879 (1974)
Angew Int *18* 809 (1979) (review)

Zn

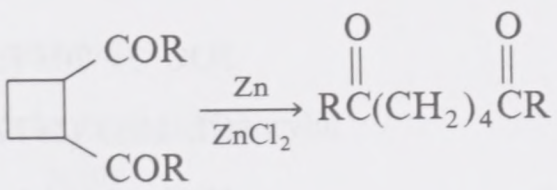
TL *22* 695 (1981)

Zn, HCl

JOC *35* 2986 (1970)

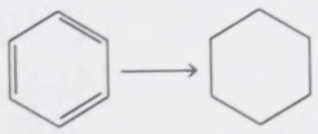
Zn, $ZnCl_2$

TL 2489 (1975); *22* 695 (1981)



TL 2489 (1975)

2. Arenes



Review: Acct Chem Res *12* 324 (1979)

H_2, cat π-$C_3H_5CoL_3$

Inorg *15* 2379 (1976)

H_2, cat $RhCl_3$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	TL *24* 4139 (1983) J Mol Catal *34* 221 (1986) (naphthalenes); *39* 185 (1987) (polycyclic arenes) JOC *52* 2804 (1987)
H_2, cat $[ClRh(C_7H_8)]_2$-polymer	CL 603 (1982)
H_2, cat Rh(I)-polymer	JOC *44* 239 (1979) JACS *103* 5096 (1981)
H_2, cat $[Rh(C_5Me_5)Cl_2]_2$	CC 427 (1977) Acct Chem Res *11* 301 (1978)
H_2, cat [Si]-ORh(allyl)H	JACS *103* 5253 (1981)

3. Alkenes

3.1. Catalytic Hydrogenation

Reviews:

R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York (1965)
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3.1.1. Selective hydrogenation catalysts

5% Ru on Norit	JOC *24* 708 (1959)
$RuCl_2(PPh_3)_3$	CL 1083 (1977) (polyenes to monoenes)
$NaBH_4$, $CoCl_2$ (mono > di > tri > tetrasubstituted)	JOC *44* 1014 (1979) JACS *108* 67 (1986)
$ClRh(PPh_3)_3$ (Wilkinson's catalyst)	Discuss Faraday Soc *46* 60 (1968) Chem Rev *21* 73 (1973) Syn 329 (1978)
$[Rh(NBD)Ph_2P(CH_2)_4PPh_2]BF_4$	CC 348 (1982) (syn to allylic, homoallylic OH) JACS *106* 3866 (1984) (syn to OH); *107* 4339 (1985) (syn to OH); *108* 2476 (1986) TL *28* 3659 (1987)

$[Ir(COD)py(PCy_3)]PF_6$	TL *22* 303 (1981) (α face of steroids) JACS *105* 1072 (1983) (syn to OH); *106* 3866 (1984) (syn to OH); *109* 6493 (1987) (syn to $CONR_2$) Organomet *2* 681 (1983) (syn to OH) JOC *50* 5905 (1985) (syn to CO_2R, $CONR_2$); *51* 2655 (1986) (syn to OH, CO_2R, C=O, OMe)
nickel boride (P-2)	JOC *38* 2226 (1973); *46* 1263 (1981)
$LaNi_5H_6$	JOC *52* 5695 (1987) (least substituted double bond)
NaH, NaO-*t*-Am, $Ni(OAc)_2$	JOC *45* 1937, 1946 (1980)

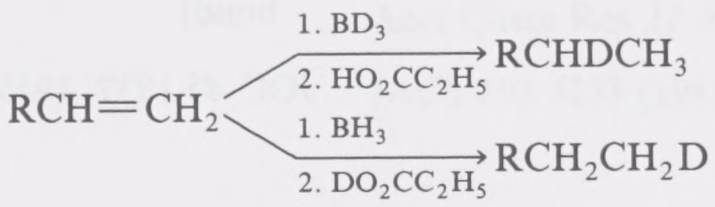
3.1.2. Enantioselective hydrogenation catalysts

Catalyst	Substrate	
$Ru_2Cl_4(BINAP)_2(NEt_3)$	α-amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL *28* 1905 (1987)
$RuHCl(BINAP)_2$	α-amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL *28* 1905 (1987)
$Ru(OAc)_2(BINAP)$	enamides	JACS *108* 7117 (1986)
	allylic and homoallylic alcohols	JACS *109* 1596 (1987)
	α,β- and β,γ-unsaturated carboxylic acids	JOC *52* 3174 (1987)
$[Rh(NBD)(S,S\text{-chiraphos})]ClO_4$	α-amidoacrylic acid and ester	JOC *52* 5143 (1987)
$[Rh(NBD)(BINAP)]ClO_4$	α-amidoacrylic acids	JACS *102* 7932 (1980)
	α-amidoacrylic acids and esters	Tetr *40* 1245 (1984)
$[Rh(NBD)(BINAP)]BF_4$	α,β-unsaturated ester	JACS *108* 2476 (1986)
$Rh(O_2CCF_3)_2$(tolbinap)	enamides	TL *28* 4829 (1987)
chiral (aminoalkyl)-ferrocenylphosphine-Rh	trisubstituted acrylic acids	JACS *109* 7876 (1987)
chiral pyrrolidinodi-phosphines-Rh	itaconic acid	CL 567 (1978)
	α-amidoacrylic acids	Ber *119* 3326 (1986)
$Ph_2PCH(CH_2OR)CH_2PPh_2$-Rh	α-amidoacrylic acids and esters	J Chem Res (S) 117 (1982)
{R,R-1,2-bis((phenyl-O-anisoyl)phosphino)-ethane}-Rh(I)	α-amidoacrylate	JACS *109* 1746 (1987)

3.2. Diimide Reduction (HN=NH)

JOC *30* 3965 (1965)
J Chem Ed *42* 254 (1965) (review)
Angew Int *4* 271 (1965) (review)
Syn Commun *12* 287 (1982) ($HONH_2$, EtOAc)
JOC *52* 4665 (1987) ($TsNHNH_2$, NaOAc)

3.3. Hydroboration–Protonolysis



JACS *81* 4108 (1959)

3.4. Transition Metal Salts and Metal Hydrides

LiH, VCl_3 ($RCH=CH_2$ only)	JOC *45* 1041 (1980)
NaH, NaO-*t*-Bu, $FeCl_3$	TL 3947 (1977)
NaH, NaO-*t*-Am, $Ni(OAc)_2$	TL 1069 (1977)
$NaBH_4$, $CoCl_2$	JACS *108* 67 (1986)
$LiAlH_4$, $TiCl_4$ or $ZrCl_4$	TL 15 (1976) JOMC *142* 71 (1977)
$LiAlH_4$, $CoCl_2$	JOC *43* 2567 (1978)
$LiAlH_4$, $NiCl_2$	TL 4481 (1977)
$LaNi_5H_6$	CC 163 (1984)

3.5. Miscellaneous Reagents

Na, *t*-BuOH, amide	JOC *44* 2369 (1979)
$NaH_2PO_2 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O	JOC *50* 3408 (1985)
R_3SiH, CF_3CO_2H	Tetr *23* 2235 (1967) Syn 633 (1974) Org Prep Proc Int *12* 13 (1980) JACS *108* 1239 (1986)

3.6. Conjugate Reduction

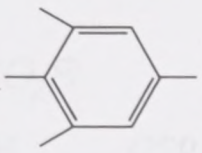
$$RCH=CHX \longrightarrow RCH_2CH_2X$$

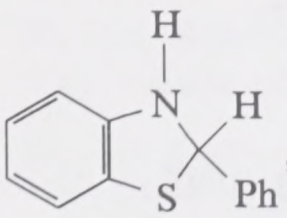
X = CHO

H_2, CO, cat $Co_2(CO)_8$	Compt Rend C *281* 877 (1975)
H_2, cat Rh-Al_2O_3	Compt Rend C *284* 577 (1977)

H_2, cat $ClRh(PPh_3)_3$	JCS C 270 (1967) JOC *34* 3684 (1969)
H_2; cat $HRhCO(PPh_3)_3$, $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$; cat diphosphine	J Mol Catal *16* 51 (1982) (chiral)
H_2, $NaBH_4$-cat $Ni(OAc)_2$ or $PdCl_2$	JOC *42* 551 (1977)
$(Et_3NH)O_2CH$, cat Pd-C	JOC *43* 3985 (1978)
i-Bu_2AlH, HMPA	JOC *51* 537 (1986)
Et_3SiH, cat $ClRh(PPh_3)_3/K_2CO_3$	TL 5035 (1972) Organomet *1* 1391 (1982)
Ph_2SiH_2, cat $Pd(PPh_3)_4$, cat $ZnCl_2$	JACS *108* 7314 (1986)
polymethylhydrosiloxane, cat $RhCl_3$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	J Mol Catal *37* 359 (1986)
n-Bu_3SnH, cat $Pd(PPh_3)_4$	TL *23* 477 (1982)
n-Bu_3SnH, cat $Pd(PPh_3)_4$, HOAc	TL *23* 1825 (1982)
$NaHFe_2(CO)_8$	JACS *100* 1119 (1978)
$HCo(CO)_4$	JOC *27* 3698 (1962) JACS *85* 2782 (1963)
$LaNi_5H_6$	CC 163 (1984)
$LiHCuC{\equiv}C(CH_2)_2CH_3$	JACS *96* 1623 (1974)
$Fe(CO)_5$, NaOH	JOC *37* 1542 (1972) Syn 596 (1976)
CO, H_2O, cat $Rh_6(CO)_{16}$	CL 379 (1973)
Li, NH_3	Org Rxs *23* 1 (1976) JOC *46* 5371 (1981)
$Na_2S_2O_4$, $NaHCO_3$, cat Aliquat®	TL *26* 831 (1985)
NaTeH	CL 847 (1980)
X = COR	
electrolysis	JOC *52* 276 (1987)
Li, NH_3 (Birch reduction)	JCS 3045 (1954) Org Rxs *23* 1 (1976) (review) JACS *108* 4561 (1986)
Li·4 NH_3	JOC *43* 4647 (1978)
Na or Li, HMPA or NH_3	JACS *92* 2800 (1970)
Li, NH_3, EtOH	JACS *86* 1761 (1964)
Li, NH_3, *t*-BuOH	JOC *32* 2851 (1967); *42* 183 (1977); *50* 2607 (1985); *52* 2263, 3346 (1987) JACS *106* 3539 (1984)
Li, $EtNH_2$, *t*-BuOH	Syn 400 (1980)

Na, HMPA, (ROH)	JACS *92* 2783 (1970)
Yb, NH_3	JOC *43* 4555 (1978)
C_8K, $HN(SiMe_3)_2$	Syn 30 (1979)
Mg, $TiCl_4$, *t*-BuOH	TL *27* 4153 (1986)
$TiCl_3$, MeOH, NH_3	Helv *13* 1308 (1930)
Zn, HCl	Quart Rev *23* 522 (1969)
Zn, cob(I)alamin, HOAc	Helv *62* 2361 (1979)
Zn, $NiCl_2$, H_2O, $CH_3OCH_2CH_2OH$, ultrasound	TL *28* 2347 (1987)
Zn, $NiCl_2$, H_2O, $CH_3OCH_2CH_2OH$, NH_3-NH_4Cl or Et_3N, ultrasound	TL *28* 2351 (1987)
H_2, cat $HRuClL_4$ or H_2RuL_4 (chiral ligands)	TL *27* 5497 (1986) (chiral)
H_2, cat $H_2Ru(PPh_3)_4$ or $RuCl_2(PPh_3)_3$, glycoside	TL 4083 (1976) (chiral)
H_2, CO, cat $Co_2(CO)_8$	Compt Rend *281* 877 (1975)
H_2, cat $Co_2(CO)_6(PR_3)$	JOMC *284* 101 (1985) (chiral)
H_2, cat $K_3Co(CN)_5H$	TL 115 (1979) JOC *45* 3860 (1980)
H_2, cat bis(dimethylglyoximato)-cobalt(II)-quinine	CL 265 (1973) (chiral)
H_2, cat Rh-C, Na_2CO_3	JOC *50* 2438 (1985)
H_2, cat Rh-Al_2O_3	Compt Rend C *284* 577 (1977)
H_2, cat $ClRh(PPh_3)_3$	JCS C 1894 (1966) JOC *34* 3684 (1969) JACS *107* 8066 (1985)
H_2, cat $[Rh(diolefin)L_2]BF_4$ (L = chiral phosphine)	JOC *43* 1787 (1978) (chiral)
H_2, cat $RhCl_3 \cdot 3\ H_2O$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	J Mol Catal *34* 229 (1986) TL *28* 1321 (1987)
H_2, cat $HRh(PPh_3)_4$, $PhCHOHCH_3$	Can J Chem *57* 218 (1979)
H_2, cat $[Ir(COD)py(PCy_3)]PF_6$	TL *22* 303 (1981)
H_2, cat NaH-NaO-*t*-Am-$Ni(OAc)_2$	JOC *45* 1946 (1980)
H_2, cat Pd-C	JOC *23* 1853 (1958); *52* 2875, 5594 (1987) JACS *107* 7967 (1985); *108* 4561 (1986)
H_2, cat PtO_2	JOC *23* 1853 (1958) JACS *108* 7967 (1985)
NaH, NaO-*t*-Am, $Ni(OAc)_2$, ($MgBr_2$)	JOC *44* 2203 (1979)

NaH, *t*-AmOH, $Ni(OAc)_2$, (Me_3SiCl)	TL *27* 5487 (1986)
HBI_2	TL 3865 (1976)
$NaBH_4$	JCS C 616 (1968)
$NaBH_4$, diglyme, amine base	JCS 5280 (1965)
$LiHB(sec\text{-}Bu)_3$	JACS *109* 6389 (1987)
$KHB(sec\text{-}Bu)_3$	JOC *40* 146 (1975); *41* 2194 (1976)
$KHBPh_3$	JOC *52* 5564 (1987)
$NaBH_3CN$, $ZnCl_2$	JOC *50* 1927 (1985)
i-Bu_2AlH, (cat MeCu), HMPA	JOC *51* 537 (1986) Syn Commun *16* 639 (1986)
i-Bu_3Al, cat $Ni(mesal)_2$	JOC *47* 4640 (1982)
$HAl(OR)_2$ (R = *t*-Bu, *i*-Pr)	TL 3865 (1976)
$HAl[N(i\text{-}Pr)_2]_2$	TL 3865 (1976)
$LiAlH_4$, 4 CuI	TL 4453 (1975) JOC *41* 1939 (1976)
$LiAlH_4$, cat CuI, HMPA	CC 1013 (1980)
$LiAlH_4$, 	JOC *46* 192 (1981)
$LiHAl(SR)_3$ (R = Me, *t*-Bu)	TL 2397 (1974)
2 $LiHAl(OMe)_3$, CuBr	JOC *40* 3619 (1975); *42* 3180 (1977)
$NaH_2Al(OCH_2CH_2OCH_3)_2$, CuBr	JOC *40* 3619 (1975); *42* 3180 (1977)
$PhSiH_3$, cat $Mo(CO)_6/H_2O$	JOC *52* 2576 (1987)
Ph_2SiH_2, cat $Pd(PPh_3)_4$, cat $ZnCl_2$	TL *26* 1353 (1985) JACS *108* 7314 (1986)
R_3SiH (R = Me, Et), $TiCl_4/H_2O$	Chem Pharm Bull *25* 1468 (1977)
Et_3SiH, cat $ClRh(PPh_3)_3$	TL 5035 (1972) Organomet *1* 1390 (1982) JACS *105* 7358 (1983); *107* 3731 (1985); *108* 4586 (1986)
polymethylhydrosiloxane, cat $RhCl_3$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	J Mol Catal *37* 359 (1986)
Ph_2SnH_2	TL 2221 (1966)
Ph_3SnH	TL 2221 (1966) BSCF 1928 (1967) Helv *56* 1062 (1973)
n-Bu_3SnH	TL *28* 1313 (1987)
n-Bu_3SnH, cat $Pd(PPh_3)_4$	TL *23* 477 (1982)

n-Bu_3SnH, cat $Pd(PPh_3)_4$, $ZnCl_2$	TL *23* 1825 (1982) Nouv J Chim *8* 611 (1984)
n-Bu_3SnH, cat $Cl_2Pd(PPh_3)_2$, cat n-$Bu_3SnO_3SCF_3$	Nouv J Chim *8* 611 (1984)
NaTeH	CL 847 (1980) TL *27* 3411 (1986)
$MHCr_2(CO)_{10}$ (M = Na, K)	Syn 596 (1976)
$MHFe(CO)_4$ (M = Na, K)	JCS Perkin I 1273 (1975) Syn 596 (1976)
$NaHFe_2(CO)_8$, HOAc	JACS *100* 1119 (1978)
$(Et_4N)HFe_3(CO)_{11}$	JOMC *171* 85 (1979)
$HCo(CO)_4$	JACS *85* 2782 (1963)
$LaNi_5H_6$	CC 163 (1984) JOC *52* 5695 (1987)
LiHCu(n-Bu)	JACS *96* 3686 (1974)
$LiHCuC{\equiv}C(CH_2)_2CH_3$	JACS *96* 1623 (1974)
Li_2CuH_3	JOC *43* 183 (1978)
$(R_3NH)O_2CH$ (R = Et, n-Bu), cat Pd-C	JOC *43* 3985 (1978)
$Fe(CO)_5$, NaOH	JOC *37* 1542 (1972)
$Na_2Fe(CO)_4$, $Fe(CO)_5$, HOAc	Acct Chem Res *8* 342 (1975)
CO, H_2O, cat $Rh_6(CO)_{16}$	CL 379 (1973)
CO, cat $Rh_4(CO)_{12}$-resin	CL 203 (1975)
benzylic alcohol, cat $Cl_2Ru(PPh_3)_3$	JOC *40* 1887 (1975)
$Na_2S_2O_4$, $NaHCO_3$, Adogen 464®, H_2O, benzene	Tetr *42* 4603 (1986)
$Na_2S_2O_4$, $NaHCO_3$, cat Aliquat®	TL *26* 831 (1985)
 , $AlCl_3$, CH_3OH	Syn 308 (1984)
$PhCH_2NH_2/KO$-t-Bu/H_3O^+	JACS *89* 2794 (1967)
baker's yeast	TL *27* 4737 (1986) (α-chloro enones, chiral)
Beauveria sulfurescens	JOC *47* 792 (1982) (enantiospecific); *52* 4893 (1987) (enantiospecific)
$X = CO_2H$	
Li, NH_3	Org Rxs *23* 1 (1976)
Na, NH_3, t-BuOH	TL *27* 3923 (1986)

C_8K/H_3O^+	Syn 30 (1979)
$TiCl_3$, MeOH, NH_3	Helv *13* 1308 (1930)
$CrSO_4$, H_2O	JACS *88* 4964 (1966)
cob(I)alamin, Zn, HOAc	Helv *62* 2361 (1979)
SmI_2, CH_3OH	JACS *102* 2693 (1980)
H_2, cat $RuCl_2$	JACS *88* 5150 (1966)
H_2, cat Ru-BINAP	JOC *52* 3174 (1987) (chiral)
H_2, cat $ClRh(PPh_3)_3$	JOC *34* 3684 (1969)
H_2, cat Raney Ni-NaBr-tartaric acid	JOC *52* 1139 (1987) (chiral)
$PhSiH_3$, cat $Mo(CO)_6/H_2O$	JOC *52* 2576 (1987)
NaTeH	Syn 545 (1978)
$HCo(CN)_5^{3-}$	Catal Rev *1* 37 (1967) (review)
$HONH_2$, EtOAc	Syn Commun *12* 287 (1982)
$X = CO_2Na$	
H_2, cat Raney Ni-NaBr-tartaric acid	JOC *52* 1139 (1987) (chiral)
$X = CO_2R$	
Mg, CH_3OH	CL 633 (1983) (lactone) TL *27* 2409 (1986); *28* 5287 (1987) JOC *52* 4641 (1987)
Mg, CH_3OH, ultrasound	CC 344 (1986)
cob(I)alamin, Zn, HOAc	Helv *62* 2361 (1979)
$CrSO_4$, H_2O	JACS *88* 4964 (1966) Org Syn Coll Vol *5* 993 (1973)
Zn, $NiCl_2$, H_2O, $CH_3OCH_2CH_2OH$, ultrasound	TL *28* 2347 (1987)
SmI_2, CH_3OH	JACS *102* 2693 (1980)
H_2, cat bis(dimethylglyoximato)-cobalt(II)-quinine	CL 265 (1973) (chiral)
H_2, cat $RhCl_3 \cdot 3\ H_2O$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	TL *28* 1321 (1987)
H_2, cat $ClRh(PPh_3)_3$	JACS *90* 1673 (1968) Discuss Faraday Soc *46* 60 (1968) JOC *34* 3684 (1969)
H_2, cat $[Rh(NBD)Ph_2P(CH_2)_4PPh_2]BF_4$	JACS *108* 2476 (1986)
H_2, cat [Rh(NBD)(+)-BINAP]BF_4	JACS *108* 2476 (1986) (chiral)
H_2, cat $PdCl_2$	JACS *91* 2579 (1969)

H_2, cat Pd-C	JOC *52* 4603 (1987) (lactone)
H_2, cat PtO_2	JOC *52* 4641 (1987)
$NaBH_4$	JOC *31* 620 (1966)
$NaBH_4$, CF_3CH_2OH, EtOH	JOC *50* 3948 (1985)
$NaBH_4$, cat $NiCl_2$	JACS *106* 5585 (1984) (lactone) TL *28* 4037 (1987) (lactone)
$LiHB(sec\text{-}Bu)_3$, *t*-BuOH	JOC *40* 2846 (1975); *41* 2194 (1976)
$i\text{-}Bu_2AlH$, cat MeCu, HMPA	JOC *51* 537 (1986)
$LiAlH_4$, CuI	CC 1013 (1980)
$NaH_2Al(OCH_2CH_2OCH_3)_2$, CuBr	JOC *40* 3619 (1975); *42* 3180 (1977) JACS *109* 5432 (1987)
$LiHAl(OMe)_3$, CuBr	JOC *42* 3180 (1977)
$PhSiH_3$, cat $Mo(CO)_6/H_2O$	JOC *52* 2576 (1987)
Ph_2SiH_2, cat $Pd(PPh_3)_4$, cat $ZnCl_2$	JACS *108* 7314 (1986)
Et_3SiH, cat $ClRh(PPh_3)_3/H_3O^+$	Chem Pharm Bull *22* 2767 (1974) Syn Commun *15* 965 (1985) JACS *109* 5432 (1987)
polymethylhydrosiloxane, cat $RhCl_3$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	J Mol Catal *37* 359 (1986)
NaTeH	Syn 545 (1978); 847 (1980)
$KHCr_2(CO)_{10}$	Syn 596 (1976)
$NaHFe_2(CO)_8$	JACS *100* 1119 (1978)
$(Et_4N)HFe_3(CO)_{11}$	JOMC *171* 85 (1979)
$HCo(CN)_5^{3-}$	Catal Rev *1* 37 (1967) (review)
$LaNi_5H_6$	CC 163 (1984) JOC *52* 5695 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)
$LiHCuC{\equiv}C(CH_2)_2CH_3$	JACS *96* 1623 (1974)
$(R_3NH)O_2CH$, cat Pd-C	JOC *43* 3985 (1978)
CO, H_2O, cat $Rh_6(CO)_{16}$	CL 379 (1973)
CO, cat $Rh_4(CO)_{12}$-resin	CL 203 (1975)
$Fe(CO)_5$, NaOH	JOC *37* 1542 (1972)
$Na_2Fe(CO)_4$, $Fe(CO)_5$, HOAc	JACS *100* 1119 (1978)
baker's yeast	TL *28* 1447 (1987) (enantioselective on methyl 2,4,4-trichloro-2-butenoates)

X = CONR$_2$

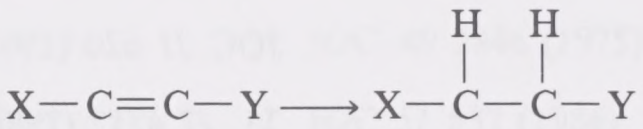
Mg, CH_3OH	TL *21* 2915 (1980) JCS Perkin I 2912 (1981)
$TiCl_3$, CH_3OH, NH_3	Helv *13* 1308 (1930)
cob(I)alamin, Zn, HOAc	Helv *62* 2361 (1979)
H_2, cat nickel boride	JOC *37* 3552 (1972)
$NaBH_4$	JOC *31* 620 (1966)
$LiHB(sec\text{-}Bu)_3$	TL *27* 4717 (1986)
$PhSiH_3$, cat $Mo(CO)_6/H_2O$	JOC *52* 2576 (1987)
Ph_2SiH_2, cat $Pd(PPh_3)_4$, cat $ZnCl_2$	JACS *108* 7314 (1986)
NaTeH	Syn 545 (1978)
$NaHFe_2(CO)_8$	JACS *100* 1119 (1978)
CO, H_2O, cat $Rh_6(CO)_{16}$	CL 379 (1973)
CO, cat $Rh_4(CO)_{12}$-resin	CL 203 (1975)

X = CN

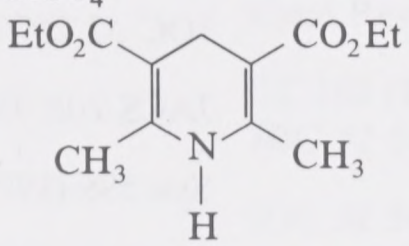
Mg, CH_3OH	JOC *40* 127 (1975); *51* 449 (1986)
$CrSO_4$, H_2O	JACS *88* 4964 (1966)
H_2, cat $ClRh(PPh_3)_3$	Discuss Faraday Soc *46* 60 (1968) JOC *34* 3684 (1969)
$NaBH_4$	JOC *31* 620 (1966) Can J Chem *56* 41 (1978)
$NaH_2Al(OCH_2CH_2OCH_3)_2$, CuBr/*sec*-BuOH	JOC *45* 167 (1980)
$PhSiH_3$, cat $Mo(CO)_6/H_2O$	JOC *52* 2576 (1987)
Ph_2SiH_2, cat $Pd(PPh_3)_4$, cat $ZnCl_2$	JACS *108* 7314 (1986)
$KHCr_2(CO)_{10}$	Syn 596 (1976)
$NaHFe(CO)_4$	JCS Perkin I 1273 (1975)
$NaHFe_2(CO)_8$	JACS *100* 1119 (1978)
$HCo(CN)_5^{3-}$	Catal Rev *1* 37 (1967) (review)
$(R_3NH)O_2CH$, cat Pd-C	JOC *43* 3985 (1978)
CO, H_2O, cat $Rh_6(CO)_{16}$	CL 379 (1973)
$Fe(CO)_5$, NaOH	JOC *37* 1542 (1972)
$Na_2Fe(CO)_4$, $Fe(CO)_5$, HOAc	JACS *100* 1119 (1978)
$NaH_2PO_2 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O	JOC *50* 3408 (1985)

$X = NO_2$

H_2, cat $ClRh(PPh_3)_3$	JCS C 1894 (1966) JOC *34* 3684 (1969)
$NaBH_4$	JACS *108* 1039 (1986)
n-Bu_3SnH/H_2F_2, MeOH	TL *28* 5365 (1987)



X	Y	Reagent(s)	
CHO	COR	NaI, HCl	Syn 245 (1980)
RCO	COR	NaI, HCl	Syn 245 (1980)
		$SnCl_2$, HCl, HOAc	Ber *89* 822 (1956) JOC *51* 4169 (1986)
		$TiCl_3$, H_2O	JOC *39* 258 (1974) Syn 956 (1982) JACS *109* 7230 (1987)
RCO	CO_2R	$TiCl_3$, H_2O	JOC *39* 258 (1974)
HO_2C	CO_2H	H_2, catalyst	M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," Wiley-Interscience, New York, (1978), pp 16–18
		H_2, cat $RuCl_2$	JACS *88* 5150 (1966)
		Ti, electrolysis	Can J Chem *56* 2269 (1978)
		$TiCl_3$, H_2O	JOC *39* 258 (1974)
		$CrSO_4$	JACS *88* 4964 (1966)



JCS 3257 (1960)

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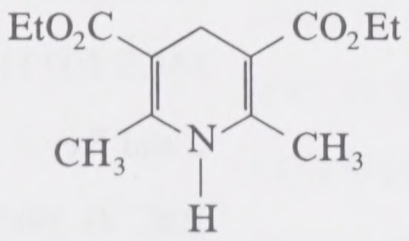
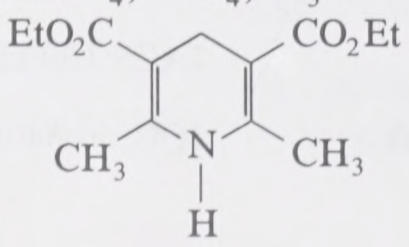


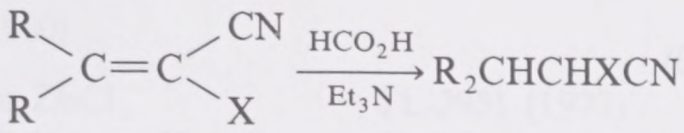
JCS 3257 (1960)

RO_2C	CO_2R	$CrSO_4$	JACS *88* 4964 (1966) Org Syn *49* 98 (1969)
		$LiAlH_4$, $TiCl_4$, Et_3N	TL *28* 2393 (1987)



JCS 3257 (1960)

CN	CN	$CrSO_4$	JACS *88* 4964 (1966)



$X = CO_2Et, CN, SO_2Ph$

Chem Pharm Bull *25* 2396 (1977)

4. Alkynes

4.1. Catalytic Hydrogenation

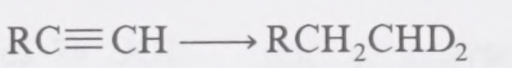
Reviews:

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley-Interscience, New York (1971), Chpt 8
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley and Sons, New York (1978), Chpt 3
P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 3

4.1.1. Catalysts

Ni	JCS 5032 (1952)
PtO_2	JACS *74* 3636 (1952)
Ru	JOC *24* 708 (1959)
Re_2S_7	JACS *76* 1519 (1954); *81* 3587 (1959)

4.2. Hydroalumination–Protonolysis



i-Bu_2AlH/D_2O	Ann *618* 267 (1958)
i-$Bu_2AlH/Cp_2TiCl_2/D_2O$	CL 429 (1982)

4.3. Miscellaneous Reagents

NaH, NaO-*t*-Am, $Ni(OAc)_2$	TL 1069 (1977)
NaH, NaO-*t*-Bu, $FeCl_3$	TL 3947 (1977)
$LaNi_5H_6$	CC 163 (1984) JOC *52* 5695 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)
$KO_2CN{=}NCO_2K, H^+$	TL *28* 5457 (1987)

5. Organic Halides

Review: Syn 425 (1980)

$$R-X \longrightarrow R-H$$

5.1. Low-Valent Metals

Li, THF, *t*-BuOH (alkyl, vinyl, aryl)	Chem Ind 405 (1960) JACS *109* 7230 (1987)
Li, THF, *t*-BuOH, NH_3 (3° alkyl)	JOC *52* 4784 (1987)
Li(Hg), EtOH (dihalocyclopropanes)	JACS *91* 1767 (1969)
Na, THF, *t*-BuOH (alkyl, vinyl, aryl)	Org Syn *48* 68 (1968) JACS *108* 1265 (1986)
Na-K, tris(3,6-dioxaheptyl)amine (2° alkyl)	TL *28* 2503 (1987)
K, crown ether, toluene (alkyl F and Cl)	TL *22* 2583 (1981)
Mg/D_2O (aryl)	JACS *106* 1750 (1984)
Mg, *i*-PrOH (alkyl, vinyl, aryl)	Proc Chem Soc 219 (1963)
Mg, $TiCl_3$, THF (alkyl, aryl)	CC 781 (1975)
Zn, D_2O (2° alkyl)	JOC 50 2557 (1985)
Zn, HOAc (alkyl, allylic, aryl)	Org Syn Coll Vol *2* 320 (1943) JACS *91* 1767 (1969) TL *28* 3225 (1987)
Zn, KOH, ROH (cyclopropyl)	JOC *37* 1734 (1972)
Zn, KI, CH_3OH (RCOCH=CClR)	JACS *72* 1645 (1972)
Zn-Ag, CH_3OH (RCOCH=CClR)	JOC *41* 636 (1976)
Zn, H_2O, cat $NiCl_2$-NaI-PPh_3 (aryl, 3° alkyl)	JOC *47* 2622 (1982)
$CrSO_4$, DMF, H_2O (1°, 2° alkyl; allylic; benzylic)	JACS *85* 2768 (1963)
$Cr(ClO_4)_2(EDA)_2$, DMF, H_2O (alkyl, aryl)	JACS *88* 4094 (1966); *92* 137 (1970) Angew Int *7* 247 (1968) Tetr *24* 3503 (1968)
$Cr(ClO_4)_2$, EDA, *n*-BuSH, (electrolysis) (1°, 2° alkyl)	Angew Int *19* 46 (1980)
SmI_2, THF (1° RBr, RI; benzylic chloride, bromide)	JACS *102* 2693 (1980)

5.2. Metal Hydrides

Review: JOC *45* 849 (1980)

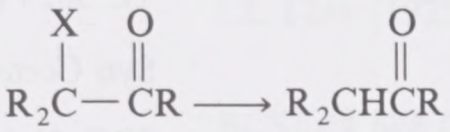
NaH, NaO-*t*-Am, $Ni(OAc)_2$ or $ZnCl_2$ (1°, 2°, 3° alkyl; vinylic; allylic; benzylic; aryl)	TL 3951 (1977) JOC *46* 1270 (1981)
KH (1° alkyl)	JOC *52* 4299 (1987)
MgH_2, $HMgOC_6H_3[CH(CH_3)_2]_2$-2,6 (1° RI)	JOC *43* 1557 (1978)
$NaBH_4$, DMSO (3° alkyl, allylic, benzylic)	TL 3495 (1965) JACS *88* 1473 (1966) JOC *34* 3923 (1969); *51* 3502 (1986) CC 338 (1970)
$NaBH_4$, DMSO or HMPA or sulfolane (1°, 2° alkyl)	JOC *43* 2259 (1978)
$NaBH_4$, sulfolane (3° alkyl)	JOC *36* 1568 (1971)
$NaBH_4$ (phase transfer) (1°, 2° alkyl; benzylic)	JOC *46* 3909 (1981)
$NaBH_4$, H_2O, CH_3CN, hν (aryl)	JACS *95* 5085 (1973)
$NaBH_4$, (t-BuO)$_2$, hν (aryl)	TL *27* 109 (1986)
$NaBH_4$, cat R_3SnCl (R = Me, *n*-Bu), hν (1°, 2° alkyl; aryl)	JOC *40* 2554 (1975)
$NaBH_4$, $PdCl_2$ (aryl)	TL 4699 (1973) CL 1029 (1981)
$Zn(BH_4)_2$ (3° alkyl, benzylic)	Angew Int *22* 562 (1983)
$NaBH_3CN$ (1° RCl, RBr, RI; 2° RBr, RI; allylic; benzylic)	Syn 35 (1975) JOC *42* 82 (1977)
$NaBH_3CN$-polymer (1° RBr, RI)	JOC *42* 82 (1977) CC 1088 (1979)
(n-Bu_4N)BH_3CN (1° RCl, RBr, RI; 2° RBr, RI; allylic; benzylic)	JOC *42* 82 (1977)
$NaBH_3CN$, $ZnCl_2$ (3° alkyl, allylic, benzylic)	TL *24* 3369 (1983)
Na or K[H(CN)B⟨ ⟩], HMPA (allylic, benzylic)	JOC *42* 82 (1977)
LiR_2B⟨ ⟩ (3° alkyl, allylic, benzylic)	JACS *97* 2558 (1975) Tetr *37* 2261 (1981)
$LiHBEt_3$ (1°, 2° alkyl; 1°, 2° benzylic)	JACS *95* 1669 (1973); *107* 2046 (1985) JOC *45* 849 (1980); *47* 2590 (1982)
$LiHBEt_3$, cat $Pd(PPh_3)_4$ (1° allylic Cl)	JOC *47* 4380 (1982)

$KHB(sec\text{-}Bu)_3$, CuI (1° alkyl, aryl)	CC 762 (1974)
$KHBPh_3$ (1° alkyl)	JOC *52* 5564 (1987)
$NaHB(OMe)_3$ (1° allylic)	TL *28* 5977 (1987)
$LiAlH_4$ (1°, 2°, 3° alkyl; benzylic)	JACS *70* 3664, 3738 (1948); *71* 1675 (1949); *94* 8905 (1972) TL 2483 (1973); *28* 3883 (1987) JOC *45* 849 (1980); *47* 276 (1982); *49* 3545 (1984)
$LiAlH_4$ (aryl)	JOC *33* 619 (1968); *34* 3918 (1969) TL 1223 (1969)
$LiAlH_4$, ultrasound (aryl)	TL *23* 1643 (1982)
$LiAlH_4$, $TiCl_3$ (aryl)	Rec Trav Chim *101* 112 (1982)
$LiAlH_4$, $TiCl_4$ (aryl, vinylic)	CL 291 (1973)
$LiAlH_4$, $CoCl_2$ (2° alkyl)	JACS *108* 67 (1986)
$LiAlH_4$, $NiCl_2$ or $CoCl_2$ (1°, 2°, 3° alkyl; aryl)	TL 4481 (1977) JOC *43* 1263 (1978)
$LiHAl(i\text{-}Bu)_2(n\text{-}Bu)$ (1° alkyl, benzylic, allylic)	JOC *49* 1717 (1984)
$LiHAl(OCH_3)_3$, CuI (1°, 2°, 3° alkyl; aryl; allylic; vinylic)	JACS *95* 6452 (1973)
R_3SiH (R = Et, *n*-Bu) or $n\text{-}BuSiH_3$, cat $AlCl_3$ (1°, 2°, 3° alkyl)	JOC *41* 1393 (1976)
polymethylhydrosiloxane, cat $Pd(PPh_3)_4$, $(PhCH_2)_3N$, Δ (aryl)	JOC *51* 734 (1986)
R_3SnH (R = *n*-Bu, Ph) (alkyl, aryl)	JOC *28* 703, 2332 (1963) Adv Organometal Chem *1* 47 (1964) JACS *87* 4007 (1965) Acct Chem Res *1* 299 (1968) CC 875 (1969) Syn 499 (1970) TL *28* 3883 (1987)
$HFe(CO)_4^-$-polymer (2° benzylic)	JOC *43* 1598 (1978)
$LiHCu(n\text{-}Bu)$ (2°, 3° alkyl; aryl)	JACS *96* 3686 (1974)
Li_4CuH_5 (1° alkyl)	TL 3695 (1977) JOC *43* 183 (1978)

5.3. Miscellaneous Reagents

H_2, cat Raney Ni (aryl)	JOC *52* 3200 (1987)
N-benzyl-1,4-dihydronicotinamide; cat $ClRh(PPh_3)_3$ or $Pd(OAc)_2$ (allylic, benzylic, aryl, vinylic)	JOC *50* 3283 (1985)

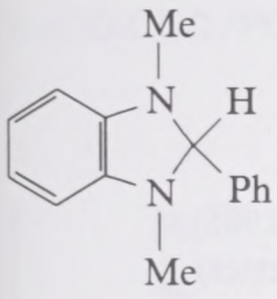
$NaH_2PO_2 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O (benzylic, aryl)	JOC *50* 3408 (1985)
NaO_2CH, cat $Pd(PPh_3)_4$, Δ (aryl)	TL 1913 (1978) JOC *51* 734 (1986)
HCO_2H, cat Pd-C, DMF, Δ (aryl)	Syn 876 (1982)
$(Et_3NH)O_2CH$, cat Pd-C or $(Ar_3P)_2Pd(OAc)_2$ (aryl)	JOC *42* 3491 (1977)
$NaOCH_3$, cat $Pd(PPh_3)_4$ (aryl)	JOC *43* 1619 (1978)
$KPPh_2$ (1,1-dichlorocyclopropanes to chlorocyclopropanes)	JOC *52* 3923 (1987)
$KP(O)(OMe)_2$ (1,1-dibromocyclopropanes to bromocyclopropanes)	JOC *50* 3713 (1985)
$AlCl_3$, EtSH (polycyclic aryl)	TL *23* 689 (1982)
hν, Et_3N, anthracene (aryl)	CC 1703 (1987)
electrolysis (dihalo to monohalo cyclopropanes)	JACS *91* 1767 (1969)

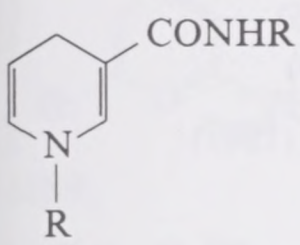


Review: Org Rxs *29* 163 (1983)

H_2, cat Pd-C (X = Br)	JOC *23* 1938 (1958)
HI (X = Br, I)	JCS 4356 (1956) JACS *81* 3634 (1959)
NaI, R_3N (R = Me, Et), SO_2 (X = Cl, Br)	Syn 59 (1979)
NaI, C_5H_5N, SO_3 (X = Cl, Br)	Syn 59 (1979)
LiI, BF_3 (X = Cl, Br, I)	TL 137 (1971)
NaI, $SnCl_2$, H_2O, THF (X = Cl, Br)	Syn 570 (1986)
NaI, HOAc (X = Br)	JOC *16* 573 (1951)
NaI, aq H_2SO_4 (X = Cl, Br, I)	TL *21* 3195 (1980)
NaI, Me_3SiCl (X = Cl, Br)	JOC *45* 3531 (1980)
NaI, $MeSiCl_3$ (X = Br)	JOC *48* 3667 (1983)
Me_3SiI (X = Cl, Br)	Syn Commun *11* 101 (1981)
PI_3 or P_2I_4 (X = Br, I)	TL *22* 1431 (1981)
Zn, H^+ (X = Br)	JACS *81* 3127, 3634, 3644 (1959) JOC *36* 1153 (1971)
Zn, H_2O, DMSO, C_6H_6 (X = Cl)	JOC *52* 5280 (1987)
Zn, HOAc (X = Cl, Br)	Ann *681* 196 (1965) JOC *37* 2363 (1972); *45* 2036 (1980); *48* 2590 (1983); *50* 3957 (1985); *52* 4772 (1987) JACS *101* 4003 (1979); *105* 2435 (1983)

Zn, HOAc, KI (X = Cl)	JACS *83* 3114 (1961)
Zn, HOAc, EtOH, TMEDA (X = Cl)	TL *28* 3299 (1987) (4,4-dichloro-cyclobutenones)
Fe graphite (X = Br)	JOC *47* 876 (1982)
$SnCl_2$, HCl (X = Br)	JACS *68* 1813 (1946)
$SnCl_2$, *i*-Bu_2AlH (X = Br)	CL 2069 (1984)
$TiCl_3$ (X = Cl, Br)	Syn Commun *3* 237 (1973) JACS *108* 1239 (1986) TL *28* 1541 (1987)
$Ti_2(SO_4)_3$ (X = Cl, Br)	TL *28* 1541 (1987)
VCl_2 (X = Cl, Br)	Syn 807 (1976)
$CrSO_4$, H_2O, DMF (X = Cl, Br)	JACS *85* 2768 (1963)
$CrCl_2$ (X = Br)	JACS *67* 1728 (1945) JCS 3869 (1953)
$CrCl_3$, $LiAlH_4$ (X = Br)	TL 3829 (1977)
$Ce_2(SO_4)_3$, NaI (X = Cl, Br)	Syn Commun *9* 241 (1979)
SmI_2, MeOH (X = Cl)	JOC *51* 1135 (1986)
$NaBH_4$, $Pd(OAc)_2$ or $Pd(NO_3)_2$ or $Hg(OAc)_2$ or $Ni(OAc)_2$ (X = Br)	TL 513 (1961)
$PhSiH_3$, cat $Mo(CO)_6$, (cat PPh_3), $NaHCO_3$ (X = Cl, Br)	JOC *52* 5570 (1987)
Ph_2SiH_2, cat $Pd(PPh_3)_4$ (X = Br)	JOC *52* 5570 (1987)
polymethylhydrosiloxane or NaO_2CH, cat $Pd(PPh_3)_4$, Δ (X = Br)	JOC *51* 734 (1986)
R_3SnH or R_2SnH_2 (R = *n*-Bu, Ph) (X = Cl, Br)	JOC *28* 2165 (1963)
n-Bu_3SnH (X = Cl)	JOC *52* 307 (1987)
Ph_3SnH (X = Cl, Br)	JOC *51* 5182 (1986)
$HFe(CO)_4^-$-polymer (X = Br)	JOC *43* 1598 (1978)
$(Et_4N)HFe_3(CO)_{11}$ (X = Br)	JOMC *171* 85 (1979)
$Fe(CO)_5$ (X = Br)	JOC *44* 641 (1979)
$Fe(CO)_5$, KOH (X = Br)	TL 2257 (1975)
$Fe_2(CO)_9$, H_2O, DMF (X = Br)	JACS *94* 7202 (1972); *100* 1759 (1978)
$Mo(CO)_6$, Al_2O_3 (X = Br)	JOC *44* 2568 (1979)
cat $Co_2(CO)_8$, NaOH, $(PhCH_2NEt_3)Cl$ (X = Br)	TL 2861 (1977)
$PhNMe_2$ (X = Br)	Chimia *21* 464 (1967)


(X = F, Cl, Br) — JOC *51* 5400 (1986) (α-halo aldehydes, ketones)


(X = F, Cl, Br) — JOC *52* 2142 (1987)

N-benzyl-1,4-dihydronicotinamide; cat $ClRh(PPh_3)_3$ or $Pd(OAc)_2$ (X = Cl, Br) — JOC *50* 3283 (1985)

Ph_2PH (X = Cl, Br) — JOC *34* 2687 (1969)

Ph_3P, MeOH, C_6H_6 (X = Cl, Br) — TL 471, 583 (1962); JACS *85* 2183 (1963); JCS 1379 (1965); JOC *31* 4031 (1966)

PhSH, iron polyphthalocyanine (X = Cl, Br) — CL 1241 (1975)

RS^- (X = Cl, Br, I) — BCSJ *44* 828 (1971); JOC *46* 2596 (1981)

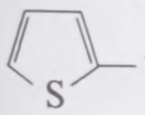
$NaHSO_3$ (X = I) — JACS *72* 362 (1950)

$Na_2S_2O_4$, H_2O, DMF (X = Cl, Br) — Syn Commun *12* 261 (1982)

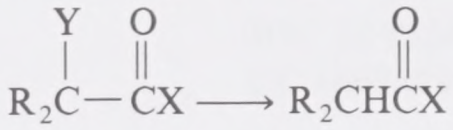
$C_5H_5N/Na_2S_2O_4$ (X = Cl, Br) — JOC *39* 562 (1974)

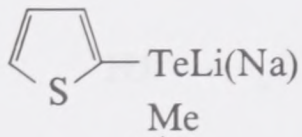
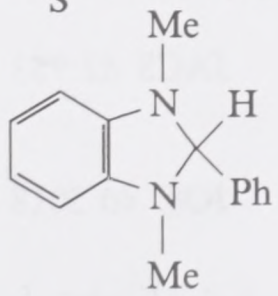
PhSeH, K_2CO_3 (X = I) — JOC *46* 2596 (1981)

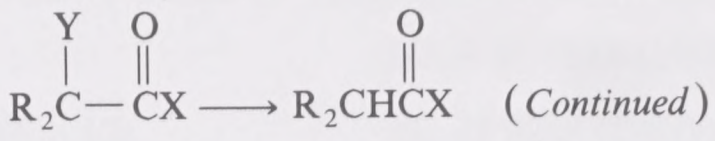
NaTeH (X = Cl, Br) — CL 119 (1983)


(X = Cl, Br, I) — JOC *47* 3946 (1982)

$(EtO)_2P(O)TeNa$ (X = Cl, Br) — JOC *47* 1124 (1982)



X	Y	Reagent(s)	
OH	Cl	Zn, HOAc	TL *28* 5339 (1987)
	Cl, Br		JOC *47* 3946 (1982)
			JOC *51* 5400 (1986)
OR	Cl	H_2, cat Pd-C	JOC *52* 3777 (1987)
		Zn, HOAc	TL *28* 5339 (1987)



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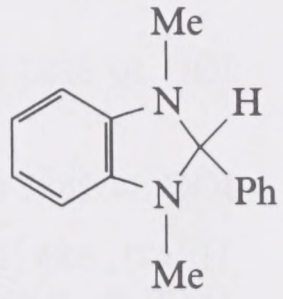
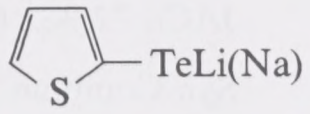
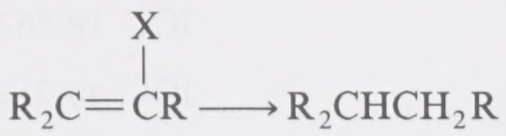
X	Y	Reagent(s)	
		$NaH_2PO_4 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O	JOC *50* 3408 (1985) (α,α-dihalo ester)
		NaI, $SnCl_2$, H_2O, THF	Syn 570 (1986)
		NaTeH	CL 119 (1983)
	Cl, Br	$PhSiH_3$, cat $Mo(CO)_6$, cat PPh_3, $NaHCO_3$	JOC *52* 5570 (1987)
			JOC *51* 5400 (1986)
	Br	SmI_2, CH_3OH	JOC *51* 1135 (1986)
		$HFe(CO)_4^-$-polymer	JOC *43* 1598 (1978)
$CONR_2$	Cl	Zn, HOAc	TL *28* 5339 (1987)
		$NaH_2PO_4 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O	JOC *50* 3408 (1985) (α,α-dihalo amide)
	Br	NaTeH	CL 119 (1983)
			JOC *47* 3946 (1982)

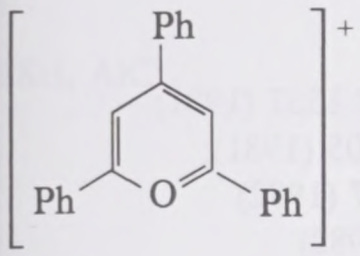


H_2, cat Pd-C	Can J Chem *37* 1870 (1959) JACS *104* 2198 (1982); *109* 4752 (1987)
Li, NH_3, EtOH	TL *28* 3209 (1987)

6. Amines

$$RNH_2 \longrightarrow RH$$

RSO_2Cl (R = Ph, *p*-Tol, Me)/H_2NOSO_3H, NaOH	JACS *82* 753 (1960); *86* 1152 (1964)
RSO_2Cl (R = CF_3, *p*-Tol, *p*-BrC_6H_4, *p*-$NO_2C_6H_4$) (disulfonimide)/$NaBH_4$, HMPA	JOC *40* 2018 (1975); *43* 2259 (1978)
H_2NOSO_3H, OH^-	JACS *100* 341 (1978)

$MeCO_2CHO/POCl_3/n\text{-}Bu_3SnH$, AIBN	JACS *90* 4182 (1968) TL 2291 (1979) CC 345 (1979) Syn 68 (1980)
 $ClO_4^-/NaBH_4/\Delta$	TL 2689 (1976)
HNF_2	JACS *85* 97 (1963); *86* 2233 (1964)
$NaNO_2$, H_3PO_2, cat Cu_2O (R = aryl)	JACS *108* 1000 (1986)
i-AmONO, H_2SO_4, hydroquinone, dioxane (R = aryl)	CC 605 (1973)
n-AmONO, THF (R = aryl)	JCS Perkin I 541 (1973)
RONO (R = *t*-Bu, $PhCH_2$), DMF (R = aryl)	JOC *42* 3494 (1977)

$$ArNH_2 \longrightarrow (ArN_2)X \xrightarrow[\text{agent}]{\text{reducing}} Ar{-}H$$

Review: Org Rxs *2* 262 (1944)

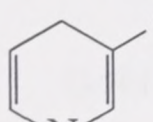
H_3PO_2	JACS *71* 2137 (1949); *72* 3013 (1950); *76* 290 (1954) Org Syn Coll Vol *3* 295 (1955); *4* 947 (1963)
H_3PO_3	JACS *74* 3074 (1952)
$Ca(H_2PO_2)_2$	Ber *35* 162 (1902)
$NaBH_4$, DMF	JACS *83* 1251 (1961)
Et_3SiH or $n\text{-}Bu_3SnH$	Tetr *26* 4609 (1970)
$SnCl_2$, NaOH	JACS *64* 376 (1942)
cat $ClRh(PPh_3)_3$ or $ClRh(CO)(PPh_3)_2$, DMF	JOC *36* 1725 (1971)
cat Cu_2O, dioxane	JOC *32* 3844 (1967)
$NaOCH_3$, CH_3OH	JOC *33* 1924 (1968) CC 1469 (1971)
KO-*t*-Bu, *t*-BuOH, Et_2O	JOC *33* 1924 (1968)
PhSH	CL 1051 (1979)
H_2CO	JACS *61* 2418 (1939)
HMPA	JOC *39* 1317 (1974)
DMF	Ind J Chem B *20* 767 (1981)
$Me_2NCONMe_2$	JOC *28* 568 (1963) Ind J Chem B *20* 767 (1981)
various ethers and 3° amines	Angew *70* 211 (1958)

$$ArCH_2NR_2 \xrightarrow[\text{catalyst}]{H_2} ArCH_3$$

Review: Org Rxs *7* 263 (1953)

7. Nitro Compounds

$$RNO_2 \longrightarrow RH$$

Reagent(s)	R	
n-Bu_3SnH, AIBN	3° alkyl, 2° α-ketoalkyl, 1° allylic or benzylic	JACS *103* 1557 (1981) TL *22* 1705 (1981); *23* 2957 (1982) CC 33 (1982) JOC *50* 3692 (1985); *51* 2832 (1986); *52* 5061 (1987) Tetr *41* 4013 (1985) Syn 693 (1986) (review)
$AlCl_3$ or $SnCl_4$, Et_3SiH	benzylic, α- or β-thiophenyl alkyl	TL *28* 2277 (1987)
NaTeH, EtOH	3° alkyl	BCSJ *58* 1067 (1985)
NaSMe, DMF or HMPA	3° alkyl	JACS *100* 289 (1978); *101* 647 (1979)
KOH, $HOCH_2CH_2OH$, Δ	2°, 3° alkyl	TL 3203 (1971); 1243 (1979)
 , hν	α-cyano, -keto or -ester	JACS *102* 2851 (1980); *105* 4017 (1983)

$$R_2CCH{=}CH_2 \xrightarrow[\text{cat } Pd(PPh_3)_4]{(NH_4)O_2CH,\ PPh_3} R_2CHCH{=}CH_2$$

JOC *51* 3734 (1986);

See page 115, Section 4 for reduction with double bond transposition.

8. Ethers

$$ROR' \xrightarrow[\text{2. Zn, HOAc}]{\text{1. } Me_3SiCl,\ NaI} RH$$

R′ = Me, $SiMe_3$; R = 1°, 2° alkyl or benzylic

Syn 32 (1981)

$$RCH{=}CHCH_2OR' \xrightarrow[\text{cat } Pd(PPh_3)_4]{LiHBEt_3} RCH{=}CHCH_3$$

R′ = Me, Ph, $SiMe_2(t\text{-Bu})$

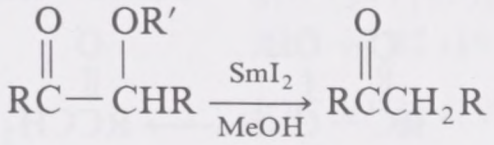
JOC *47* 4380 (1982)

$$RCH{=}CHCH_2OPh \textit{ or } RCHCH{=}CH_2 \xrightarrow[\text{cat } PdCl_2(PPh_3)_2]{(Et_3NH)O_2CH} RCH_2CH{=}CH_2$$

TL 613 (1979)

$$ArOR \longrightarrow ArH$$

K, THF	CC 1549 (1987)
Na, ROH	Ber *69* 1643 (1936) Can J Chem *52* 2136 (1974)
EtSH, $AlCl_3$	TL *23* 689 (1982)



$R' = Me, SiMe_3, Ts$

JOC *51* 1135 (1986)
TL *28* 3065 (1987)

9. Alcohols and Phenols

9.1. Direct Reduction

H_2, cat PtO_2, CF_3CO_2H	JOC *29* 2325 (1964) (3° alkyl)
Li, NH_3, NH_4Cl	JOC *40* 3151 (1975) (1°, 2°, 3° benzylic)
K, $Fe(CO)_5$/HCl	TL *21* 801 (1980) (2°, 3° benzylic)
$BH_3 \cdot py$, CF_3CO_2H	Chem Pharm Bull *27* 2405 (1979) (2° benzylic)
BH_3, $BF_3 \cdot OEt_2$	TL 1849 (1967) (3° benzylic cyclopropyl)
$NaBH_4$, $BF_3 \cdot OEt_2$	Proc Chem Soc 357 (1962) (2° benzylic) J Sci Ind Res B *21* 583 (1962) (2° benzylic)
$NaBH_4$, $PdCl_2$	CL 1029 (1981) (benzylic)
$NaBH_4$, CF_3CO_2H	Syn 172 (1977) (2°, 3° benzylic)
$NaBH_3CN$, ZnI_2	JOC *51* 3038 (1986) (1°, 2° benzylic; 2° allylic; 3° alkyl)
$LiAlH_4$, $AlCl_3$	JOC *29* 121 (1964) (3° alkyl, benzylic) TL 2447 (1967) (allylic)
$AlCl_3$, cat Pd-C, 	Syn 397 (1978) (1°, 2°, 3° benzylic)
$AlCl_3$, EtSH	TL *23* 689 (1982) (polycyclic ArOH)
R_3SiH, BF_3	TL 2955 (1976) (2° alkyl; 3° benzylic)
R_3SiH (R = Ph, Et), HOAc	JACS *90* 2578 (1968) (benzylic)
Et_3SiH, CF_3CO_2H	JOC *34* 4 (1969) (3° benzylic); *36* 758 (1971) (3° alkyl); *52* 2226 (1987) (2° benzylic) JACS *91* 2967 (1969) (3° alkyl; benzylic) J Gen Chem USSR *43* 2294 (1973) (2° ferrocenyl carbinol) Syn 633 (1974) (review)

Me_3SiCl, NaI, CH_3CN, hexane	TL *28* 3817 (1987) (2°, 3° benzylic)
Me_3SiCl, NaI/Zn, HOAc	Syn 32 (1981) (1°, 2° alkyl or benzylic)
Me_2SiI_2	TL 4941 (1979) (2°, 3° benzylic)
P_2I_4	CL 247 (1983) (1°, 2°, 3° benzylic)
PPh_3, I_2	Ber *109* 1586 (1976) (1° allylic, 2° benzylic)

$$RC(=O)-CHR(OH) \longrightarrow RCCH_2R(=O)$$

HI, HOAc, H_2O	JACS *109* 4690 (1987)
Zn, HOAc	JCS 3045 (1954)
SmI_2, Ac_2O	JOC *51* 1135 (1986) JACS *109* 4424 (1987)
$Me_3SiI/Na_2S_2O_3$, H_2O	Syn Commun *9* 665 (1979)
P, I_2	Syn 161 (1975)
Ph_2PLi/HOAc, MeI	JOC *51* 2378 (1986)

9.2. Via Phosphorus Compounds

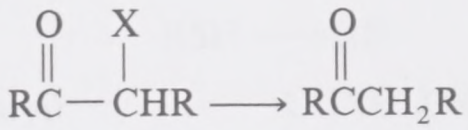
$$ROH \xrightarrow[2.\ ClPOX_2]{1.\ NaH\ or\ RLi} ROPX_2(=O) \xrightarrow{Reagent(s)} RH$$

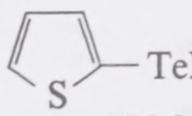
X	Reagent(s)	
OEt	electrolysis	JOC *44* 4508 (1979) (phenol)
	Li, NH_3, Et_2O	JOC *42* 344 (1977) (phenol)
	Li or Na, NH_3	JCS 522 (1955) (phenol)
	Li, Na or K; NH_3; Et_2O	JOC *38* 2314 (1973) (phenol)
	Ti, THF	JOC *43* 4797 (1978) (phenol)
NMe_2	Li, NH_3	JOC *45* 1172 (1980) (2° alcohol)
	Li, NH_3, EtOH, THF	JACS *94* 5098 (1972) (2° alcohol)
	Li, $MeNH_2$	CC 1342 (1987) (1° alcohol)
	Li, $EtNH_2$	JACS *94* 5098 (1972) (2° alcohol)
	Li, $EtNH_2$, *t*-BuOH, THF	JACS *94* 5098 (1972) (1°, 2°, 3° alcohol); *108* 3835 (1986) (3° alcohol) TL *28* 2863 (1987) (1° alcohol)

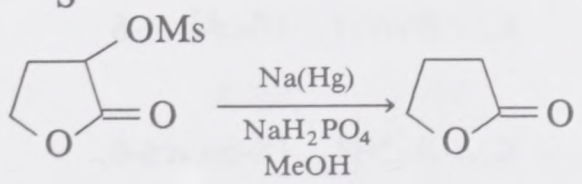
9.3. Via Sulfonates

MsCl/electrolysis (1°, 2° alkyl)	TL 2157 (1979)
Me_2NSO_2Cl/Na, NH_3 (2° alkyl)	TL 3365 (1978)
TsCl or MsCl/NaI, Zn (1°, 2° alkyl)	TL 3325 (1976) Coll Czech Chem Commun *44* 246 (1979) JACS *107* 2471 (1985)

MsCl/KO-*t*-Bu/H_2, cat Pd-C (2° alkyl)	JOC *47* 2685 (1982)
MsCl/$NaBH_4$, *t*-BuOH, $CH_3OCH_2CH_2OCH_3$ (1° alkyl)	JOC *52* 1309 (1987)
TsCl/$NaBH_4$, DMSO or HMPA or sulfolane (1°, 2° alkyl)	JOC *43* 2259 (1978)
TsCl/$NaBH_3CN$ (1° alkyl; benzylic)	Syn 135 (1975) JOC *42* 82 (1977)
TsCl/(*n*-Bu_4N)BH_3CN (1° alkyl)	JOC *42* 82 (1977)
TsCl/$LiHBEt_3$ (1°, 2° alkyl)	JOC *41* 3064 (1976); *45* 1 (1980); *50* 2668, 5646 (1985) JOMC *156* 171 (1978) Carbohydr Res *110* 19 (1982) JACS *108* 468 (1986); *109* 6858, 8102 (1987) CC 1786 (1987)
MsCl/$LiHBEt_3$ (1°, 2° alkyl)	JOC *42* 2166 (1977) CC 1139 (1987) JACS *109* 6858 (1987) TL *28* 5161 (1987)
$C_5H_5N \cdot SO_3$/$LiAlH_4$ (allylic, benzylic)	JOC *34* 3667 (1969) TL 1837 (1969); *27* 4813 (1986) JACS *92* 6636, 6637 (1970)
TsCl or MsCl/$LiAlH_4$ (1°, 2° alkyl)	JACS *73* 2872 (1951); *77* 1820 (1955); *92* 553 (1970); *107* 686 (1985) JOC *47* 2685 (1982); *52* 4776 (1987)
TsCl/$LiAlH_4$, LiH (1° alkyl)	JACS *108* 468 (1986)
MsCl/2 $LiHAl(OMe)_3$, CuI (1°, 2° alkyl)	JACS *95* 6452 (1973)
TsCl or MsCl/LiHCu(*n*-Bu) (1°, 2° alkyl; allylic)	JACS *96* 3686 (1974)
TsCl/Li_4CuH_5 (1° alkyl)	JOC *43* 183 (1978)
$(R_fSO_2)_2$/cat $(Ph_3P)_2PdCl_2$ or $Pd(PPh_3)_4$, *n*-Bu_3N, HCO_2H (aryl)	CC 1452 (1986)



X	Reagent(s)	
OTs	SmI_2, MeOH	JOC *51* 1136 (1986)
OMs		JOC *47* 3946 (1982)



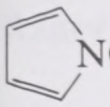
JACS *109* 1564 (1987)

9.4. Via Other Derivatives

$$ROH \longrightarrow ROX \xrightarrow[\text{agent}]{\text{reducing}} RH$$

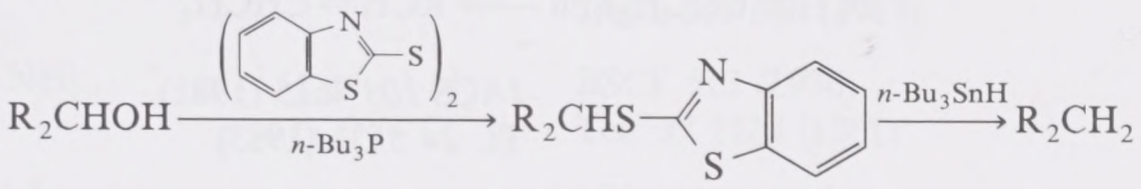
Review: Pure Appl Chem *53* 15 (1981)

X	Reducing Agent	
PhC=S	*n*-Bu_3SnH	JCS Perkin I 1574 (1975) (2° alkyl); 885 (1980) (2° alkyl) JOC *46* 4300 (1981) (2° alkyl)
ClC=O	*n*-Pr_3SiH, (*t*-BuO)$_2$, Δ	JCS Perkin I 1207 (1980) (1°, 2° alkyl)
R′OC=S	*n*-Bu_3SnH	JCS Perkin I 1718 (1977) (2° alkyl)
PhOC=S	*n*-Bu_3SnH	JACS *103* 932 (1981); *105* 4059 (1983) (both 2° alkyl) JOC *52* 3706 (1987) (2° alkyl)
PhSC=S	*n*-Bu_3SnH	Chem Pharm Bull *26* 1786 (1978) (2° alkyl)
MeSC=S	*n*-Bu_3SnH	JCS Perkin I 1574 (1975); 1718 (1977) (both 2° alkyl) Austral J Chem *30* 1269 (1977) (2° alkyl) Chem Pharm Bull *26* 1786 (1978) (2° alkyl) JACS *101* 6116 (1979) (2° alkyl); *108* 3443 (1986) (2° alkyl) Nouv J Chim *4* 59 (1980) (2° alkyl) Org Syn *64* 57 (1985) (2° alkyl) JOC *51* 2148 (1986) (2° alkyl); *52* 1057 (2° benzylic), 3096 (2° alkyl), 4647 (2° alkyl) (1987) TL *27* 2679 (2° alkyl), 3057 (2° alkyl) (1986); *28* 3615 (2° alkyl), 3883 (2° alkyl) (1987) CC 1351 (2° alkyl), 1802 (2° alkyl) (1987)
	K, *t*-$BuNH_2$, 18-crown-6	CC 1175 (1979) (1°, 2° alkyl) TL *28* 2937 (1987) (2° alkyl)
$R_2NC{=}S$	K, *t*-$BuNH_2$, 18-crown-6	CC 1175 (1979) (1°, 2° alkyl) JCS Perkin I 1510 (1981) (1°, 2° alkyl)

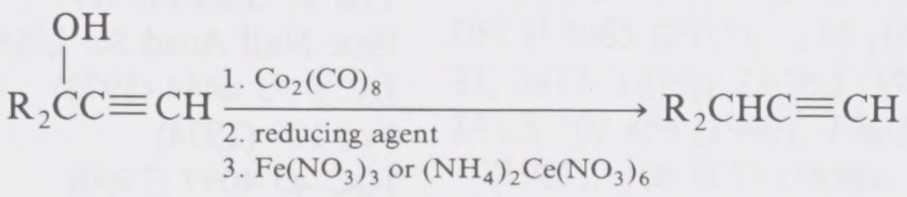


	n-Bu_3SnH	JCS Perkin I 1574 (1975) (1°, 2° alkyl); 1109 (1984) (2° alkyl) JOC *46* 4843 (1981) (2° alkyl) TL *24* 865 (1983) (2° alkyl); *28* 6425 (1987) (2° alkyl)
	n-Bu_3SnH, cat $Pd(PPh_3)_4$	JACS *107* 2471 (1985) (2° allylic)
R′N=CNHR′	H_2, cat Pd-C	Ber *107* 1353 (1974) (1°, 2°, 3° alkyl; benzylic)

See also page 41, Section 15.



TL *27* 5385 (1986)



$BH_3 \cdot SMe_2$, CF_3CO_2H	Syn Commun *16* 1535 (1986) TL *28* 1857 (1987)
$NaBH_4$, CF_3CO_2H	JACS *107* 4999 (1985)

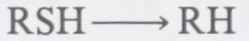
10. Sulfur Compounds

See also pages 28–31, Sections 9.3 and 9.4, for reduction of sulfur-containing derivatives of alcohols and phenols.

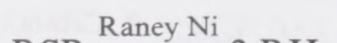
Raney nickel reviews:

E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., New York (1958), Vol 1, p 115

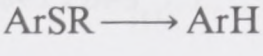
N. Kharasch and C. Y. Meyers, "The Chemistry of Organic Sulfur Compounds," Pergamon Press, New York (1966), Vol 2, p 35



R_2CHMgX, cat $NiCl_2$-PPh_3 (R = aryl)	CC 840 (1982)
$Mo(CO)_6$, HOAc or SiO_2 (R = alkyl, aryl)	CC 169 (1980)
$P(OEt)_3$, hν (R = 1° alkyl, benzyl)	JACS *78* 6414 (1956)



TL *28* 1799 (1987)



Raney Ni	TL *26* 39 (1985); *28* 1459 (1987)
R_2CHMgX, cat $NiCl_2$-PPh_3 (R = Me)	CC 840 (1982)

$AlCl_3$, EtSH (R = Et, *i*-Pr; Ar = polycyclic) TL *23* 689 (1982)

$$R_2C{=}CRSR' \xrightarrow[LiAlH_4]{TiCl_4} R_2CHCH_2R$$

CL 291 (1973)

$$R_2C{=}CRSR' \xrightarrow[\text{Ni catalyst}]{R_2CHMgX} R_2C{=}CHR$$

TL *22* 3463 (1981)
CC 840 (1982)

$$RCH{=}CHCH_2SPh \longrightarrow RCH{=}CHCH_3$$

Li, NH_3 JACS *103* 4615 (1981)
TL *24* 5531 (1983)

Li, $EtNH_2$ TL 3707 (1969)
Tetr *27* 5861 (1971)
Proc Natl Acad Sci USA *68* 1294 (1971)
JACS *95* 4444 (1973)
Syn 129 (1974)
JOC *45* 4097 (1980)

Na, *i*-PrOH, THF TL *28* 5665 (1987)

$LiHBEt_3$, cat $Pd(PPh_3)_4$ JOC *47* 4380 (1982)

$$\begin{array}{l} \text{SAr} \\ | \\ RCHC{\equiv}CH \end{array} \xrightarrow[NH_3]{Li} RCH_2C{\equiv}CH$$

JOC *46* 5041 (1981)

$$RR'CHSAr \longrightarrow RR'CH_2$$

Raney Ni Tetr *37* 4027 (1981)
Syn 937 (1982)

$LiAlH_4$, $TiCl_4$ CL 291 (1973)

$LiAlH_4$, $CuCl_2$ BCSJ *44* 2285 (1971)

$$ArSAr \longrightarrow 2\ ArH$$

$Mo(CO)_6$, SiO_2 Pure Appl Chem *52* 607 (1980)

$TiCl_4$, $LiAlH_4$ CL 291 (1973)

$$ArSOCH_3 \xrightarrow[\text{cat } NiCl_2\text{-}PPh_3]{R_2CHMgX} ArH$$

CC 840 (1982)

$$R_2CHSOAr \longrightarrow R_2CH_2$$

Al(Hg) JOC *46* 5244 (1981)

Raney Ni — CC 1688 (1986)

$$ArSO_2CH_3 \xrightarrow[\text{cat } NiCl_2\text{-}PPh_3]{R_2CHMgX} ArH$$

CC 840 (1982)

$$R_2CHSO_2Ar \longrightarrow R_2CH_2$$

Li, $EtNH_2$	JOC *39* 2135 (1974) BSCF 513 (1976) JCS Perkin I 761 (1981) CL 25, 1711 (1981) JACS *107* 686 (1985)
Li, $H_2NCH_2CH_2NH_2$	BSCF 513 (1976) Tetr *37* 1233 (1981)
Na(Hg), MeOH, (phosphate)	JCS 4881 (1952) JOC *38* 2747 (1973); *51* 5100 (1986) BSCF 3065 (1973); 1363 (1975); 513, 525 (1976) TL 3477 (1976); *28* 813 (1987) JACS *102* 853 (1980); *106* 3811 (1984); *107* 2033 (1985); *108* 1035 (1986); *109* 6205 (1987) JCS Perkin I 761 (1981) Syn 55 (1981) CC 451 (1986)
Na, EtOH	CL 2105 (1984) TL *27* 4817 (1986)
Raney Ni	BSCF 525 (1976)

$$RCH{=}CHSO_2Ar \longrightarrow RCH{=}CH_2$$

Na(Hg), Na_2HPO_4, MeOH	TL *27* 2187 (1986)
Al(Hg), H_2O	CC 351 (1973)
$LiAlH_4$, $CuCl_2$	CC 351 (1973)
n-BuMgCl, cat $Ni(acac)_2$	TL *28* 6273 (1987)
RMgX (R = *i*-Pr, *n*-Bu), Ni or Pd catalyst	TL *24* 4311 (1983)
$Na_2S_2O_4$, H_2O	TL *23* 3265 (1982)

$$RCH{=}CHCH_2SO_2Ph \longrightarrow RCH{=}CHCH_3$$

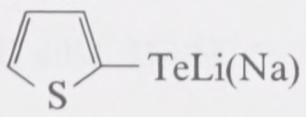
Li, $EtNH_2$	JOC *39* 2135 (1974) BSCF 513 (1976) JCS Perkin I 761 (1981) CL 25 (1981)
Li, $H_2NCH_2CH_2NH_2$	BSCF 513 (1976)
Na, EtOH	BCSJ *55* 1325 (1982)
Na(Hg), CH_3OH	BSCF 513 (1976)

$Na(Hg)$, CH_3OH, Na_2HPO_4	JCS Perkin I 761 (1981) JOC *51* 5100 (1986)
$LiHBEt_3$, cat $Pd(PPh_3)_4$	JOC *47* 4380 (1982)

$$R_2C(SR)_2 \longrightarrow R_2CH_2$$

Li, $EtNH_2$	JCS 4413 (1960)
Na, NH_3, EtOH	JACS *80* 4604 (1958)
Raney Ni	JACS *66* 909 (1944); *84* 2938 (1962); *109* 3025 (1987) Can J Chem *37* 1870 (1959) Org Rxs *12* 356 (1962) Chem Rev *62* 347 (1962) JOC *33* 3551 (1968); *50* 2359, 2607 (1985); *52* 2875, 3346 (1987)
$LiAlH_4$, Δ	JACS *86* 478 (1964)
$LiAlH_4$, $TiCl_4$	CL 291 (1973)
$LiAlH_4$, $CuCl_2$	BCSJ *44* 2285 (1971)
$LiAlH_4$, $CuCl_2$, $ZnCl_2$	Int J Sulfur Chem *7* 173 (1972)
n-Bu_3SnH, AIBN	JOC *45* 3393 (1980)
N_2H_4, KOH	JACS *81* 5834 (1959)

$$\begin{array}{c} X \\ | \\ YCHR \longrightarrow YCH_2R \end{array}$$

X	Y	Reagent(s)	
SR	COR	Li, NH_3/H_2O	Syn Commun *3* 265 (1973)
		Na(Hg), Na_2HPO_4, MeOH	TL 3477 (1976)
		Zn, NH_4Cl, H_2O	JOC *52* 2317 (1987)
		Zn, Me_3SiCl	Syn Commun *7* 427 (1977)
		Raney Ni	Syn Commun *3* 265 (1973) JOC *47* 4384 (1982); *50* 2589 (1985) CC 717 (1985)
		SmI_2, MeOH	JOC *51* 1135 (1986)
		NaSR	BCSJ *44* 828 (1971)
			JOC *47* 3946 (1982)
	CO_2R	Li, NH_3/H_2O	Syn Commun *3* 265 (1973)
		Raney Ni	CC 717 (1985)
		NaSR	BCSJ *44* 828 (1971)
	CN	Li, naphthalene/H_2O	Syn Commun *3* 265 (1973)
SOPh	COR	Al(Hg), H_2O	JACS *103* 2886 (1981); *104* 4180 (1982) JOC *46* 5244 (1981)
		Zn, NH_4Cl, H_2O	JOC *52* 2317 (1987)
		SmI_2, MeOH	JOC *51* 1135 (1986)
	CO_2R	Al(Hg), H_2O	JACS *103* 2886 (1981)

SO_2Ph	COR	Al(Hg), H_2O	JOC *45* 4002 (1980); *49* 1246 (1984)
		Al(Hg), Na_2HPO_4, MeOH	TL *28* 5017 (1987)
		SmI_2, MeOH	JOC *51* 1135 (1986)
	CO_2R	Na(Hg), Na_2HPO_4, MeOH	TL 3477 (1976)

11. Selenium Compounds

See also page 39, Section 12.7.

$$RSeR' \longrightarrow RH$$

$$R' = Me, Ph$$

Li, $EtNH_2$	TL 2643 (1976)
Raney Ni	TL 2643 (1976)
Ph_3SnH	CC 41 (1978) JACS *102* 4438 (1980)

$$RCH{=}CHCH_2SePh \xrightarrow[\text{cat } Pd(PPh_3)_4]{LiHBEt_3} RCH{=}CHCH_3$$

JOC *47* 4380 (1982)

$$R_2C(SeR')_2 \longrightarrow R_2CH_2$$

Li, $EtNH_2$	TL 2643 (1976)
Raney Ni	TL 2643 (1976)
Ph_3SnH	JACS *102* 4438 (1980) TL *22* 1623 (1981)

12. Aldehydes and Ketones

12.1. Direct Reduction

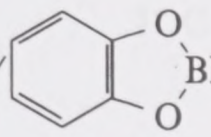
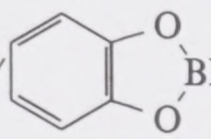
$$RCHO\ (R_2CO) \longrightarrow RCH_3\ (R_2CH_2)$$

H_2, various catalysts (aryl aldehydes and ketones)	Org Rxs *7* 263 (1953) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York (1965)
H_2, cat Pd-C (aryl ketones)	Can J Chem *49* 2712 (1971) Tetr *38* 3555 (1982) Syn 940 (1982)
D_2, cat Pd-C, DOAc (aryl ketones)	JOC *52* 2938 (1987)
H_2, cat PtO_2 (aryl ketones)	TL *23* 2415 (1982)

cyclohexene or limonene, cat Pd-C, $FeCl_3$ (aryl aldehydes or ketones)	CC 757 (1976)
Raney Ni, aq EtOH (aryl aldehydes and ketones)	TL *21* 2637 (1980)
HI, P (diaryl ketone)	JOC *13* 786 (1948)
HI, P, I_2 (aryl ketones)	Ber *92* 1705 (1959) Can J Chem *52* 1229 (1974)
Li, NH_3/NH_4Cl (aryl ketones)	JOC *36* 2588 (1971)
Zn, HCl	CC 919 (1969)
Zn, HCl, H_2O	Org Rxs *1* 155 (1942) JACS *76* 6368 (1954) Angew *71* 726 (1959) Quart Rev *23* 522 (1969) CC 893 (1986) (mechanism)
Zn, HCl, Ac_2O	JCS C 2887 (1968)
Zn, NaOH or KOH (diaryl ketones)	JOC *51* 3502 (1986); *52* 3205 (1987)
BH_3 (diaryl ketone)	J Sci Ind Res B *21* 583 (1962)
$BH_3 \cdot py$, CF_3CO_2H (aryl ketones)	Chem Pharm Bull *27* 2405 (1979)
BH_3, $BF_3 \cdot OEt_2$ (cyclopropyl or aryl ketones)	TL 1849 (1967)
$NaBH_4$, $BF_3 \cdot OEt_2$ (aryl ketones)	Proc Chem Soc 357 (1962) J Sci Ind Res B *21* 583 (1962)
$NaBH_4$, $AlCl_3$ (diaryl ketone)	J Sci Ind Res B *21* 583 (1962)
$NaBH_4$, CF_3CO_2H (aryl ketones)	Syn 763 (1978) JOC *50* 5451 (1985)
$NaBH_4$, $PdCl_2$ (aryl ketones)	CL 1029 (1981)
$NaBH_3CN$, ZnI_2 (aryl aldehydes and ketones)	JOC *51* 3038 (1986)
$LiAlH_4$, $AlCl_3$ (allyl or aryl ketones)	JCS 3755 (1957); 1406 (1960); 1405 (1961); 1658 (1962) JACS *80* 2896 (1958) Tetr *21* 2641 (1965) TL *28* 2937 (1987)
Et_3SiH, BF_3 (ketones and aryl aldehydes)	JOC *43* 374 (1978) Org Syn *60* 108 (1981)
Et_3SiH, $BF_3 \cdot OEt_2$ (enone)	JOC *52* 1984 (1987)

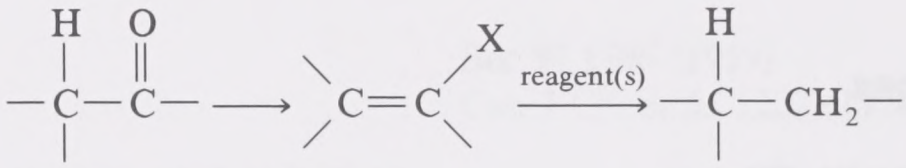
Et_3SiH, CF_3CO_2H (aryl aldehydes and ketones)	Bull Acad Sci USSR, Div Chem Sci 1245 (1966) Tetr *23* 2235 (1967) JOC *38* 2675 (1973) Syn 633 (1974) (review)
$PhSiMe_2H$, CF_3CO_2H (aryl aldehydes)	JOC *38* 2675 (1973)

12.2. Via Hydrazones

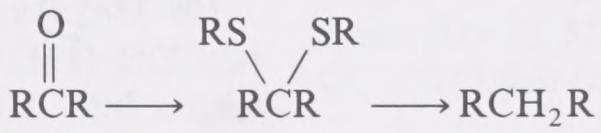
NH_2NH_2, K_2CO_3, $(HOCH_2CH_2)_2O$	JACS *105* 7352, 7358 (1983); *106* 6690, 6702 (1984)
NH_2NH_2, K_2CO_3, $HO(CH_2CH_2O)_3H$	JOC *48* 1404 (1983)
NH_2NH_2, KOH, $(CH_2OH)_2$	Org Rxs *4* 378 (1948) JACS *71* 3301 (1949); *107* 7978 (1985); *108* 3385 (1986) JCS 2056 (1955) Angew Int *7* 120 (1968)
NH_2NH_2, $HO(CH_2CH_2O)_nH$ ($n = 2$ or 3), NaOH or KOH	JACS *68* 2487 (1946) Ind J Chem *2* 229 (1964) JOC *50* 2359 (1985); *52* 3205 (1987)
NH_2NH_2, KO-*t*-Bu	JOC *51* 5019 (1986)
$TsNHNH_2/BH_3$	BCSJ *47* 2323 (1974)
$TsNHNH_2$/  /$NaOAc \cdot 3\ H_2O$	JOC *40* 1834 (1975) Syn 124 (1977) JACS *107* 5732 (1985)
$TsNHNH_2$/  /MeOH/*n*-Bu_4NOAc	Syn Commun *9* 275 (1979)
$TsNHNH_2/(PhCO_2)_2BH/NaOAc \cdot 3\ H_2O$	JOC *46* 1217 (1981)
$TsNHNH_2/(PhCO_2)_2BH/NaOH$	JACS *107* 1721 (1985)
$TsNHNH_2/NaBH_4$	Chem Ind 153, 1689 (1964) Ber *98* 3236 (1965) Org Syn *52* 122 (1972) BCSJ *47* 2323 (1974) TL *28* 4759 (1987)
$TsNHNH_2/NaBH_3CN$ (aliphatic aldehydes and ketones only)	JACS *93* 1793 (1971); *95* 3662 (1973); *106* 2115 (1984); *109* 7270 (1987) Syn 35 (1975) Org Prep Proc Int *11* 201 (1979) JOC *50* 2607 (1987)
$TsNHNH_2/NaBH_3CN$, $ZnCl_2$ (aliphatic aldehydes and ketones only)	JOC *50* 1927 (1985)

$TsNHNH_2/LiAlH_4$	Tetr *19* 1127 (1963); *22* 487 (1966) Ber *98* 3236 (1965)
$2,4,6\text{-}(i\text{-}Pr)_3C_6H_2SO_2NHNH_2/CuBH_4(PPh_3)_2$	TL *21* 4031 (1980)

12.3. Via Oxygen and Sulfur Derivatives

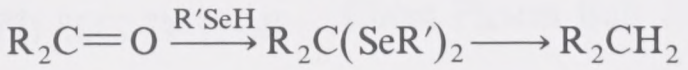


X	Reagent(s)	
OSO_2CF_3	H_2, cat Pd-C	TL *23* 117 (1982)
$OPO(OEt)_2$	H_2, cat Pt-C	JACS *104* 2198 (1982)
	Li, *t*-BuOH, $EtNH_2$	JACS *108* 5650 (1986)



See page 31, Section 10.

12.4. Via Selenium Derivatives



See page 35, Section 11.

12.5. Decarbonylation



Review: Syn 157 (1969)

Reagent(s)	R	
R′SH, hν	alkyl	JACS *85* 4010 (1963)
$Fe(CO)_5$	vinylic	TL 447 (1973)
cat $ClRh(PPh_3)_3$	alkyl, aryl, vinylic	TL 3969 (1965); 2173 (1967); 1899 (1968); 2145 (1969); 823 (1970); *28* 5669 (1987) CC 129 (1966); 856 (1974) JACS *89* 2338 (1967); *90* 99 (1968); *93* 5465 (1971); *95* 1229, 2038, 7862 (1973); *106* 1421, 5312, 6364 (1984) JCS A 348 (1968); 612 (1969) JOC *41* 2288 (1976); *45* 315 (1980); *52* 3303 (1987) JCS Perkin I 700 (1977)

cat $ClRh(Ph_2PCH_2CHRPPh_2)_2$ (R = H, Me)	aryl	JACS *100* 7083 (1978) Fund Res Homogeneous Catal *3* 909 (1979) JOC *49* 3195 (1984)
cat $(Ph_3P)_2Rh(CO)Cl$, $Ph_2P(CH_2)_3PPh_2$	alkyl	TL *28* 6089 (1987)
cat Pd-C	alkyl, aryl	JOC *25* 2215 (1960); *52* 1201 (1987)

12.6. Ketone Cleavage

$$RCR' \xrightarrow{\text{base}} RH + H_2NCR'$$

$NaNH_2$	Org Rxs *9* 1 (1957) (review)
$NaNH_2$, DABCO	Syn 395 (1975)
MNH_2 (M = Li, Na, K) or KO-*t*-Bu	JACS *109* 6858 (1987)

12.7. Reductive Coupling

$$RCR \xrightarrow[\text{or ArMgX}]{\text{ArLi}} \xrightarrow[NH_4Cl]{Li,\ NH_3} R_2CHAr$$

JOC *40* 271, 3306 (1975); *41* 3465 (1976); *46* 4139, 5060 (1981)

$$ArCR \xrightarrow{R'Li} \xrightarrow[NH_4Cl]{Li,\ NH_3} ArCHRR'$$

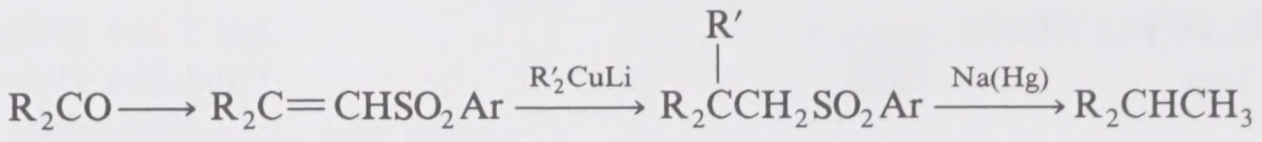
JOC *38* 1735, 1738 (1973); *41* 1494 (1976)
Org Syn *55* 7 (1976)

$$RCR \longrightarrow R_2C(CH_3)_2$$

$(CH_3)_3Al$	JOC *35* 532 (1970) CC 595 (1972)
$(CH_3)_2TiCl_2$ or $(CH_3)_2TiCl_2$-$TiCl_4$ or $(CH_3)_2Zn$	CC 237 (1981) JOC *48* 254 (1983)
$(CH_3)_2Zn$, $TiCl_4$	JOC *50* 5727 (1985) (enone)

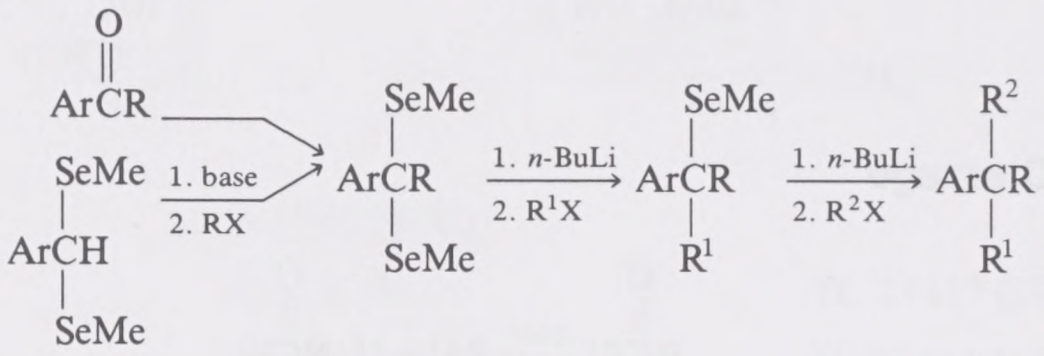
$$ArCR \xrightarrow[2.\ MeTiCl_3,\ Me_2TiCl_2]{1.\ R'Li} ArC(R')(CH_3)R$$

JOC *48* 254 (1983)



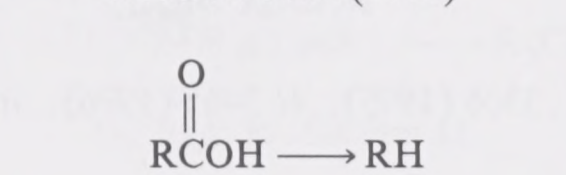
Ar = *p*-ClC_6H_4

JOC *38* 2747 (1973)



TL *27* 1719, 1723 (1986)

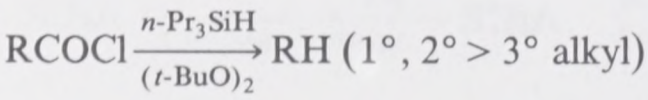
13. Carboxylic Acids



JACS *92* 3232 (1970)

hν (R = ArCONRCHR)	Syn 141 (1982)
R_2CO, Δ (RH = tryptamine)	Heterocycles *6* 1167 (1977)
Cu, quinoline, Δ (R = ArCH=CH)	Org Syn Coll Vol *4* 732 (1963)
Cu chromite, quinoline, Δ (R = heterocyclic)	TL *27* 3045 (1986)
Cu_2O (R = stabilized carbanion)	Tetr *40* 3229 (1984)
H_2, cat Ni or Pd, Δ (R = 1°, 2°, 3° alkyl; aryl)	Ber *115* 808 (1982)
$PhOPOCl_2$/PhSeH, Et_3N/*n*-Bu_3SnH (R = tetrahydrofuranyl)	JACS *107* 3285 (1985)

14. Acid Halides



JCS Perkin I 1137 (1979)

15. Esters

$$ArCO_2R \xrightarrow{Me_3SiI} \xrightarrow[n\text{-}Pr_3N]{HSiCl_3} \xrightarrow{KOH} ArCH_3$$

JOC *44* 2185 (1979)

$$ROCR' \longrightarrow RH$$

hν, *N*-methylcarbazole (R′ = Ph; R = 2° alkyl)	JACS *108* 3115 (1986)
Li, NH_3/EtOH (R = benzylic)	JOC *52* 4879 (1987)
Li, $EtNH_2$ (R = hindered alkyl, allylic)	JCS 1969 (1957) CC 68 (1978); 1173 (1979) JACS *106* 723 (1984) TL *27* 5471 (1986)
Li, $(CH_2NH_2)_2$	Ind J Chem B *18* 179 (1979)
Na, *t*-BuOH, HMPA	CC 567 (1978)
K, *t*-$BuNH_2$, 18-crown-6	CC 1173 (1979)
Na-K, tris(3,6-dioxaheptyl)amine	TL *28* 2503 (1987)
Zn, HOAc, THF (R = 3° allylic, R′ = CF_3)	JACS *109* 6187 (1987)
H_2, cat Pd-C, $HClO_4$ (R = benzylic)	Syn Commun *12* 983 (1982)
Ph_3SiH, (*t*-BuO)$_2$, Δ	CL 77 (1986)
$HMe_2SiOSiMe_2H$, cat Me_3SiOTf	CC 1743 (1987) (4-acetoxyazetidin-2-ones)

$$RO_2CCO_2CH_3 \xrightarrow{n\text{-}Bu_3SnH} RH$$

R = 1°, 2° alkyl

CC 1588 (1985)
JACS *109* 7534 (1987)

$$RCHCH{=}CH_2 \text{ or } RCH{=}CHCH_2OAc \longrightarrow RCH_2CH{=}CH_2$$

$(NH_4)O_2CH$, cat $PdCl_2(PPh_3)_2$	TL 613 (1979)
SmI_2, cat $Pd(PPh_3)_4$, *i*-PrOH	TL *27* 601 (1986)

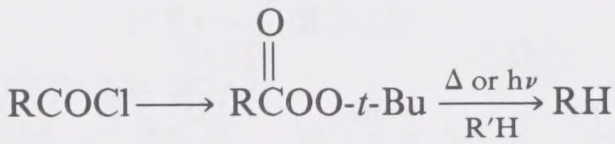
$$RC{=}CHR \xrightarrow{Fe(CO)_5} RCH{=}CHR$$

TL 447 (1973)

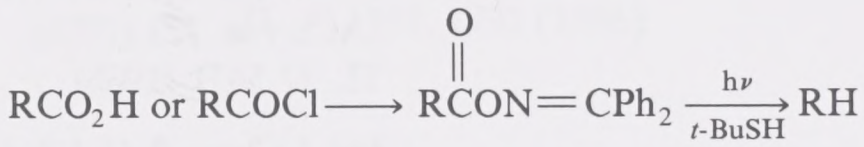
$$RC(=O)CH(O_2CR')R \longrightarrow RC(=O)CH_2R$$

Ca, NH_3	JCS 4344 (1956)

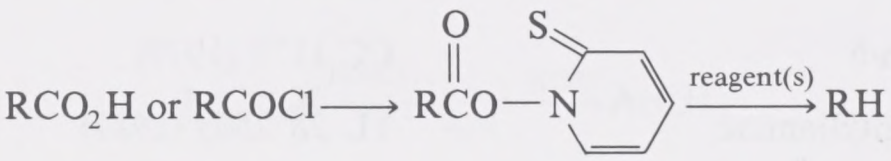
Zn, HOAc	JACS *77* 4367 (1955); *79* 5540 (1957)
Zn(Hg), HOAc	JACS *97* 1101 (1975)
$Fe(CO)_5$	TL 447 (1973)
SmI_2, MeOH	JOC *51* 1135 (1986)
n-Bu_3SnH	Ber *110* 2911 (1977) CC 1290 (1987)



JACS *83* 3998 (1961); *86* 3157 (1964); *102* 678 (1980)
JOC *33* 99 (1968)
Ber *108* 2156 (1975)

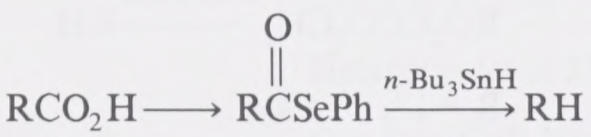


TL *28* 6207 (1987)



Reagent(s)

n-Bu_3SnH	Heterocycles *21* 1 (1984) Tetr *41* 3901 (1985)
t-BuSH, hν	CC 1298 (1984); 1041 (1987)



Helv *63* 1562, 2328 (1980)
JACS *107* 3285 (1985)

16. Nitriles

$RCN \longrightarrow RCH_3$

H_2, cat Ni-Al_2O_3	Syn 802 (1980)
H_2, cat Pd-C	Ann *707* 26 (1967)
$(NH_4)O_2CH$, cat Pd-C	Syn 1036 (1982)

$RCN \longrightarrow RH$

electrolysis, $EtNH_2$	TL 1975 (1968)
Li, NH_3, EtOH	TL *28* 547 (1987) (α-amino nitrile)
Li, $EtNH_2$	JACS *89* 6794 (1967); *91* 2059 (1969)

Li naphthalenide	TL *27* 2199 (1986)
Li, Na or K; HMPA; (*t*-BuOH)	Compt Rend *274* 797 (1972) BSCF 1174 (1973) TL 3851 (1975) Syn 391 (1976)
Na, NH_3	JACS *89* 6794 (1967); *91* 2059 (1969) BSCF 178 (1975) JOC *40* 1162 (1975); *42* 3309 (1977) TL 57 (1976); 61 (1976) (α-amino nitrile); 27 (1979); *23* 3369 (1982) (α-amino nitrile) Chem Pharm Bull *25* 2689 (1977) (α-amino nitrile)
Na, $Fe(acac)_3$	JACS *93* 7113 (1971)
K, crown ether, toluene	TL *26* 6103 (1985)
K, Al_2O_3	JOC *45* 3227 (1980)
NaOH	Syn 290 (1979) (*o*-hydroxyaryl nitrile)
KOH	Syn Commun *10* 939 (1980)
$NaBH_4$	TL 3105 (1969) (α-amino nitrile); *23* 3369 (1982) (α-amino nitrile)

2. COUPLING REACTIONS

See also page 39, Section 12.7.

1. Symmetrical or Intramolecular Coupling

$$2\,RH \xrightarrow[Hg]{h\nu} R{-}R$$

CC 970 (1987)
TL *28* 5599 (1987)

$$2\,ArH \longrightarrow Ar{-}Ar$$

Review: Tetr *36* 3327 (1980)

$Pb(OAc)_4$, $BF_3 \cdot OEt_2$	JACS *102* 6504 (1980)
$PhI(OAc)_2$	JOC *52* 5662 (1987) (intramolecular)
$(Et_4N)[I(O_2CCX_3)_2]$ (X = H, F, Cl)	TL *21* 3509 (1980)
VOF_3, CF_3CO_2H, $[(CF_3CO)_2O]$	JACS *95* 6861 (1973); *97* 5622, 5623 (1975); *98* 267 (1976) (all intramolecular) JOC *41* 3772, 4047 (1976); *43* 2521, 4076 (1978); *52* 5662 (1987) (all intramolecular) TL *27* 1785 (1986) (intramolecular)
$VOCl_3$	TL *27* 1785 (1986) (intramolecular) JOC *52* 5662 (1987) (intramolecular)
$FeCl_3$, SiO_2 (ArOH, ArOR)	JOC *45* 749 (1980); *46* 4545 (1981)
$FeCl_3$, Ac_2O	Chem Pharm Bull *33* 3599 (1985)
$Fe(ClO_4)_3 \cdot 6\,H_2O$, CH_3CN	Chem Pharm Bull *33* 3599 (1985)
$K_3Fe(CN)_6$ (ArOH)	JOC *46* 2547 (1981)
RuO_2, CF_3CO_2H, $(CF_3CO)_2O$, $BF_3 \cdot OEt_2$	TL *27* 1785, 5377 (1986); *28* 543, 5161 (1987) (all intramolecular)
CoF_3, CF_3CO_2H	JACS *102* 6504 (1980)
$Tl(O_2CCF_3)_3$	JACS *107* 4984 (1985) (intramolecular) JOC *52* 5662 (1987) (intramolecular)

$Tl(O_2CCF_3)_3$, $BF_3 \cdot OEt_2$	JOC *42* 764 (1977) (inter- and intramolecular); *49* 3220 (1984) (intramolecular) CC 538 (1977) (intramolecular) JACS *102* 6504, 6513 (intramolecular) (1980) Syn Commun *10* 827 (1980) (intramolecular) Austral J Chem *37* 1775 (1984) (intramolecular) TL *27* 1465, 1781, 1785 (1986); *28* 543, 5161 (1987) (all intramolecular)
$Tl(O_2CCF_3)_3$, cat $Pd(OAc)_2$	TL *22* 3793 (1981)

$$2\ RCH{=}CH_2 \longrightarrow (RCH_2CH_2)_2$$

$BH_3/AgNO_3$, NaOH	JACS *83* 1001, 1002 (1961)
$LiAlH_4$, $TiCl_4$ or $Cp_2TiCl_2/Cu(OAc)_2$	CL 1155, 1337 (1978)

$$2\ ArX \longrightarrow Ar{-}Ar$$

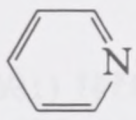
Review: Tetr *36* 3327 (1980)

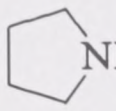
Cu (Ullman)	Chem Rev *38* 139 (1946); *64* 613 (1964) (reviews) Syn 9 (1974) Ann 329 (1977) BCSJ *54* 3522 (1981) JACS *106* 3297 (1984)
Co	JOC *48* 4904 (1983)
Ni	TL *23* 4215 (1982) JOC *48* 840, 4904 (1983)
$Ni(COD)_2$	JACS *93* 5908 (1971); *103* 6460 (1981)
$Ni(PPh_3)_4$	JACS *97* 3873 (1975); *103* 6460 (1981) TL 3375 (1975); *21* 631 (1980) JOC *52* 4665 (1987) (intramolecular)
$Ni(ClO_4)_2$, electrolysis	JCS Dalton 1074 (1981)
$Ni(acac)_2$, electrolysis	JOC *41* 719 (1976)
$NiCl_2(PPh_3)_2$, electrolysis	JOMC *202* 435 (1980) J Chem Res (S) 26 (1980)
NaH, NaO-*t*-Am, $Ni(OAc)_2$, bipy	TL 3951 (1977)
NaH, Na-O-*t*-Bu, $Ni(OAc)_2$, PPh_3	TL *27* 5483 (1986) (heteroaromatic)
NaH, *t*-AmOH, $Ni(OAc)_2$, PPh_3 or bipy	JOMC *264* 263 (1984)
Pd(Hg), N_2H_4	BCSJ *53* 1767 (1980)
cat Pd-C, NaOH, NaO_2CH, surfactant	Syn 537 (1978) JOC *47* 4116 (1982) (bipyridines)
cat $Pd(OAc)_2$, R_3N	JCS Perkin I 121 (1975)
cat $Pd(PPh_3)_4$, electrolysis	TL *26* 1655 (1985)
cat $Pd(PPh_3)_4$, 0.5 $(Me_3Sn)_2$, LiCl	JACS *109* 5478 (1987)

Zn, $NiBr_2$, KI	CL 917 (1979) BCSJ *53* 3691 (1980)
Zn, $NiCl_2$, PPh_3	Syn 736 (1984) (bipyridines)
Zn, cat $NiCl_2(PPh_3)_2$	TL 4089 (1977)
Zn, cat $NiCl_2(PEt_3)_2$, KI	BCSJ *57* 1887 (1984)
Zn, $NiCl_2(PPh_3)_2$, *n*-Bu_4NI	CC 1476 (1987) (bithiophenes)
Zn, $NiBr_2(PPh_3)_2$, *n*-Bu_4NI	TL *26* 3829 (1985)
Zn, Mg or Mn; cat $NiCl_2$; PPh_3	JOC *51* 2627 (1986)

$$2\,RX \longrightarrow R{-}R$$

For R = allylic and vinylic, see also page 241, Section 7.

Na (Wurtz) (R = alkyl)	JACS *80* 622 (1958)
O_2, Et_3B (R = allylic, benzylic)	JACS *93* 1508 (1971)
Ti, V (review) (R = allylic, benzylic)	Org Prep Proc Int *12* 361 (1980)
$TiCl_3$ or $TiCl_4$, $LiAlH_4$ (R = allylic, benzylic)	Syn 607 (1976)
$VCl_2(py)_4$ (R = benzylic)	JACS *95* 4158 (1973)
VCl_3, $LiAlH_4$ (R = allylic, benzylic)	Syn 170 (1977)
$CrCl_2$ (R = benzylic)	Tetr *20* 1005 (1964)
$CrCl_2$, electrolysis (R = allylic, benzylic)	Syn 901 (1978)
$CrCl_3$, $LiHBEt_3$ (R = 3° alkyl, allylic, benzylic)	TL *22* 5167 (1981)
$CrCl_3$, $LiAlH_4$ (R = allylic, benzylic)	TL 3829 (1977) BCSJ *55* 561 (1982)
$Fe_3(CO)_{12}$,  (R = allylic, benzylic)	CL 1309 (1978)
$Fe(acac)_3$, electrolysis (R = 1° alkyl)	JOC *41* 719 (1976)
$CoCl(PPh_3)_3$ (R = benzylic)	CL 1277 (1981)
Ni (R = benzylic)	TL *23* 4215 (1982) JOC *48* 4904 (1983)
$Ni(CO)_4$, DMF (R = allylic)	JACS *73* 2654 (1951); *86* 1641 (1964); *89* 2757, 2758 (1967); *90* 2416, 2417 (1968); *96* 4724 (1974) TL 6237 (1966) Org Rxs *19* 115 (1972) (review)
$Ni(PPh_3)_4$ (R = allylic, aryl, vinylic)	TL 3375 (1975) JACS *103* 6460 (1981)

$Ni(acac)_2$, electrolysis (R = benzylic)	JOC *41* 719 (1976)
$Ni(ClO_4)_2$, electrolysis (R = 1°, 3° alkyl; benzylic)	JCS Dalton 1074 (1981)
cat $PdCl_2$, NaOH, N_2H_4 (R = 1° alkyl)	BCSJ *54* 3599 (1981)
 NLi, CuI (R = allylic)	TL 783 (1979)

$$RX \longrightarrow RM \xrightarrow{\text{reagent(s)}} R\text{—}R$$

RM	Reagent(s)	
$ArCH_2Li$	$CoCl_2$	BSCF 1331 (1964)
ArLi	$Fe(acac)_3$	JACS *106* 2160, 3286 (1984); *109* 7068 (1987)
	$CoCl_2$	BSCF 1331 (1964)
	$CuCl_2$	CC 1476 (1987) (bithiophenes)
RMgX (R = 1° alkyl)	AgOTf	JOC *41* 2882 (1976) (cyclobutanes and -pentanes)
	RX, Ag or AgX	Syn 303 (1971)
RMgX (R = 2° alkyl, aryl)	TlBr	JACS *90* 2423 (1968) Tetr *26* 4041 (1970) JOC *51* 1618 (1986)
RMgX (R = 1° alkyl, benzylic, aryl)	$CoCl_2$	BSCF 1331 (1964)
RMgX (R = 1° alkyl, benzyl, vinyl, phenyl)	CuCl	Angew Int *6* 85 (1967) BCSJ *44* 3063 (1971)
	AgBr	BCSJ *44* 3063 (1971)
ArMgX	$Ni(acac)_2$ or $NiCl_2L_2$	JOC *41* 2252 (1976)
	$ClCH_2CH{=}CHCH_2Cl$ or $ClCH_2C{\equiv}CCH_2Cl$	JOC *46* 2194 (1981)
RCu or R_2CuLi (R = 1°, 2° alkyl; aryl; vinylic; alkynyl)	Δ, O_2, or $PhNO_2$ or $CuCl_2 \cdot$TMEDA	JACS *88* 4541 (1966); *89* 5302 (1967); *93* 1379 (1971) Angew Int *13* 291 (1974) JOC *44* 2705 (1979)
$(ArCu)_n$	CuO_3SCF_3	CC 203 (1977)

$$2\ ROH \longrightarrow \text{“}(RO)_2Ti\text{”} \longrightarrow R\text{—}R$$

R = allylic, benzylic

JACS *87* 3277 (1965); *90* 209, 3284 (1968)
CC 53 (1969)
JOC *40* 2687 (1975); *43* 3249 (1978)
J Med Chem *23* 841 (1980)
Org Prep Proc Int *12* 361 (1980) (review)

$$2\ ROH \xrightarrow[NaAlH_4]{NbCl_5} R-R$$

R = allylic, benzylic

CL 157 (1982)

$$RM \longrightarrow R-R$$

RM	Reagent	
$K_2(PhSiF_5)$	$PdCl_2$	Organomet *1* 542 (1982)
RHgX (R = aryl, vinylic)	cat $[RhCl(CO)_2]_2$	JOC *42* 1680 (1977)
R_2Hg (R = aryl, alkynyl, benzylic, vinylic)	cat $[RhCl(PPh_3)_3$	BCSJ *50* 2741 (1977)

$$2\ RCO_2H \xrightarrow{electrolysis} R-R$$

"Organic Electrochemistry," Ed. M. M. Baizer, M. Dekker, New York (1973), p 469
"Techniques of Chemistry," Ed. N. L. Weinberg, J. Wiley, New York (1974), Vol. 5, Part 1, p 793
Org Syn *60* 1 (1981)
Can J Chem *59* 945 (1981)
Angew Int *20* 911 (1981)

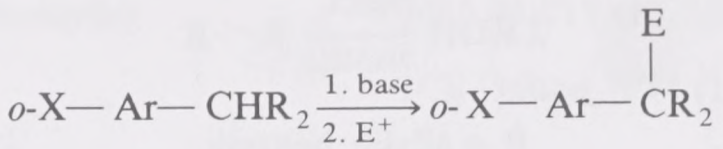
2. Unsymmetrical Coupling

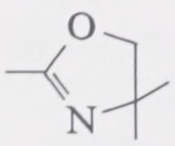
2.1. Organolithium Reagents

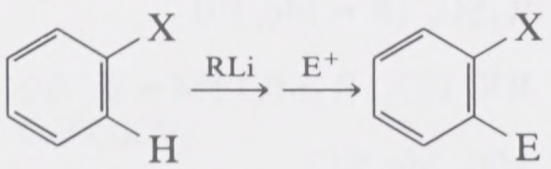
See also page 39, Section 12.7.

$$ArCH_3 \xrightarrow{Li\ base} ArCH_2Li \xrightarrow{E^+} ArCH_2E$$

Ar	E^+	
benzene	R_2SO_4 (R = Me, Et)	JOC *47* 3949 (1982)
phenol	RX, CO_2, R_3MCl (M = Si, Sn)	JOC *51* 1432 (1986)
naphthalene	MeI, Me_3SiCl	JOC *44* 3483 (1979); *48* 903 (1983)
pyridine	RBr	TL *24* 31 (1983)
pyrazine	RCHO	JOC *52* 3971 (1987)
oxazole	MeOD, RX, RCHO, R_2CO	TL *24* 4391 (1983); *28* 3585 (1987) JACS *107* 1423 (1985)
thiazole	RX	TL *28* 3585 (1987)



X	E^+	
CH_2OH	D_2O, RX, RCHO, R_2CO, CO_2 Me_3SiCl	TL *24* 1233 (1983) JACS *109* 2738 (1987)
CO_2H	RX, R_2CO	JACS *92* 1396 (1970) (also *m* and *p* isomers)
	RCHO	JACS *104* 4708 (1982) CC 479 (1986)
	$(RO)_2CO$	JACS *99* 4533 (1977) Syn 245 (1977) JOC *42* 4155 (1977)
CO_2R	RX	JCS Perkin I 1043 (1984) JACS *108* 4953 (1986)
	RCHO, R_2CO	CC 764 (1983), 520 (1987) JCS Perkin I 1043 (1984)
	RCOCl, CO_2	JCS Perkin I 1043 (1984)
	other electrophiles	CC 406 (1978); 205, 206 (1979) JCS Perkin I 1043 (1984)
CONHMe	RCHO, R_2CO	JOC *29* 3514 (1964); *52* 5378 (1987) J Heterocyclic Chem *6* 83 (1969)
	ArCH=NR	JOC *52* 5378 (1987)
	RCN	JOC *47* 3787 (1982)
$CONR_2$	RX, R_2CO	JOC *38* 1668 (1973) (also *m* and *p* isomers)
	ArCH=NR	JOC *52* 5378 (1987)
	RCN	JACS *108* 7100 (1986)
	O_2	JOC *52* 674 (1987)
	Me_3SiCl	JOC *51* 3325 (1986)
$CONEtCH_2CH_2NEt_2$	RX, RCHO, $HCONMe_2$	JOC *51* 3566 (1986)
	RX	CC 388 (1986)



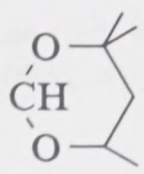
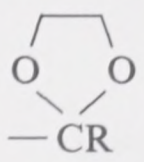
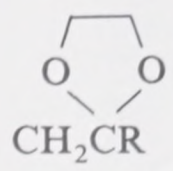
E^+ = RX, RCHO, R_2CO, CO_2, DMF, RCO_2R, $(RCO)_2O$, $(RS)_2$, $ClSiMe_3$, I_2, TsN_3

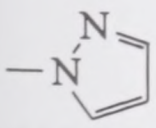
Reviews:

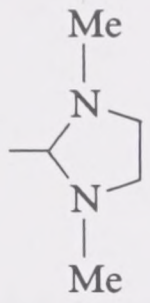
Org Rxs *8* 258 (1954); *26* 1 (1979)
Chem Rev *69* 693 (1969)
TL 3443 (1970)
Adv Chem Ser *130* 222 (1974)
JOC *41* 3653 (1976)

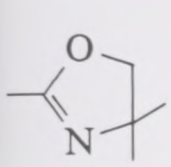
Z Chem *17* 1 (1977)
Tetr *39* 2009 (1983) (π-deficient heteroaromatics)
Syn 957 (1983) (synthesis of heterocycles)

X	
C≡CH	CC 366 (1981)
F	JOC *22* 1915 (1957); *46* 203 (pyridines), 4494 (pyridines) (1981); *50* 805 (1985); *52* 713 (1987) J Med Chem *11* 814 (1968); *29* 1982 (1986) Compt Rend C *275* 1535 (1972) (pyridines) JOMC *171* 273 (1979) (quinolines); *215* 139 (1981) (pyridines) Tetr *39* 2009 (1983) (heteroaromatics) TL *28* 4139 (1987)
Cl	TL *21* 4137 (1980) (pyridines) JOMC *216* 139 (1981) (pyridines)
Br	TL *21* 4137 (1980) (pyridines); *24* 3291 (1983) (pyridines) Tetr *38* 3035 (1982) (pyridines) J Chem Res (S) 278 (1982) (pyridines)
I	TL *21* 4137 (1980) (pyridines)
CF_3	JACS *68* 1658 (1946) JOMC *11* 209 (1968)
OH	JOC *19* 510 (1954) Chem Rev *57* 583 (1957) (review) J Chem Eng Data *14* 388 (1969) Org Prep Proc Int *13* 426 (1981) JACS *107* 2571 (1985)
OMe	JACS *62* 667, 987 (1940); *80* 4537 (1958); *106* 7150 (1984); *107* 2712 (1985); *109* 7068 (1987) Ber *73* 1197 (1940); *112* 1841 (1979) JOMC *9* 193 (1967); *11* 209, 217 (1968); *132* 321 (1977); *182* 155 (1979) Tetr *25* 3509 (1969) TL 3443 (1970); *27* 1971, 5125 (1986); *28* 5551 (1987) JOC *38* 1675 (1973); *43* 3205, 3717 (1978); *46* 203, 783 (1981); *47* 2396 (1982); *50* 2690 (1985); *52* 547, 674 (1987) J Heterocyclic Chem *17* 1333 (1980)
OR	JOC *45* 2739 (1980) Syn 235 (1982) (pyridines)
OCH_2CH_2OMe	Chem Pharm Bull *33* 1016 (1984) (arenes, pyridines)
$OCH_2CH_2NMe_2$	Chem Pharm Bull *33* 1016 (1984) (arenes, pyridines)

OCH_2OMe	JACS *79* 5792 (1957); *108* 7100 (1986) JOC *44* 2480 (1979); *47* 2101 (1982) (arenes, pyridines) Syn 906 (1979) TL *22* 811, 3923 (1981); *24* 3795 (1983); *28* 5093 (1987) Tetr *39* 2031 (1983) CC 1234 (1986)
OCH_2OR	JACS *101* 257 (1979) JOC *45* 2224, 5067 (1980)
$OCH(CH_3)OEt$	JOC *44* 2480 (1979)
OTHP	JACS *70* 4187 (1948); *79* 5797 (1957); *80* 4537 (1958); *107* 2712 (1985)
$OCONEt_2$	JOC *48* 1935 (1983); *50* 5436 (1985) (pyridines) TL *24* 3795 (1983); *28* 5093, 5097 (1987) JACS *107* 6312 (1985)
$OPO(NMe_2)_2$	TL *27* 1391 (1986) (furans)
CH_2OH	Angew Int *17* 521 (1978) JOC *45* 1835 (1980) Ber *113* 1304 (1980)
CHOHR	Syn 59 (1981)
$CHOHCH_2NMeR$	CC 968 (1974)
$CR(OLi)NR_2$	Acta Chem Scand *22* 1353 (1968) (thiophene) Arkiv Kemi *32* 283 (1970) (furan, thiophene) JOC *41* 3651 (1976) TL *23* 3979 (1982)
CH_2OMe	Syn Commun *5* 65 (1975) TL 3973 (1975); *28* 5551 (1987) JOC *48* 3653 (1983); *50* 2690 (1985)
$CH_2OCH(CH_3)OCH_2CH_3$	JOC *48* 3653 (1983)
CPh_2OMe	JACS *74* 6282 (1952)
$CH(OMe)_2$	TL 4921 (1979) JOC *48* 3653 (1983); *50* 805 (1985)
	TL *27* 2963 (1986)
	JOC *48* 3653 (1983)
$CH_2CH(OMe)_2$	JOC *48* 3653 (1983)
	JOC *48* 3653 (1983)

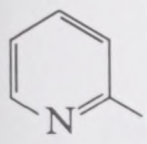
SR	Arkiv Kemi *13* 269 (1958) (thiophenes) JOMC *132* 321 (1977); *182* 155 (1979)
CR_2SMe	JACS *101* 257 (1979)
SO_2R	JACS *75* 278 (1953) Arkiv Kemi *13* 269 (1958) (thiophenes) JOC USSR *5* 313 (1969) Tetr *27* 433 (1971)
SO_3H	JOC *45* 3728 (1980)
SO_3R	Bull Acad Sci USSR, Div Chem Sci 129 (1980) JOC *51* 2833 (1986)
SO_2NHR	JOC *33* 900 (1968)
SO_2NR_2	Can J Chem *47* 1543 (1969) Angew Int *13* 270 (1974) TL 1499 (1975) Bull Acad Sci USSR, Div Chem Sci 129 (1980) Tetr *39* 2073 (1983) Syn 822 (1983) (pyridines)
NMe_2	Ber *75* 1491 (1942) JOC *31* 2047 (1966); *35* 1288 (1970); *44* 237 (1979) TL 3443 (1970) Org Syn *53* 56 (1973)
NR_2	JOC *50* 2690 (1985)
$NMeCH_2CH_2NMe_2$	TL *24* 5465 (1983)
$NHCOC(CH_3)_3$	JOC *44* 1133 (1979); *45* 4798 (1980); *46* 3564 (1981) (pyridines); *48* 3401 (1983) (pyridines) J Heterocyclic Chem *17* 1333 (1980) Chem Pharm Bull *30* 1257 (1982) (arenes, pyridines) Syn 499 (1982) (pyridines) TL *28* 5435 (1987) CC 1528 (1987)
$NHCO_2C(CH_3)_3$	JOC *44* 1133 (1979); *45* 4798 (1980); *51* 2781 (1986) Syn 499 (1982) (pyridine) TL *28* 5093 (1987)
	Helv *57* 1988 (1974)
CH_2NHMe	JOC *36* 1607 (1971)
CH_2NMe_2	JACS *85* 2467 (1963) JOC *27* 701 (1963); *28* 663, 3461 (1963); *32* 1479 (1967); *45* 5067 (1980); *52* 704 (1987) TL 4159 (1968); 3443 (1970); *22* 2797 (1981) JOMC *54* 1 (1973) Tetr *39* 1975 (1983)

CH=NR	JOC *41* 1564 (1976); *45* 5067 (1980)
	JOC *44* 2004 (1979)
$(CH_2)_2NMe_2$	TL 603 (1966); 3443 (1970); *27* 1971 (1986) Chem Ind 120 (1967) Austral J Chem *21* 2319 (1968) Acta Chem Scand B *31* 514 (1977)
CO_2H	TL *26* 1777 (1985) (furans, thiophenes)
CONHR	JOC *29* 853 (1964); *40* 1427 (1975); *44* 4463 (1979); *46* 2799 (1981); *47* 34 (1982); *50* 4362 (1985); *51* 2011 (1986) CC 564 (1968); 1552 (1970); 1042 (1980) TL 4159 (1968); 2559, 3965 (1978); *22* 1779 (1981); *23* 1647 (1982); *25* 2127 (1984) (pyridines); *27* 501 (1986) J Heterocyclic Chem *6* 475 (1969) Tetr *27* 6171 (1971); *39* 1983 (1983) Chem Ind 75 (1974) Syn 797 (1975); 127 (1981) (pyridines) Ind J Chem B *15* 512 (1977) JACS *103* 4247 (1981) JCS Perkin I 2227 (1982)
$CONR_2$	JOC *41* 3651 (1976); *42* 1823 (1977); *44* 4463, 4802 (1979); *47* 34, 2120, 3335, 5009 (1982); *48* 1565 (1983); *49* 318 (1984); *50* 805, 2690, 4362, 5902 (1985); *51* 271, 2011, 3325, 3566 (1986); *52* 183, 283, 674, 3181 (naphthalenes), 5668 (1987) TL 5099, 5103, 5107 (1978); *21* 3335, 4739 (pyridines) (1980); *22* 1093, 2349 (1981); *24* 2649 (pyridines), 2945, 3795, 4515, 4735 (pyridines) (1983); *26* 1149 (thiophenes), 6213 (1985); *28* 5093, 5097 (1987) Can J Chem *57* 1598 (1979) Heterocycles *14* 1649 (1980) (review) JACS *102* 1457 (1980); *104* 5531 (1982); *107* 6312 (1985); *108* 7100 (1986); *109* 3402 (1987) CC 1215 (1981) Acct Chem Res *15* 306 (1982) (review) Tetr *39* 1955, 1983 (1983)
CSNHR	JOC *41* 4029 (1976)

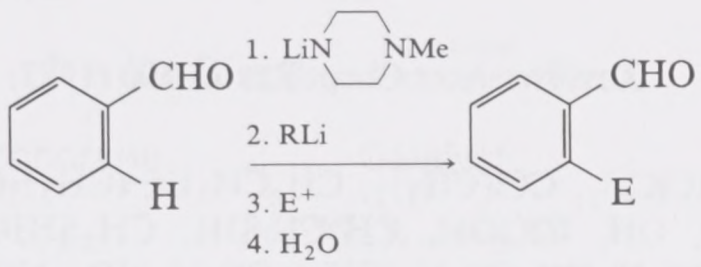


Arkiv Kemi *21* 335 (1963) (thiophene)
BSCF 628 (1976) (thiophene, selenophene)
JOC *47* 2681 (1982) [m-$C_6H_4(CN)_2$]

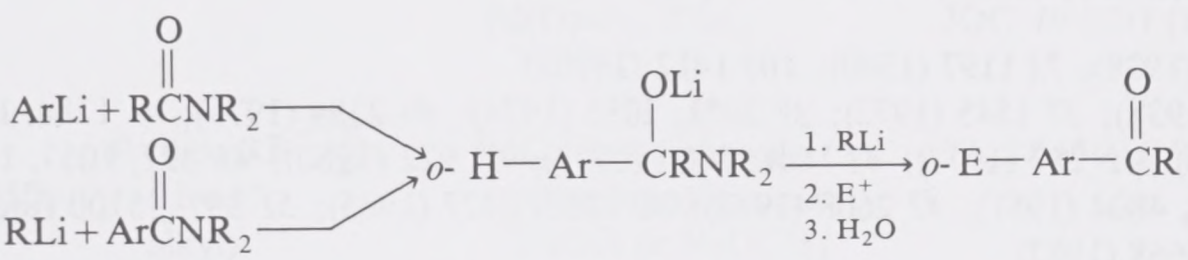
JOC *40* 2008, 3158 (1975); *42* 2649 (1977) (thiophenes); *43* 727 (1978); *44* 4464 (1978); *46* 3881 (1981); *47* 1585, 2633 (pyridines), 2837 (1982); *52* 713 (1987)
Angew Int *15* 270 (1976)
Heterocycles *11* 133 (1978) (pyridines)
TL 227 (1978); *21* 3335 (1980); *23* 2091 (1982); *24* 3795 (1983); *26* 5335 (1985); *27* 3431 (1986)
JCS Perkin I 1343 (1982); 173 (1985)
Tetr *40* 2107 (1984)
JACS *104* 4015 (1982); *108* 2662, 4138 (furan) (1986)
CC 388 (1986)



Tetr *39* 3593 (1983) (furans)



TL *23* 3979 (1982)
JOC *49* 1078 (1984); *52* 104 (1987)

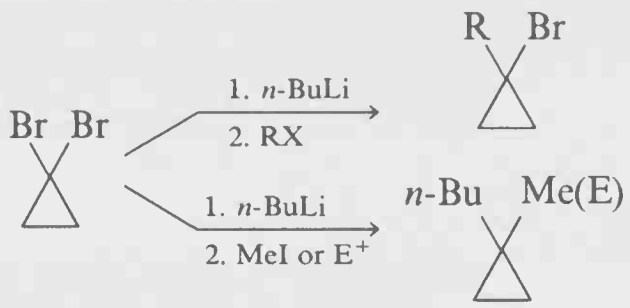


Acta Chem Scand *22* 1353 (1968) (thiophene)
Arkiv Kemi *32* 283 (1970) (furan, thiophene)
JOC *41* 3651 (1976)
TL *24* 5465 (1983); *27* 1793 (1986)

$$RLi + R'X \longrightarrow R{-}R'$$

R = allylic, benzylic

JACS *91* 4871 (1969)
TL 4115 (1973); 2215 (1974)
JOC *39* 1168, 3452 (1974)

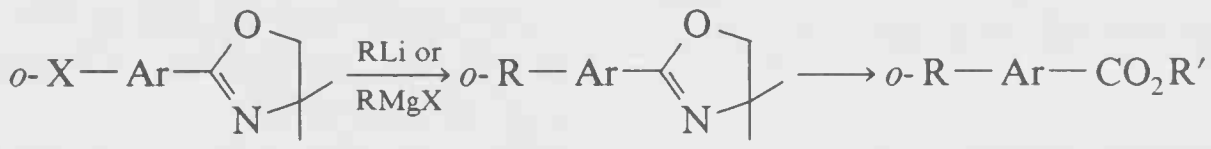


JACS *97* 949 (1975)

BCSJ *50* 2158 (1977)

$$1^\circ\ RLi + ArX \longrightarrow R{-}Ar$$

JACS *91* 4871 (1969)
JOC *39* 3452 (1974)



X = F, OMe

JACS *97* 7383 (1975); *104* 879, 881 (1982); *107* 682, 4238 (1985); *109* 3098, 5446 (1987)
JOC *43* 1372 (1978); *46* 783 (1981)

$$X{-}Ar{-}Y \xrightarrow[2.\ E^+]{1.\ RLi} X{-}Ar{-}E$$

Review: Acct Chem Res *15* 300 (1982)

X = H, R, Br, CH_2Cl, $CHClCH_3$, $CCl(CH_3)_2$, CH_2CH_2Br, $(CH_2)_3Cl(Br)$, $(CH_2)_2CHBrCH_3$, OR, $O(CH_2)_nBr$ ($n = 2,3$), OH, CR_2OH, CH_2CH_2OH, CH_2SH, $CH(OLi)NR'_2$, CN, CR_2CN, CH_2CH_2CN, CO_2R, CO_2H, CH_2CO_2H, $(CH_2)_2CO_2H$, NO_2, NH_2, NHCOR, SO_2NR_2, pyrrole

Y = Br, I

E^+ = H_2O, D_2O, Br_2, RX, $RCH\text{—}CH_2$ (O), RCHO, R_2CO, RCO_2H, RCO_2R, RCOCl, $HCONR_2$, CO_2, RCN, PhNCO, imines, Michael acceptors

Ber *71* 1903 (1938); *73* 1197 (1940); *103* 1412 (1970)
JOC *3* 108 (1938); *37* 1545 (1972); *39* 2051, 2053 (1974); *40* 2394 (1975); *41* 1184, 1187, 1268, 2628, 2704 (1976); *42* 257 (1977); *43* 1606, 3800 (1978); *45* 922 (1980); *46* 327, 1057, 1384, 2730, 2826, 4600, 4608, 4804 (1981); *47* 2608 (1982); *50* 2423, 2427 (1985); *51* 3973, 5100 (indoles) (1986); *52* 586, 704, 5668 (1987)
JACS *61* 106, 1371 (1939); *62* 344, 346, 446, 1843, 2327 (1940); *63* 1553, 2844 (1941); *64* 1007 (1942); *69* 1537 (1947); *70* 4177 (1948); *99* 4822 (1977); *106* 7150 (1984)
TL 4573 (1977); *22* 1475, 3707, 4213 (1981); *28* 1937, 2933, 4507, 6089 (1987)
Org Prep Proc Int *10* 267 (1978)
JOMC *212* 1 (1981); *215* 281 (1981)
Syn Commun *12* 49, 231 (pyrroles) (1982)

$$ROH \xrightarrow[3.\ R'Li]{\substack{1.\ MeLi\\2.\ CuI}} R{-}R' \xrightarrow{4.\ (Ph_3PNMePh)I}$$

R = allylic, benzylic, cyclopropylcarbinyl

R′ = 1° alkyl, aryl, alkynyl

JACS *99* 2361 (1977)

2.2. Grignard Reagents

$$RMgX + R'OTs \longrightarrow R{-}R'$$

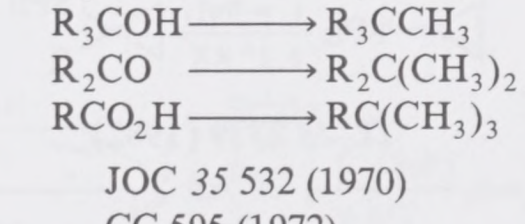
Org Syn Coll Vol *1* 471 (1932); *2* 47 (1943)

$$RMgX + H_2C{=}CHCH_2X \longrightarrow RCH_2CH{=}CH_2$$

Org Syn Coll Vol *1* 186 (1941)
TL 1393 (1969)

$$RMgBr + R'Br \longrightarrow R{-}R'$$

TL 1857 (1978)



R = aryl, alkenyl, alkynyl

TL *26* 29 (1985)
JOC *50* 3104, 5524 (1985); *51* 3162 (1986); *52* 4311 (1987)

2.3. Organoboron Reagents

$$R{-}X + R'{-}B\!\!<\!\!\!> \xrightarrow{\text{Pd catalyst}} R{-}R'$$

R—X	Organoborane	Catalyst	
ArBr, ArI	$ArB(OH)_2$	$Pd(PPh_3)_4$, Na_2CO_3	Syn Commun *11* 513 (1981) Organomet *3* 1261 (1984) JOC *49* 5237 (1984) Chem Scripta *24* 5 (1984) TL *26* 5997 (1985); *28* 5093, 5097 (1987)
		$Pd(OAc)_2$, PAr_3, NEt_3	JOC *49* 5237 (1984)
ArBr, ArI, RCH=CHBr	R_3B or RB (R = 1° alkyl)	$PdCl_2$[bis(diphenylphosphino)ferrocene], NaOH or $NaOCH_3$	TL *27* 6369 (1986)

2.4. Organoaluminum Reagents

$$R_3CCl \xrightarrow{(CH_3)_3Al} R_3CCH_3$$
$$R_3COH \longrightarrow R_3CCH_3$$
$$R_2CO \longrightarrow R_2C(CH_3)_2$$
$$RCO_2H \longrightarrow RC(CH_3)_3$$

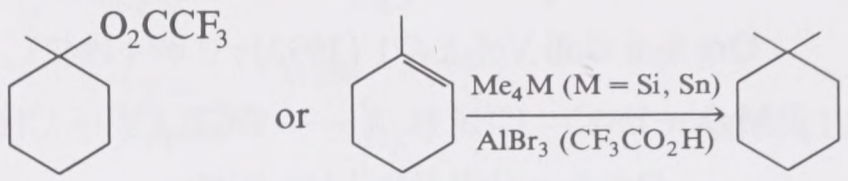
JOC *35* 532 (1970)
CC 595 (1972)

2.5. Organothallium Reagents

$$ArH \xrightarrow{Tl(O_2CCF_3)_3} ArTl(O_2CCF_3)_2 \xrightarrow[Ar'H]{h\nu} Ar{-}Ar'$$

JACS *92* 6088 (1970)

2.6. Organosilicon and -tin Reagents



CC 748 (1980)

$$ArCH_2SiMe_3 \xrightarrow[\text{KF, 18-crown-6 or } n\text{-}Bu_4NF, \text{ silica}]{PhCH_2Br} ArCH_2CH_2Ph$$

TL *23* 577 (1982)

$$R-Br + R'-SnR''_3 \xrightarrow{\text{Pd catalyst}} R-R'$$

R = benzylic, aryl; R′ = Me, $PhCH_2$, Ph, $CH{=}CH_2$

JACS *101* 4992 (1979)

$$(ArN_2)X + RSnR'_3 \xrightarrow{\text{Pd catalyst}} Ar-R$$

R = Me, Ph, $CH{=}CH_2$

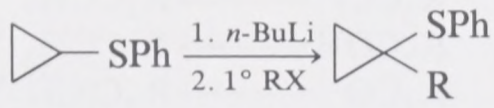
JOC *48* 1333 (1983)

2.7. Organolead Reagents

$$ArH \text{ or } ArHgO_2CR \xrightarrow{Pb(O_2CR)_4} ArPb(O_2CR)_3 \longrightarrow ArX$$

X	Reagent(s)	
Ar′	Ar′H, CF_3CO_2H, ($AlCl_3$)	Austral J Chem *32* 1531 (1979)
CR_2NO_2	R_2CHNO_2	TL *22* 783 (1981)
$CH(COR)_2$	$RCOCH_2COR$	Austral J Chem *32* 1561 (1979)
$CH(COR)CO_2R$	$RCOCH_2CO_2R$	Austral J Chem *33* 113 (1980)
$CR(CO_2R)_2$	$\overline{C}R(CO_2R)_2$	TL *21* 965 (1980)

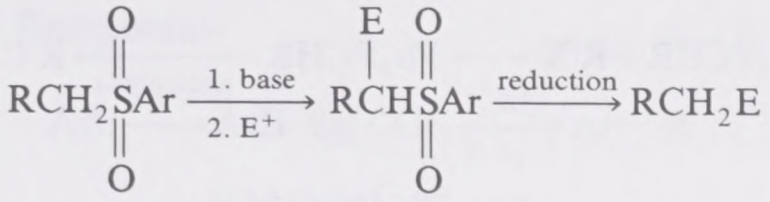
2.8. Sulfur, Selenium and Phosphorus Reagents



TL *23* 2379 (1982)

$$ArCH_2SCH_2Ar \xrightarrow[P(OR)_3]{h\nu} ArCH_2CH_2Ar$$

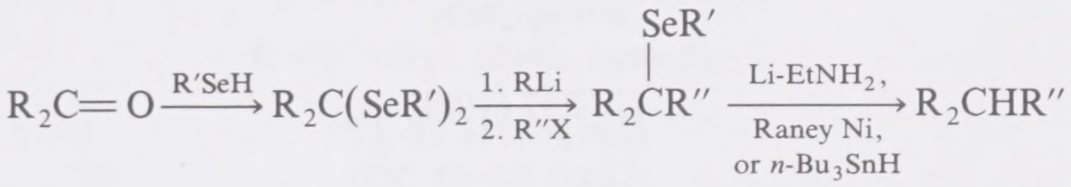
TL 1215 (1973)
Syn Commun *6* 591 (1976)
CL 977 (1977)



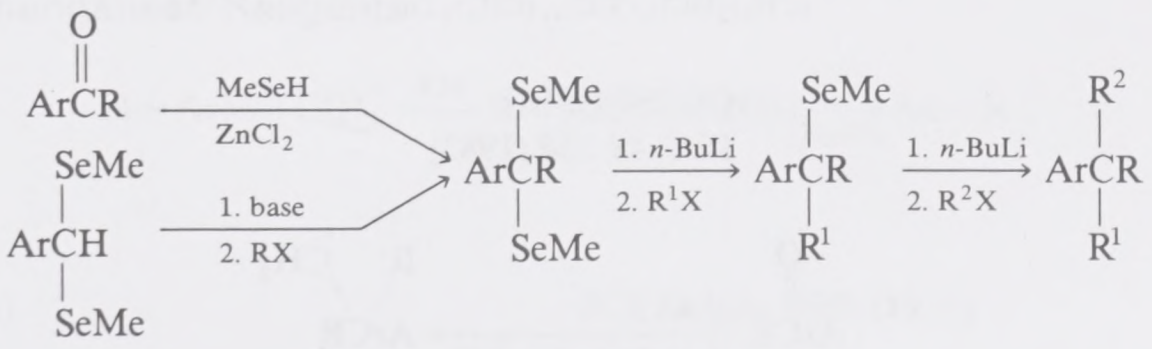
E^+	
RX	BSCF 3065 (1973); 1363 (1975) Tetr *37* 1233 (1981) JCS Perkin I 1846 (1981) CL 1711 (1981) JACS *106* 3811 (1984); *108* 1035 (1986) JOC *52* 3541 (1987) TL *28* 813, 6069 (1987)
epoxide	TL 2275 (1975) BSCF 513 (1976)
RCO_2R	JOC *45* 4002 (1980)

$$ArCH_2SO_2CH_2Ar' \longrightarrow ArCH_2CH_2Ar'$$

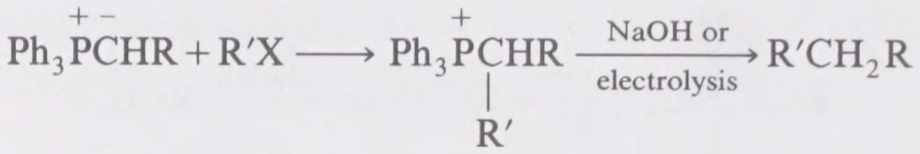
hν	Angew *85* 831 (1973) TL 861, 865 (1978); *27* 3341 (1986) (all intramolecular) JACS *86* 3173 (1979); *106* 1779, 1789 (1984) JOC *44* 1608 (1979) (intramolecular) Org Photochem *5* 227 (1981)
hν, $P(OR)_3$	Angew *85* 831 (1973)
Δ	Angew Int *8* 274 (1969); *18* 515 (1979) (review) Angew *85* 831 (1973) CL 977 (1977) JOC *50* 2939 (1985) (intramolecular); *52* 3196 (1987)



TL 2643 (1976); *28* 1337 (1987)

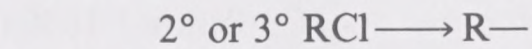


TL *27* 1719, 1723 (1986)
CC 457 (1986)

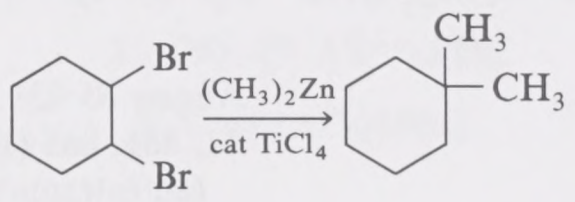


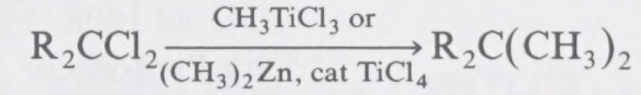
Ann *704* 109 (1967)

2.9. Organotitanium and -zinc Reagents

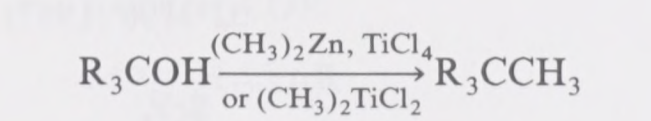


R'_2Zn	CC 1202 (1980)
$(CH_3)_2Zn$, (cat) $TiCl_4$	Angew Int *19* 900, 901 (1980) Syn Commun *11* 261 (1981)
CH_3TiCl_3	Angew Int *19* 900, 901 (1980)
$(CH_3)_2TiCl_2$	Angew Int *19* 900, 901 (1980)

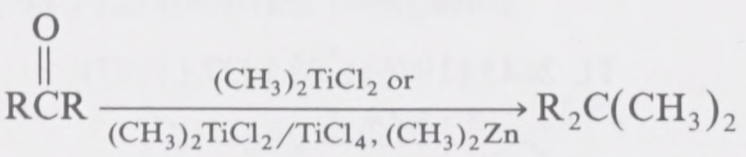




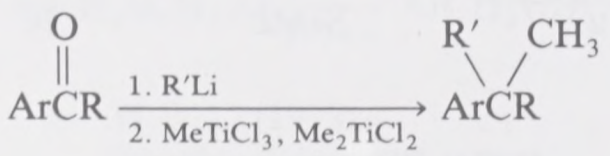
Syn Commun *11* 261 (1981)



CC 237 (1981)



CC 237 (1981)
JOC *48* 254 (1983)



JOC *48* 254 (1983)

2.10. Organochromium Reagents

$$ArH \longrightarrow ArH \cdot Cr(CO)_3 \xrightarrow[2.\ I_2]{1.\ RLi} Ar-R$$

JACS *96* 7091, 7092 (1974); *97* 1247 (1975); *98* 6387 (1976); *99* 959, 1675 (1977); *101* 217, 3535 (1979)
JOC *44* 3275 (1979)
Tetr *37* 3957 (1981)
Pure Appl Chem *53* 2379 (1981) (review)
JOMC *221* 147 (1981); *226* 183 (1982); *240* C5 (1982) (heterocycles)
CC 1361 (1982)
Organomet *2* 467 (1983)

$$ArH \longrightarrow ArH \cdot Cr(CO)_3 \xrightarrow[2.\ E^+]{1.\ RLi} E-Ar \cdot Cr(CO)_3 \xrightarrow[Ce(IV)]{I_2\ or} Ar-E$$

$$E^+ = RX,\ CO_2,\ RCHO,\ Me_3SiCl,\ RO_2CCl,\ PhSCl$$

JACS *101* 769 (1979)
JOC *45* 2555, 2560 (1980)
TL *21* 2069 (1980); *23* 1605 (1982); *27* 5525 (1986)
CC 1260 (1981) (indoles); 467 (1982) (indoles); 1235 (1986)

$$ArCH_2X \longrightarrow ArCH_2X \cdot Cr(CO)_3 \xrightarrow[2.\ E^+]{1.\ base} \underset{\displaystyle E}{\underset{|}{ArCHX}} \cdot Cr(CO)_3 \longrightarrow \underset{\displaystyle E}{\underset{|}{ArCHX}}$$

$$E^+ = D_2O,\ RX,\ RCHO,\ RCO_2R$$

$$X = H,\ R,\ CO_2R,\ OMe,\ SEt$$

JACS *94* 2897 (1972); *106* 2207 (1984)
CC 813 (1975); 1264 (1981); 1316 (1983)
TL 2727 (1975)
Tetr *35* 2249 (1979)
BSCF II 357 (1982)

$$ArCH_2X + RX \xrightarrow[LiHBEt_3\ or\ LiAlH_4]{CrCl_3} ArCH_2R$$

$$R = 3^\circ \text{ alkyl, allylic, benzylic}$$

TL *22* 5167 (1981)
JOC *52* 511 (1987)

2.11. Organomanganese Reagents

$$H-ArMn(CO)_3^+ \xrightarrow{RM} R-ArHMn(CO)_3 \xrightarrow[H_2SO_4]{CrO_3} Ar-R$$

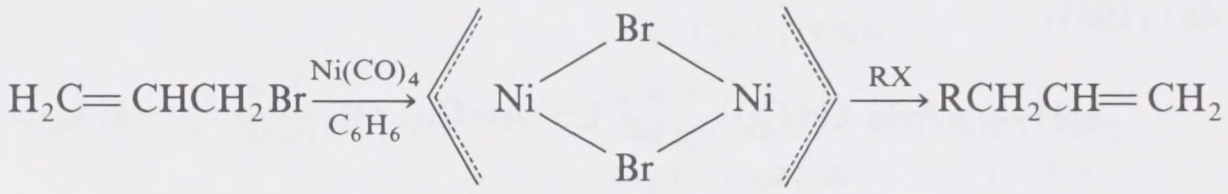
RM	
RLi (R = Me, Ph)	JCS Dalton 1683 (1975)
RMgX (R = Me, Ph)	Organomet *1* 1053 (1982)
$RCOCH_2Li$	Organomet *1* 1053 (1982)

2.12. Organoiron Reagents

$$1°, 2°, 3°\ \text{RMgBr} + \text{BrCH}{=}\text{CHR}' \xrightarrow{\text{cat Fe(PhCOCHCOPh)}_3} \underset{\text{retention}}{\text{RCH}{=}\text{CHR}'}$$

JOC *40* 599 (1975)

2.13. Organonickel Reagents



R = alkyl, vinyl, aryl

Org Rxs *19* 115 (1972) (review)

$$\text{RM} + \text{ArX} \xrightarrow{\text{Ni catalyst}} \text{Ar—R}$$

X	RM	Catalyst	
halogen	CH_3Li	$NiCl_2L_2$	JACS *97* 7262 (1975)
	RO_2CCH_2Li	$NiBr_2$ + *n*-BuLi	JACS *99* 4833 (1977)
	RMgX (R = 1°, 2° alkyl; aryl; vinylic; benzylic; allylic)	$NiCl_2L_2$	JACS *94* 4374 (1972); *97* 7262 (1975); *106* 3286, 7150 (1984) JOMC *50* C12 (1973) Helv *56* 460 (1973) J Heterocyclic Chem *10* 243 (1973); *12* 443 (1975) TL 3 (1974); *22* 4449 (1981); *23* 4629 (1982) BCSJ *49* 1958 (1974) CL 133 (1975) Pure Appl Chem *52* 669 (1980) (review) Tetr *38* 3347 (1982); *39* 2699 (1983) JOC *47* 4319 (1982); *50* 2086, 5370 (1985); *51* 142, 921 (1986)
		$Ni(acac)_2$	CC 144 (1972) JOC *41* 2252 (1976) TL *22* 4449 (1981)
	ArMgX	Ni(acaen)	BCSJ *55* 845 (1982)
	n-BuZnCl	$NiCl_2(PPh_3)_2$	Bull Acad Sci USSR, Div Chem Sci 620 (1986)
	RZnX (R = aryl, benzylic)	$Ni(PPh_3)_4$	JOC *42* 1821 (1977)
SH	RMgX (R = Me, Ph)	$NiCl_2L_2$	CC 637 (1979)

SR	RMgX (R = Me, aryl, allyl)	$NiCl_2L_2$	CC 637 (1979) TL *23* 4629 (1982); *26* 39 (1985)
SOR	RMgX (R = Me, Tol)	$NiCl_2L_2$	CC 637 (1979)
SO_2R	RMgX (R = Me, Tol)	$NiCl_2L_2$	CC 637 (1979)

2.14. Organopalladium Reagents

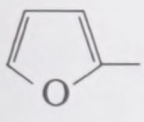
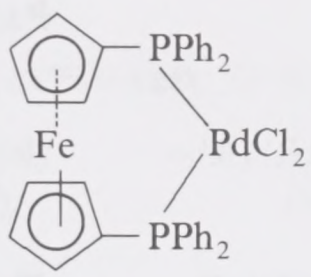
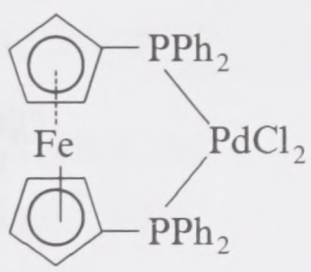
See also page 57, Section 2.3; and page 58, Section 2.6.

$$R_fI + RX \xrightarrow[\text{Pd catalyst}]{Zn} R_f{-}R$$

$RX = RCH{=}CHCH_2Br$ (with rearrangement), $RCH{=}CHBr$, ArI

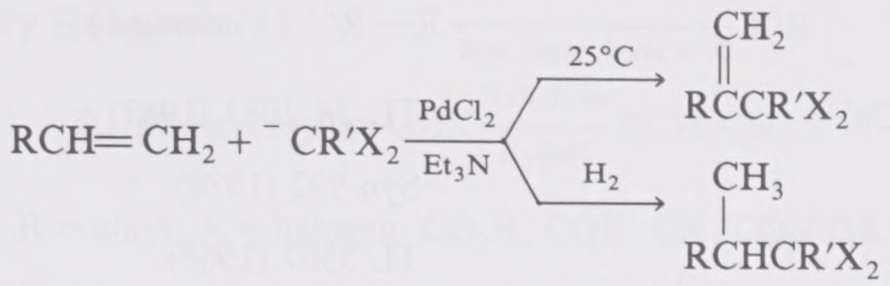
CL 137 (1982)

$$RM + R'X \xrightarrow{\text{Pd catalyst}} R{-}R'$$

RM	R′X	Catalyst	
	RBr (R = 1° alkyl, allylic, benzylic, aryl)	$Pd(PPh_3)_4$	Syn 51 (1987) TL *28* 1203 (1987)
RMgBr (R = 1°, 2° alkyl; aryl)	RI (R = 1°, 2° alkyl)		TL *27* 6013 (1986)
RMgCl(ZnCl) (R = 1°, 2° alkyl)	R′Br (R′ = aryl, vinylic)		JACS *106* 158 (1984)
RMgX (R = 1°, 2° alkyl)	ArX	$PdCl_2L_2$	TL 1871 (1979) JACS *104* 180 (1982); *106* 158 (1984)
RMgX (R = 1°, 2° alkyl; PhC≡C; Ar)	ArX	$PhPdI(PPh_3)_2$	JOMC *118* 349 (1976)
ArMgX, 1° RMgX	ArX	$Pd(PPh_3)_4$ or $PdCl_2L_2$	TL *21* 845 (1980)
ArMgX	ArX	$PdCl_2[Ph_2P(CH_2)_4PPh_2]_2$	CC 511 (1984)

$$RM + R'X \xrightarrow{\text{Pd catalyst}} R{-}R' \quad (\textit{Continued})$$

RM	R′X	Catalyst	
ArMgBr	ArI	cat $PdCl_2$	JOMC *125* 281 (1977)
ArMgBr(ZnCl)	ArBr	$PdCl_2[Ph_2P(CH_2)_4$-$PPh_2]_2$	TL *22* 5319 (1981)
n-BuZnCl	PhI	$PdCl_2L_2$	Bull Acad Sci USSR, Div Chem Sci 620 (1986)
RZnX (R = Ph, $PhCH_2$)	ArX	$Pd(PPh_3)_4$ or $PdCl_2L_2$	TL *21* 845 (1980)
RZnX (R = Ph, $PhCH_2$)	ArX	$PdCl_2(PPh_3)_2$, *i*-Bu_2AlH	JOC *42* 1821 (1977)
$EtO_2C(CH_2)_nZnI$ ($n = 2,3$)	ArI	$PdCl_2L_2$	TL *27* 955 (1986)
$(RO_2CCHRCH_2)_2Zn$	ArX	$PdCl_2(PAr_3)_2$	JACS *109* 8056 (1987)
RZnX (R = alkynyl, benzyl, $EtO_2CCH_2CH_2$)	ArO_3SR_f	$Pd(PPh_3)_4$, LiCl	TL *28* 2387 (1987)
RZnX [R = aryl·$Cr(CO)_3$]	ArX (Ar = heterocyclic)	$Pd(PPh_3)_4$	TL *28* 2645 (1987)
RZnX (R = heterocyclic)	ArX	$Pd(PPh_3)_4$	Syn 51 (1987) TL *28* 2645, 5213 (1987)
R_4Sn (R = Me, Et)	PhCHBrR′ (R′ = H, Me)	(bipy)Pd (NCCH=CHCN)	TL *27* 5207 (1986)
R_4Sn (R = Me, Ph, $CH{=}CH_2$, $PhCH_2$)	ArX, $ArCH_2X$	$PhCH_2PdCl(PPh_3)_2$	JACS *101* 4992 (1979)
R_4Sn or $RSnR'_3$ (R = 1° alkyl, alkynyl, aryl, vinylic)	ArOTf	$Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$, LiCl	JACS *109* 5478 (1987)
$RSnMe_3$ (R = Me, aryl)	ArI	$ArPdI(PPh_3)_2$	Proc Acad Sci USSR, Chem Sec *272* 333 (1983)
$RSnMe_3$ (R = heterocyclic)	ArX·$Cr(CO)_3$	$Pd(PPh_3)_4$	TL *28* 2645 (1987)
$RSn(n\text{-}Bu)_3$ (R = *n*-Bu, $H_2C{=}CH$)	ArCl·$Cr(CO)_3$	$Pd(PPh_3)_4$	CC 1755 (1987)
$RSnR'_3$ (R = heterocyclic)	ArX	$PdCl_2(PPh_3)_2$	TL *27* 4407 (1986)



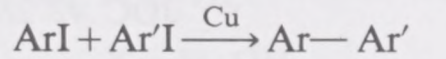
$$X = CO_2R, COR$$

JACS *99* 7093 (1977); *102* 4973 (1980)
Organomet *1* 1175 (1982)
TL *23* 939 (1982)

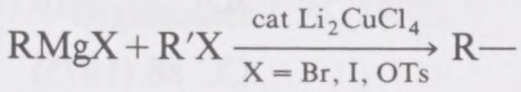
2.15. Organocopper Reagents

Reviews:

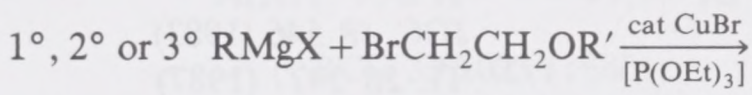
Syn 63 (1972)
Org Rxs *22* 253 (1975)



Tetr *38* 2569 (1982) (intramolecular)

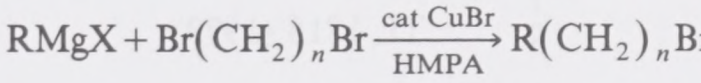


Syn 303 (1971)
JACS *96* 7101 (1974); *109* 7477 (1987)
Angew Int *13* 82 (1974)
JOC *41* 3505 (1976); *52* 2337, 4369 (1987)
TL 4697 (1976); *23* 3115, 3587 (1982); *27* 3903, 6193 (1986); *28* 651, 1175 (R′X = allylic acetate), 2281 (1987)
Ber *111* 1446 (1978)
Ann 1532 (1982)
J Chem Res (S) 93 (1982)



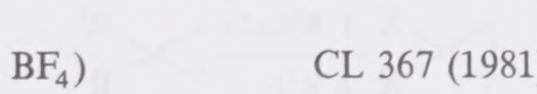
$$R' = H, alkyl, Ac$$

TL 3263 (1977)



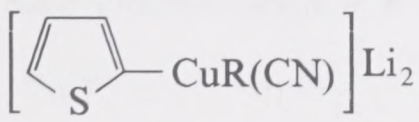
$$R = i\text{-Pr}, Ar;\ n = 3\text{–}6$$

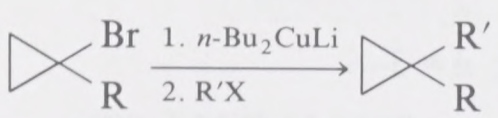
BCSJ *59* 2035 (1986)



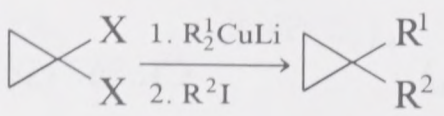
$NaCH(CO_2Et)_2$, CuX (X = Br, I, BF_4) (R′ = Ar)	CL 367 (1981)
NaO_2CCF_3, CuI (R′ = Ar; R = CF_3)	CL 1719 (1981); 135 (1982)
RMgX, cat CuX (X = Br, CN)	JOC *52* 3847 (1987) (heterocycles)

$$R'X \xrightarrow[R' = \text{alkyl, vinyl, aryl}]{} R{-}R' \quad (\textit{Continued})$$

$H_2C{=}CHCH_2MgCl$, CuI	TL *28* 2083 (1987)
CF_3Cu	Syn 932 (1980)
ArCu	TL 3307 (1968) JACS *90* 2186 (1968); *102* 790 (1980) Org Syn *59* 122 (1980) JOC *52* 547 (1987)
R_2CuLi	JACS *89* 3911 (1967); *90* 5615 (1968); *91* 4871 (1969); *94* 2520 (1972); *95* 7777, 7783 (1973); *104* 4696 (1982); *48* 546 (1983) JOC *39* 400 (1974); *44* 2705 (1979); *50* 127 (1985); *52* 4554 (1987) TL 683 (1974); *23* 415 (1982); *24* 3717 (1983); *27* 4273 (1986); *28* 3135 (1987) Syn 752 (1982) JOMC *251* 133 (1983)
R_3CuLi_2	JOC *42* 2805 (1977)
Me_3Cu_2Li, Me_3CuLi_2, $Me_5Cu_3Li_2$	JOC *42* 2805 (1977)
$(RCuC{\equiv}CCMe_2OMe)Li$	JOC *43* 3418 (1978)
(RCuCN)Li	CC 88 (1973) JOMC *251* 133 (1983)
(ArCuCN)Li	JACS *107* 2712 (1985)
$(R_2CuCN)Li_2$	JACS *103* 7672 (1981); *104* 4696 (1982) JOC *48* 3334 (1983); *49* 3928 (1984)
	JOMC *285* 437 (1985) TL *28* 945 (1987)
$[CH_3SOCH_2Cu(CN)R]Li_2$	JOC *52* 1885 (1987)
$(R_2CuSCN)Li_2$	JOC *48* 546 (1983) TL *28* 2977 (1987)
$(RCuNCy_2)Li$	JACS *104* 5824 (1982)
$(RCuPPh_2)Li$	JACS *104* 5824 (1982)
(RCuO-*t*-Bu)Li	TL 1815 (1973)



JACS *99* 5816 (1977)
BCSJ *52* 3632 (1979)



$X = Cl, Br\ (R^1 \neq CH_3, CH{=}CH_2)$

BCSJ *50* 1600 (1977)

2.16. Organomercury Reagents

$$RHgOAc + H_2C{=}CHX \xrightarrow[R_3SnH]{NaBH_4\ or} RCH_2CH_2X$$

R = alkyl; X = halogen, CO_2R, COR, CN, CO_2COR

Ber *110* 2588 (1977); *112* 3759, 3766 (1979); *113* 1192, 2787 (1980); *114* 1572 (1981); *117* 859, 2132, 3160, 3175 (1984); *118* 1289, 1345, 1616 (1985); *119* 1291 (1986)
Angew Int *16* 178 (1977); *18* 154 (1979); *20* 965 (1981); *26* 479 (1987)
TL 2779, 2783 (1977); *21* 1829, 3569 (1980); *22* 2155 (1981); *24* 11, 15, 2051, 3221 (1983); *25* 2743 (1984)
Organomet *1* 675 (1982)
Tetr *41* 4025 (1985)
Ann 427 (1987)

$$ArH \longrightarrow ArHgX \xrightarrow{R_2CuLi} Ar{-}R$$

R = 1°, 2° alkyl; vinylic

$$RCH{=}CH_2 \longrightarrow \underset{\displaystyle X}{RCHCH_2HgCl} \xrightarrow{Li_2Cu(CH_3)_3} \underset{\displaystyle X}{RCHCH_2CH_3}$$

X = H, OH

TL *22* 3435 (1981)
Organomet *1* 74 (1982)

2.17. Miscellaneous Reactions

$$R_fI(Ph)OSO_2CF_3 + ArH \longrightarrow R_f{-}Ar$$

CL 1663 (1981)

$$ArI + Ar'H \xrightarrow{h\nu} Ar{-}Ar'$$

JOC *30* 2493 (1965)

$$ArNH_2 + Ar'H \xrightarrow{t\text{-}BuSNO_2} Ar{-}Ar'$$

BCSJ *53* 2023 (1980)

$$\underset{\displaystyle O}{RCR} \longrightarrow \underset{\displaystyle NNHCPh_2(t\text{-}Bu)}{RCR} \xrightarrow[2.\ R'X]{1.\ base} \underset{\displaystyle R'}{\underset{\displaystyle N{=}NCPh_2(t\text{-}Bu)}{RCR}} \xrightarrow[\Delta]{PhSH} \underset{\displaystyle R'}{\underset{\displaystyle H}{RCR}}$$

CC 176 (1986)

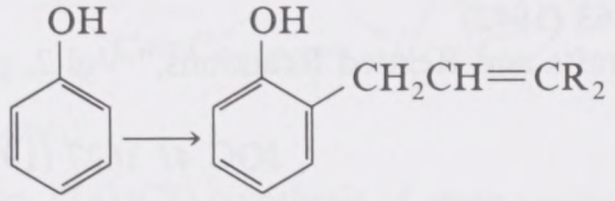
$$RCO_2H + R'CO_2H \xrightarrow{electrolysis} R{-}R'$$

"Organic Electrochemistry," Ed. M. M. Baizer, M. Dekker, New York (1973), p 469
"Techniques of Chemistry," Ed. N. L. Weinberg, J. Wiley, New York (1974), Vol 5, Part 1, p 793
Angew Int *20* 911 (1981)
Ann 1532 (1982)

3. FRIEDEL-CRAFTS AND RELATED ALKYLATION REACTIONS

Reviews:

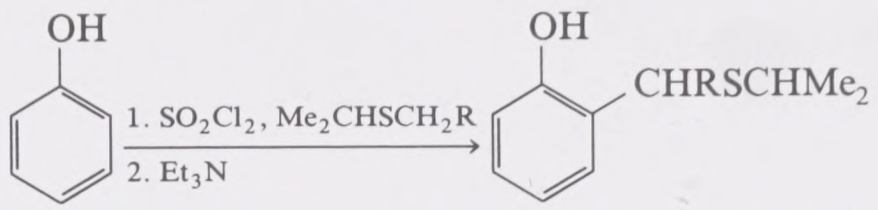
Org Rxs *3* 1 (1946)
Quart Rev *8* 355 (1954)
"Friedel-Crafts and Related Reactions," Ed. G. A. Olah, Interscience, New York (1964), Vol 2
G. A. Olah, "Friedel-Crafts Chemistry," Wiley-Interscience, New York (1973)
R. M. Roberts, A. A. Khalaf, "Friedel-Crafts Alkylation Chemistry," Marcel Dekker, New York (1984)



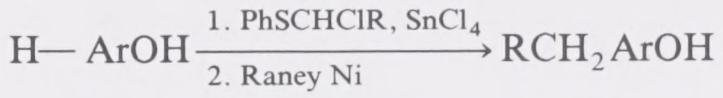
$NaH/R_2C{=}CHCH_2X$, toluene	JCS Perkin I 1601 (1982)
$KOH/R_2C{=}CHCH_2X$	TL *23* 4567 (1982) (*m*-diphenol)
$NaOMe/R_2C{=}CHCH_2X$	Ind J Chem *7* 1072 (1969) JOC *39* 2215 (1974)
$K/ZnCl_2/R_2C{=}CHCH_2X$	Syn 310 (1981)
Al_2O_3, $R_2C{=}CHCH_2X$	JOC *51* 4481 (1986)
Ag_2O, $R_2C{=}CHCH_2X$	Tetr *28* 4395 (1972) (*m*-diphenol)
$H_2C{=}CHC(CH_3){=}CH_2$, Me_3SiCl, NaI	TL *25* 5581 (1984)
$H_2C{=}CHC(CH_3){=}CH_2$, TsOH, NaI	TL *25* 5581 (1984)

$$ArH + ROH \longrightarrow Ar - R$$

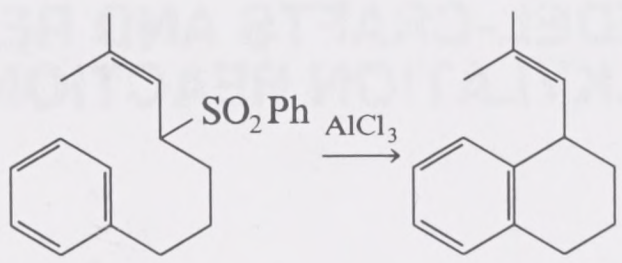
HOAc	Org Syn Coll Vol *4* 47 (1963)
HF	JACS *72* 5232 (1951)
P_2O_5	JCS 2520 (1932) (intramolecular)
$AlCl_3$	JACS *60* 1421 (1938)



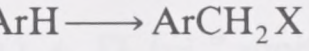
JACS *100* 7611 (1978)
JOC *52* 5495 (1987)



Syn 937 (1982)



JACS *106* 7260 (1984)

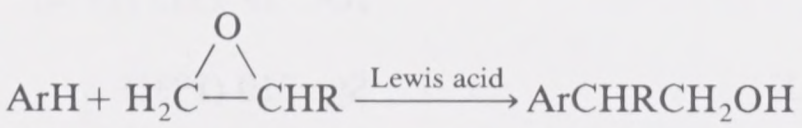


X = Cl, Br, I

Reviews:

Org Rxs *1* 63 (1942)
"Friedel-Crafts and Related Reactions," Vol 2, pp 659–784

$ClCH_2OCH_2Cl$, $SnCl_4$	JOC *41* 1627 (1976)
$(XCH_2OCH_2CH_2)_2$ (X = Cl, Br), Lewis acid	Syn 560 (1974) JOC *41* 1627 (1976) Org Prep Proc Int *14* 3 (1982)
H_2CO, HCl, $ZnCl_2$, HOAc	JACS *75* 6292 (1953)
H_2CO, HBr, HOAc	JOC *47* 578 (1982); *52* 3200 (1987)



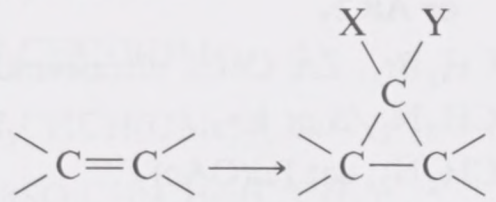
JCS 5404 (1964) (intramolecular)
Tetr *25* 1807 (1969)
JOC *48* 2449, 4572 (1983); *52* 425 (1987) (all intramolecular)

4. RING-FORMING REACTIONS

See also page 653, Section 6.

1. Three-Membered Rings

Review: Houben-Weyl, Vol IV/3 (1971)

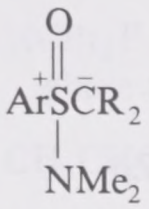
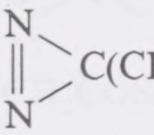


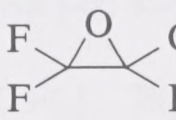
Reviews:

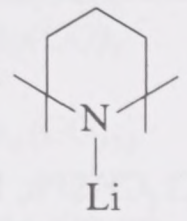
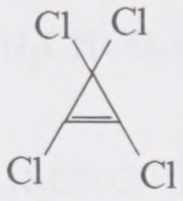
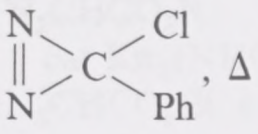
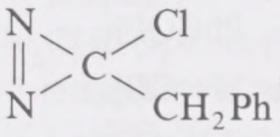
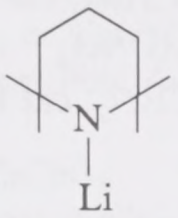
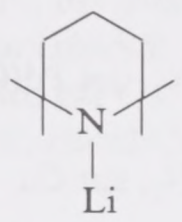
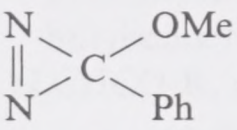
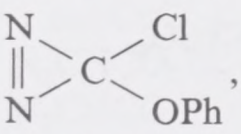
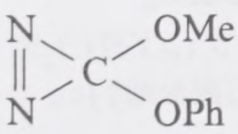
Syn 77 (1978) (synthesis of spiro compounds)
Tetr *36* 2531 (1980)
Acct Chem Res *13* 58 (1980); *19* 348 (1986)
Chem Rev *86* 919 (1986)

CXY	Reagent(s)	
CH_2	CH_2I_2, hν	JACS *100* 655 (1978) Tetr *37* 3229 (1981)
	CH_2I_2, R_3Al (R = Me, Et, *i*-Bu)	JOC *50* 4412 (1985) CC 157 (1987)
	CH_2I_2, Cu	JACS *98* 2676 (1976); *101* 2139 (1979)
	CH_2I_2, Cu, ultrasound	CC 1460 (1987)
	CH_2I_2, Zn, ultrasound	TL *23* 2729 (1982) Org Prep Proc Int *16* 25 (1984)
	CH_2I_2, Zn-Cu	JACS *80* 5323 (1958); *81* 4256 (1959); *85* 468 (1963); *91* 6892 (1969); *107* 4984, 8256 (chiral) (1985); *108* 3443 (1986) JOC *24* 1825 (1959); *33* 1767, 2141 (1968); *51* 2721 (1986) (diastereoselective); *52* 3000 (1987) (diastereoselective) Org Rxs *20* 1 (1973) (review) Org Syn Coll Vol *5* 855 (1973) J Chem Res (S) 179 (1978)

CXY	Reagent(s)	
CH_2 (*continued*)	CH_2I_2, Zn-Ag	Syn 549 (1972) JACS *104* 4290 (1982) TL *28* 1865 (1987) JOC *52* 603 (1987)
	CH_2I_2, EtZnI	TL *23* 259 (1982) JACS *109* 3025 (1987)
	CH_2I_2, Et_2Zn	TL 3353 (1966) Tetr *24* 53 (1968) JACS *106* 3869, 6006 (1984); *107* 8254 (1985) (chiral); *108* 6343 (1986); *109* 7553 (1987) JOC *52* 3603 (1987)
	CH_2I_2, Sm or Sm(Hg)	JOC *52* 3942 (1987) (allylic alcohols)
	CH_2Br_2, $CoCl_2$ or $NiBr_2$, Zn, NaI	CL 395 (1981)
	CH_2Br_2, cat $Ni(COD)_2$, NaI	CL 761 (1979)
	CH_2Br_2; cat $Ni(PPh_3)_4$; NaI, ZnX_2 (X = Cl, Br or I) or $AlCl_3$	CL 761 (1979)
	CH_2Br_2, Zn, CuCl, ultrasound	JOC *50* 4640 (1985)
	CH_2N_2/Δ or hν	TL *23* 2103 (1982)
	CH_2N_2, cat $Pd(OAc)_2$	TL 1465 (1972); 629 (1975); *23* 502 (1982); *28* 4547 (1987) Syn 636 (1975); 714 (1981) JOC *51* 4836 (1986)
	CH_2N_2, CuBr, cat $Cu(OTs)_2,\cdot 2\ H_2O$	Helv *59* 1953 (1976)
	CH_2N_2, cat $(CuOTf)_2$	JACS *95* 3300 (1973); *107* 996 (1985)
	$[CpFe(CO)_2CH_2\overset{+}{S}Me_2]BF_4^-$	JACS *101* 6473 (1979); *109* 3739 (1987) JOC *50* 5898 (1985)
	$\bar{C}H_2\overset{+}{S}Me_2$ (on Michael acceptors)	TL 661 (1962) Ber *96* 1881 (1963) JOC *29* 3277 (1964); *33* 3849 (1968); *34* 3324 (1969); *37* 2354 (1972) Ind J Chem B *19* 563 (1980)
	$\bar{C}H_2\overset{+}{S}OMe_2$ (on Michael acceptors)	JACS *84* 3822 (1962); *87* 1353 (1965); *106* 5335 (1984); *107* 4984 (1985) Z Naturforsch B *18* 976 (1963) JOC *31* 3467 (1966); *43* 2839 (1978); *50* 5898 (1985) JCS C 2495 (1967) Angew Int *12* 845 (1973) BSCF 888 (1974) TL *28* 3201 (1987)

CH_2, CHR, CR_2		Acct Chem Res *6* 341 (1973) JACS *95* 7692 (1973)
CH_2, CR_2, $CHCO_2R$	R_2CN_2, cat Cu(II)	Tetr *24* 3655 (1968) Can J Chem *47* 1242 (1969)
CHR (R = H, Me)	$RCHI_2$, R'_3Al	JOC *50* 4412 (1985)
CHR (R = H, Me, Ph)	$RCHI_2$, Et_2Zn	Tetr *27* 1799 (1971) JOC *42* 3031 (1977); *47* 1615, 2426 (1982)
$CHCH_3$	CH_3CHI_2, Zn, CuCl	JOC *47* 1615, 2426 (1982) JACS *107* 4230 (1985)
	$CpFe(CO)_2CH(CH_3)SPh$, $MeSO_3F$ or $(Me_3O)BF_4$	JACS *103* 1862 (1981) JOMC *285* 231 (1985)
CHR	$RCHN_2$, CuI	CL 863 (1982) (intramolecular)
	$CpFe(CO)_2CHRSPh$, $(Me_3O)BF_4$	JOC *50* 5898 (1985) (intramolecular)
$CHCF_3$	CF_3CHN_2, hν	JCS 1881 (1964)
$CHCH(OMe)_2$	$N_2CHCH(OMe)_2$, Δ	TL *23* 503 (1982)
	$N_2CHCH(OMe)_2$, hν	TL *21* 2239 (1980)
$CHCH{=}C(CH_3)_2$	$PhSO_2CH_2CH{=}C(CH_3)_2$, KO-*t*-Bu (on Michael acceptors)	BSCF 985 (1967)
	$NO_2CH(K)CH{=}C(CH_3)_2$ (on Michael acceptors)	JOC *50* 2806 (1985)
CHR (R = vinylic)	$RCH(K)NO_2$ (R = vinylic) (on Michael acceptors)	JOC *50* 2806 (1985)
$C(CH_3)_2$	$Ph_2\overset{+}{S}\overset{-}{C}(CH_3)_2$ (on Michael acceptors)	JACS *89* 3912 (1967)
	$(CH_3)_2CBr_2$, *n*-BuLi	Angew Int *20* 863 (1981)
	$(CH_3)_2CH(K)NO_2$, DMSO (on Michael acceptors)	JOC *50* 2806 (1985)
$C(CF_3)_2$		JACS *88* 3617 (1966)
CR_2	$R_2CH(K)NO_2$, DMSO (on Michael acceptors)	JOC *50* 2806 (1985)
CHF	$CHFI_2$, hν	TL 1819 (1975)
CHCl	CH_2Cl_2, *n*-BuLi	JACS *82* 5729 (1960) Can J Chem *59* 621 (1981)
CHBr	CH_2Br_2, $NaN(SiMe_3)_2$	Syn 201 (1972)
CHX (X = Cl, Br)	$XCHN_2$	JACS *84* 4350 (1962); *87* 4270 (1965)

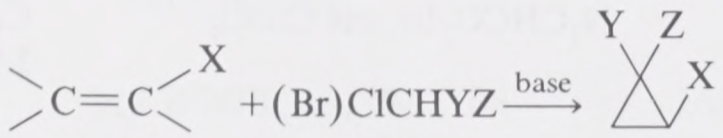
CXY	Reagent(s)	
CHX (X = F, Cl, Br, I)	$HCXI_2$, Cu	Tetr *35* 1919 (1979)
	HCX_3 or $HCXI_2$, Et_2Zn	CC 1375 (1971) (X = F, Cl, Br, I); 364 (1975) (X = Br) BCSJ *47* 1500 (1974) (X = I)
CF_2		JOC *35* 678 (1970) JCS Perkin I 2203 (1982)
	$ClCF_2CO_2Na$, Δ	JACS *85* 1851 (1963)
CCl_2	$HCCl_3$, NaOH, ultrasound	JOC *47* 1587 (1982)
	$HCCl_3$, NaOH, phase transfer	TL 4659 (1969); 1461 (1972); *27* 893 (1986) Ann *744* 42 (1971); 591 (1981) Tetr *28* 175 (1972) JOC *44* 447 (1979); *52* 3579 (1987) Syn 1004 (1981) J Chem Res (S) 354 (1982)
	$HCCl_3$, KO-*t*-Bu	JACS *76* 6162 (1954); *78* 1437 (1956); *80* 5274 (1958)
	$XCCl_3$ (X = Br, I), RLi (R = Me, *n*-Bu)	JACS *81* 5009 (1959)
	Cl_3CCO_2Na, Δ	JACS *85* 1851 (1963)
	Cl_3CCO_2Na, R_4NBr, Δ	J Chem Res (S) 72 (1977) Helv *65* 1191 (1982)
	Cl_3CCO_2Et, NaOR (R = Me, Et) or KO-*t*-Bu	JOC *24* 1733 (1959); *40* 2234 (1975) JACS *82* 4085 (1960) Org Syn Coll Vol *5* 874 (1973)
CBr_2	$HCBr_3$, NaOH, phase transfer	TL 1367 (1973) Syn 296 (1982) JOC *47* 3211 (1982); *52* 4732 (1987)
	$HCBr_3$, NaOH, *n*-Bu_3N	JACS *107* 8066 (1985)
	$HCBr_3$, KO-*t*-Bu	JOC *47* 3211 (1982)
CX_2 (X = Cl, Br)	HCX_3, NaOH	TL 1749 (1965)
CXY (X, Y = F, Cl, Br, I)	PhHgCXYZ (Z = F, Cl, Br, I)	Acct Chem Res *5* 65 (1972) (review) Russ Chem Rev *46* 941 (1977) (review) R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1985), Chpt 10 (review)
CFCl	$FCCl_2COCCl_2F$, KO-*t*-Bu	JOC *28* 2494 (1963)
	$HCCl_2F$, NaOH	TL 1749 (1965)

CFBr	$HCBr_2F$, NaOH, phase transfer	Ann 591 (1981)
$CClCH_3$	CH_3CHCl_2, RLi	Syn 801 (1974) Can J Chem *60* 1933 (1982) JACS *108* 1251 (1986) JOC *52* 1475 (1987)
$CClCH{=}CH_2$	$Cl_2CHCH{=}CH_2$, 	Syn 425 (1979)
$CClCCl{=}CCl_2$	 , Δ	TL *23* 3341 (1982)
CClPh	 , Δ	Org Syn *60* 53 (1981) TL *25* 901 (1984); *27* 4395 (1986)
$CClCH_2Ph$	 , hν or Δ	JOC *52* 4223 (1987)
$CHMMe_3$ (M = Si, Sn)	$ClCH_2MMe_3$, 	TL 1677 (1978)
CHOR	$ClCH_2OR$, 	TL 3779 (1976)
	$ClCH_2OR$, RLi	Angew *73* 27, 765 (1961) Ber *96* 2266 (1963); *97* 636 (1964)
	Cl_2CHOR, MeLi	Ber *98* 2221 (1965)
C(Ph)OMe	 , hν or Δ	CC 432 (1982) JACS *109* 4341 (1987)
$C(CH_3)OSiMe_3$	$CH_3COSiMe_3$, hν	JACS *103* 699 (1981)
CClOPh	 , Δ	JOC *47* 4177 (1982)
	$HCCl_2OPh$, NaOH, phase transfer	Angew Int *21* 916 (1982)
C(OMe)OPh	 , Δ	JACS *109* 3811 (1987)
CHSPh	$ClCH_2SPh$, NaOH, $(PhCH_2NEt_2)Cl$	TL 4247 (1975); *28* 4797 (1980)
	$ClCH_2SPh$, NaH	Compt Rend C *275* 283 (1972)

CXY	Reagent(s)	
CHSAr	$ClCH_2SAr$, KO-*t*-Bu	Angew *73* 765 (1961) TL 165 (1962) Ber *97* 1527 (1964) BCSJ *52* 3434 (1979)
	$ClCH_2SAr$, *n*-BuLi	Angew *73* 765 (1961) TL *165* (1962) Ber *97* 1527 (1964)
CClSPh	Cl_2CHSPh, NaOH, $(PhCH_2NEt_3)Cl$	TL 4517 (1971)
	Cl_2CHSPh, KO-*t*-Bu	Ber *99* 806 (1966)
$CHSO_2C_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4SO_2CHN_2$, cat $Cu(acac)_2$	JOC *52* 4760 (1987)
CHCOR	$RCOCHN_2$	Org Rxs *26* 361 (1980) (intramolecular, review)
	$RCOCHN_2$, hν, PhCOPh	JACS *90* 2200 (1968)
	$RCOCHN_2$, cat $Mo(CO)_6$	JOC *45* 1538 (1980)
	$PhCOCHN_2$, cat $Mo(CO)_6$ or $Mo_2(OAc)_4$	JOC *47* 4059 (1982)
	$RCOCHN_2$, cat $Rh_2(OAc)_4$	TL *27* 2075 (1986) JOC *51* 3878 (1986) JACS *109* 5432 (1987) (all intramolecular)
	$RCOCHN_2$, cat $Pd(OAc)_2$	Tetr *36* 3269 (1980) TL *23* 2411 (1982)
	$RCOCHN_2$, cat Cu	JACS *103* 1808, 1813 (1981) (both intramolecular)
	$RCOCHN_2$, cat Cu-bronze or $CuSO_4$	Tetr *28* 4653 (1972) (intramolecular)
	$RCOCHN_2$, cat Cu, cat $CuSO_4$	Tetr *26* 2815 (1970) JACS *109* 3147 (1987) JOC *52* 4634 (1987) (all intramolecular)
	$RCOCHN_2$, cat $Cu(acac)_2$	JOC *45* 5020 (1980) (intramolecular)
	$RCOCHN_2$, cat $CuSO_4$, cat $Cu(acac)_2$	JOC *47* 1522 (1982); *52* 4641 (1987)
CRCOR	N_2CRCOR, hν, PhCOPh	JACS *90* 2200 (1968)
	N_2CRCOR, cat $CuSO_4$	TL 1363 (1972) (intramolecular)
	N_2CRCOR, cat $Cu(acac)_2$	JOC *45* 5020 (1980) (intramolecular)
	N_2CRCOR, cat Cu(II) bis(*N*-*n*-butylsalicyl-ideneaminate)	JACS *106* 6006 (1984) (intramolecular)

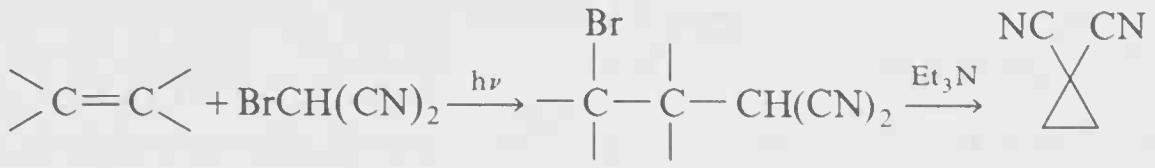
$CHCO_2R$	Br_2CHCO_2Me, Cu	JACS *98* 2676 (1976); *101* 2139 (1979)
	N_2CHCO_2R, hν or Δ	Org Rxs *18* 217 (1970) (review) Org Syn *50* 94 (1970) Chem Rev *75* 431 (1974)
	N_2CHCO_2R, $(Ar_3N)SbCl_6$	JACS *108* 4234 (1986)
	N_2CHCO_2Et, cat $Mo(CO)_6$	JOC *45* 1538 (1980)
	N_2CHCO_2Et, cat $Mo(CO)_6$ or $Mo_2(OAc)_4$	JOC *47* 4059 (1982)
	N_2CHCO_2Et,cat $Rh_6(CO)_{16}$	TL *22* 1783 (1981); *23* 2261 (1982) Syn 787 (1981)
	N_2CHCO_2R, cat $Rh_2(OAc)_4$	Syn 787 (1981) TL *23* 2261 (1982); *28* 833 (1987)
	N_2CHCO_2R, cat $Rh_2(O_2CCF_3)_4$	TL *28* 833 (1987)
	N_2CHCO_2R, cat $Rh_2(NHCOCH_3)_4$	TL *28* 833 (1987)
	N_2CHCO_2Et, cat Rh(III)-porphyrins	Tetr *38* 2365 (1982)
	N_2CHCO_2R, cat Rh(III)-tetraphenylporphyrin	TL *21* 3489 (1980)
	N_2CHCO_2R, cat $Rh_2(OAc)_4$ or $Pd(OAc)_2$ or $Cu(OTf)_2$	JOC *45* 695 (1980)
	N_2CHCO_2Et, cat $Pd(OAc)_2$	TL 1465 (1972); 629 (1975)
	N_2CHCO_2Et, cat $PdCl_2(PhCN)_2$	TL *23* 2261 (1982)
	N_2CHCO_2Et, cat π-allylpalladium chloride	JOC *52* 5158 (1987)
	N_2CHCO_2Et, cat Cu	JOC *38* 2221 (1973)
	N_2CHCO_2R, chiral Cu catalyst	Tetr *24* 3655 (1968) TL 1707 (1975); *23* 685 (1982) JACS *104* 1362 (1982); *106* 1421, 5312, 6364 (1984)
	N_2CHCO_2R, cat Cu(II) bis(salicylaldehyde-*t*-butylimine)	TL *25* 3559 (1984) (intramolecular) JACS *107* 5574 (1985)
	N_2CHCO_2R, cat $Cu(acac)_2$	TL *27* 2139 (1986) (intramolecular)
	N_2CHCO_2Et, cat $CuCl\cdot(i\text{-}PrO)_3P$	TL *23* 2261 (1982)
	N_2CHCO_2Et, cat CuI	JOC *50* 2026 (1985)
	N_2CHCO_2Et, cat $CuSO_4$	Can J Chem *60* 2383 (1982) JACS *106* 1421 (1984); *107* 734 (1985) JOC *52* 4898 (1987)
	N_2CHCO_2Et, cat $(CuOTf)_2\cdot C_6H_6$	JACS *95* 3300 (1973); *107* 996 (1985)
CHCONHAr	$N_2CHCONHAr$, cat $Rh_2(O_2CR)_4$	JOC *51* 5362 (1986)

CXY	Reagent(s)	
$CHCONR_2$	$N_2CHCONR_2$; cat $Rh_2(OAc)_4$, $Rh_2(O_2CCF_3)_4$ or $Rh_2(NHCOCH_3)_4$	TL *28* 833 (1987)
$CRCO_2R$	$RCHXCO_2R$ (X = Cl, Br), NaH or NaOMe	JACS *80* 6568 (1958)
$C(CH{=}CH_2)CO_2Et$	$CH_3CH{=}CBrCO_2Et$, LDA (on Michael acceptors)	JOC *51* 4746 (1986); *52* 4397, 4641 (1987)
$C(COR)SO_2Ph$	$N_2C(COR)SO_2Ph$, cat $Rh_2(OAc)_4$	TL *28* 3459 (1987) (intramolecular)
$C(COR)_2$	$N_2C(COR)_2$, hν, PhCOPh	JACS *106* 6006 (1984) (intramolecular)
$C(COR)CO_2R$	$N_2C(COR)CO_2R$, hν, PhCOPh	JACS *106* 6006 (1984) (intramolecular)
	$N_2C(COR)CO_2R$, cat Cu(II)	Tetr *37* 2079 (1981) JACS *106* 6006 (1984); *109* 4717, 6187 (1987) (all intramolecular)
$C(CO_2R)_2$	$BrCH(CO_2Et)_2$, DBU, $CuBr_2$	BCSJ *55* 2687 (1982)
	$Br_2C(CO_2R)_2$, Cu	Tetr *36* 3517 (1980)
	$MeSCl/NaCH(CO_2R)_2$ / Me_2SO_4/NaOEt	Syn 690 (1980) JACS *106* 5335 (1984)
$CPhCO_2R(CN)$	PhCHClCO$_2$R(CN), NaOH (on enones)	Syn 34 (1980)
CXY (X, Y = CO_2Et, CN)	Br_2CXY, Cu_2Br_2, DMSO	BCSJ *54* 2539 (1981)
CHCN	$(Me_3\overset{+}{N}CH_2CN)I^-$, NaH (on enones)	Syn 301 (1982)
$C{=}C{=}C{=}CR_2$	$HC{\equiv}CC(OSO_2CF_3){=}CR_2$, KO-*t*-Bu	Acct Chem Res *15* 348 (1982)

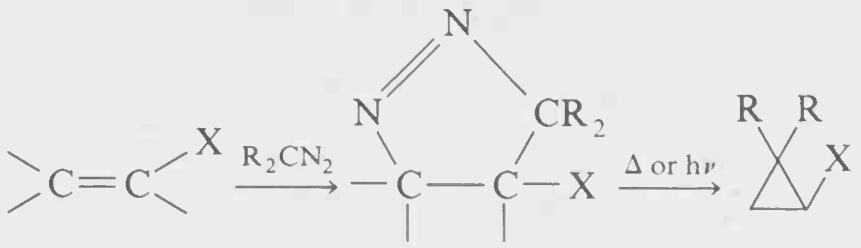


X = CHO, COR, CO_2R, CN; Y = COR, CO_2R; Z = H, R, CO_2R, Cl

Ber *51* 907, 533 (1918)
JACS *70* 3470 (1948); *80* 6568 (1958); *82* 6416 (1960); *84* 2246 (1962)
BSCF 986 (1957); 1102 (1959); 418, 788 (1960); 200 (1961); 2462 (1964)
JOC *24* 1536 (1959); *25* 2078 (1960); *27* 4312 (1962); *29* 240 (1964)
Compt Rend *248* 887, 1465, 2840 (1959)



JACS *87* 1394 (1965)
TL 1415 (1966); 4351 (1967)
JOC *31* 2784 (1966)
Ber *100* 1281 (1967)

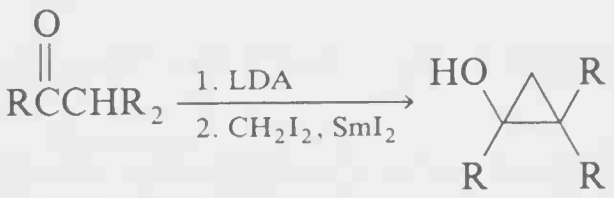


X = Ar, COR, CO_2R, CN

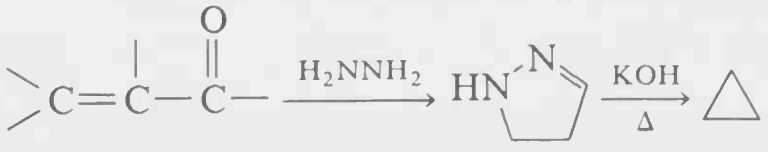
Reviews:

Newer Methods Prep Org Chem *1* 513 (1948)
Heterocyclic Compounds, Ed. R. Elderfield, J. Wiley, New York (1957), Vol 5
Houben-Weyl, Vol IV/3, p 43

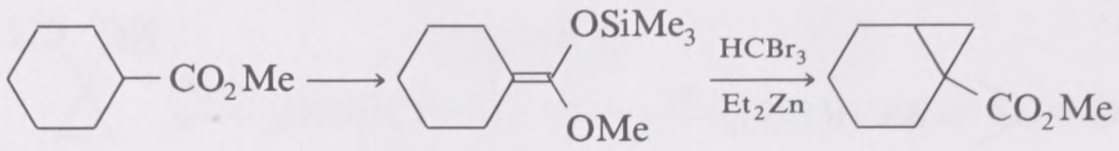
Ber *21* 2637 (1888); *23* 701 (1890); *27* 868, 877, 879 (1894); *36* 3774, 3782 (1903); *49* 1928 (1916); *70* 1688 (1937); *71* 2673 (1938); *88* 49 (1955); *93* 883, 1710 (1960); *100* 3495 (1967)
Ann *273* 239 (1893); *496* 252 (1932); *618* 105 (1958); *678* 78 (1964); *703* 104 (1967)
J Prakt Chem [2] *133* 291 (1932) (1,3-diene); [4] *36* 73 (1967)
JACS *56* 2710 (1934); *65* 159 (1943); *72* 3815 (1950); *73* 2383 (1951); *79* 4994 (1957); *80* 6687 (1958); *81* 3776, 5153, 5472 (1959); *82* 3136, 5251 (1960); *84* 869, 3736 (1962); *86* 658 (1964); *87* 4119 (1965)
JCS 829 (1936); 5186 (1962)
Rec Trav Chim *62* 210 (1943)
JOC *25* 852 (1960); *26* 1831, 3669 (1961); *27* 213, 1030 (1962); *31* 3467 (1966); *50* 2220, 2600 (1985); *52* 120 (1987)
Can J Chem *38* 2410 (1960); *45* 691 (1967) (1,3-diene)
BSCF 550 (1960) ($BF_3 \cdot OEt_2$ promoted elimination); 1761 (1962)
Helv *43* 2178 (1960); *49* 1049 (1966)
TL 1719 (1964); 3947 (1965)
Angew *79* 815 (1967); *80* 42 (1968)
Z Chem *7* 421 (1967)



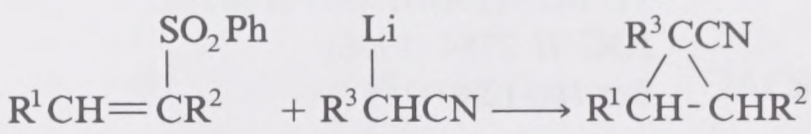
TL *28* 1307 (1987)



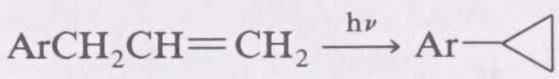
J Russ Phys Chem Soc *44* 165 [CA *6* 1431 (1912)], 849 [CA *6* 2915 (1913)] (1912); *45* 949 [CA *7* 3964 (1913)], 957 [CA *7* 3965 (1913)] (1913); *47* 1102 [CA *9* 3051 (1915)]; 1819 [CA *10* 1338 (1916)] (1915); *50* 1 (1918) [CA *18* 1485 (1924)]; *61* 781 (1929) [CA *23* 4698 (1929)]
Helv *25* 732 (1942)
JACS *66* 488 (1944); *69* 2544 (1947); *73* 3840 (1951)
JCS 4686 (1952)



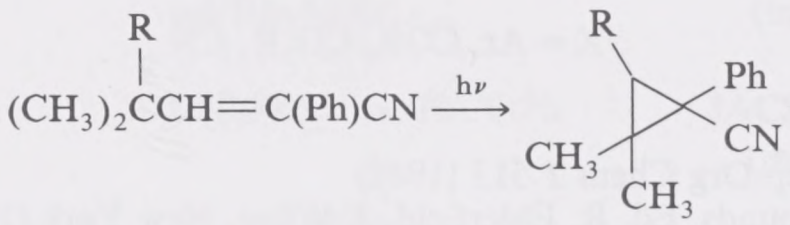
JACS *106* 7283 (1984)



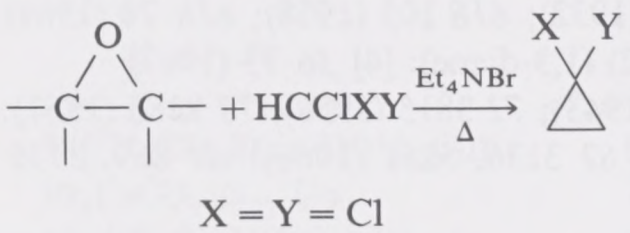
JCS Perkin I 751 (1981)



Chimia *35* 52 (1981)



JOC *43* 2839 (1978)
Can J Chem *60* 1657 (1982)
TL *27* 6225 (1986)

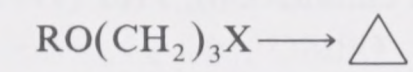


$X = Y = Cl$

$X = F, Y = Cl$

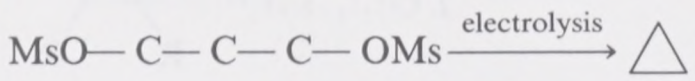
$X = Y = F$

Ber *100* 1858 (1967)

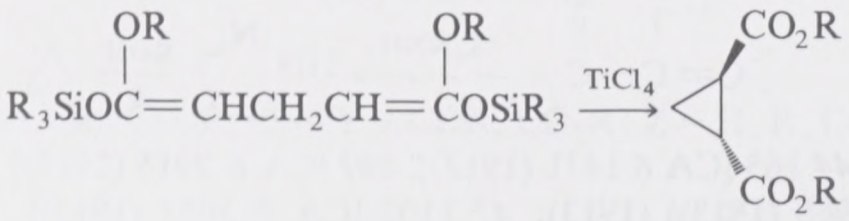


Mg — JACS *74* 6290 (1952); JOC *20* 275 (1955)

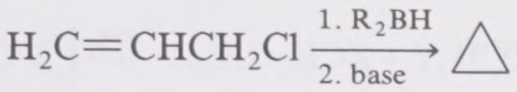
$EtMgBr, CoBr_2$ — JACS *83* 2734 (1961)



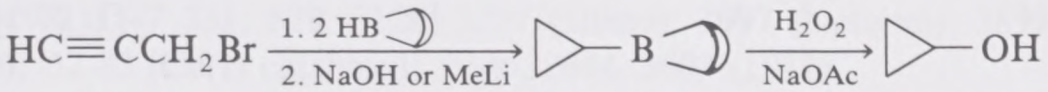
JOC *47* 3090 (1982)



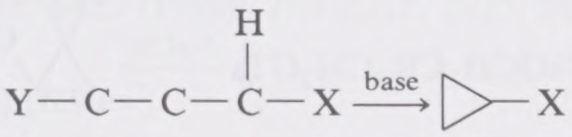
TL *23* 799 (1982)
Tetr *39* 847 (1983)



JACS *80* 5830 (1958); *82* 1886 (1960); *86* 1791 (1964); *91* 2149, 4306 (1969)
Israel J Chem *6* 691 (1968)



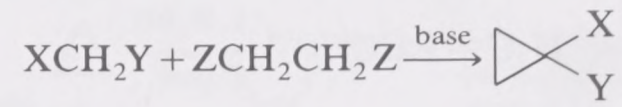
JACS *91* 4306 (1969)



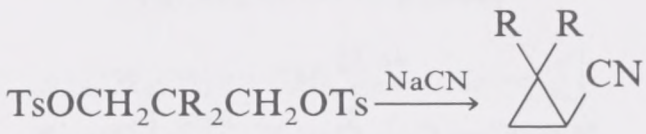
Review: Houben-Weyl, Vol IV/3, p 89

X	Y	
COR	OTs	BSCF 1340, 1347 (1957) JACS *83* 4678 (1961); *85* 41 (1963) JCS C 909 (1967) JOC *37* 2911 (1972)
	$OTs, \overset{+}{N}Me_3$	JOC *22* 1146 (1957)
	OAc	JACS *80* 1264, 5304 (1958)
	Cl	JOC *19* 1628 (1954) JACS *78* 112 (1956); *79* 1455 (1957) BSCF 1634 (1962) Org Syn Coll Vol *4* 597 (1963) JCS Perkin II 579 (1982)
	Br	JCS 1060 (1954); 2620 (1956) JACS *76* 4115 (1954) Ber *91* 768 (1958) JCS Perkin II 579 (1982)
	I	JACS *87* 4601 (1965)
CO_2R	$O_3SC_6H_4Br$	JOC *22* 1146 (1957)
	O_2CR	TL 2441 (1976)
	Cl	Compt Rend *245* 2304 (1957) BSCF 1487 (1964) Syn 955 (1982) (phase transfer)
	Br	BSCF 681 (1957)
CN	OTs, OMs	BSCF 1854 (1961)
	O_2CR	BSCF 1476 (1964)
	Cl	JACS *67* 1587 (1945); *109* 7483 (1987) (bicyclobutane)
SO_2Ph	OMs	TL *22* 4339 (1981)
$(SO_2Ph)_2$	Cl, I	CC 1374 (1983) JCS Perkin II 605 (1986)

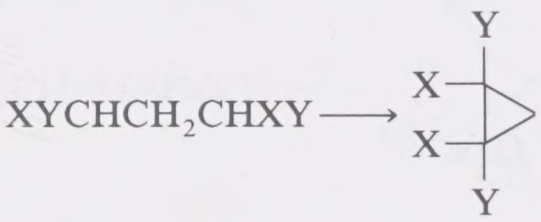
For analogous opening of epoxides see page 512 Section 4.1.



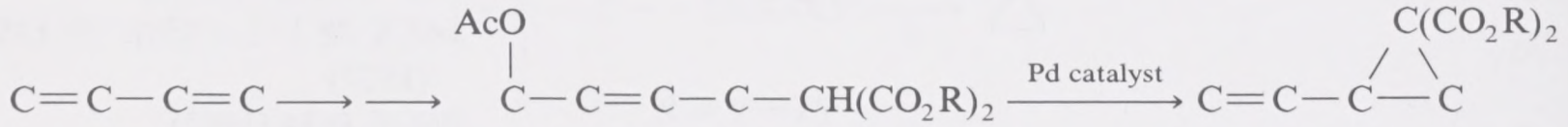
X	Y	Z	
CN	Ar	Cl	JACS *67* 1249 (1945)
CO_2R, CN	Ar	Br	TL *27* 3685 (1986)
CH=CHCH=CH		Br	JCS 646 (1958)



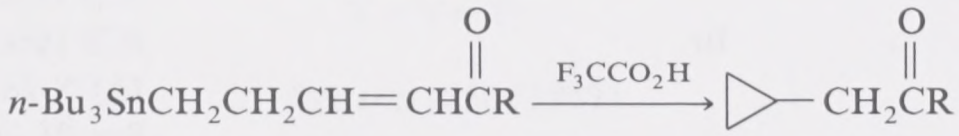
JACS *79* 3467 (1957)



X	Y	Reagent(s)	
CN	CN	Br_2	JOC *22* 1130 (1957)
RCO	H	Br_2/NaI	JCS 2620 (1956)



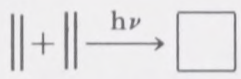
JOC *52* 5430 (1987)



TL *23* 2577 (1982)

2. Four-Membered Rings

Review: Houben-Weyl, Vol IV/4 (1971)



Reviews:

Chem Rev *66* 373 (1966) (intramolecular)
Acct Chem Res *1* 50 (1968) (enones); *4* 41 (1971) (enone photoannelation); *15* 135 (1982) (intramolecular)
Syn 287 (1969) (enones)
Photochem Photobiol *25* 605 (1977)
Org Photochem *5* 123 (1981)
Rev Chem Intermed *4* 369 (1981)
A. C. Weedon in "Synthetic Organic Photochemistry," Ed. W. M. Horspool, Plenum, New York (1984), Chpt 2

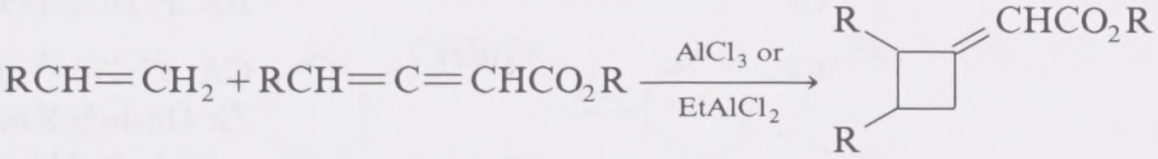
Recent references:

Intramolecular

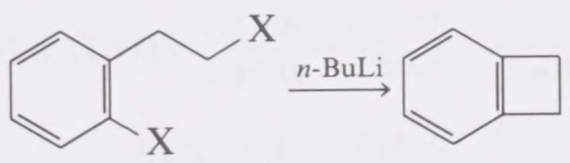
CC 235 (1979); 1195 (1980); 118 (1981); 1578 (1987)
Helv *63* 1198 (1980)
Org Photochem *5* 123 (1981) (enones, review)
JOC *46* 4821 (1981); *47* 331, 829, 3121, 3297 (allene), 3597 (lactones), 3893 (1982); *50* 3155 (1985) (allene); *52* 83 [Cu(I) catalyzed], 2346, 2644, 3603 (1987)
Tetr *37* 4543 (1981)
JACS *103* 82 (1981); *104* 998, 6841 (1982); *105* 1292, 1299 (1983); *107* 5732 (1985); *108* 800, 1311 [Cu(I) catalyzed], 3385, 3435, 6425 (1986); *109* 2212, 2523, 2850, 6199, 7230 (1987)
Can J Chem *60* 425 (1982)
Acct Chem Res *15* 135 (1982) (review)
J Chem Ed *59* 313 (1982) (review)
TL *23* 23 (enones), 711 (1982); *24* 2961 (1983); *26* 989 (allene), 1429 (allene), 5883 (1985); *27* 2703 (allene), 5177, 6393 (1986); *28* 1295, 5083, 5087, 5497 (1987)

Intermolecular

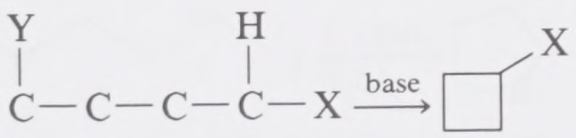
JACS *102* 3634 (1980); *107* 1308 (1985); *108* 306 (1986)
Can J Chem *60* 425 (micelles), 872 (allene-lactone) (1982)
JCS Perkin I 1697 (1984)
JOC *50* 3026 (1985); *51* 5226 (1986); *52* 1993, 2639, 3595 (1987)
TL *26* 4707, 6163 (1985); *27* 5975, 6049 (1986); *28* 581 (allene), 2833 (chiral), 2857, 5017 (1987)
Tetr *42* 3547 (1986)



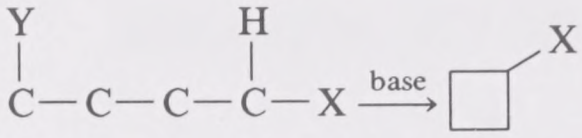
JOC *45* 5017 (1980); *51* 3643 (1986)
TL *22* 1953 (1981)



JOC *41* 1184 (1976)
TL 4573 (1977)
JACS *109* 7137 (1987)

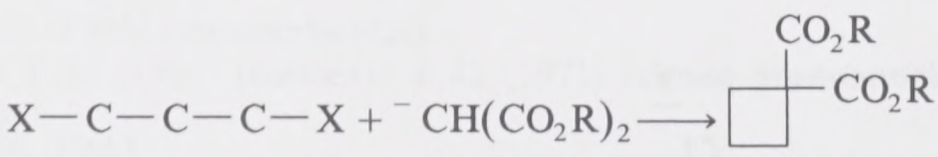


X	Y	
RCO	Cl	JACS *83* 938 (1961) TL 2525 (1964) Ber *100* 720 (1967) JCS C 2350 (1969)
	Br	Ber *91* 1616 (1958) Tetr *25* 613 (1969)



(*Continued*)

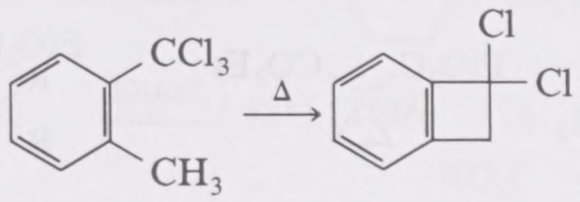
X	Y	
	I	Angew Int *1* 457 (1962) Tetr *26* 1589 (1970)
	$O_3SC_6H_5$	JOC *27* 1883 (1962)
	OTs	Angew Int *1* 457 (1962) TL 1043 (1963); 2525 (1964); 2043 (1966); 3627 (1969) JACS *88* 4110 (1966); *89* 4133 (1967) BSCF 147 (1966) Ber *100* 720, 2978 (1967) Tetr *25* 5267 (1969); *26* 1589 (1970) JOC *37* 2911 (1972)
	$\overset{+}{N}Me_3$	Angew Int *1* 457 (1962) Ber *100* 720 (1967)
enone	OMs	JOC *34* 3837 (1969)
	OTs	Tetr *25* 5281 (1969)
CO_2R	Cl	BSCF 1833 (1959); 979 (1960)
$(CO_2R)_2$	Cl	CA *37* 4705[6] (1943) Zh Obshch Khim *22* 122 (1952) [CA *46* 11119d (1952)] Bull Acad Sci USSR, Div Chem Sci 1585 (1966)
	Br	JACS *71* 2941 (1949); *106* 1051 (1984) JOC *26* 2335 (1961)
CN	Cl	Compt Rend *231* 703 (1950) BSCF 1833 (1959)
	OTs	BSCF 979 (1960)
1,3-dithiane	Cl	JOC *33* 300 (1968)
$(SO_2Ph)_2$	Cl, I	CC 1374 (1983) JCS Perkin II 605 (1986)
$\overset{+}{P}Ph_3$	Br	JOC *30* 3215 (1965); *33* 3082 (1968)



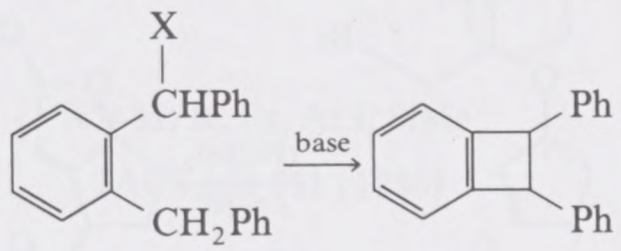
X = halogen, OTs

JCS *51* 1 (1887); *61* 36 (1892); *127* 2387 (1925); 1487 (1929); 1211 (1938); 3002 (1953)
Ber *40* 3883 (1907); *98* 2651 (1965); *99* 1509 (1966)

Rec Trav Chim *50* 921 (1931)
JACS *63* 1698 (1941); *84* 4982 (1962)
JOC *14* 1036 (1949); *21* 1371 (1956); *22* 1029 (1957); *26* 54 (1961); *27* 1647 (1962); *30* 1945, 3308, 4212 (1965); *31* 4069 (1966)
Org Syn Coll Vol *3* 213 (1955); *4* 288 (1963)
Ann *648* 36 (1961); *666* 81 (1963); *678* 53 (1964); *685* 74 (1965); *692* 53 (1966); *694* 1 (1966)
Naturwiss *50* 441 (1963)
Angew Int *5* 127 (1966)
Bull Acad Sci USSR, Div Chem Sci 1585 (1966)

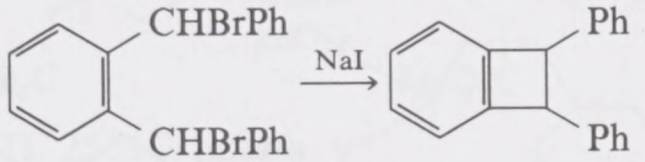


JACS *82* 749 (1960)
JOC *31* 2244 (1966); *34* 2906 (1969)

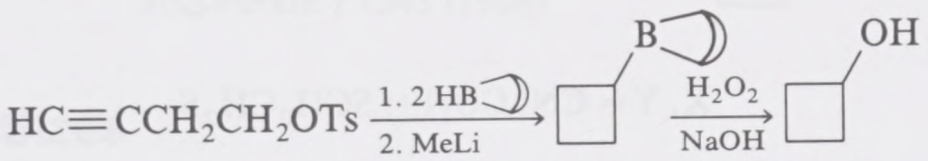


X = Cl, Br

JACS *80* 6149 (1958); *85* 4031 (1963)

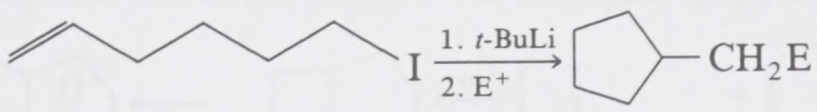


JACS *80* 6149 (1958)



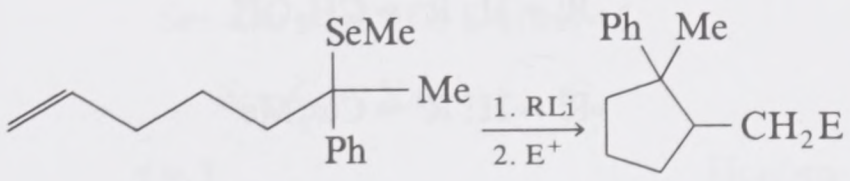
JACS *91* 4306 (1969)

3. Five-Membered Rings



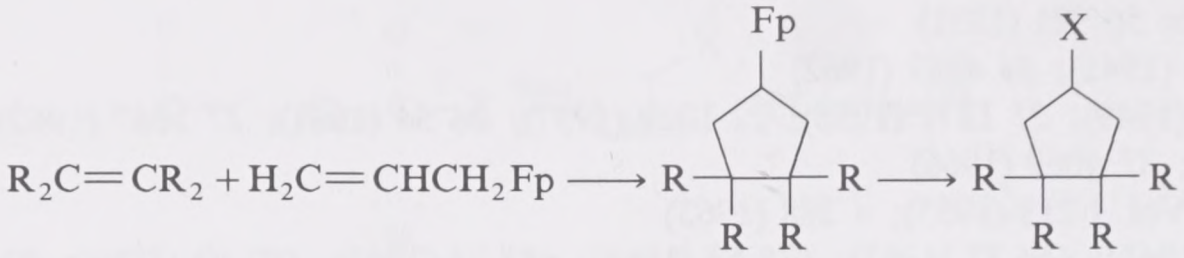
$E^+ = CH_3OH, CH_3OD, CO_2, O_2$

JACS *109* 2442 (1987)



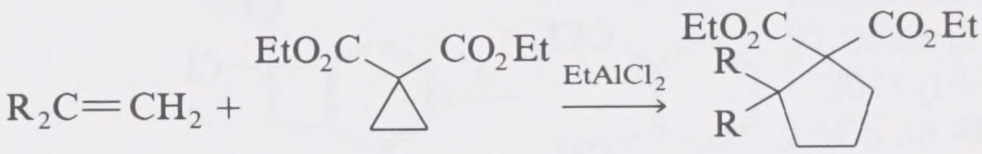
$E^+ = H_2O$, PhCHO

CC 1214 (1987)

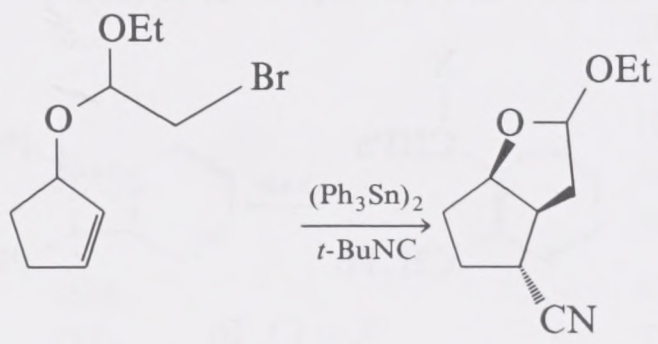


R = H, CN, CO_2R; Fp = $CpFe(CO)_2$; X = H, Br, CO_2R'

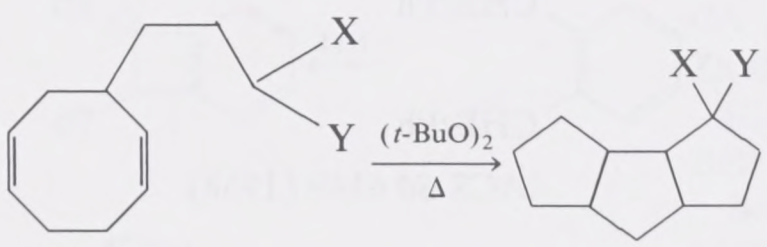
JCS Perkin I 285, 295, 301 (1982)



JOC *51* 4391 (1986)



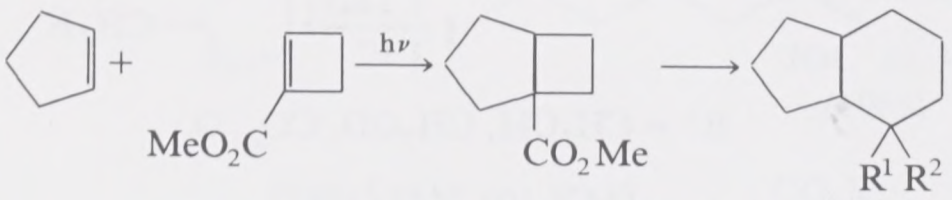
JACS *105* 6765 (1983)



X, Y = CN, CO_2Et; SCH_2CH_2S

JACS *108* 1708 (1986)

4. Six-Membered Rings

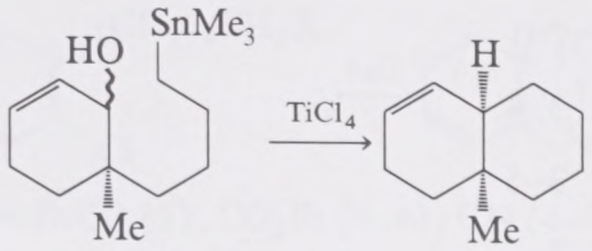


R^1 = H; R^2 = CH_2OH

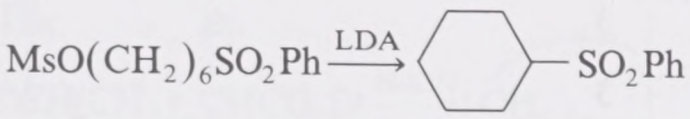
R^1 = H; R^2 = CO_2Me

R^1 = Me; R^2 = CO_2Me

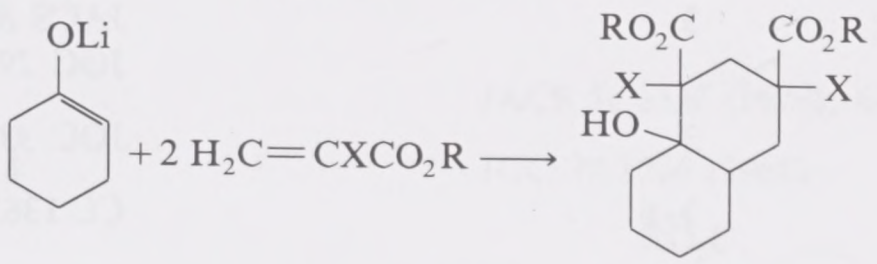
JACS *100* 4321 (1978)



TL *22* 2077 (1981)
JACS *103* 6767 (1981)

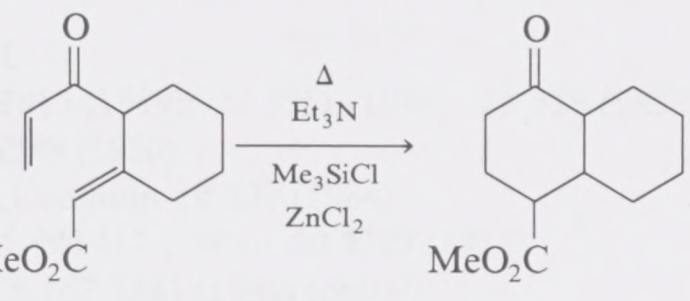


JOC *51* 5311 (1986)



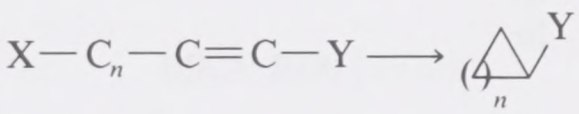
X = H, R, Br, ArS, $SiMe_3$

JACS *108* 511 (1986)



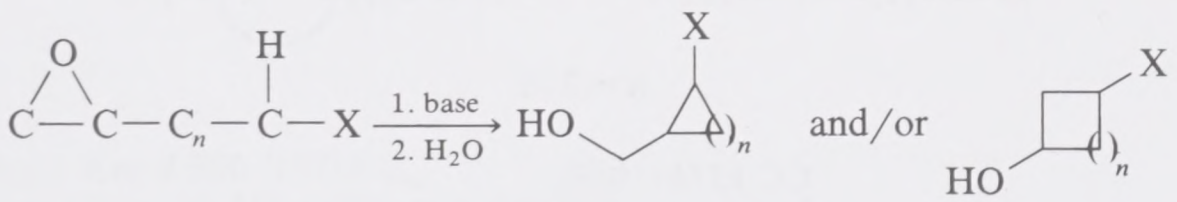
TL *25* 2167 (1984)
CC 1159 (1985); 721, 1467 (1987)
JCS Perkin I 1543 (1986)

5. Various Ring Sizes

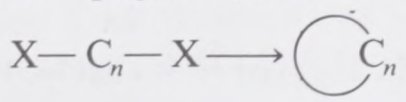


X = Br, I; Y = COR, CO_2R, CN

See the appropriate functional group Y for conjugate addition reactions



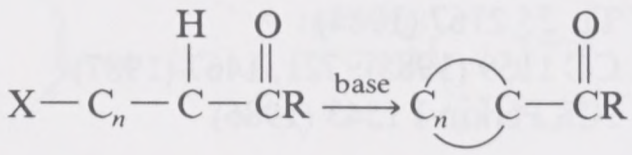
See also page 512, Section 4.1.



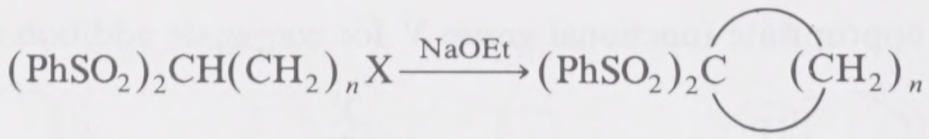
Reviews:

$n = 3$	Houben-Weyl, Vol IV/4 (1971), p 32 Russ Chem Rev *51* 368 (1982)
$n = 4$	Houben Weyl, Vol IV/4 (1971), p 31

Reagent(s)	n	
electrolysis	3, 4	TL 1119 (1974)
Li(Hg)	3–5	TL 4925 (1967); *28* 5263 (1987)
MeLi	3	TL *28* 5411 (1987)
t-BuLi	3–5	TL *23* 5123 (1982)
Na	3	TL 2173 (1963)
Mg	3	JACS *75* 3344 (1953)
Mg/AgOTf	4–6	JOC *41* 2882 (1976)
RMgBr, $FeCl_3$	3	JACS *83* 3232 (1961) JOC *29* 2813 (1964)
$Cr(ClO_4)_2$, EDA	3	JOC *33* 1027 (1968)
$Ni(COD)_2$, bipy	3–6	CL 1363 (1974)
Zn	3	J Prakt Chem *36* 300 (1887); *58* 458 (1898) JACS *66* 812 (1944); *68* 1335 (1946); *70* 946 (1948) JOC *23* 1715 (1958) BSCF 116 (1966) Syn Commun *11* 865 (1981)
Zn-Cu	3	Org Syn *44* 30 (1964)

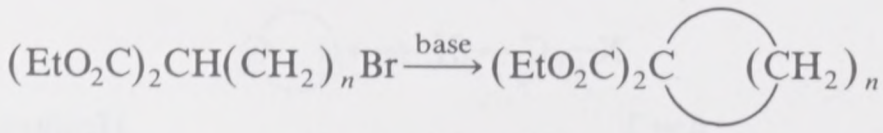


n	X	
4	Cl	JCS Perkin II 579 (1982)
	Br	Ber *91* 1616 (1958) JCS Perkin II 579 (1982)
5	Br	Ber *91* 1616 (1958)



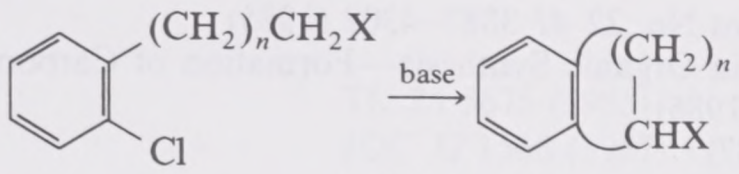
$n = 2–6$

CC 1374 (1983)
JCS Perkin II 605 (1986)



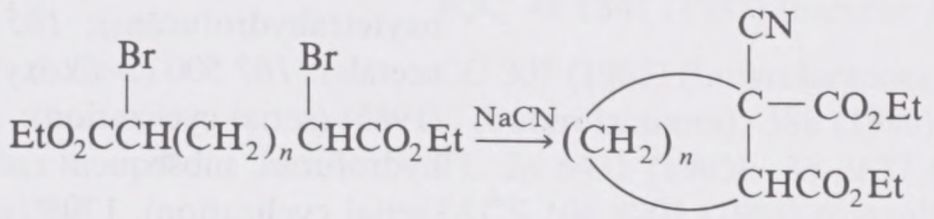
$n = 3–12, 16, 20$

JACS *106* 1051 (1984)

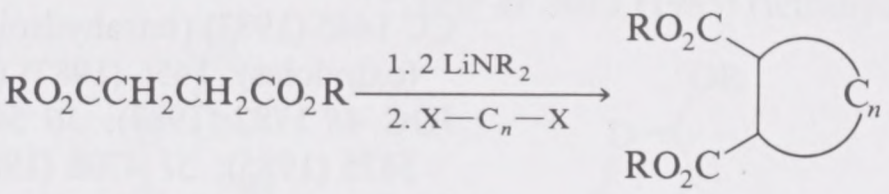


X (ring size) = PhCO (5), CO_2Et (4–6), CN (4–7), SO_2Ph (4, 5)

JOC *27* 3836 (1962)

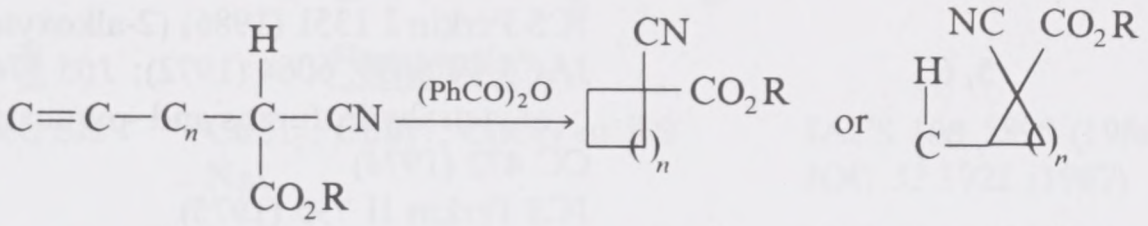


n	
2	JACS *51* 1536 (1929); *64* 2696 (1942)
2–4	JOC *30* 1206 (1965)



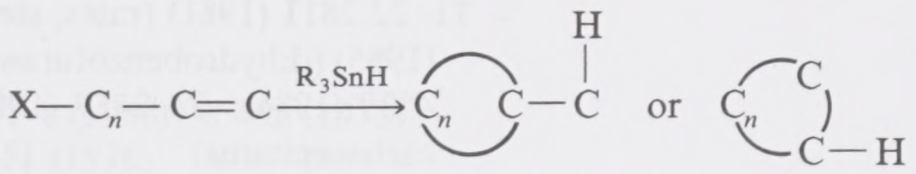
$n = 1–5$

TL 1815 (1979); *27* 5951 (1986); *28* 589 (1987)
Syn 389 (1980)
Syn Commun *14* 227 (1984)
JOC *49* 1412 (1984); *50* 5727 (1985)
JACS *107* 3343 (1985) (chiral)



$n = 3$ $n = 4$

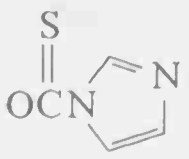
BSCF 3070 (1970)



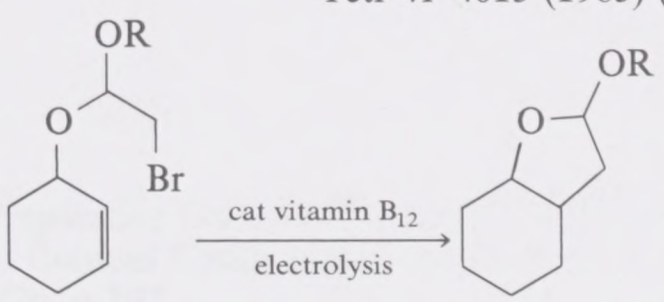
Reviews:

Acct Chem Res *4* 386 (1971)
Pure Appl Chem *40* 553 (1974) (mechanism)
A. L. J. Beckwith and K. U. Ingold in "Rearrangements in Ground and Excited States," Ed. P. de Mayo, Academic Press, New York (1980), pp 162–310
CC 482 (1980) (steric and stereoelectronic effects)
Tetr *37* 3073 (1981); *41* 3925 (1986) (theory)
J.-M. Surzur in "Reactive Intermediates," Ed. R. A. Abramovitch, Plenum, New York (1981), Vol 2, Chpt 3
Angew Int *22* 753 (1983); *24* 553 (1985)
Science *223* 883 (1984)

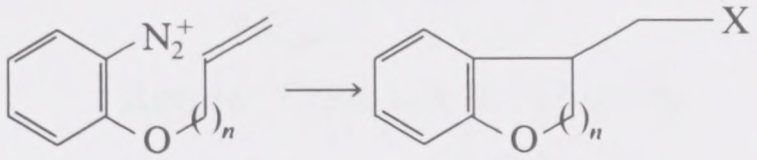
Tetr Symposia-in-Print No. 22 *41* 3887–4302 (1985)
B. Giese, "Radicals in Organic Synthesis—Formation of Carbon-Carbon Bonds," Pergamon Press, New York (1986)
Curr Sci *56* 392 (1987)

X	Ring size	
halogen	5	JACS *96* 1613 (1974); *104* 5564 (1982) (2-alkoxytetrahydrofurans); *105* 3741 (1983) (bicyclic acetals); *107* 500 (2-alkoxytetrahydrofurans), 1448 (1985) (serial cyclization); *108* 303 (2-alkoxytetrahydrofuran, subsequent radical trapping), 1106 (serial cyclization), 1708 (serial cyclization), 2116 (serial cyclization), 3102, 5890 (dihydrobenzofurans), 8098 (1986)
		J Chem Res (S) 78 (1981)
		Austral J Chem *36* 545 (1983) (rates, stereochemistry)
		CC 1445 (1983) (tetrahydroindanes); 115 (1986) (oxindoles); 1456 (1987) (bicyclic alkane)
		JOC *48* 1782 (1983); *50* 546, 5620 (pyrrolidines), 5875 (1985); *51* 4708 (1986) (tetrahydrofurans)
		TL *25* 4317 (1984) (2-alkoxytetrahydrofurans); *26* 957 (pyrrolidines); 3349 (serial cyclization, *n*-Bu_3GeH), 4991 (serial cyclization) (1985); *27* 3715 (1986) (tetrahydrofurans); *28* 671 (2-alkoxytetrahydrofurans), 1317 (2-alkoxytetrahydrofurans), 1623 (2-alkoxytetrahydrofurans), 2127, 3953 (pyrrolidines), 6389 (oxindole) (1987)
		CL 1725 (1985)
		JCS Perkin I 1351 (1986) (2-alkoxytetrahydrofurans)
	5, 6	JACS *94* 6059, 6064 (1972); *105* 3741 (1983) (2-alkoxytetrahydrofurans and -pyrans); *108* 5893 (1986)
		CC 472 (1974)
		JCS Perkin II 795 (1975)
		Tetr *31* 1737 (1975); *37* 3073 (1981)
		JOC *43* 6 (1978); *49* 2299 (1984) (diols); *52* 4072 (1987)
		TL *22* 2811 (1981) (rates, stereochemistry); *26* 6001 (1985) (dihydrobenzofurans and -pyrans); *27* 4525, 4529 (1986); *28* 2637 (1987) (carbapenams and carbacephams)
		CC 85 (lactones), 464 (1986); 1456 (1987) (bicyclic alkane)
	6	JOC *41* 3261 (1976)
		TL *26* 4413 (1985); *28* 1035 (1987)
		CC 1438 (1987) (lactone)
	6, 7	JOC *48* 1841 (1983) (bicyclic β-lactams)
	7	CC 472 (1974)
	10, 14, 18	JACS *108* 2787 (1986) (ketones)
	5	JACS *109* 609 (1987)

	6	TL *26* 5675 (1985) JOC *52* 1568 (1987)
SR	5, 6	JACS *104* 1430 (1982) (pyrrolizidinones, indolizidinones); *106* 8201 (pyrrolizidinones, indolizidinones), 8209 (pyrrolizidinones) (1984)
	7	JOC *48* 1841 (1983) (bicyclic β-lactams)
SePh	5	CC 307 (1983) (butyrolactones); 1205 (1985) (butyrolactones); 588 (1986) TL *26* 6431 (1985); *28* 2637 (1987) (carbapenam)
	5, 6	JACS *106* 8201 (1984) (pyrrolizidinones, indolizidinones) CC 353 (1987)
	7	JOC *48* 1841 (1983) (bicyclic β-lactams)
NO_2	5	CL 635 (1985) (tetrahydrofurans) Tetr *41* 4013 (1985) (tetrahydrofurans)



TL *28* 1313, 1317 (1987)



n	X	Reagent(s)	
1	Cl, Br, CN, SR	$CuCl_2$, $CuBr_2$, CuCN or RS^-	JACS *108* 5890 (1986)
	I	NaI	JOC *52* 1922 (1987)
2	I	NaI	JOC *52* 2568 (1987)

5.1. Carbocationic Cyclization

Reviews:

Acct Chem Res *1* 1 (1968); *8* 152 (1975)
Bioorg Chem *5* 51 (1976)
Angew *88* 33 (1976)
P. A. Bartlett in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, p 341

Some recent references

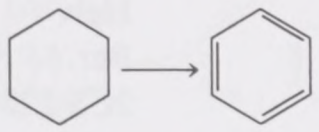
JACS *103* 4615 (1981); *104* 3508 (1982); *107* 522, 2712 (1985) (both Hg promoted); *109* 2517, 5852 (1987)
JOC *46* 2709 (1981); *52* 4878 (1987) (Hg promoted)
JCS Perkin I 2956 (1981)
J Chem Res (S) 20 (1981)
TL *28* 4053 (Sn promoted), 6413 (Hg promoted) (1987)

5. AROMATIZATION

1. Dehydrogenation

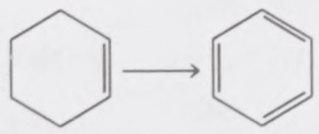
Reviews:

"Newer Methods of Preparative Organic Chemistry," Vol 1 (1963) (S, Se, Pt)
"The Chemistry of the Quinoid Compounds," Ed. S. Patai, J. Wiley (1974), Chpt 7
Houben-Weyl, Vol V/2b, p 107



Review: Chem Rev *78* 317 (1978)

cat $[Ni_3(PO_4)_2 + H_2]$	CL 967 (1976)
cat Ni-Al_2O_3, C_6H_6	JACS *63* 1320 (1941)
cat Ni-Cr_2O_3, C_6H_6	JACS *63* 1320 (1941); *71* 2962 (1949)
cat Ni-Cr_2O_3, C_6H_6, PhSPh or thiophene	JACS *70* 381 (1948)
cat Pd-asbestos	JCS 583 (1957)
cat Pd-C	JCS 583 (1957) Helv *51* 1102 (1968); *52* 1023 (1969)
cat Pd, C_6H_6	JACS *71* 2962 (1949)
cat Pt-C	JCS 583 (1957)
cat Pt, C_6H_6	JACS *63* 1320 (1941); *71* 2955, 2962 (1949)
S	JCS 1832 (1932) Tetr *30* 3303 (1974)
Se	JCS 1431 (1936)



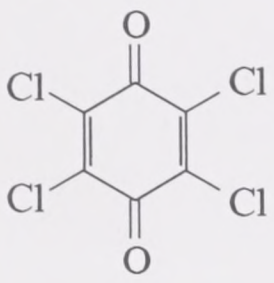
Review: Chem Rev *78* 317 (1978)

cat Pd-C	JACS *90* 6992 (1968)
cat Pt-alumina	Ann *670* 23 (1963) TL 3491 (1973)

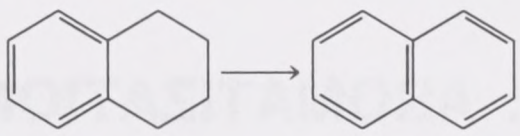
S — JCS 1832 (1932)
JACS *60* 940 (1938)
JOC *38* 1430 (1973)

Se — Ber 1471 (1933)

quinones — Adv Org Chem *2* 239 (1960) (review)



JACS *61* 1407 (1939); *62* 983 (1940)
BCSJ *44* 2841 (1971)



Review: Chem Rev *78* 317 (1978)

cat Ni-Al_2O_3, C_6H_6 — JACS *63* 1320 (1941)

cat Pd-C — Ber *96* 707 (1963)
Syn 307 (1971)

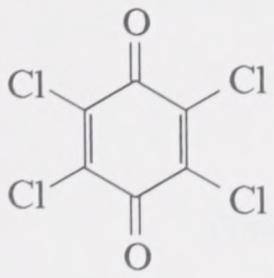
cat Pd, C_6H_6 — JACS *71* 2962 (1949)

cat Pt, C_6H_6 — JACS *71* 2955 (1949)

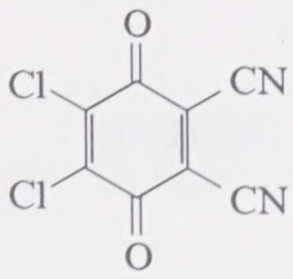
S — Helv *10* 915 (1927)
Ber *65* 883 (1932)
JCS 1286 (1938)

Se — Ber *60* 2323 (1927)
JCS 1125 (1932); 1012 (1933); 365 (1934); 62 (1936); 1845 (1959)

$(i\text{-AmS})_2$ — JACS *59* 2351 (1937)

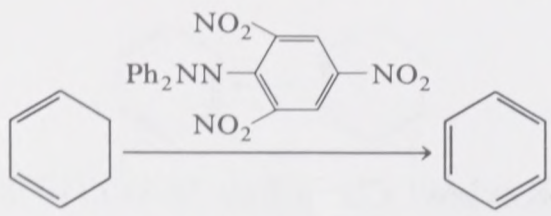


JACS *61* 1407 (1939)

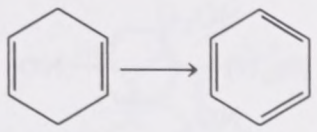


JCS 3569 (1954)
Chem Rev *67* 153 (1967) (review)

Ph_3COH, CF_3CO_2H — TL 3217 (1974)



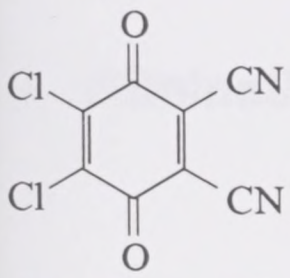
JCS 3574 (1954)



Review: Chem Rev *78* 317 (1978)

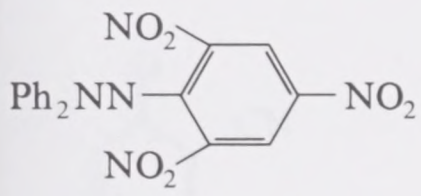
cat Pd-C — TL 191 (1969)

quinones — Adv Org Chem *2* 239 (1960) (review)



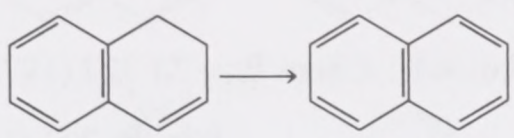
JACS *107* 5305 (1985)
JOC *51* 5100 (1986)

$(NC)_2C{=}C(CN)_2$ — TL 205 (1962)
JACS *85* 3436 (1963); *87* 2751 (1965); *102* 886 (1980)



JCS 3574 (1954)

act MnO_2 — Syn Commun *12* 637 (1982)



Review: Chem Rev *78* 317 (1978)

cat Pd-C — Ann *686* 40 (1965)

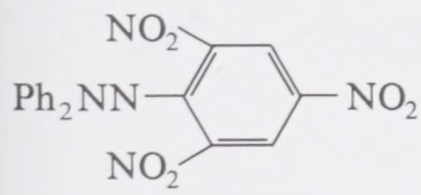
cat Pt — JCS 1431 (1936)

cat Pt, C_6H_6 — JACS *71* 2955 (1949)

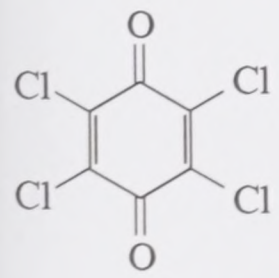
S — JOC *23* 797 (1958)

Se — JCS 62, 1431 (1936)

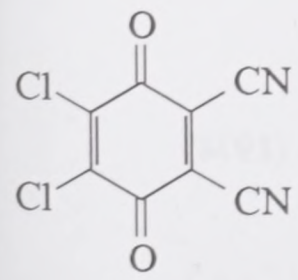
SeO_2 — Z Chem *13* 216 (1973)



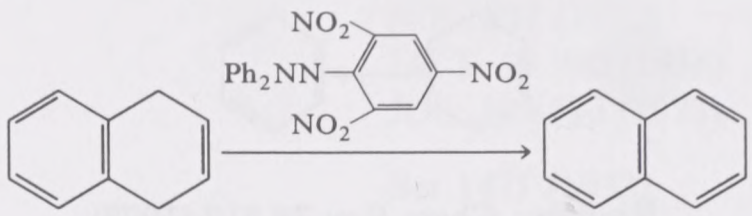
JCS 3574 (1954)



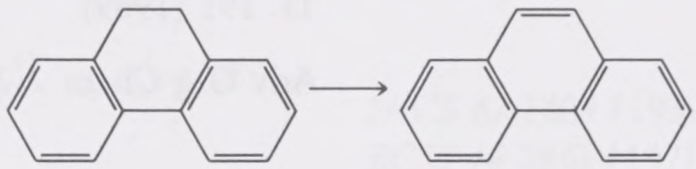
Ann *686* 40 (1965)



JOC *52* 2226, 3205 (1987)

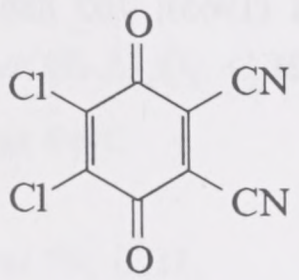


JCS 3574 (1954)

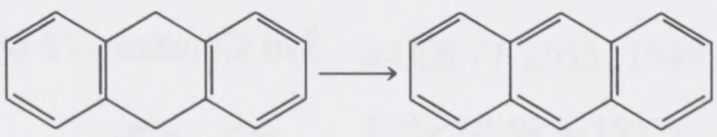


Review: Chem Rev *78* 317 (1978)

$(Ph_3C)ClO_4$	JCS 2773 (1959)
Ph_3COH, CF_3CO_2H	TL 3217 (1974)
n-BuLi	JACS *95* 2376 (1973); *96* 2434 (1974)

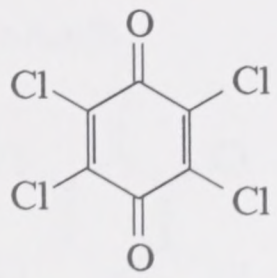


JOC *52* 3196 (1987)

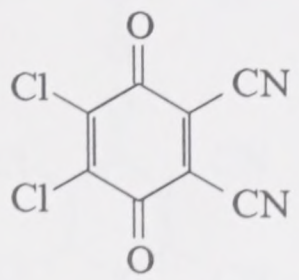


Review: Chem Rev *78* 317 (1978)

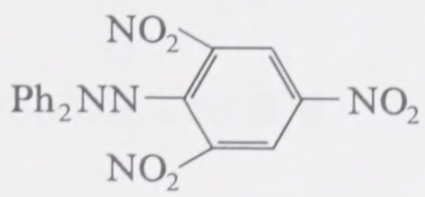
cat Pd-C	Ber *96* 707 (1963)
Cu	Ber *72* 1817 (1939); *96* 707 (1963)
SeO_2	JCS 764 (1947)



JACS *61* 1407 (1939)
Ber *96* 707 (1963)

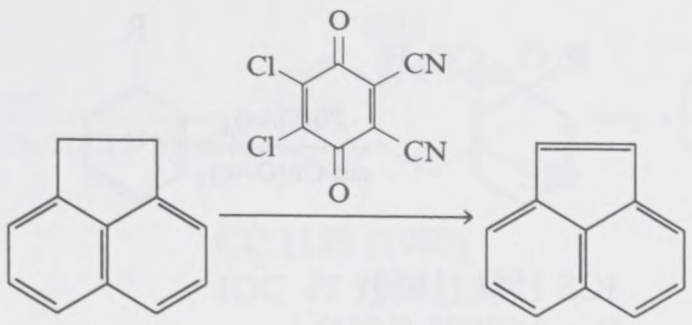


JOC *52* 3205 (1987)



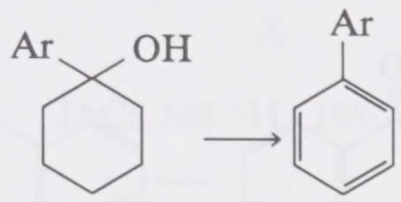
JCS 3574 (1954)

$(Ph_3C)ClO_4$	JCS 2773 (1959)
Ph_3COH, CF_3CO_2H	TL 3217 (1974)
$PhSO_3H$, $PhNO_2$	Ber *91* 2109 (1958)
n-BuLi/$CdCl_2$	JACS *95* 2376 (1973); *96* 2434 (1974)



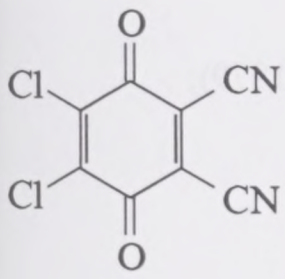
JOC *52* 3205 (1987)

2. Elimination

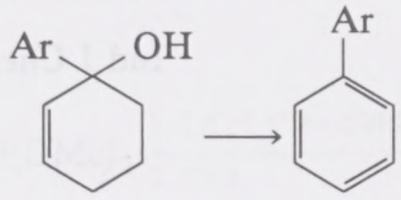


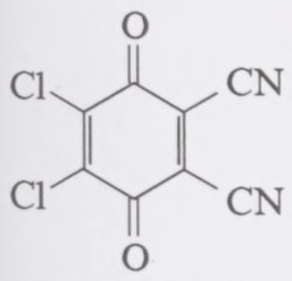
JCS 1832 (1932)

S



JOC *30* 2942 (1965)

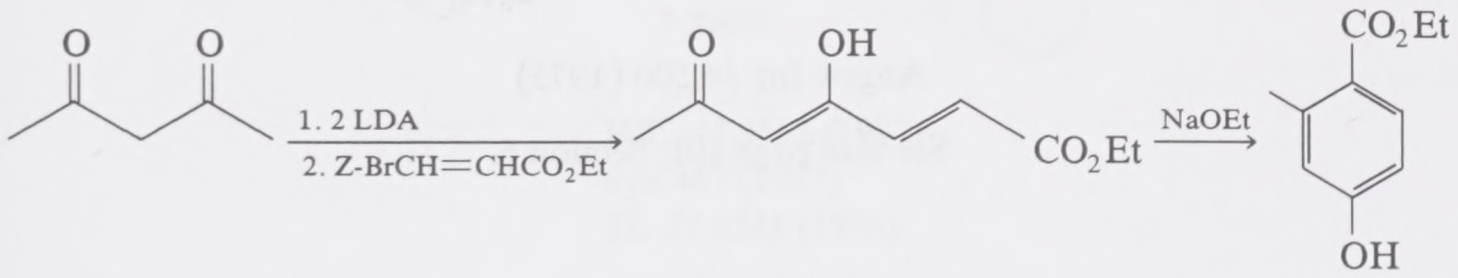




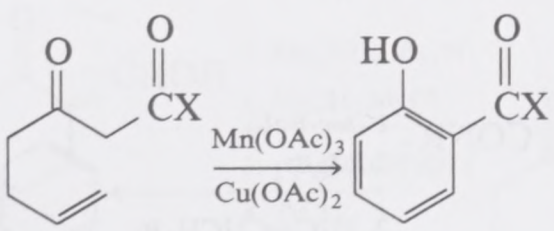
JOC *28* 2403 (1963)

Ph_3COH, CF_3CO_2H

TL 3217 (1974)

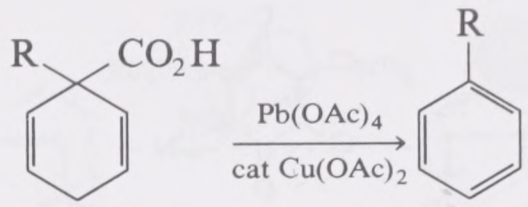


TL *26* 4419 (1985)



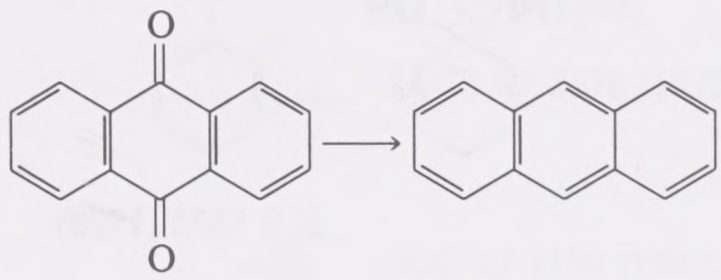
X = R, OR

TL *28* 845, 6109 (1987)



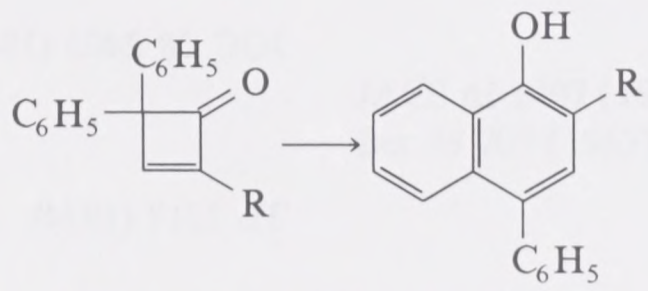
JCS 1551 (1950)
Ber *94* 2095 (1961)
TL 2079 (1976); *27* 3923 (1986)

3. Reductive Elimination



HI, HOAc	JOC *43* 3423 (1978); *44* 4813 (1979); *52* 3205 (1987)
Ph_2SiH_2, Δ	JOC *26* 4817 (1961)
$NaBH_4/HCl/NaBH_4$	JOC *39* 770 (1974)
$NaBH_4$, $BF_3 \cdot OEt_2$ or $AlCl_3$	Ind J Chem *1* 19 (1963)

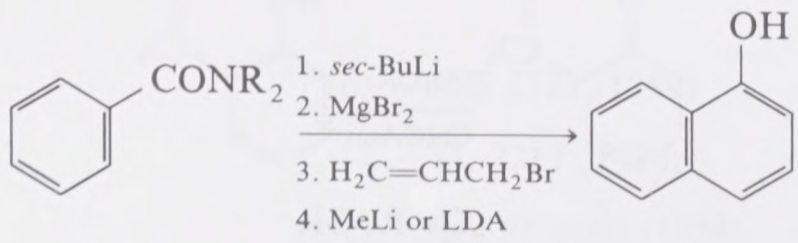
4. Rearrangement



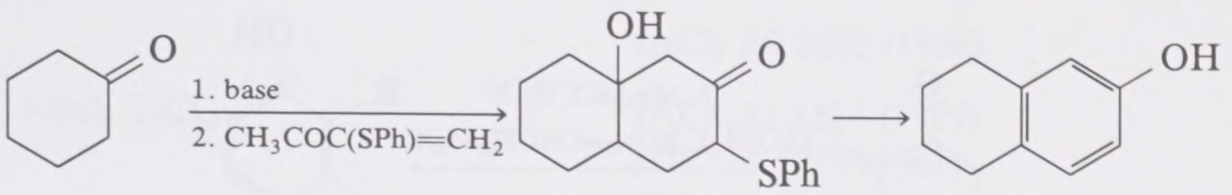
Angew Int *14* 500 (1975)

See also page 101, Section 6.

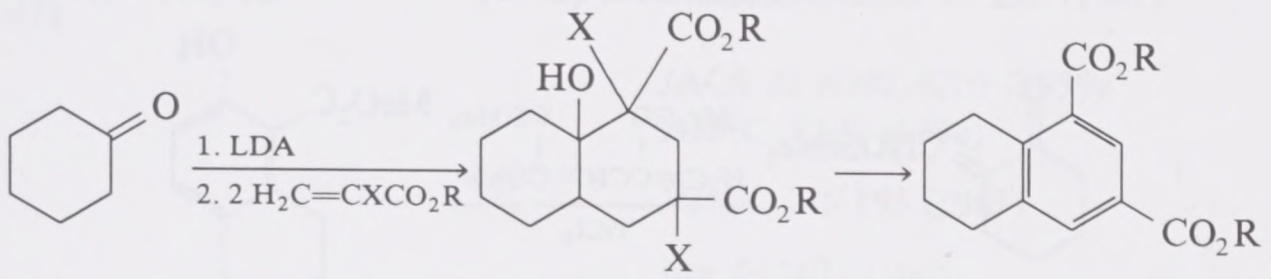
5. Cyclization and Annulation



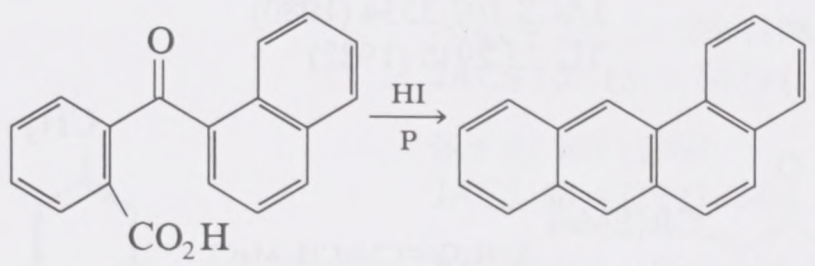
JOC *51* 271 (1986)



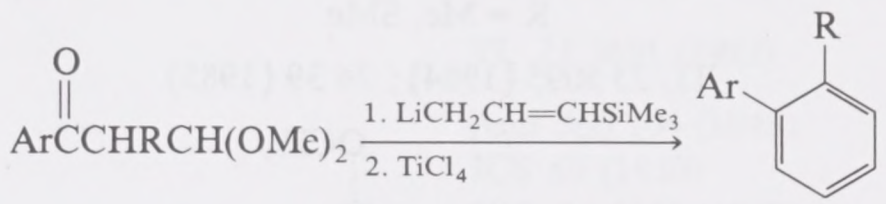
CC 1183 (1980)
JOC *47* 1200 (1982)



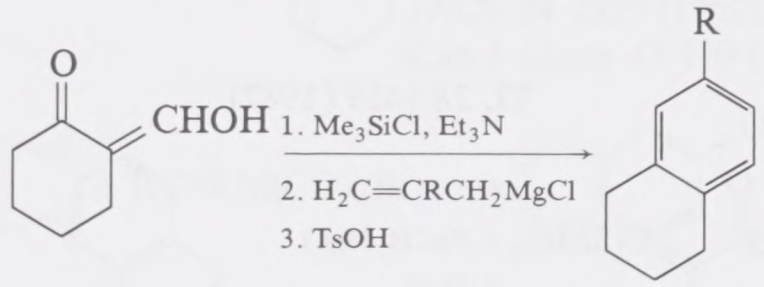
JACS *108* 511 (1986)



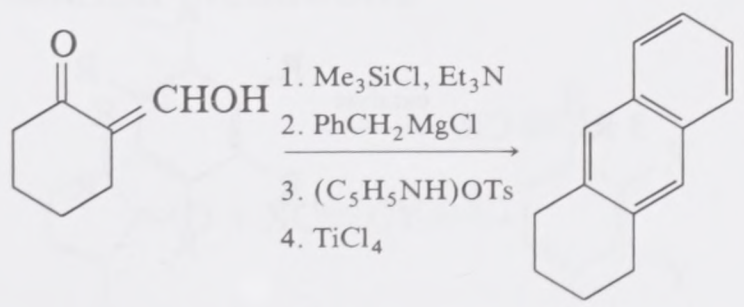
JOC *46* 2601 (1981)



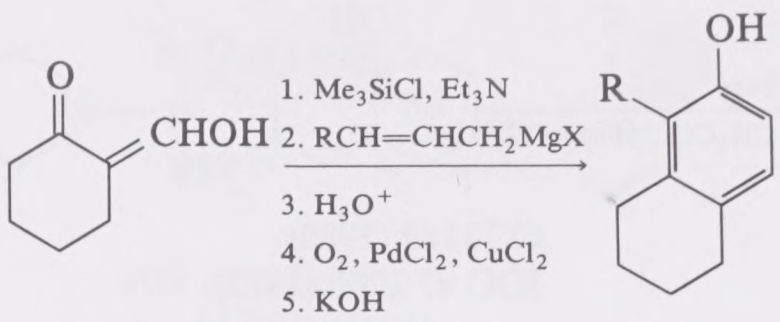
TL *22* 3335 (1981)



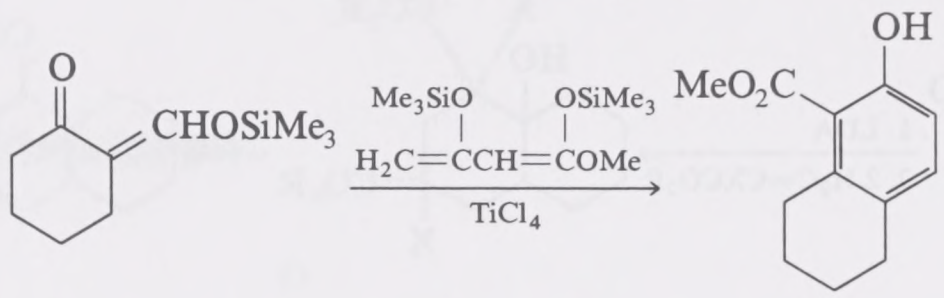
JOC *47* 3163 (1982)
Syn 467 (1983)
TL *27* 4541 (1986)



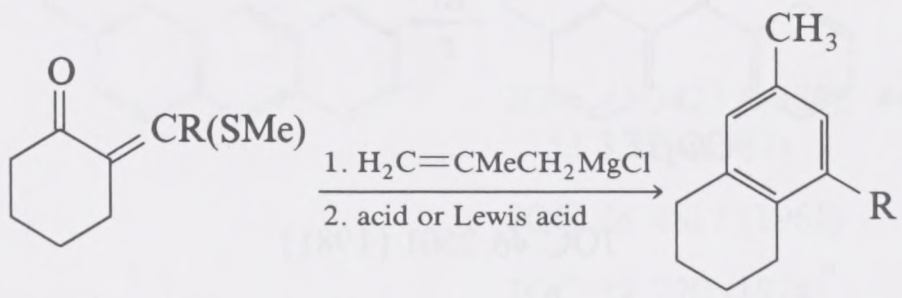
TL *27* 2571 (1986)



TL *23* 2823 (1982)

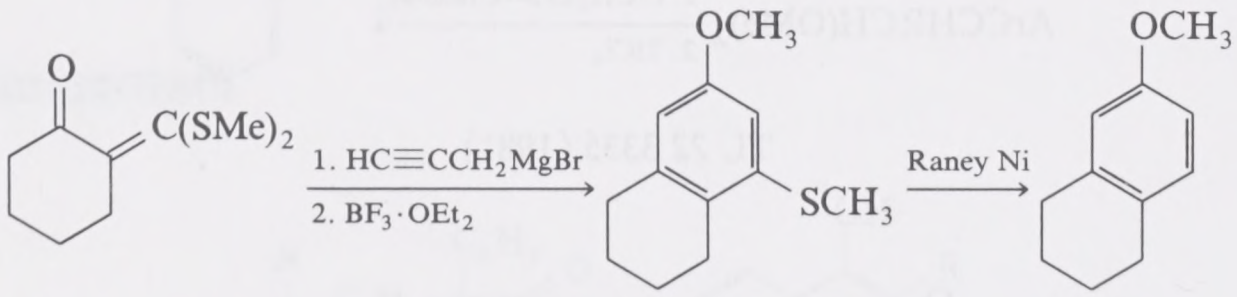


CC 578 (1979)
JACS *102* 3534 (1980)
TL *23* 2935 (1982)

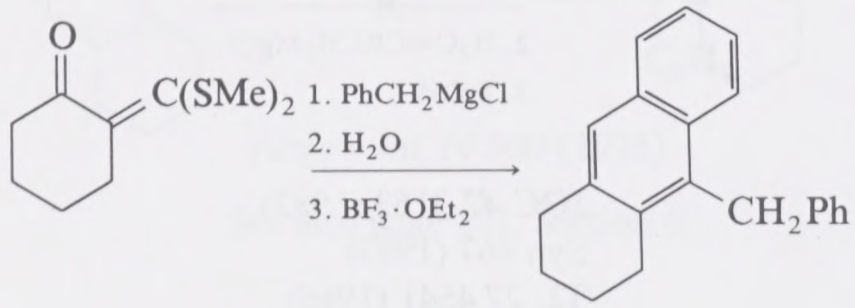


R = Me, SMe

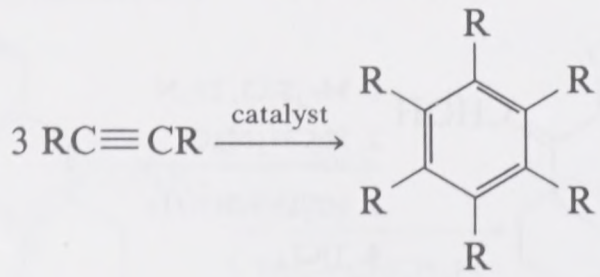
TL *25* 5095 (1984); *26* 39 (1985)



TL *28* 1459 (1987)

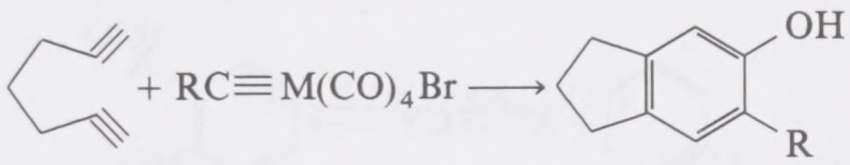


TL *27* 117 (1986)



Reviews: Russ Chem Rev *35* 510 (1966); *43* 48 (1974)
Acct Chem Res *10* 1 (1977)
JOC *52* 1161 (1987)

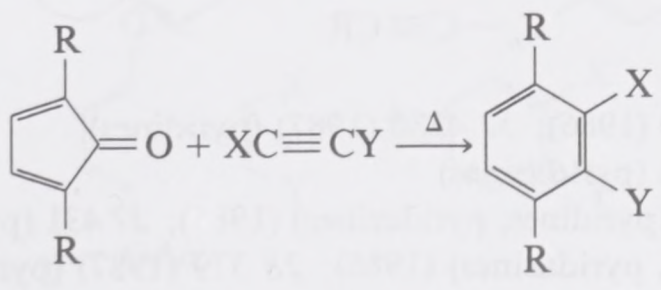
$i\text{-Bu}_2\text{AlH}$, Δ	JACS *88* 2213 (1966)
R_3Al (R = Et, *i*-Bu), $TiCl_4$	JACS *81* 1514 (1959) JOC *26* 2234 (1961) Helv *48* 509 (1965)
Me_3SiCl, cat Pd-C	JOC *52* 1161 (1987)
$M_2Cl_6\left(\text{S}\right)_2$ M = Nb, Ta	Macromolecules *14* 235 (1981)
R_3Cr	JACS *81* 6090, 6203 (1959) JOMC *5* 176 (1966)
Fe	JOMC *249* 195 (1983)
$Fe_3(CO)_{12}$	Ber *93* 103 (1960)
$CpCo(CO)_2$	Acct Chem Res *10* 1 (1977) (review) CC 953 (1982) Angew Int *23* 539 (1984) JACS *107* 1379, 5670 (1985); *108* 856, 3150 (1986)
$Co_2(CO)_8$	Ber *93* 103 (1960) JACS *86* 4729 (1964)
$Hg[Co(CO)_4]_2$	Ber *93* 103 (1960); *94* 2829 (1961) Helv *48* 509 (1965)
Co carbonyl alkyne complexes	Ber *93* 103 (1960); *94* 2817, 2829 (1961)
$ClRh(PPh_3)_3$	TL *23* 2691 (1982)
$Ni(CO)_2(PPh_3)_2$	Ann *560* 104 (1948) JCS *69* (1950) JOC *26* 5155 (1961)
$Ni(H_2C{=}CHCN)_2$	Ber *94* 1403 (1961)
$PdCl_2(PhCN)_2$	JACS *84* 2329 (1962); *92* 2276 (1970) Can J Chem *43* 470 (1965)



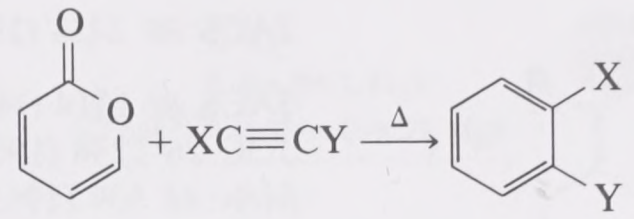
M = W, Cr

TL *26* 2159 (1985)

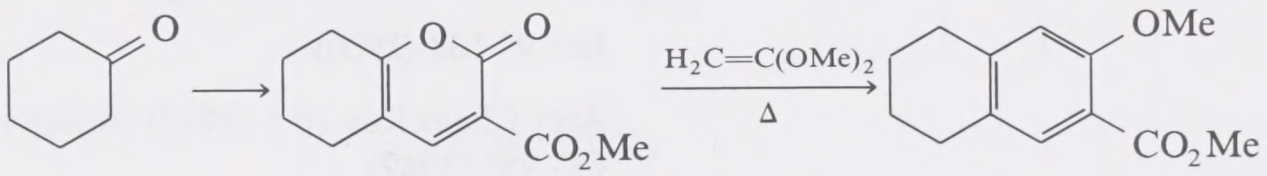
6. Diels-Alder and Related Reactions



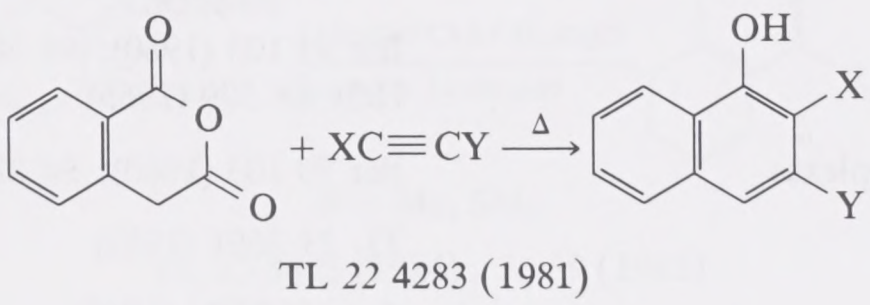
JOC *52* 496 (1987)



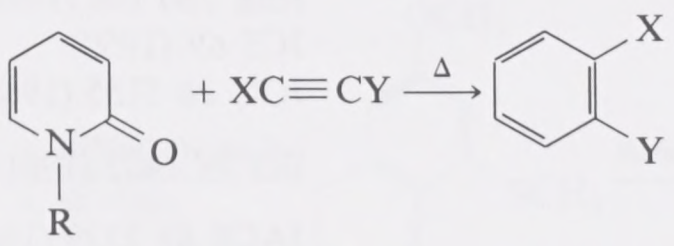
Ber *70* 1354 (1937)
JOC *29* 2534 (1964); *42* 2930 (1977); *47* 1150 (1982)
JACS *89* 952, 4793 (1967)
JOMC *34* 119 (1972)
CC 95 (1978)
TL *22* 3355 (1981)
Ann 914 (1982)



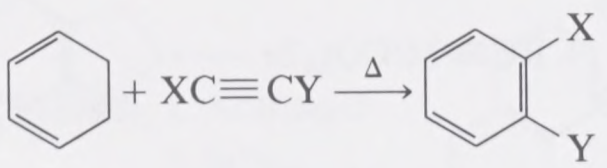
TL *23* 4551, 4555, 4559 (1982); *24* 4939 (1983)
JOC *49* 4033, 4055 (1984)
Org Syn *65* 98 (1987)



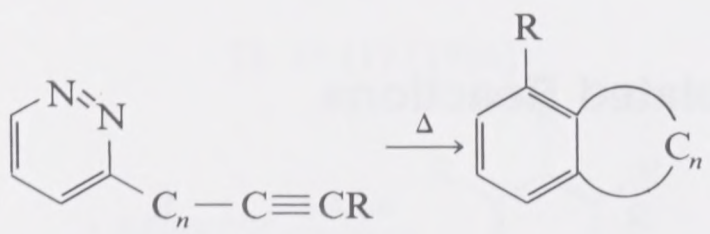
TL *22* 4283 (1981)



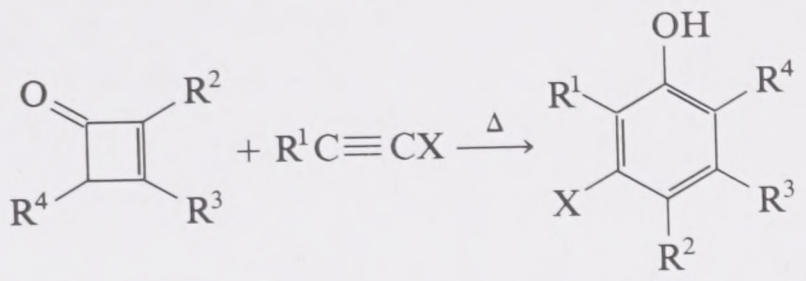
JCS Perkin I 169 (1982)



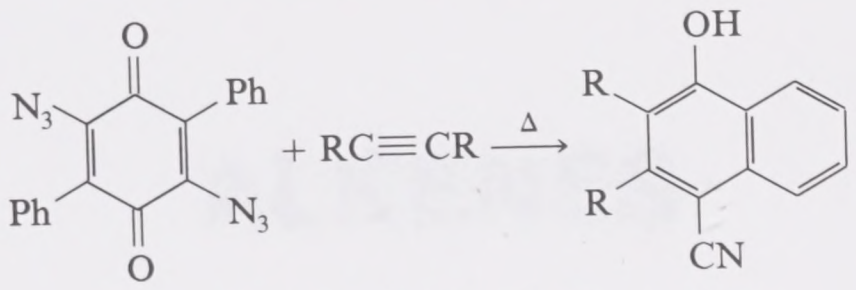
Syn 223 (1982)
JACS *107* 2712 (1985)



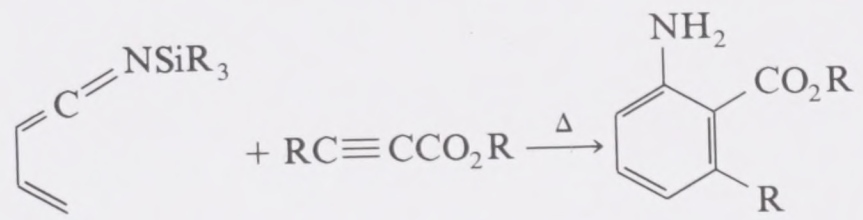
JOC *49* 2240 (1984); *51* 3250 (1986); *52* 4280 (1987) (pyridines)
Chem Zeitung *108* 331 (1984) (pyridazines)
TL *26* 2419 (pyridines), 4355 (pyridines, pyridazines) (1985); *27* 431 (pyridines), 1967 (pyridines), 2107 (pyridines), 2747 (pyridines, pyridazines) (1986); *28* 379 (1987) (pyridines)
JACS *109* 2717 (1987)



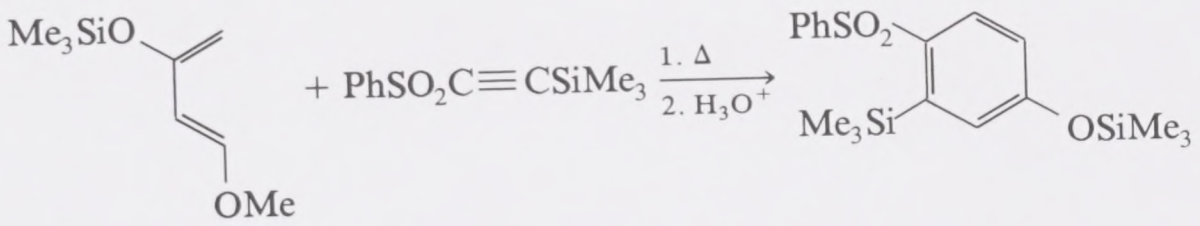
JOC *49* 1672 (1984)
JACS *108* 806 (1986)



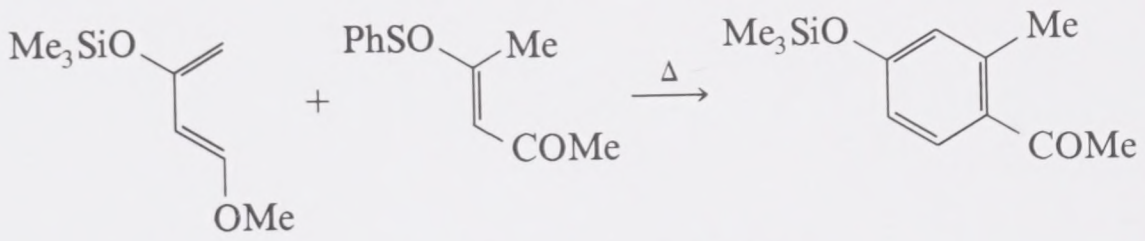
TL *28* 5013 (1987)



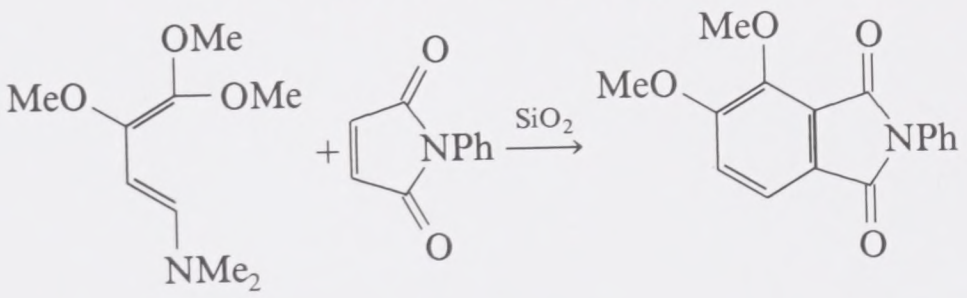
TL *28* 397 (1987)



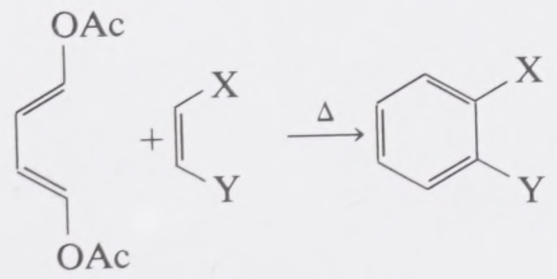
JACS *101* 7001 (1979)
JOC *46* 1951 (1981)



JACS *101* 7008 (1979)



Syn 649 (1981)



TL 1157 (1964)

ALKENES

GENERAL REFERENCES

"The Chemistry of Alkenes," Ed. S. Patai, Interscience, New York (1964)

F. Asinger, "Olefins," Pergamon Press, New York (1966)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1c (dienes), G. Thieme, Stuttgart (1970)

Quart Rev *25* 135 (1971)

Syn 175 (1971)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1b (alkenes), G. Thieme, Stuttgart (1972)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1d (polyenes), G. Thieme, Stuttgart (1972)

1. ISOMERIZATION OF ALKENES

Review: Syn 405 (1970)

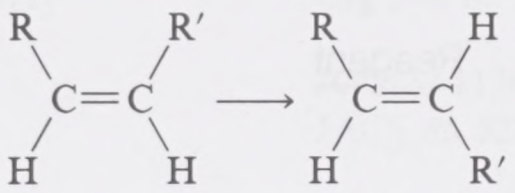
For reactions of allylic organometallics which proceed with allylic transposition see page 185, Section 5.

1. Alkene Inversion

See also page 129, Section 2, for elimination via diols, epoxides, β-dihalides, β-halo esters and bromohydrins.

Reviews:

Chem Rev *55* 625 (1955)
Tetr *36* 557 (1980)

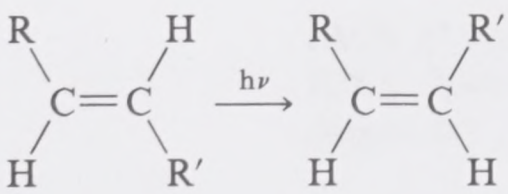


$h\nu$ — JACS *107* 1034 (1985)

$h\nu$, $(PhS)_2$ — JCS C 260 (1966); JACS *89* 2758 (1967); Helv *51* 548 (1968); Org Syn *63* 192 (1984); TL *28* 47, 6437 (1987)

PhSH, AIBN — JOC *51* 260 (1986) (R = 3° alkyl); *52* 4674 (1987)

cat Ph_3GeH, cat BEt_3 — TL *28* 3709 (1987)

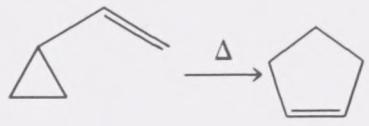


Helv *38* 1338 (1955)
JACS *79* 2318 (1957); *86* 2087 (1964); *107* 1034 (1985); *108* 3005 (R = Ph, R′ = CO_2R; added $BF_3 \cdot OEt_2$ or $EtAlCl_2$), 3016 (R = alkyl, R′ = CO_2R; added $EtAlCl_2$) (1986)
JOC *38* 1247 (1973)
Tetr *31* 193 (1975)

2. Simple Rearrangement

2.1. Thermal

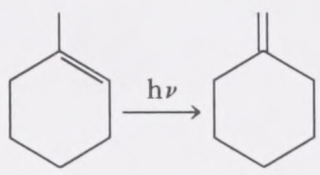
"Molecular Rearrangements," J. Wiley and Sons, New York (1963), Vol 1, Chpt 11
Angew Int *2* 115 (1963)



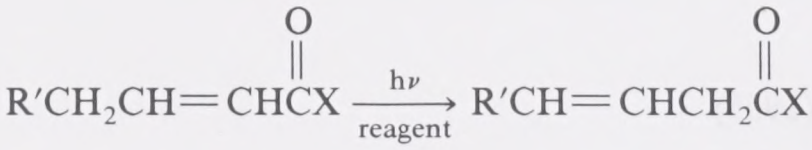
See page 273, Section 9.

2.2. Photochemical

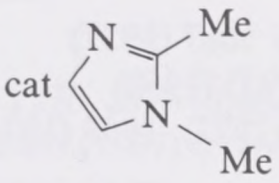
See also page 109, Section 1 (Alkene Inversion).



JACS *89* 5199 (1967)



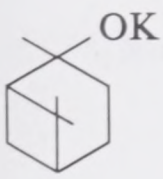
X	Reagent	
R	—	Helv *46* 678 (1963) TL 1203 (1964) Pure Appl Chem *9* 481 (1964) BSCF 1185 (1973) Can J Chem *54* 2127 (1976) JACS *109* 2479 (1987)
OH	—	JACS *85* 1210 (1963) (dienoic acid → allenic acid) Pure Appl Chem *9* 481 (1964) JOC *33* 1671 (1968)
OR	—	Pure Appl Chem *9* 481 (1964) CC 137 (1965) JOC *32* 3222 (1967); *33* 1671 (1968); *34* 609 (1969); *38* 2558 (1973) TL 4987, 4991 (1968); 489 (1970) JACS *91* 198 (1969); *93* 5490 (1971)

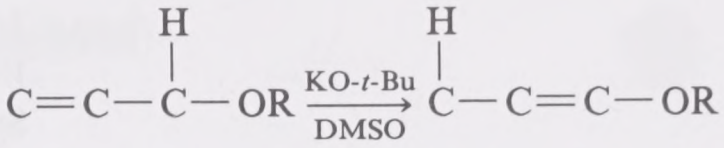
	J Photochem *1* 433 (1972/73) BCSJ *46* 2181 (1973) (lactone) Syn 1019 (1983) (lactones)
	TL *24* 4299 (1983); *27* 5555 (1986) Can J Chem *62* 1933 (1984) JOC *50* 873 (1985)
ephedrine	TL *26* 4945 (lactones), 6079 (1985); *27* 2997, 3001 (1986) (all enantioselective) Pure Appl Chem *58* 1257 (1986) (esters and lactones)
various amino alcohols	TL *27* 3001 (1986); *28* 4825 (1987) (both enantioselective) Pure Appl Chem *58* 1257 (1986) (esters and lactones)

See also page 867, Section 1; and page 873, Section 2, for reactions with strong bases followed by protonation.

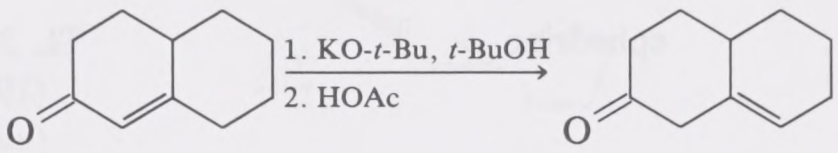
2.3. Base-Promoted

Review: Syn 97 (1969)

KNH_2, NH_3	JCS 1642 (1947) Acct Chem Res *1* 231 (1968) Syn 97 (1969)
$KNH(CH_2)_3NH_2$, $H_2N(CH_2)_3NH_2$	Org Syn *65* 224 (1987)
LiNHEt	JOC *23* 1136 (1958) JACS *86* 5281 (1964)
KO-*t*-Bu, DMSO	JACS *83* 3731 (1961); *84* 3164 (1962); *85* 1553 (1963) JCS 4234 (1963) Ber *99* 1737 (1966) JOC *33* 221 (1968)
	JOC *45* 900 (1980)
$NaCH_2Ph$	TL 467 (1964)
Na, alumina	JACS *87* 4107 (1965) JCS C 2149 (1967) Angew Int *24* 320 (1985)
K, alumina	Angew Int *24* 320 (1985)
MgO	CL 133 (1979)



TL 1191 (1964); *28* 5887 (1987)
JCS C 82 (1966); 1903 (1968)
JCS Perkin I 1535 (1972); 1858 (1973)



TL 669 (1962)
JOC *30* 2513 (1965)

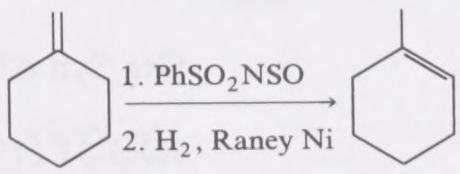
2.4. Acid-Catalyzed

acid alumina	JACS *87* 4107 (1965)
$(CO_2H)_2$, EtOH	JACS *75* 5421 (1953)

2.5. Sulfur Dioxide

JACS *99* 5219 (1977)

2.6. Ene Reaction–Reduction



TL *28* 5017 (1987)

2.7. Iodine

JCS 2760 (1957)
JCS C 260 (1966) (plus hν)
JOC *52* 2586 (1987)

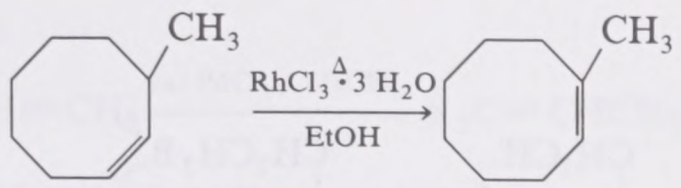
2.8. Transition Metal-Catalyzed

Review:

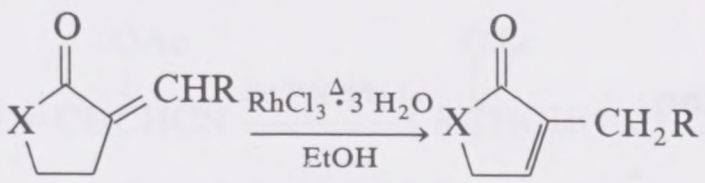
C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York (1967), Chpt 3

$$H_2C{=}CHCH_2R \longrightarrow CH_3CH{=}CHR$$

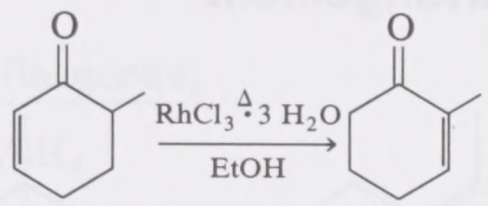
$[(o\text{-}CH_3C_6H_4O)_3P]_2Ni(C_2H_4)$, HCl	JOC *41* 3020 (1976)
$PdCl_2(PhCN)_2$	TL *28* 5473 (1987)



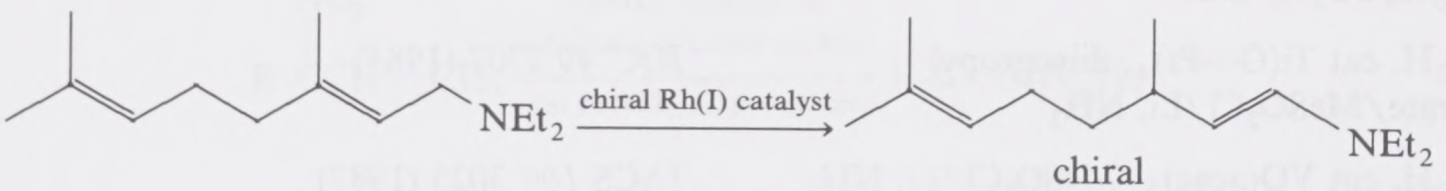
JACS *86* 1776, 2516 (diene) (1964); *107* 7352 (1985)
Helv *50* 2445 (1967) (diene)
JOC *52* 2875 (1987)



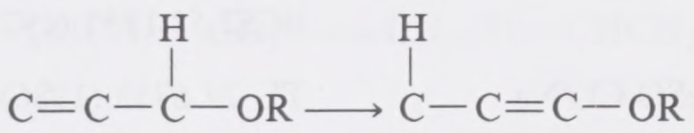
X	
CH_2	JCS Perkin I 359 (1977) JOC *45* 3017 (1980) Syn 952 (1983)
O	JOC *52* 1429 (1987)



JACS *98* 7102 (1976); *109* 3025 (1987)
TL *28* 31 (1987)

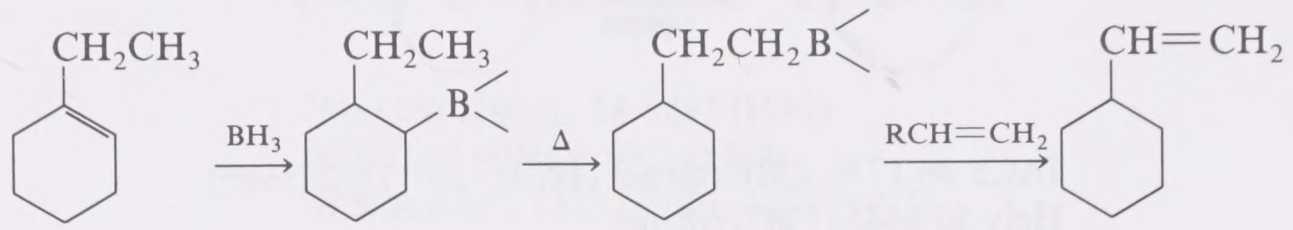


JACS *106* 5208 (1984)



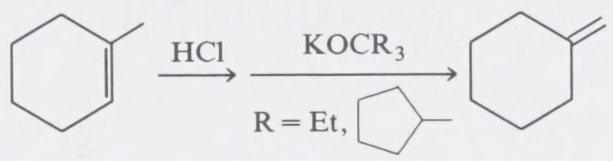
cat $H_2Ru(PPh_3)_4$	TL 1415 (1979); *21* 4927 (1980); *23* 1079 (1982); *28* 239 (1987) CL 1435 (1981) JACS *109* 5280 (1987) JOC *52* 5700 (1987)
cat $H_2Ru(CO)(PPh_3)_3$	TL *21* 4927 (1980)
cat $HRuCl(CO)(PPh_3)_3$	TL *21* 4927 (1980)
cat $ClRh(PPh_3)_3$	JOC *38* 3224 (1973) CC 277 (1974) JACS *109* 5446 (1987)
cat $PdCl_2(PhCN)_2$	JCS Perkin I 2870 (1973)

2.9. Organoboranes



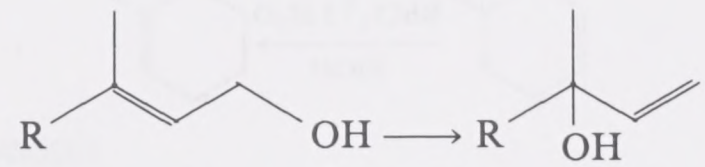
JACS *82* 2074 (1960); *89* 561, 567 (1967)

2.10. Addition–Elimination

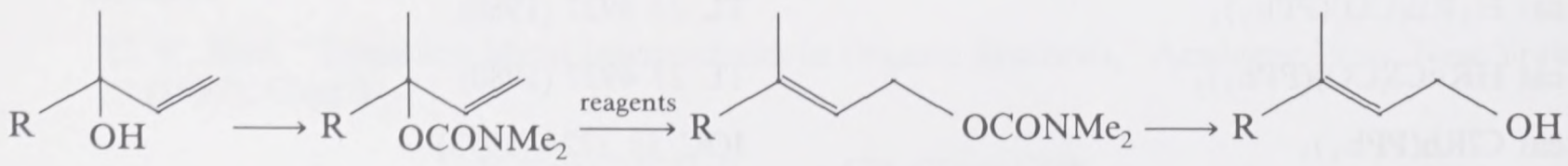


CC 305 (1968)

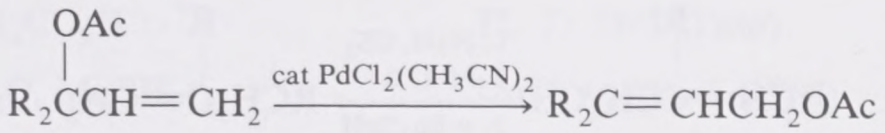
3. Functional Group Rearrangement



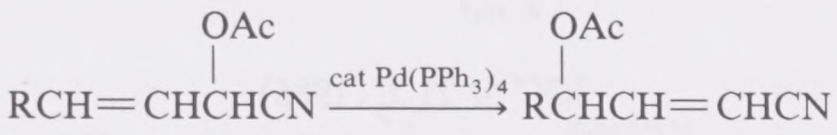
NaH, CS_2, MeI/*n*-Bu_3SnH/*m*-$ClC_6H_4CO_3H$/HCl	Syn 1011 (1980)
t-BuO_2H, cat Ti(O-*i*-Pr)$_4$, diisopropyl tartrate/$MeSO_2Cl$/Li, NH_3	JOC *49* 1707 (1984)
t-BuO_2H, cat $VO(acac)_2$/$MeSO_2Cl$/Li, NH_3	JACS *109* 3025 (1987)
t-BuO_2H, cat $VO(acac)_2$/$MeSO_2Cl$/Na, NH_3	TL 2621 (1976) CL 465 (1977) BCSJ *52* 1757 (1979)
t-BuO_2H, cat $VO(acac)_2$/$MeSO_2Cl$/Na naphthalene	TL *27* 6353 (1986)
$PhCMe_2O_2H$; cat $VO(acac)_2$; 2,6-lutidine/ CBr_4, PPh_3/Zn, HOAc, THF	JACS *109* 6187 (1987)
o- or *p*-$NO_2C_6H_4SeCN$, *n*-Bu_3P/H_2O_2	CC 770 (1978) JOC *50* 2981 (1985)



$Hg(O_2CCF_3)_2/PPh_3$	JACS *100* 4822 (1978)
$PdCl_2(CH_3CN)_2$	Can J Chem *62* 791 (1984)

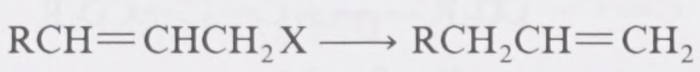


JACS *94* 5200 (1972); *102* 7587 (1980)
TL 321 (1979); *28* 4131, 5655 (1987)
JOC *46* 5005 (1981)
Tetr *40* 1791 (1984)
Can J Chem *62* 791 (1984) (carbonates also)

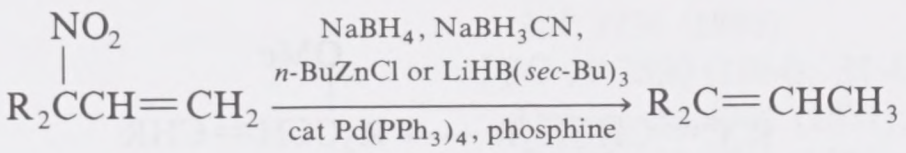


Syn 687 (1982)

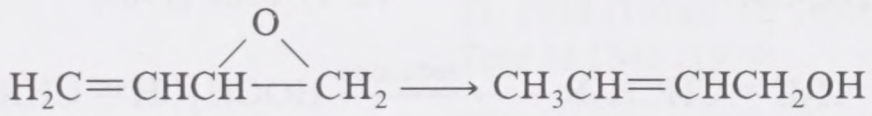
4. Reductive Transposition



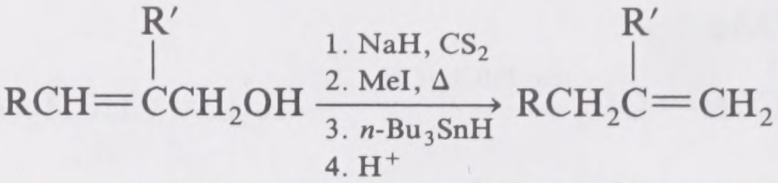
X	Reagent(s)	
$\overset{+}{P}Ph_3$	$LiAlH_4$	JOC *49* 4084 (1984)
SO_2Ph	$LiAlH_4$, $CuCl_2$	JACS *107* 1034 (1985)



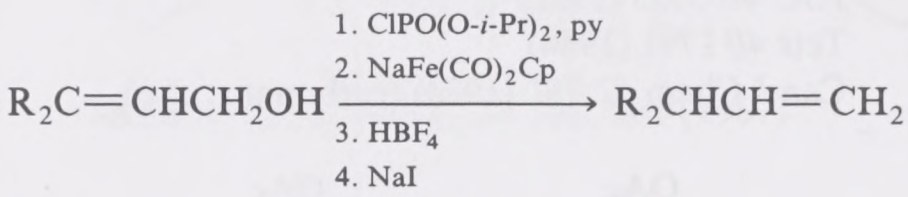
JOC *51* 3734 (1986)



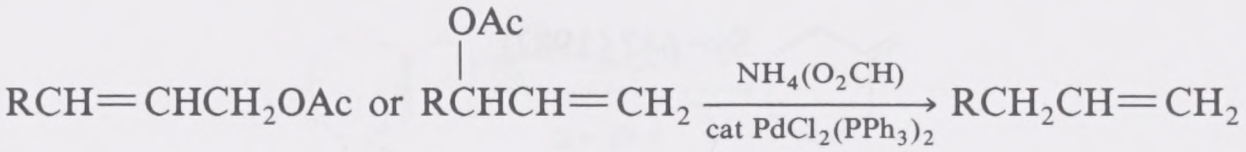
BH_3	Rocz *47* 771 (1973); *48* 467 (1974) Syn 62 (1979)
$NaBH_3CN$, $BF_3 \cdot OEt_2$	JOC *46* 5214 (1981)
$LiHBEt_3$	TL 3775 (1976)
i-Bu_2AlH	JACS *95* 957 (1973)
$LiAlH_4$	TL 3775 (1976)
Li/NH_3	JACS *95* 957 (1973)
Ca, NH_3	JACS *95* 957 (1973) TL *28* 2021 (1987)
SmI_2, ROH	JOC *51* 5259 (1986)



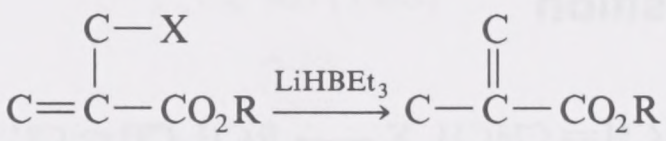
TL *21* 1767 (1980)



JOC *51* 2126 (1986)



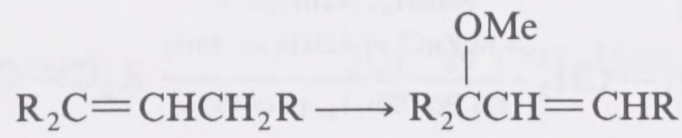
TL 613 (1979)



X = Br, OAc

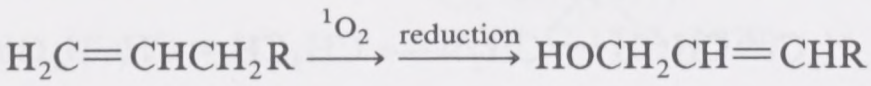
Angew Int *22* 796 (1983)

5. Oxidative Transposition

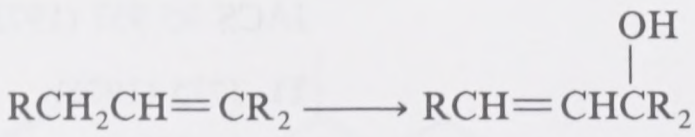


$(PhSe)_2$, $MgSO_4$, MeOH, electrolysis — JACS *103* 4606 (1981)

PhSeCl, MeOH/*m*-$ClC_6H_4CO_3H$ — TL *27* 6361 (1986)



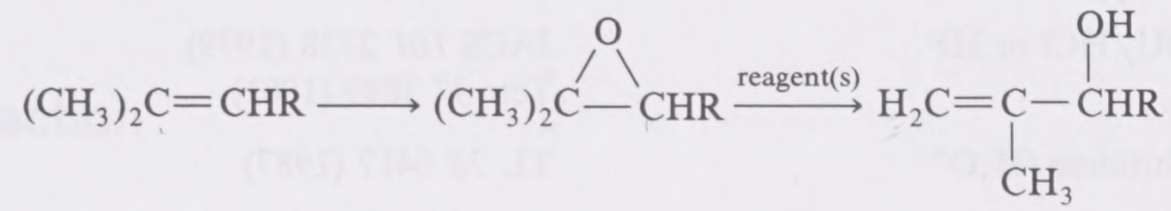
Angew *69* 579 (1957)
A. Schonberg, "Preparative Organische Photochemie," Springer Verlag, Berlin (1958), p 47
JACS *90* 975 (1968)
Adv Photochem *6* 1 (1968)
Acct Chem Res *1* 104 (1968); *13* 419 (1980) (mechanism)
Tetr *37* 1825 (1981)



"PhSeOH"/*t*-BuO_2H — TL 3967 (1978)
JOC *43* 1688 (1978)

$(PhSe)_2$, $MgSO_4$, H_2O, CH_3CN, electrolysis — JACS *103* 4606 (1981)

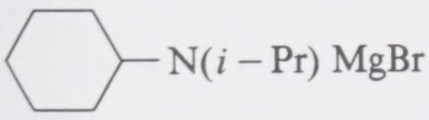
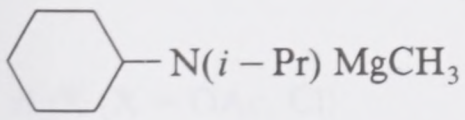
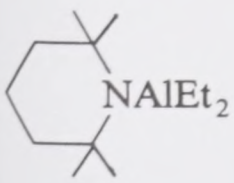
PhSeCl, $H_2O/m\text{-}ClC_6H_4CO_3H$	TL *27* 2391 (1986)
PhSeBr, AgO_2CCF_3/H_2O, MeOH, $NaHCO_3/H_2O_2$	JACS *106* 1446 (1984)
epoxidize/PhSeNa/[O]	JACS *95* 2697 (1973); *106* 7854 (1984); *107* 1691, 1777 (1985) Tetr *34* 1049 (1978) JOC *51* 2148 (1986); *52* 2644 (1987)
epoxidize/$i\text{-}Bu_2AlSePh/m\text{-}ClC_6H_4CO_3H/Et_3N$, Δ	JOC *50* 5897 (1985)

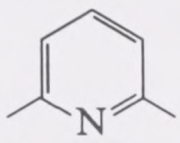


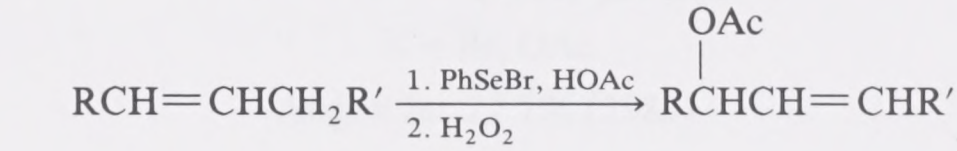
Reviews:

Russ Chem Rev *41* 403 (1972)
Tetr *39* 2323 (1983)
Org Rxs *29* 345 (1983)
Syn 629 (1984)

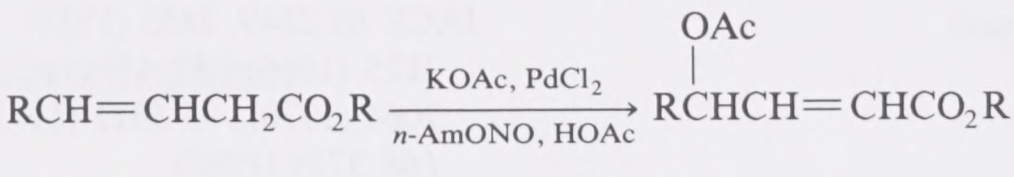
Reagent(s)

Li, $H_2NCH_2CH_2NH_2$	Helv *50* 153 (1967)
alkali metal amide bases	JACS *80* 2849, 2855 (1958); *82* 6370 (1960); *87* 3125 (1965); *89* 4526, 4527 (1967); *92* 737, 2064 (1970); *95* 5311 (1973); *106* 2949 (1984); *108* 3739 (1986) JOC *29* 2830 (1964); *32* 435, 532 (1967); *34* 3583 (1969); *36* 1365 (1971); *37* 2060, 3919, 4250 (1972); *51* 1362 (1986); *52* 1907 (1987) Syn 194 (1972); 602 (1975) Org Syn *53* 17 (1974) TL 1929 (1974); *28* 1439, 3831, 4993 (1987) Tetr *34* 1541 (1978)
LiNRR′ (chiral)	JOC *45* 755 (1980) CL 829 (1984); 389 (1987) TL *26* 5803 (1985)
	JACS *102* 1433, 7986 (1980) JOC *51* 793 (1986)
	TL *27* 299, 303 (1986)
	JACS *96* 6513 (1974) Angew Int *17* 169 (1978) BCSJ *52* 1705 (1979) JOC *52* 1106 (1987)

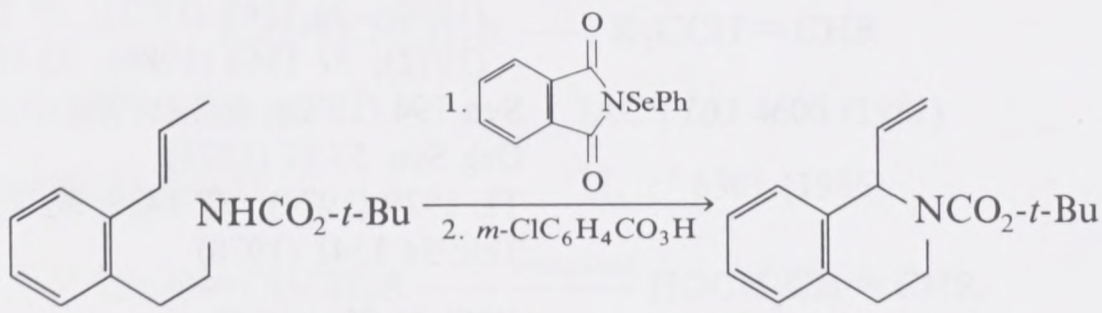
$Al(O\text{-}i\text{-}Pr)_3$	JOC *35* 1598 (1970); *44* 868 (1979); *50* 2948 (1985) JCS Perkin I 2909 (1982) JACS *105* 5510 (1983) Helv *67* 1998 (1984) CC 418, 727 (1986)
$Ti(O\text{-}i\text{-}Pr)_4$ (epoxy alcohols)	JACS *103* 462 (1981)
9-BBN-OTf, 	CL 1215 (1977)
$Me_3SiOTf/DBU/HCl$ or HF	JACS *101* 2738 (1979) Tetr *37* 3899 (1981)
$Et_3SiOTf/2,6\text{-lutidine}/H_3O^+$	TL *28* 6417 (1987)
Me_3SiBr, $PPh_3/DBU/HCl$	JACS *106* 7854 (1984)
Me_3SiI/DBU or DBN/H^+	TL *21* 2329 (1980) JOC *45* 2579 (1980)
$t\text{-}BuMe_2SiI/DBN/H^+$	JOC *45* 924 (1980)



JACS *106* 1446 (1984)

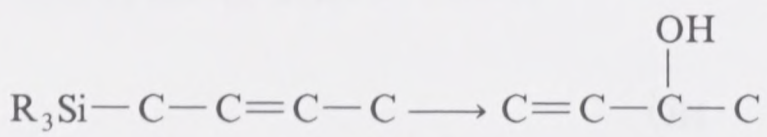


TL *22* 131 (1981)



JACS *107* 1421 (1985)

6. Heteroatom Displacement



CH_3CO_3H, buffer	CC 679 (1976)
$m\text{-}ClC_6H_4CO_3H/H^+$	CC 79 (1977) TL *23* 1267 (1982) JOC *49* 4224 (1984)
$m\text{-}ClC_6H_4CO_3H/(n\text{-}Bu_4N)F$	TL *24* 4153 (1983)

$$ArSO_2CH_2CR{=}CR_2 \xrightarrow[3.\ m\text{-}ClC_6H_4CO_3H\ \ 4.\ Na(Hg)]{1.\ n\text{-}BuLi\ \ 2.\ R'X} R'CH{=}CRCR_2OH$$

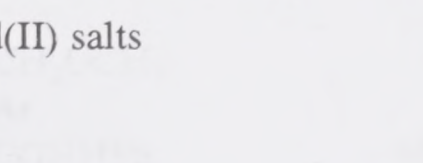
TL 441 (1979)

$$RCH{=}CHCH_2OH \xrightarrow{Cl_3CCN} RCH{=}CHCH_2OC(NH)CCl_3 \xrightarrow[HgX_2\text{ or }PdX_2]{\Delta\text{ or}} RCH(NHCOCCl_3)CH{=}CH_2$$

See page 937, Section 13.

7. Ene Reaction

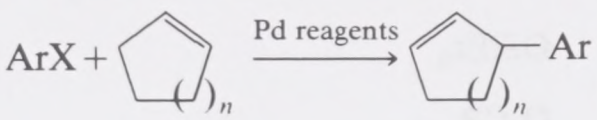
See further examples in the following Section 8



Angew Int *8* 556 (1969); *17* 476 (1978) (intramolecular); *23* 876 (1984)
Acct Chem Res *13* 426 (1980)
Tetr *37* 3927 (1981)

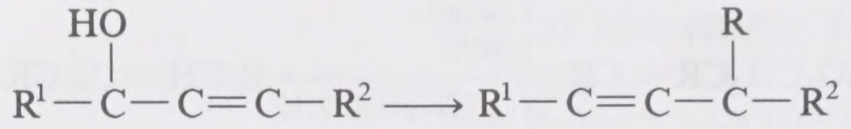
8. Alkylative Transposition

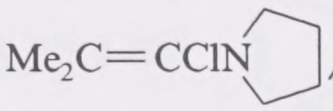
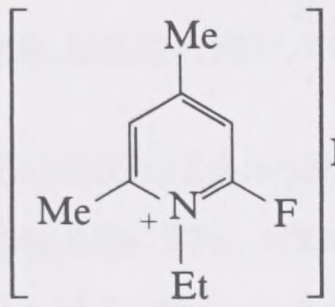
See also page 521, Section 5; page 637, Section 7.1; page 775 (Carroll Reaction); page 934, Section 10; page 936, Section 11; page 937, Section 14; and page 938, Section 15.

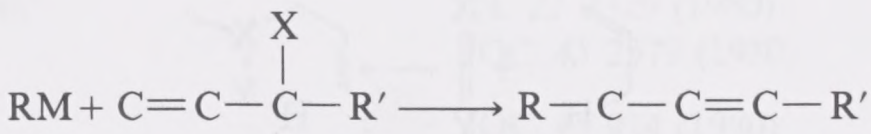


$n = 1, 2$

X	Pd reagents	
Br or I	cat $Pd(OAc)_2(PAr_3)_2$	JOC *43* 2952, 4110 (1978); *44* 21 (1979) Tetr *35* 329 (1979)
N_2^+	cat $PdCl_2$-NaO_2CH or $Pd(DBA)_2$	Tetr *37* 31 (1981)
NH_2	*t*-BuONO, cat $Pd(DBA)_2$	CL 551 (1980) JOC *46* 4885 (1981)
	t-BuONO, $Pd(OAc)_2$	JOC *45* 2359 (1980)
HgX (X = OAc, Cl)	Pd(II) salts	JACS *93* 6896 (1971); *100* 287 (1978) Organomet Chem Syn *1* 455 (1972) JOC *43* 4110 (1978); *48* 399, 2870 (1983)



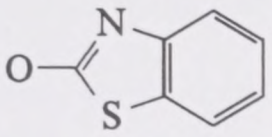
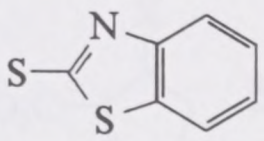
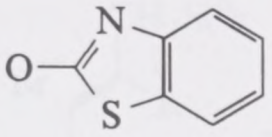
$CH_3Li/CuI/RLi/[n\text{-}Bu_3PNMePh]I$		JACS *99* 2361 (1977); *100* 4610 (1978) JOC *46* 2144 (1981) TL *23* 557 (1982); *27* 6353 (1986)
CH_3MgBr, cat $NiCl_2L_2$ ($R = CH_3$)		CC 681 (1981)
 /cat CuI, HMPA/RMgX		TL *24* 5745 (1983)
 BF_4^-/RMgBr		CL 1257 (1977)



See also page 201, Section 13.

Review: Tetr *36* 1901 (1980)

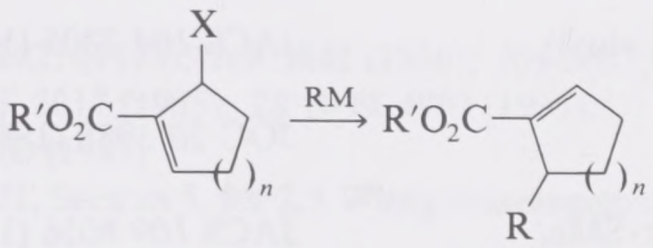
RM	X	
$RCCHLiR$, cat CuI	O_2CR	CL 1521 (1982) (lactone)
PhMgBr, Ni catalyst	Cl, OR, $OSiR_3$, OH	CC 313 (1981)
PhMgBr, cat $PdCl_2L_2$	$OSiEt_3$	CC 313 (1981)
RMgX, cat CuCl	O_2CR	TL 633 (1979) (enyne synthesis) JOC *51* 2884, 2892 (1986)
RMgX, cat CuBr	OR	TL 3831 (1975) BSCF II 309 (1979) Tetr *35* 1517 (1979) (S_N2 or S_N2')
RMgX, cat $CuBr \cdot SMe_2$	O_2CR	JOC *51* 1612 (1986)
RMgX, cat CuI	O_2CR	TL *23* 3583, 3587 (1982) CL 1521 (1982) (all lactones)
RMgX, cat CuCN	O_2CR	JOC *51* 2884, 2892 (1986)
RMgX, cat Li_2CuCl_4	Cl Br OAc	TL *23* 3115 (1982) Helv *65* 684 (1982) TL *23* 3115 (1982) CC 827 (1987)
RMgX, cat $Cu(acac)_2$	$PhSO_2$	TL 2393 (1979) Tetr *39* 3283, 3289 (1983)

$RMgX(Li), CuBr \cdot SMe_2$	O_2CR	JOC *51* 1612 (1986) (lactone)
RMgX, CuX (X = Br, I)		Syn 885 (1979) JOMC *231* 179 (1982) JOC *46* 4482 (1982)
		CC 1085 (1978); 1252 (1986) (S_N2 or S_N2')
RMgX (X = Cl, Br), CuBr, LiBr	OAc	Syn 469 (1982)
RCu	Br	JOC *49* 1838 (1984)
	O_2CR	JOC *51* 1612 (1986) (lactone)
$RC{\equiv}CCu$		TL 3873 (1979)
$RCu \cdot BF_3$	Cl, Br	JACS *99* 8068 (1977); *100* 8068 (1978); *102* 2318 (1980) JOC *49* 1838 (1984)
	OH	JOMC *156* C9 (1978) JACS *102* 2318 (1980)
	O_2CR	JOC *51* 1612 (1986) (lactone)
$RCu \cdot 2\ n\text{-}Bu_3P$	OR	TL *22* 1809 (1981)
R_2CuLi	Cl	JACS *92* 737 (1970)
	Br	JOC *52* 3394 (1987)
	O_2CR	CC 43 (1969) JACS *92* 735 (1970); *94* 5379 (1972); *95* 6832 (1973); *98* 7854 (1976); *101* 1035, 2493 (1979); *109* 8117 (1987) TL 4439 (1976); 1035 (1977); *23* 3093 (1982) JOMC *136* 103 (1977) Tetr *35* 1517 (1979) JCS Perkin I 2093 (1980); 1729 (1981) (both lactones) JOC *46* 2591, 5304 (1981); *48* 1531, 3986 (1983); *50* 5495 (1985) (relative rates); *51* 1612 (1986) (lactone); *52* 5452 (1987) Syn 469 (1982) CL 1521 (1982) (lactone)
	OCH_2OCH_3	TL *22* 119 (1981)
	OAr	JOC *45* 4026 (1980)
	OCONHPh	JACS *101* 1035 (1979) TL *23* 3093 (1982) JOC *48* 715, 1404 (1983)

RM	X	
R_2CuLi (*continued*)	OTs	JACS *108* 7420 (1986)
	SOPh	CC 434 (1980)
	SO_2Ph	CC 434 (1980) JACS *109* 6396 (1987)
$R_2CuLi \cdot BF_3$	OTs, OMs	JACS *108* 7420 (1986)
$R_2CuLi \cdot 2\ BF_3$	OTs	JACS *108* 7420 (1986)
R_2CuLi, Me_3SiCl	OH	TL *28* 5521 (1987)
R_2CuMgX	O_2CR	TL 4439 (1976); *23* 3583 (1982) (lactone) CL 1521 (1982) (lactone) Can J Chem *61* 632 (1983)
(RCuCN)MgCl	Br, OAc	TL *27* 5095 (1986)
$(RCuCH_2SOCH_3)Li$	OAc	JOC *52* 1885 (1987)
$[RCu(CN)CH_2SOCH_3]Li_2$	OAc	JOC *52* 1885 (1987)
(RCuX)Li (X = CN, SPh)	OAc	JOMC *136* 103 (1977)
(RCuCN)Li	Br	TL *27* 5095 (1986)
	O_2CR	JOC *45* 4256 (1980) (lactone); *48* 1404, 3986 (1983); *49* 422 (1984); *51* 1612 (lactone), 4492 (1986)
		TL *27* 5095 (1986)
$RCu(CN)Li \cdot BF_3$	OMs	CC 1596 (1987)
$(R_2CuCN)Li_2$	OMs	JACS *108* 7420 (1986)
$(R_2CuCN)Li_2 \cdot BF_3$	OTs, OMs	JACS *108* 7420 (1986) CC 1596 (1987)
$(RCuNCy_2)Li$	Cl	JACS *104* 5824 (1982)
$(RCuPPh_2)Li$	Cl	JACS *104* 5824 (1982)
$Li_2Cu_3Me_5$	OCONHPh	TL *23* 3093 (1982); *24* 4477 (1983) JOC *51* 1264 (1986); *52* 897 (1987)
$(R_3BMe)Li$, CuBr	Cl, Br	BCSJ *50* 2199 (1977)
RZnCl or R_2Zn, cat $CuBr \cdot SMe_2$	Cl	JACS *109* 8056 (1987)
$(RO_2CCHRCH_2)_2Zn$, cat $CuBr \cdot SMe_2$	Cl, Br	JACS *109* 8056 (1987)

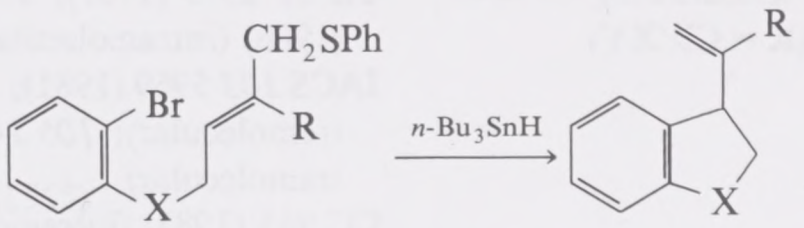
$RHgX, Li_2PdCl_4$ (R = aryl, vinylic)	Cl, OAc

JACS *90* 5531 (1968); *100* 287 (1978)
JOC *43* 2870 (1978); *46* 1432 (1981)
JOMC *156* 45 (1978)



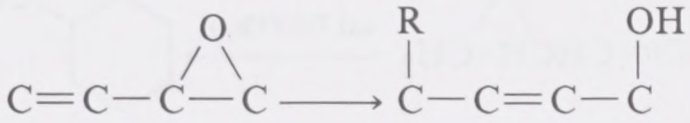
$n = 1, 2$; X = OAc, $OSiMe_3$; RM = RMgX-cat Cu(I), $RCHLiCO_2R$

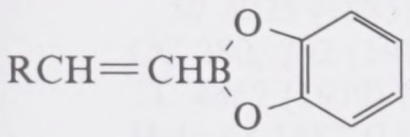
TL *28* 5521 (1987)



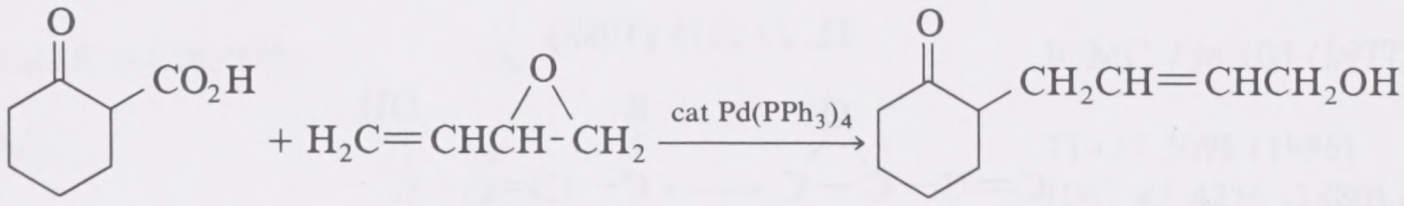
X = O, NH

TL *23* 2575 (1982)



RLi (R = alkyl, aryl)	TL 4419 (1975); *22* 577 (1981)
R_3B, O_2 (R = alkyl)	JACS *93* 2792 (1971)
 , Ni or Pd catalyst	JOMC *233* C13 (1982)
RLi or RMgX, cat CuX (X = Cl, Br, I; R = alkyl, allyl, aryl, vinyl)	TL 2027 (1978); 2051 (1979) Syn 528 (1978) CL 185 (1980) JOC *46* 239 (1981); *50* 1607 (1985) JACS *105* 3360 (1983)
RMgX, CuI, SMe_2	JACS *105* 6515 (1983) (R = i-$Pr_3SiC{\equiv}CCH_2$); *106* 723, 6006 (1984) JOC *49* 1707 (1984)
RMgX, CuCN	JOC *50* 3988 (1985); *52* 1106 (1987)
R_2CuLi (R = alkyl, vinylic, aryl)	JACS *92* 4978, 4979 (1970); *93* 3046, 3047 (1971); *103* 2114 (1981) Syn 528 (1978) TL 2027 (1978); 2051 (1979); *28* 4985 (1987) JOC *46* 122 (1981)
$R_2CuMgBr$ (R = pyridyl)	J Chem Res (S) 294 (1983)
$(RCuC{\equiv}CR')Li$ (R = alkyl, vinyl; R' = *n*-Pr, *n*-Bu)	TL 675 (1979) JCS Perkin I 2084 (1980); 683 (1983)
$(RCuCH_2SOCH_3)Li$ (R = alkyl)	JOC *52* 1885 (1987)

$(RCuCN)Li$ (R = alkyl, aryl, vinyl)	JOC *44* 4467 (1979); *46* 4389, 5379 (1981); *52* 4898 (1987) TL 675 (1979) Syn 872 (1980) JACS *103* 2907 (1981); *104* 3165 (1982)
$(R_2CuCN)Li_2$ (R = alkyl, aryl, vinyl)	JACS *104* 2305 (1982)
(RCuCN)MgX	JOC *50* 3988 (1985)
$(RO_2CCH_2CH_2)_2Zn$, cat $CuBr \cdot SMe_2$	JACS *109* 8056 (1987)
RHgCl (R = aryl, vinylic), Li_2PdCl_4	TL *27* 2211 (1986)
HCR′XY (X, Y = electron-withdrawing groups), cat $Pd(PPh_3)_4$ (R = CR′XY)	TL *22* 2575 (1981); *25* 1921 (1984); *27* 3881 (1986) (intramolecular) JACS *103* 5969 (1981); *104* 6112 (1982) (intramolecular); *105* 147, 5940 (1983) (both intramolecular) CC 985 (1983) (intramolecular)



JOC *51* 5216 (1986)

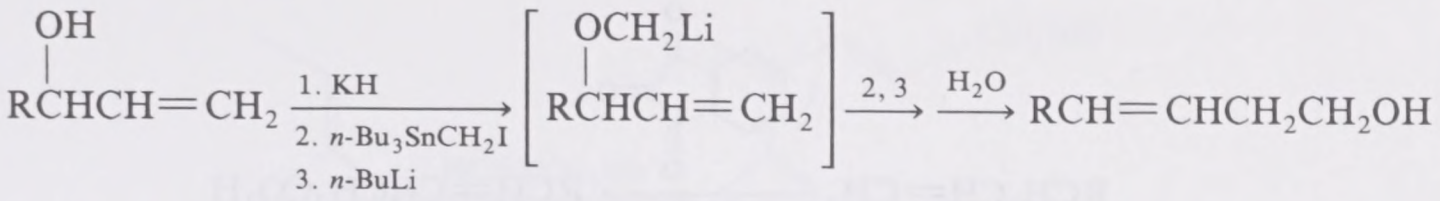
$$H_2C{=}CHCH(OR')_2 \xrightarrow{RM} RCH_2CH{=}CHOR'$$

$$H_2C{=}CHC(OR')_3 \longrightarrow RCH_2CH{=}C(OR')_2$$

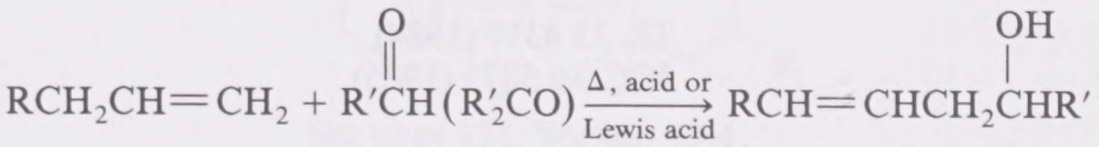
RM	
RMgX, cat CuBr	TL 3833 (1975) BSCF II 305 (1979)
E-$RR^1C{=}CHAlR^2_2$, cat $Pd(PPh_3)_4$, $(ZnCl_2)$ (R^1, R^2 = H and *i*-Bu; Me and Me)	JOC *50* 3406 (1985)
PhZnCl, (HMPA)	JOC *50* 3406 (1985)

$$H_2C{=}\underset{\displaystyle O-C=O}{\underset{|\quad|}{CHCH}}CH_2 \xrightarrow{RM} RCH_2CH{=}CHCH_2CO_2H$$

RM	
$LiCR_2CS_2Me$	CL 1901 (1983)
organocopper reagents	TL *22* 1817 (1981) CL 1307 (1981); 71, 219, 1521 (1982)



JACS *100* 1927 (1978); *108* 3841 (1986); *109* 3017, 6199 (1987)
TL *26* 5013, 5017 (1985); *28* 2099, 4993 (1987)
JOC *52* 2960 (1987)
See page 521, Section 5, for 2,3-Wittig rearrangement.



Reviews:

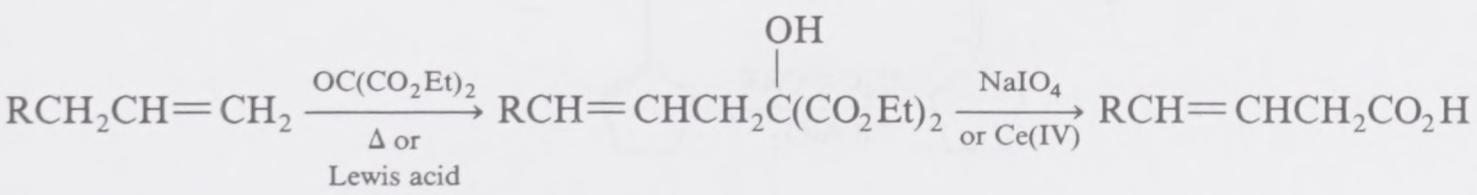
Ann Chim *10* 25 (1965)
Angew Int *8* 556 (1969)
Syn 661 (1977)
Acct Chem Res *13* 426 (1980)

Intermolecular:

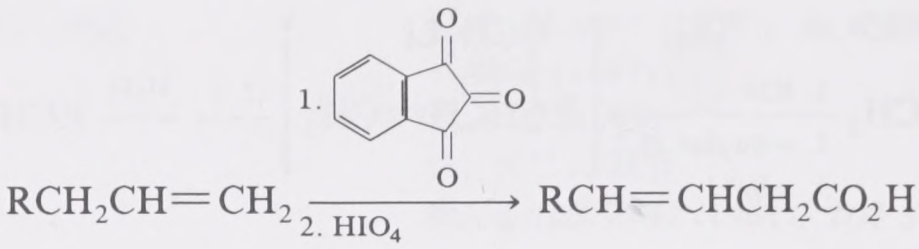
JCS 4111 (1953)
JACS *79* 4972, 4976 (1957); *81* 133 (1959); *104* 555 (1982)
Compt Rend C *263* 153 (1966)
JOC *33* 1156 (1968); *37* 964 (1972) ($R' = CO_2R$); *44* 3567 (1982) ($R' = CO_2R$); *48* 464 (1983); *50* 3025 (1985) (chiral); *51* 4779 (1986) ($R' = CO_2R$)
CC 380, 382 (1977) (both $R' = CCl_3$); 989 (1982) ($R' = CO_2R$)
TL 4867 (1979) ($R' = CCl_3$); 1815 (1980); *28* 5755 (1987)
Helv *64* 1682 (1981)
Tetr *42* 2993 (1986) ($R' = CO_2R$)

Intramolecular:

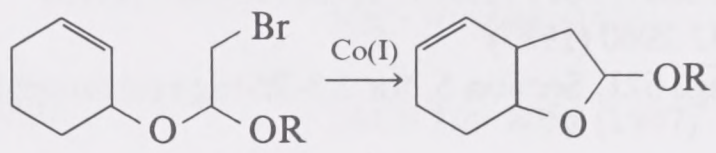
Helv *50* 153 (1967)
TL 1219 (1967); 3325 (1973); 3783 (1977); *23* 5111 (1982) ($R' = CO_2R$); *26* 4167 (1985); *28* 5945 (1987)
JACS *89* 2748 (1967); *94* 4361 (1972); *103* 1835 (1981); *105* 7358 (1983); *106* 718 (1984); *107* 2730 (1985); *109* 4424 (1987)
JOC *35* 186, 858 (1970); *42* 1794 (1977); *44* 4014 (1979); *45* 4479 (1980); *47* 745, 4538 (1982); *48* 1822 (1983); *50* 4144 (1985); *52* 5419 (1987)
CC 956 (1972)
Syn Commun *8* 449 (1978)
Tetr *42* 2951 (1986)



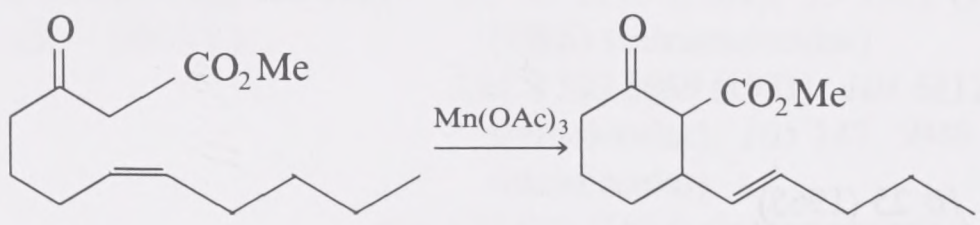
JACS *102* 2473 (1980); *106* 1092, 3797 (1984)
JOC *45* 1228 (1980); *47* 4201 (1982)



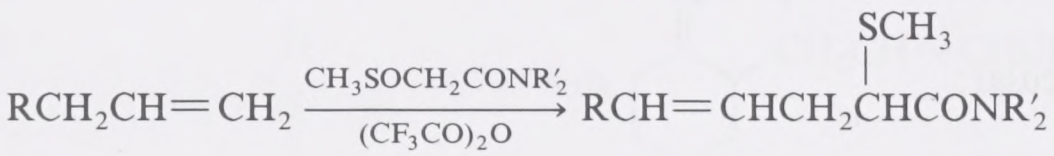
TL *23* 1399 (1982)



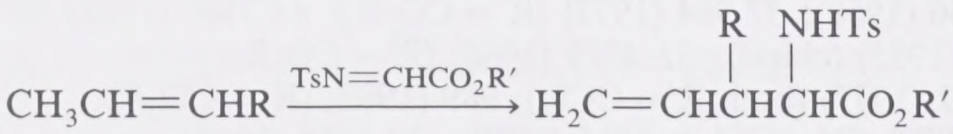
TL *25* 4317 (1984)
JOC *50* 5875 (1985)



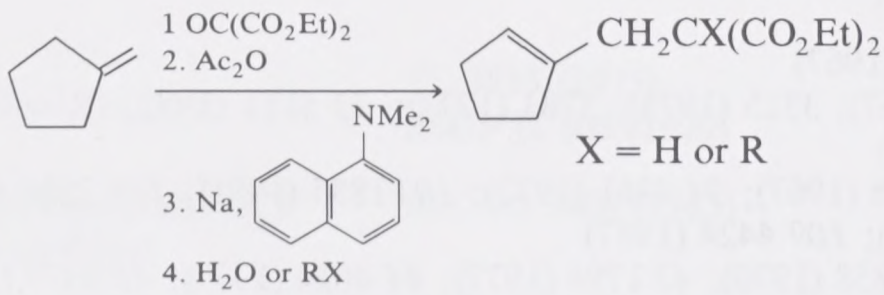
JOC *50* 3659 (1985)



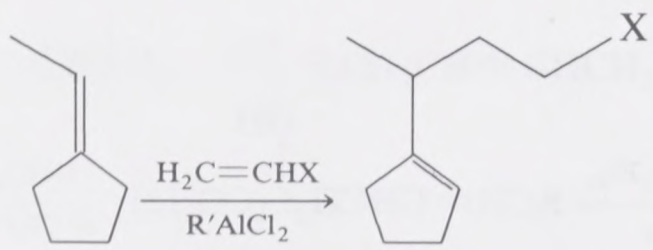
Syn 56 (1982)



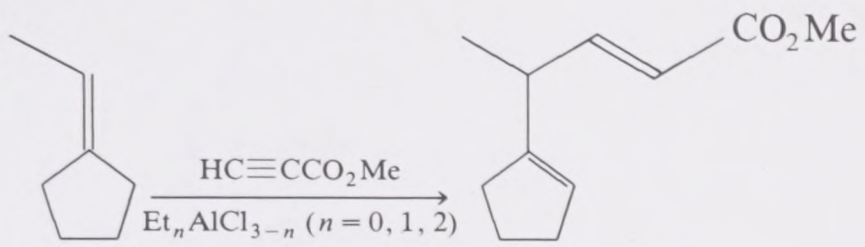
JCS Perkin I 2680 (1981)
TL *23* 3015 (1982)



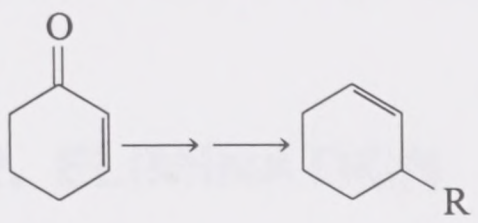
TL *22* 1885 (1981)



JOC *39* 255 (1974) (X = CHO, COMe, CO_2Me, CN); *47* 745 (1982) (X = CHO, COR)
Helv *64* 1682 (1981) (X = CO_2Me)
JACS *104* 1930 (1982) (α-substituted acrylate esters)



JOC *41* 3061 (1976); *45* 4773 (1980); *47* 3921 (1982)
JACS *101* 5283 (1979); *103* 237, 1293 (1981); *104* 2945 (1982)



See page 158, Section 45.4.

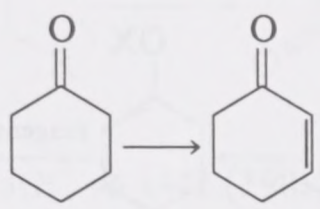
2. ELIMINATION

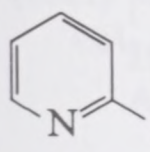
For epoxide → allylic alcohol see page 116, Section 5.

1. Dehydrogenation

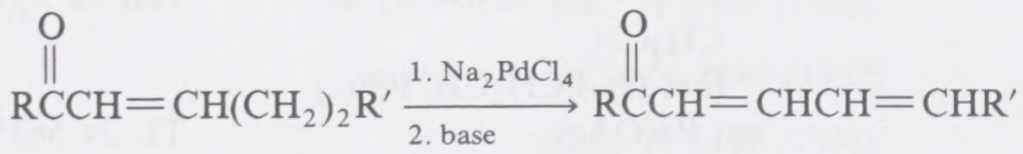
Review:

P. N. Rylander, "Organic Synthesis with Noble Metal Catalysts," Academic Press (1973), Chpt 1

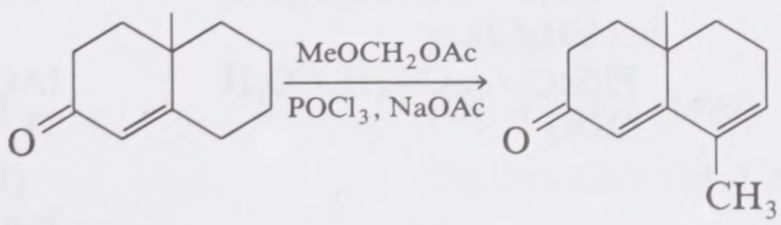


$PdCl_2$	JOC *36* 752 (1971) J Prakt Chem *314* 170 (1972) Syn 240 (1976); 773 (1977)
$PdCl_2$, $Pd(OAc)_2$	JACS *105* 2435 (1983) JOC *50* 3957 (1985)
$(PhSeO)_2O$	CC 130 (1978); 1044 (1981) JCS Perkin I 2209 (1980)
 , HCl/O_3 or $NaIO_4$	TL *23* 2105 (1982)

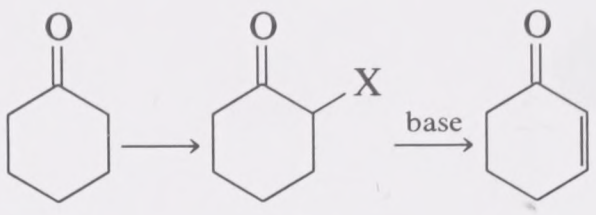
See also page 149, Section 30.



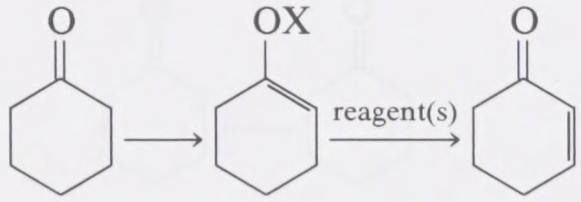
Austral J Chem *33* 1537 (1980)



Ann 712 (1983)



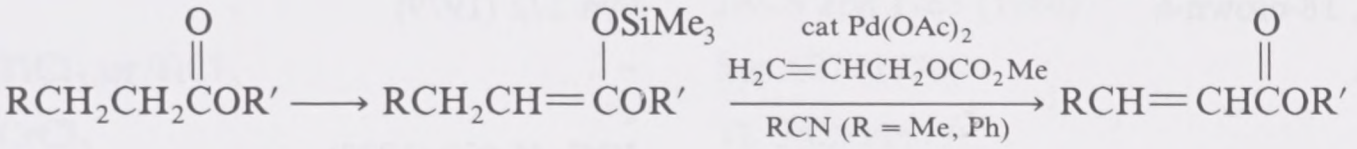
X	Base	
Cl	LiCl, DMF, Δ	TL *28* 333 (1987)
	LiBr, Li_2CO_3, DMF, Δ	JACS *101* 4003 (1979)
		Syn Commun *11* 7 (1981)
Br	LiCl, DMF, Δ	TL *23* 3405 (1982)
	LiBr, Li_2CO_3, DMF, Δ	CL 3 (1973)
		JOC *44* 71 (1979); *52* 4792 (1987)
		CC 1319 (1986)
		JACS *106* 3539 (1984)
	$CaCO_3$, CH_3CONMe_2, Δ	JCS 2532 (1961)
		JOC *35* 186 (1970); *51* 3059 (1986)
	KOH	JACS *108* 4556 (1986)
	collidine	JACS *72* 362 (1950)
	DBU	JOC *52* 1962 (1987)
		TL *28* 503 (1987)



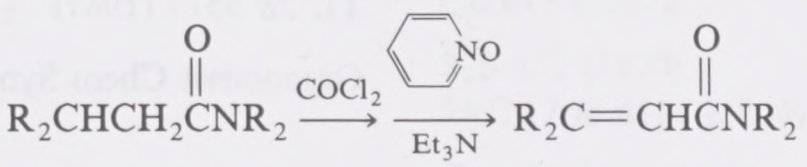
See also page 149, Section 30.

X	Reagent(s)	
$SiMe_3$	$Pd(OAc)_2$	JACS *107* 2474, 5495 (1985); *108* 3841 (1986); *109* 3017 (1987)
		JOC *52* 3346, 4647 (1987)
	cat $Pd(OAc)_2$, benzoquinone	JOC *43* 1011 (1978); *51* 4323, 5232 (1986); *52* 5588 (1987)
		JACS *108* 3443 (1986); *109* 6199 (1987)
		TL *28* 585 (1987)
	cat $Pd(OAc)_2$, $H_2C{=}CHCH_2OCO_2Me$, CH_3CN, (cat $Ph_2PCH_2CH_2PPh_2$)	CL 1133 (1984)
		Tetr *42* 2971 (1986)
	cat $Pd(OAc)_2$-$Ph_2PCH_2CH_2PPh_2$, $(H_2C{=}CHCH_2O)_2CO$, CH_3CN	TL *24* 5635 (1983); *28* 2397 (1987)
		Tetr *42* 2971 (1986)
	PhSeCl/*m*-$ClC_6H_4CO_3H$	JACS *107* 268 (1985)
	DDQ	TL 3455 (1978); *28* 31, 4943 (1987)
		Syn 736 (1979)
		JOC *50* 2981 (1985)

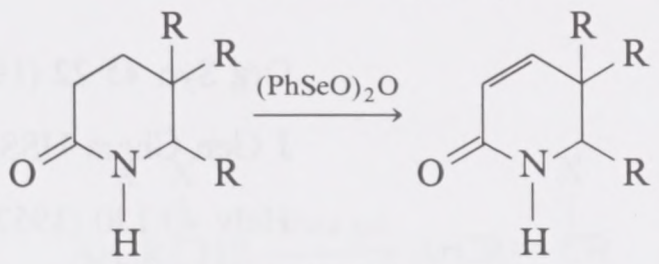
	$^1O_2$	Angew *16* 413 (1977)
	Ph_3CBF_4	JOC *42* 3961 (1977)
Ac	cat $Pd(OAc)_2$, $H_2C{=}CHCH_2OCO_2Me$, *n*-Bu_3SnOMe, CH_3CN, (cat $Ph_2PCH_2CH_2PPh_2$)	TL *24* 5635 (1983) CL 1133 (1984) Tetr *42* 2971 (1986)
$CO_2CH_2CH{=}CH_2$	cat $Pd(OAc)_2$, (cat $Ph_2PCH_2CH_2PPh_2$)	TL *24* 1797 (1983) CL 1133 (1984) Acct Chem Res *20* 140 (1987) (review)



TL *25* 4783 (1984)
Tetr *42* 2971 (1986)

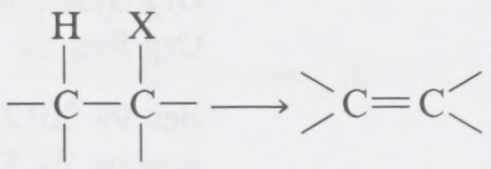


JACS *101* 4381 (1979)



JOC *46* 1442 (1981)

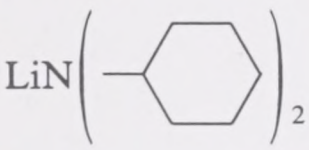
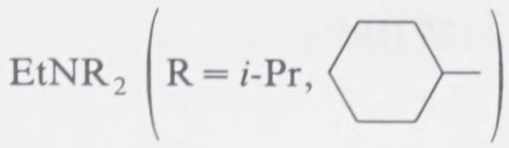
2. Dehydrohalogenation of Alkyl Halides



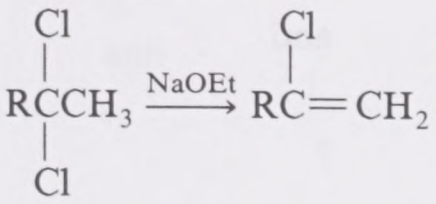
Reviews:

Chem Rev *45* 347 (1949); *80* 453 (1980)
Houben-Weyl, "Methoden der Organischen Chemie," Vol V/1b, pp 9–44, 134–180
Acct Chem Res *12* 198, 430 (1979)

DMF	JACS *86* 2309 (1964)
LiF, Li_2CO_3, HMPA	JOC *51* 3407 (1986)
KF-alumina	BCSJ *56* 1885 (1983)
Ag_2O	Helv *34* 1176 (1951)
NaOAc	Org Syn Coll Vol *3* 125 (1955)
NaOH, (*n*-$Bu_4N)HSO_4$	Syn 688 (1979)
NaOH, $HO(CH_2CH_2O)_nH$	JOC *47* 2493 (1982)
NaO-*i*-Pr, triglyme	Org Syn Coll Vol *5* 285 (1973)
KOH	Helv *60* 3060 (1977)

KOH, $HO(CH_2CH_2O)_nH$	JOC *47* 2493 (1982)
KOR	JACS *75* 4112 (1953); *78* 2199, 2203 (1956); *88* 1425 (1966) Helv *60* 3060 (1977) Coll Czech Chem Commun *46* 833, 850 (1981)
KO-*t*-Bu, DMSO	JOC *30* 2054 (1964); *32* 510 (1967); *52* 5218 (1987) JOC USSR *15* 853 (1979) JACS *108* 468, 1251 (1986)
KO-*t*-Bu, 18-crown-6	Syn 372 (1979)
	JOC *45* 900 (1980)
chiral LiNRR′	TL *28* 5517 (1987)
$LiNEt_2$	Organomet Chem Syn *1* 375 (1972)
	JOC *32* 510 (1967)
Et_3N	Org Syn *45* 22 (1965)
$PhNH_2$	J Gen Chem USSR *25* 2017 (1955)
$PhNMe_2$	Helv *40* 130 (1957)
pyridine	Org Syn Coll Vol *4* 980 (1963)
collidine	Ann *585* 132 (1954)
quinoline	Rec Trav Chim *69* 535 (1950) Org Syn Coll Vol *4* 608 (1963) Org Syn *51* 115 (1971)
DBN	Ber *99* 2012 (1966) Angew *79* 53 (1967) TL 2543 (1977) JOC *47* 4358 (1982); *52* 5624 (1987)
DBU	Angew *79* 53 (1967) Syn 591 (1972) TL 2543 (1977) JOC *47* 1944, 4358 (1982); *52* 5067 (1987) JCS Perkin I 2379 (1982) (polyene)
DBU, $NiCl_2(PPh_3)_2$-PPh_3-*n*-BuLi	CC 1621 (1986) (1° RX → terminal alkene, X = Br, I)
	Ber *91* 380 (1958)
Ph_3CLi	JCS Perkin I 1820 (1980)
Mg or $Li/NiCl_2$, $H_2C{=}CH_2$	Ber *113* 171 (1980)

3. 1,1-Dihalides

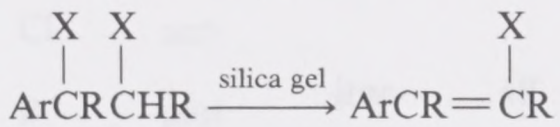


Org Mag Res *10* 192 (1977)

$$R_2CX_2 \longrightarrow R_2C{=}CR_2$$

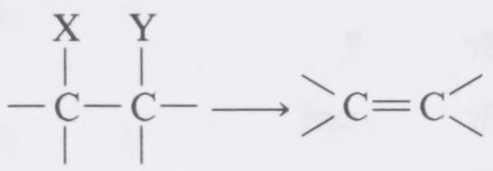
Mg	JACS *108* 1265 (1986)
$LiAlH_4$, $TiCl_3$ or $TiCl_4$	Syn 607 (1976)
$LiAlH_4$, $CrCl_3$	TL 3829 (1977)
Ni	JOC *48* 4904 (1983)
cat $Pd(PPh_3)_4$, $(ClMe_2Si)_2$	CL 613 (1982)
Zn-Cu	Syn 652 (1970) JACS *106* 8174 (1984)
CuCl	Tetr *25* 3461 (1969)

4. 1,2-Dihalides



X = Cl, Br

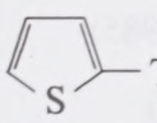
JOC *52* 1145 (1987)



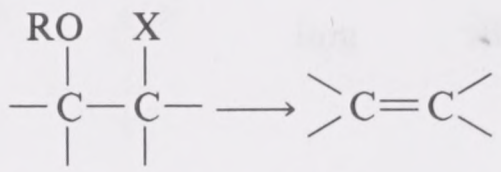
Review: Can J Chem *42* 1294 (1964)

Reagent(s)	X	Y	Stereochemistry of Elimination	
electrolysis	Br	Br	anti	Coll Czech Chem Commun *28* 1664 (1963) JOC *39* 2408 (1974) Syn 964 (1979) TL *22* 623 (1981)
Li	Br	Br	anti	TL 4269 (1968)
Na, NH_3	Br	Br	nonstereospecific	JACS *74* 4590 (1952)
Na naphthalenide	Cl	Cl	?	JOC *52* 3595 (1987)
Na naphthalenide	Br	Br	anti	JOC *37* 507 (1972)
Mg	Br	Br	anti	JACS *74* 4590 (1952) TL 4269 (1968)

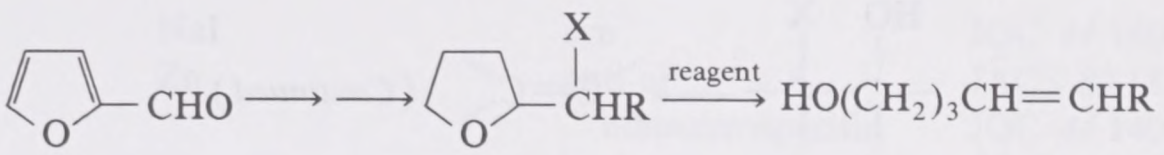
Reagent(s)	X	Y	Stereochemistry of Elimination	(*Continued*)
$LiAlH_4$	Br	Br	anti	JACS *71* 1675 (1949) Can J Chem *42* 1294 (1964)
$LiAlH_4$, $TiCl_3$ or $TiCl_4$	Cl	Cl	?	Syn 607 (1976)
$LiAlH_4$, $TiCl_3$ or $TiCl_4$	Br	Br	?	Syn 607 (1976)
$LiAlH_4$, $CrCl_3$	Br	Br	nonstereospecific	TL 3829 (1977)
$SnCl_2$	Br	Br	nonstereospecific	JACS *92* 4599 (1970)
$SnCl_2$, *i*-Bu_2AlH	Br	Br	?	CL 2069 (1984)
n-Bu_3SnH	Br	Br	nonstereospecific or anti	JACS *92* 2849 (1970)
$CrCl_2$	Br	Br	?	JACS *67* 1728 (1945)
$CrSO_4$	Cl	Cl	nonstereospecific	JACS *86* 4603 (1964)
$CrSO_4$	Cl	I	nonstereospecific	JACS *86* 4603 (1964)
$CrSO_4$	Br	Br	anti	JACS *86* 4603 (1964)
$Cr(ClO_4)_2$, $(CH_2NH_2)_2$	Cl	Br	nonstereospecific	JACS *90* 1582 (1968)
$Cr(ClO_4)_2$, $(CH_2NH_2)_2$	Br	Br	anti	JACS *90* 1582 (1968)
Fe graphite	Br	Br	anti	JOC *47* 876 (1982)
$(Et_4N)HFe_3(CO)_{11}$	Br	Br	?	JOMC *171* 85 (1979)
$Co(CN)_5^{3-}$	Br	Br	?	JACS *87* 5361 (1965)
$Pd(PPh_3)_4$	Br	Br	anti	BCSJ *52* 3629 (1979)
cat $Pd(PPh_3)_4$, $(ClMe_2Si)_2$	Cl	Cl	?	CL 613 (1982)
cat $Pd(PPh_3)_4$, $(ClMe_2Si)_2$	Br	Br	?	CL 613 (1982)
Cu	Br	Br	nonstereospecific	JOC *27* 4523 (1962)
CuCl	Br	Br	?	Tetr *25* 3461 (1969)
Zn	Br	Br	anti or nonstereospecific	JACS *63* 22 (1941); *74* 4590 (1952); *80* 182 (1958); *87* 838 (1965); *107* 516 (1987) Org Syn Coll Vol *3* 526 (1955) JOC *27* 4523 (1962); *50* 2356 (1985) TL 4269 (1968) BCSJ *52* 1752 (1979)

Zn, H_2NCSNH_2	Br	Br	?	Syn Commun *11* 901 (1981)
Zn, cat $TiCl_4$	Br	Br	anti	Syn 1025 (1982)
Zn-Cu	Br	Br	anti	JCS 3057 (1931) JACS *59* 403 (1937); *106* 5295 (1984)
NaI	Cl	Cl	nonstereospecific	JOC *27* 4523 (1962)
NaI	Cl	Br	syn	JOC *41* 3284 (1976)
NaI	Cl	Br	nonstereospecific	JOC *27* 4523 (1962)
NaI	Cl	I	nonstereospecific	JOC *27* 4523 (1962)
NaI	Br	Br	?	JACS *72* 362 (1950) JOC *30* 1658 (1965)
NaI	Br	Br	nonstereospecific	JOC *27* 4523 (1962) JACS *92* 4602 (1970)
NaI	Br	Br	syn	JOC *41* 3284 (1976)
NaI	Br	Br	anti	JACS *87* 838 (1965)
KI	Br	Br	anti	TL 4269 (1968)
$Na_2S \cdot 9\ H_2O$	Cl	Cl	anti	Syn 879 (1981)
$Na_2S \cdot 9\ H_2O$	Br	Br	anti	Syn 879 (1981)
NaSPh	Br	Br	?	J Prakt Chem *53* 1 (1896) Ber *30* 1799 (1897)
NaO_2SPh	Br	Br	?	J Prakt Chem *53* 1 (1896) Ber *30* 1799 (1897)
Na_2Se	Cl	Cl	?	JOC *31* 4292 (1966)
Na_2Se	Br	Br	?	JOC *31* 4292 (1966)
Na_2Se	I	I	?	JOC *31* 4292 (1966)
RSeNa (R = Me, Ph)	Cl	Br	syn	TL *21* 1877 (1980)
RSeNa (R = Me, Ph)	Cl	I	anti	TL *21* 1877 (1980)
RSeNa (R = Me, Ph)	Br	Br	anti	TL *21* 1877 (1980)
cat  TeNa, $NaBH_4$	Br	Br	anti	TL *23* 3601 (1982)
PPh_3	Br	Br	nonstereospecific	JOC *28* 1353, 1521 (1963)

5. β-Halo Ethers

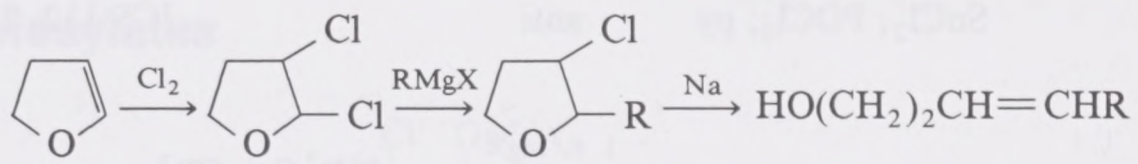


X	Reagent(s)	Stereochemistry of Elimination	
Cl	Li, NH_3	?	JOC *43* 786 (1978); *45* 48 (1980) JACS *107* 3271, 3279 (1985)
	Li; 4,4′-*t*-$BuC_6H_4C_6H_4$-*t*-Bu	?	JACS *107* 3285 (1985)
	Na	?	JCS 1707 (1950) Ann 536, 1478 (1982)
	Na, $EtNH_2$	?	JACS *107* 516 (1985)
	$Cr(ClO_4)_2$	?	JACS *109* 4752 (1987)
Cl, Br	Na or K	?	JCS Perkin I 595 (1978)
	$Na^+ C_{10}H_8^-$	?	JCS Perkin I 595 (1978)
Br	Li	?	JOC *9* 310 (1944)
	Na	nonstereospecific	Ber *43* 2175 (1910) JACS *72* 2120 (1950); *80* 182 (1958); *104* 1116 (1982) JCS 1707 (1950) CC 552 (1977)
	Na(Hg)	?	JOC *50* 5465 (1985)
	Mg	?	JACS *52* 651 (1930), *56* 126 (1934)
	Zn	nonstereospecific	JACS *52* 3396 (1930); *53* 1505, 2427 (1931); *54* 751 (1932); *55* 3293 (1933); *80* 182 (1958) JOC *17* 807 (1952); *52* 1803 (1987) Org Syn Coll Vol *4* 748 (1963) CC 1462 (1987) TL *28* 3839 (1987)
	Zn(Ag)	?	BCSJ *53* 3383 (1980) JACS *104* 1114 (1982); *105* 1058 (1983) JOC *50* 3224 (1985); *52* 598, 603 (1987) CC 1642 (1986)
	n-BuLi	?	JACS *107* 3271 (1985)
I	Zn	?	TL *28* 6497 (1987)
	t-BuLi	?	JACS *109* 4390 (1987)
	Me_2BBr, *n*-Bu_4NI	?	TL *28* 5985 (1987)

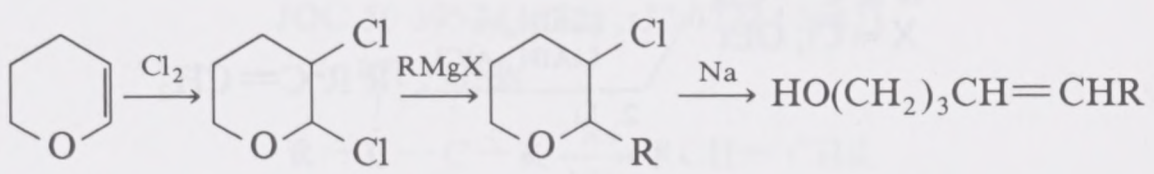


X = Cl, Br, I

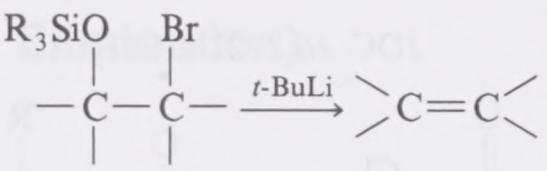
Reagent	
Na	BSCF *2* 745 (1935); *10* 484 (1943) Org Syn *25* 84 (1945) JCS 1707 (1950)
Mg	JCS 195 (1936)
Me_2BBr, n-Bu_4NI	TL *28* 5985 (1987)



JCS 1152, 1714 (1950)

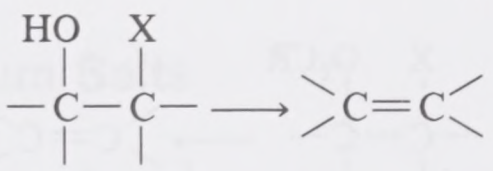


JCS 1707 (1950)
Ann 536, 1478 (1982)

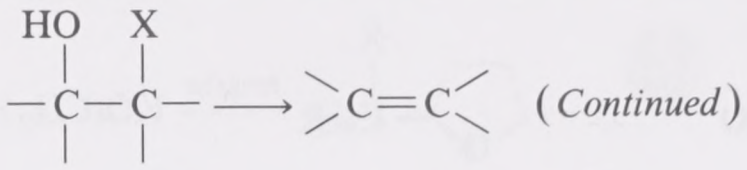


Ber *115* 1990 (1982)

6. Halohydrins

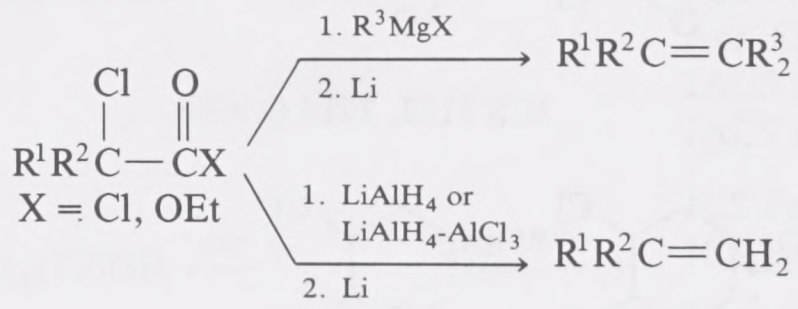


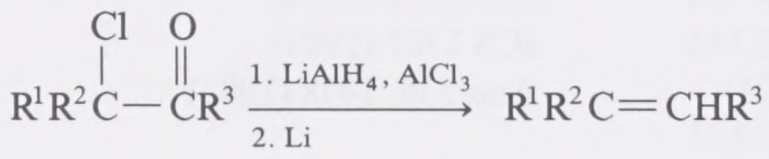
X	Reagent(s)	Stereochemistry of Elimination	
Cl	Na, NH_3	?	JACS *105* 7358 (1983)
	n-BuLi/$Li^+ C_{10}H_8^-$	?	CC 1153 (1982)
	electrolysis	?	Angew Int *16* 57 (1977)
	$Cr(ClO_4)_2$, EDA	?	JACS *105* 2435 (1983)



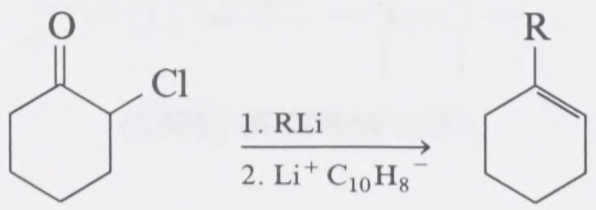
(*Continued*)

X	Reagent(s)	Stereochemistry of Elimination	
Br	Zn	?	JCS 1370 (1955)
	$Cr(ClO_4)_2$, EDA	nonstereospecific	JACS *90* 1582 (1968)
	$TiCl_3$, $LiAlH_4$	nonstereospecific	JOC *43* 3249 (1978)
	$(CF_3SO_2)_2O$, py/HMPA	anti	JACS *102* 1433 (1980)
	$KSCN/K_2CO_3$/MeI	cis	TL 2709 (1975)
	$KSeCN/K_2CO_3$	cis	TL 2709 (1975)
I	electrolysis	?	JOC *44* 1404 (1979)
	$SnCl_2$, $POCl_3$, py	anti	JCS 112, 2539 (1959)



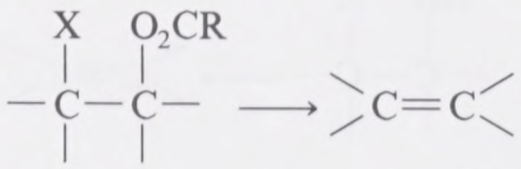


JOC *46* 2721 (1981)



CC 1153 (1982)

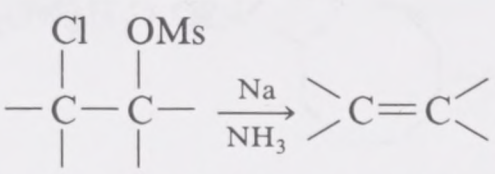
7. β-Halo Esters



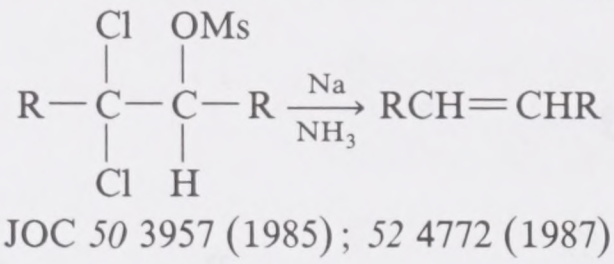
X	Reagent(s)	Stereochemistry of Elimination	
Cl	electrolysis	anti	Acta Chem Scand *17* 2139 (1963)

Cl, Br	NaI	syn	JOC *44* 1404 (1979)
	Zn	anti or nonstereospecific	JACS *80* 183 (1958) JOC *44* 1404 (1979) JCS Perkin I 1523, 1535 (1980)
Cl, Br, I	electrolysis	?	JACS *94* 5139 (1972)
Br	electrolysis	?	JOC *45* 154 (1980)
	Zn/Ag-graphite	?	CC 1149 (1986)
	$Cr(ClO_4)_2$, $(CH_2NH_2)_2$	nonstereospecific	JACS *90* 1582 (1968)
I	Zn	?	TL *27* 3297 (1986) JOC *52* 1051 (1987)

8. β-Halo Mesylates

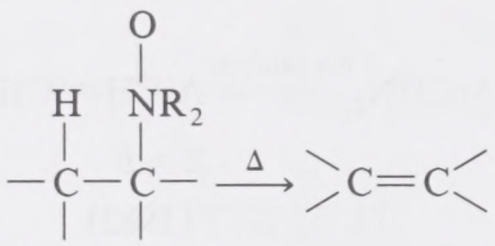


JOC *50* 3957 (1985); *52* 4772 (1987)



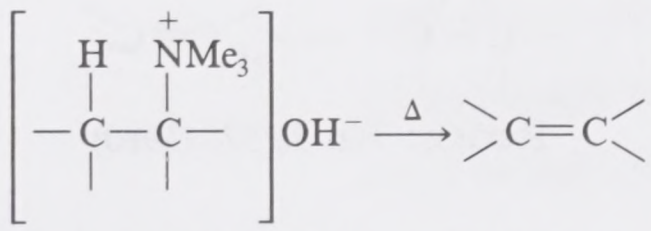
JOC *50* 3957 (1985); *52* 4772 (1987)

9. Amine Oxides (Cope Elimination)

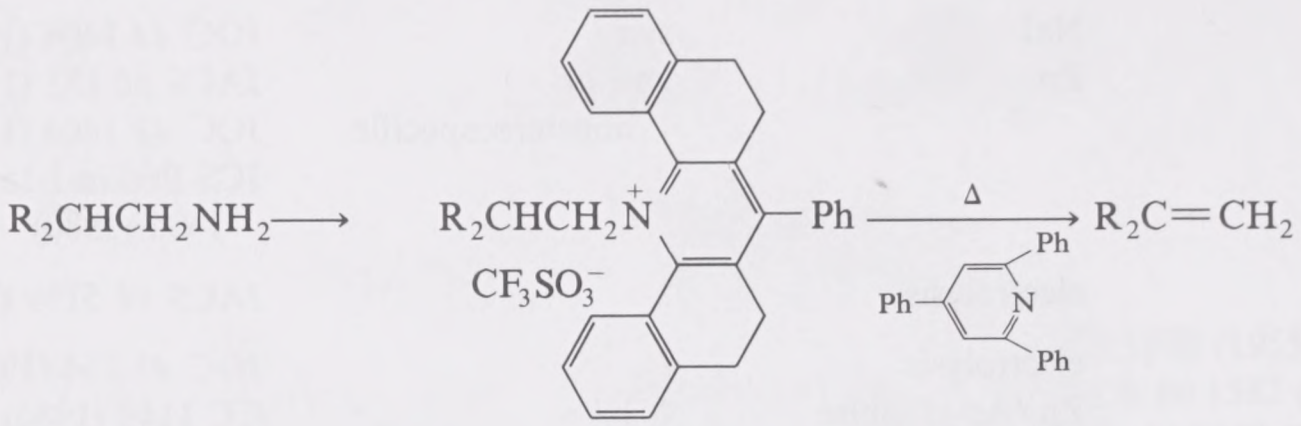


JACS *81* 2799 (1959); *108* 1039 (1986)
Org Rxs *11* 361 (1960) (review)
Org Syn Coll Vol *4* 612 (1963)

10. Quaternary Ammonium Salts

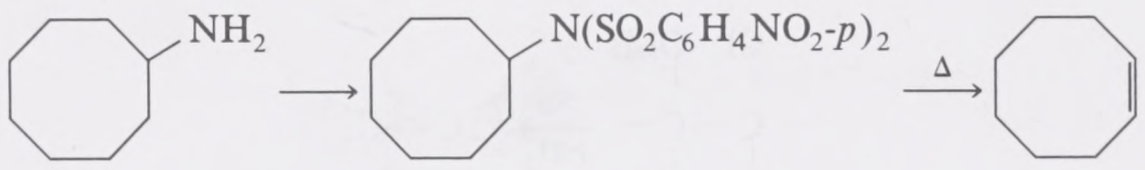


Org Rxs *11* 317 (1960) (Hofmann elimination, review)
Org Syn Coll Vol *5* 608 (1973)
Org Syn *55* 3 (1976)



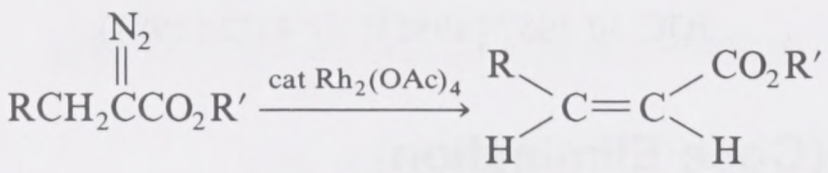
CC 96 (1981)
JOC *47* 3506 (1982)
JCS Perkin I 2347 (1982)

11. *N*-Alkyl-*N*,*N*-Disulfonimides

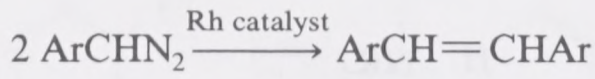


TL *22* 199 (1981)

12. Diazo Compounds



TL *22* 4163 (1981)

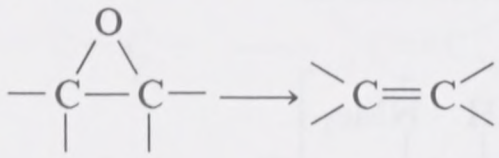


Z > *E*

TL *23* 2277 (1982)

13. Deoxygenation of Epoxides

For ring opening of epoxides to allylic alcohols see page 116, Section 5.

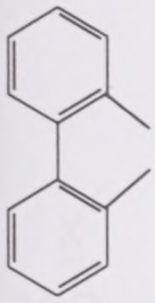


Review: Tetr *36* 575 (1980)

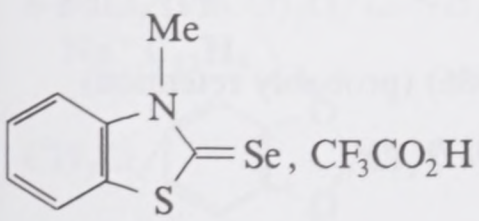
13.1. Inversion

$Ph_2PLi/HOAc, H_2O_2/NaH$

CC 142 (1974)
JACS *109* 1248 (1987)

Ph_2PLi/MeI	JACS *93* 4070 (1971); *95* 822 (1973) JOC *38* 1178 (1973)
 $PLi/H^+/EtI/NaNH_2/\Delta$	TL *28* 3445 (1987)
$Me_3SiSiMe_3$, $KOCH_3$	JACS *98* 1265 (1976) JOC *41* 3063 (1976) CC 168 (1980)
$PhSiMe_2Li$	Syn 199 (1976)
$CpFe(CO)_2Na$	JACS *94* 7170 (1972) TL 4009 (1975)
$NaBH_2S_3/LiAlH_4/PhCHO$, $H^+/LiNR_2$	JCS Perkin I 433 (1974)

13.2. Retention

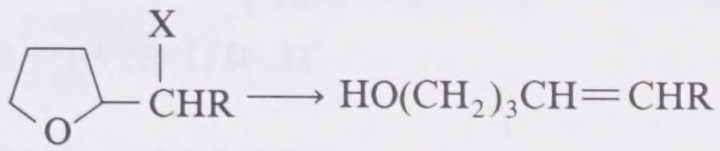
Li	TL *21* 1173 (1980)
WCl_6, *n*-BuLi	Org Syn *60* 29 (1981) CC 1084, 1642 (1986) JOC *52*, 598 (1987)
WCl_6; Li, LiI or *n*-BuLi	JACS *94* 6538 (1972)
$N_2C(CO_2Me)_2$, cat $Rh_2(OAc)_4$	TL *25* 251 (1984)
$N_2C(CO_2Me)_2$, cat $[(n\text{-}C_7H_{15}CO_2)_2Rh]_2$	JOC *51* 5503 (1986)
NaI, 18-crown-6, $BF_3 \cdot OEt_2$	JOC *43* 2076 (1978)
Me_3SiI	Nouv J Chim *3* 705 (1979)
Me_3SiCl, NaI	TL *22* 3551 (1981)
$(CF_3CO)_2O$, NaI	JOC *43* 1841 (1978)
PI_3, (py or Et_3N)	Nouv J Chim *3* 705 (1979)
P_2I_4, (py or Et_3N)	Syn 905 (1978) Nouv J Chim *3* 705 (1979)
$Ph_3P \cdot HI$, Ph_3PI_2	Syn 828 (1980)
$[(PhO)_3PCH_3]I$, $BF_3 \cdot OEt_2$	JOC *43* 2076 (1978)
KS_2CO-*n*-Bu	Chem Ind 460 (1964)
Ph_3PS, H^+/Ph_3P	JACS *94* 2880 (1972)
	Syn 200 (1976)

Ph_3PSe, CF_3CO_2H	CC 253 (1973) TL 2091 (1974)
KSeCN	JCS Perkin I 1216 (1975) JOC *51* 2712 (1986) TL *27* 4813 (1986)
RSeH (R = Me, Ph)/$(CF_3CO)_2O$ or H^+	TL 1385 (1976)
$(EtO)_2PONa(Li)$, cat Te	CC 658 (1977) JOC *45* 2347 (1980)

13.3. Non-stereospecific or Unknown Stereochemistry

R_3P (R = *n*-Bu, Ph)	Chem Ind 330 (1959) JACS *87* 2683 (1965)
$(EtO)_3P$	JOC *22* 1118 (1957)
KSCN or H_2NCSNH_2, $H^+/(EtO)_3P$	JOC *26* 3467 (1961)
H_2NCSNH_2, $NaHCO_3/PPh_3$	CC 1434 (1987)
NaTeH/TsCl, py	TL *26* 6197 (1985)
Ph_3PBr_2/Zn	JOC *41* 3279 (1976)
Zn, HOAc	CC 1450 (1970)
Zn, NaI, HOAc, NaOAc	JCS 112, 2539 (1959)
Zn-Cu, EtOH	JOC *36* 1187 (1971)
Mg(Hg), $MgBr_2$	CC 144 (1970)
$Fe(CO)_5$, $Me_2NCONMe_2$	TL 4155 (1977)
$FeCl_3$, *n*-BuLi	CL 883 (1974)
$Co_2(CO)_8$	CC 384 (1974)
Cr	JOC *41* 3647 (1976)
$Cr(ClO_4)_2$, $(CH_2NH_2)_2$	Tetr *24* 3503 (1968)
$TiCl_3$, $LiAlH_4$	JOC *40* 2555 (1975); *43* 3249 (1978)
$TiCl_4$, Zn	JOC *43* 3249 (1978)
WCl_6, $LiAlH_4$	JOC *43* 2477 (1978)
$NbCl_5$, $NaAlH_4$	CL 157 (1982)
Cp_2MX_2, Na(Hg) [M = Zr, Ti ≫ Mo > W; $X_2 = Cl_2$, O]	CC 99 (1978)
SmI_2	JACS *102* 2693 (1980)
YbI_2	JACS *102* 2693 (1980)
MeMnCl or *n*-Bu_3MnLi	TL *25* 294 (1984)
Me_3SiLi	JACS *108* 2090 (1986) (probably retention)
Et_3SiH, 300°C	JACS *109* 7534 (1987)

14. β-Mesyl or Thio Esters



X	Reagent(s)	
MsO	Na or Li, NH_3	Syn Commun *12* 915 (1982)
PhS	$Li^+ C_{10}H_8^-$	Syn Commun *12* 915 (1982)

15. Sulfides

$$RCH_2X \xrightarrow{LiCH_2SCH_3} RCH_2CH_2SCH_3 \xrightarrow[\Delta]{n\text{-BuLi}} RCH{=}CH_2$$

JACS *101* 3283 (1979)

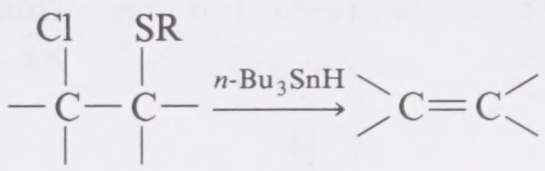
16. α-Halosulfides

$$R_2CHSH + XCHYZ \longrightarrow R_2CHSCHYZ \xrightarrow[2.\ \Delta]{1.\ SO_2Cl_2 \text{ or } Br_2} R_2C{=}CYZ$$

X = Cl, Br; Y = H, Cl, Br; Z = CO_2R, COR, CN

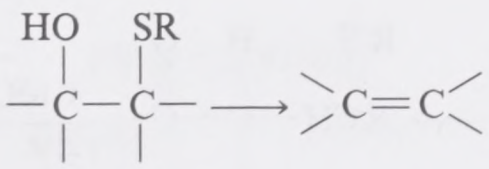
Angew Int *20* 585 (1981)

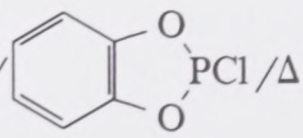
17. β-Halosulfides

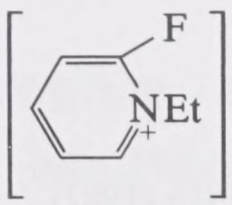


TL 4223 (1977)

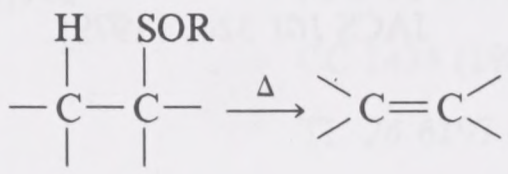
18. β-Hydroxysulfides



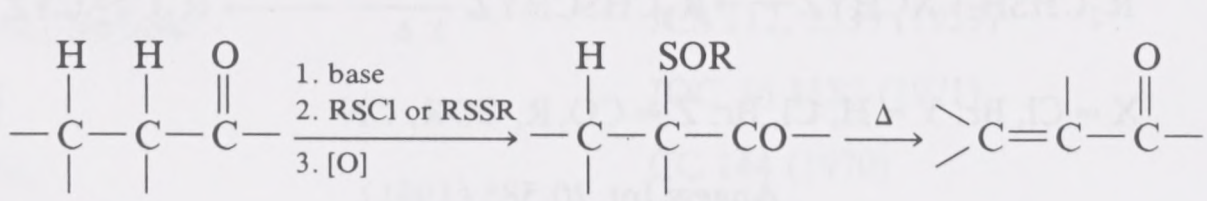
n-BuLi/$(PhCO)_2O$/Li-NH_3 or $Na^+ C_{10}H_8^-$	JACS *94* 4758 (1972) TL *27* 1343 (1986)
CH_3Li/  /Δ	TL 737 (1972)

base/CS_2/CH_3I/*n*-Bu_3SnH	TL 4223 (1977)
electrolysis	TL 2807 (1978)
PI_3, P_2I_4 or $SOCl_2$	TL 4111 (1979)
 BF_4^-, Et_3N/LiI	CL 413 (1978) JOC *45* 3549 (1980)
$TiCl_4$/Zn	CL 37, 1161, 1523 (1974)
$TiCl_4$, $LiAlH_4$, R_3N	CL 871 (1975)

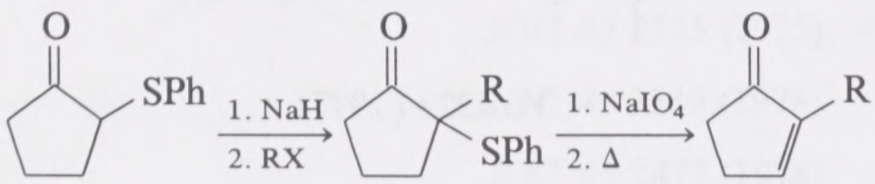
19. Sulfoxides



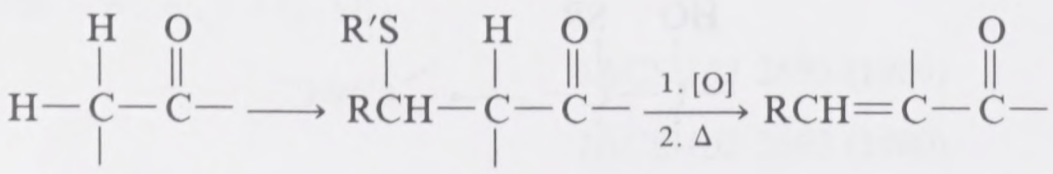
JOC *52* 1471 (1987)
TL *28* 221 (3,4-dihydrofuran), 3901 (vinyl fluorides), 4959, 5509 (α,β-unsaturated oxazolines) (1987)



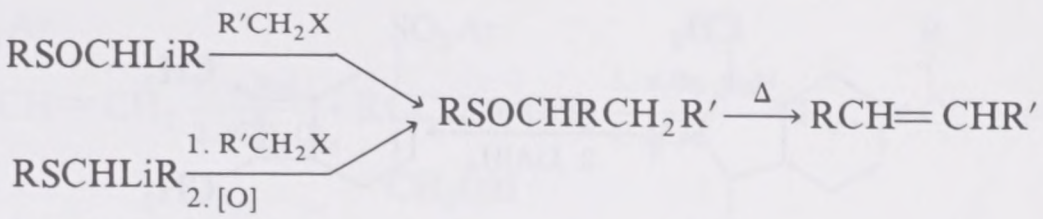
JACS *95* 6840 (1973); *98* 4887 (1976); *106* 721, 4038, 6414 (1984)
TL 5113 (1973); 1097 (1974); 4197 (1975)
Chem Rev *78* 363 (1978)
Acct Chem Res *11* 453 (1978)
JOC *44* 71 (1979); *50* 2764 (1985); *52* 1218 (1987) (on tosylhydrazone)
Syn 56 (1982)



JACS *108* 3385 (1986)

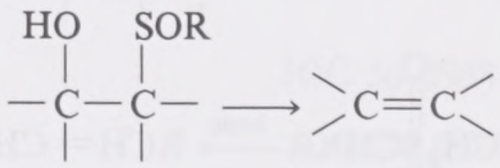


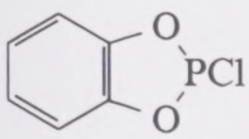
TL 993, 995, 2179 (1979)
Syn 1003 (1981)
Syn Commun *11* 315 (1981)



JACS *96* 7165 (1974)
JOC *40* 2014 (1975); *47* 4801 (1982) (diene)
Syn Commun *9* 317 (1979) (diene)

20. β-Hydroxysulfoxides



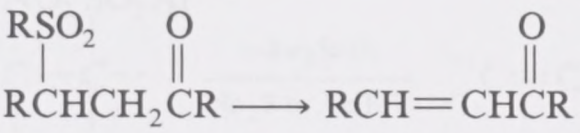


TL 649 (1972)

NBS, NCS or SO_2Cl_2

JACS *95* 3420 (1973)

21. Sulfones

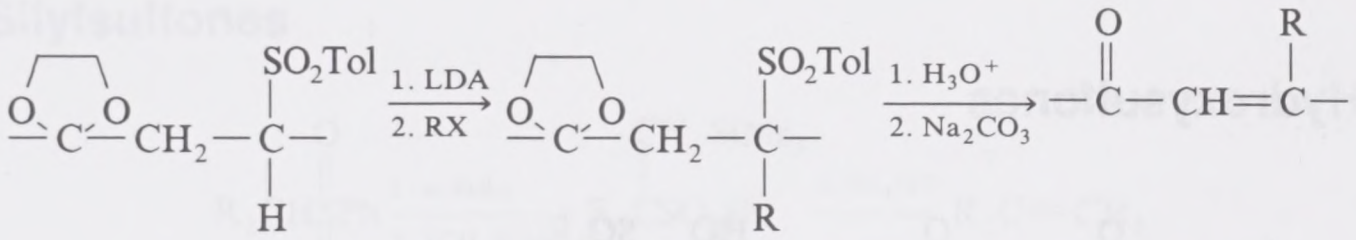


basic Al_2O_3

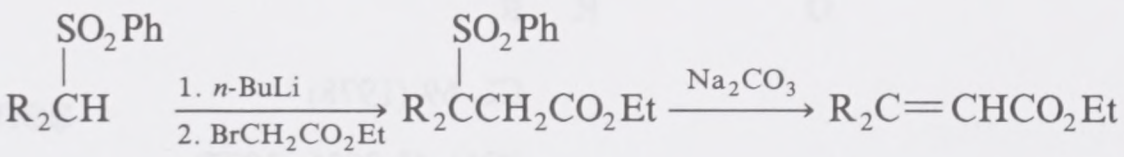
TL *27* 3733 (1986)

DBU

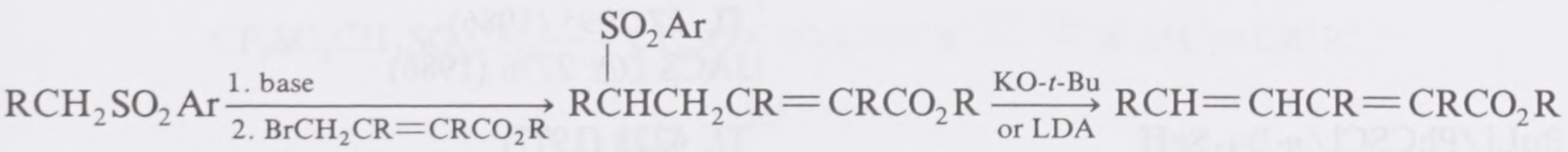
CC 1226 (1987)



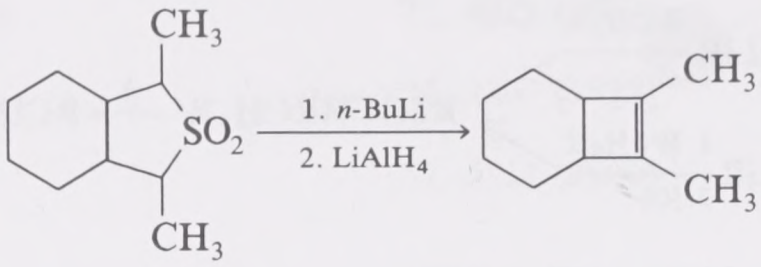
JOC *42* 1349 (1977)
CL 165 (1982)



BSCF 525 (1976)

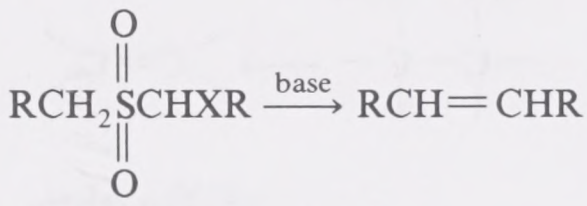


BSCF 746 (1973)
TL *27* 3337 (1986)



Org Syn *57* 53 (1977)
JACS *109* 3730 (1987)

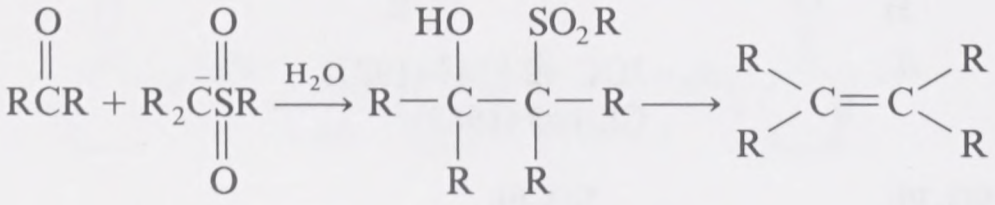
22. α-Halosulfones (Ramberg-Bäcklund Reaction)



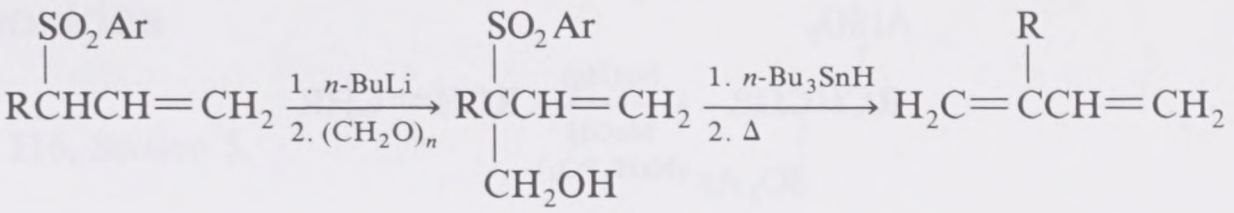
X = halogen

F. G. Bordwell in "Organosulfur Chemistry," Ed. M. J. Janssen, Interscience, New York (1967), Chpt 16 (review)
TL 4645 (1967)
Acct Chem Res *1* 209 (1968) (review)
JACS *91* 3870 (1969); *92* 2581 (1970); *96* 3332 (1972); *109* 2857 (1987)
Tetr *30* 3177 (1974)
Org Rxs *25* 1 (1977) (review)
Ber *114* 909 (1981)
Syn 504 (1982) (phase transfer)
Ann 98 (1983)
JOC *51* 2397 (1986); *52* 1703 (1987)

23. β-Hydroxysulfones

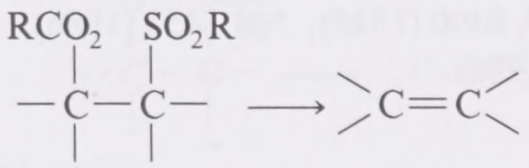


electrolysis	CL 69 (1978)
Na(Hg), MeOH	JOC *42* 2036 (1977)
Na(Hg), MeOH, Na_2HPO_4 or KH_2PO_4	JOC *50* 5465 (1985); *52* 3759 (1987) TL *27* 2095 (1986) JACS *108* 2776 (1986)
n-BuLi/PhCSCl/*n*-Bu_3SnH	TL 4223 (1977)
MsCl or TsCl/Na(Hg), MeOH	TL 4833 (1973); *23* 1963 (1982)
$SOCl_2$, py/Na(Hg), MeOH	JACS *108* 2776 (1986)



TL *22* 2675 (1981)

24. β-Acyloxysulfones



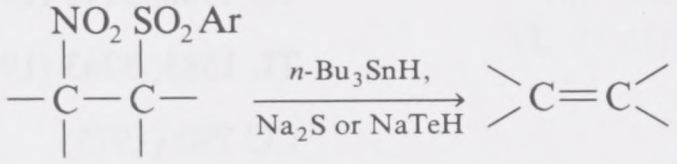
Na, EtOH

JOC *50* 2948 (1985)

Na(Hg), MeOH, (Na_2HPO_4)

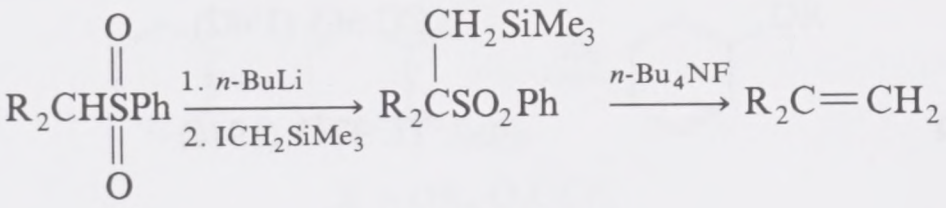
TL 4833 (1973); 4419 (1979); *27* 3903, 6345 (1986); *28* 5205, 5759, 5763 (1987)
JCS Perkin I 829, 834 (1978); 1045, 1400 (1980)
JOC *49* 3503 (1984); *52* 2838 (1987)
JACS *107* 2996 (1985); *108* 284, 4603 (1986)
CC 479 (1986); 1342 (1987)

25. β-Nitrosulfones



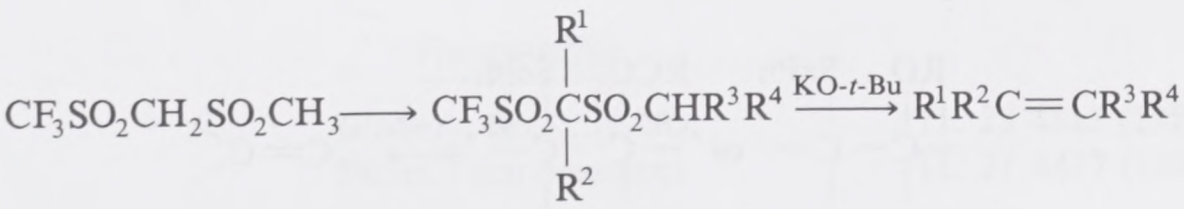
JOC *52* 5111 (1987)

26. β-Silylsulfones

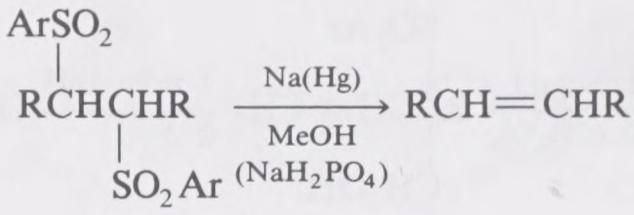


TL *23* 2223 (1982)

27. Disulfones

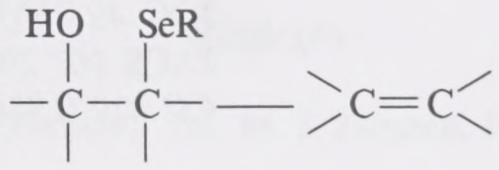


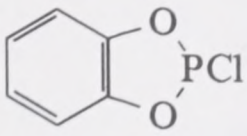
TL *25* 4617 (1984)
JOC *50* 2110 (1985)
JACS *108* 2358 (1986)



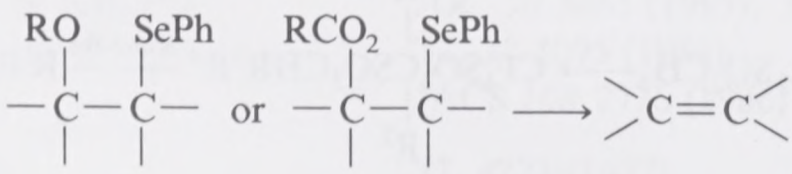
CC 914 (1982)
TL 1653 (1983)
Phosphorus and Sulfur *14* 229 (1983)
JOC *49* 596 (1984); *50* 4340 (1985); *52* 3250, 4732, 4740 (1987)
Can J Chem *62* 2487 (1984)
JACS *107* 4789, 6400 (1985); *108* 3453 (1986)
Tetr *42* 1789 (1986)

28. β-Hydroxyselenides



TsOH	TL 1385, 3227, 3743 (1976)
$HClO_4$	TL 1385, 3743 (1976)
$(CF_3CO)_2O$, Et_3N	TL 1385, 3743 (1976)
MsCl, Et_3N	CC 790 (1975)
$SOCl_2$, Et_3N	TL 3227, 3743 (1976) CC 564 (1982); 1540 (1987) JOC *51* 3108 (1986)
$POCl_3$, Et_3N	TL 2693 (1978)
PI_3, Et_3N	CC 565 (1982)
NaH/ 	TL 3743 (1976)
Me_3SiCl, NaI	JOC *46* 231 (1981)

29. β-Oxoselenides



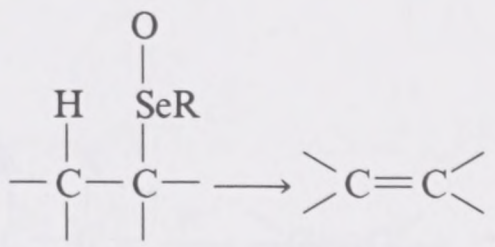
Na/NH_3	CC 83 (1979)
Me_3SiCl, NaI	JOC *46* 231 (1981)

30. Selenoxides

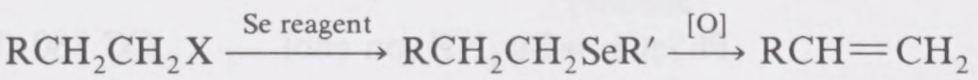
See also page 116, Section 5.

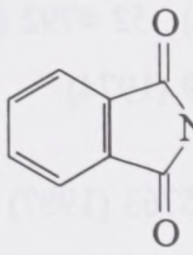
Reviews:

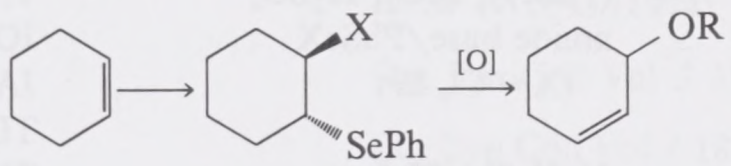
Tetr *34* 1049 (1978)
Acct Chem Res *12* 22 (1979)



JOC *36* 2561 (1971); *43* 1697 (1978)
TL 1979 (1973); 1141 (1978); *22* 1809 (1981); *27* 2949 (1986); *28* 1550, 4917, 5119 (1987)
CC 1578 (1987)

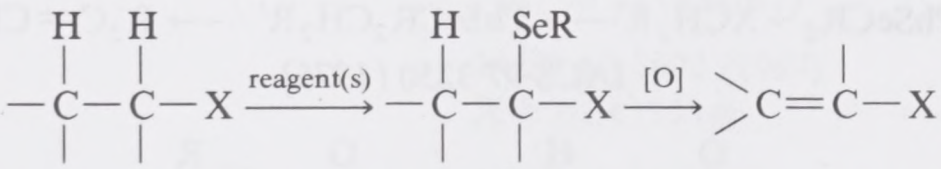


X	Se Reagent	Oxidant	
Br	NaSePh	H_2O_2	JOC *52* 2337 (1987)
OH	*o*-$NO_2C_6H_4SeCN$, *n*-Bu_3P	H_2O_2	JOC *41* 1485 (1976) JACS *105* 6723 (1983); *106* 4186, 5335 (1984); *108* 468, 1019 (1986) TL *27* 4813 (1986); *28* 3061 (1987)
	 *n*-Bu_3P	?	JOC *46* 1215 (1981)
OMs	NaSePh	KIO_4	TL *28* 3671 (1987)
	o-$NO_2C_6H_4SeCN$, $NaBH_4$	H_2O_2	JACS *98* 1612 (1976)

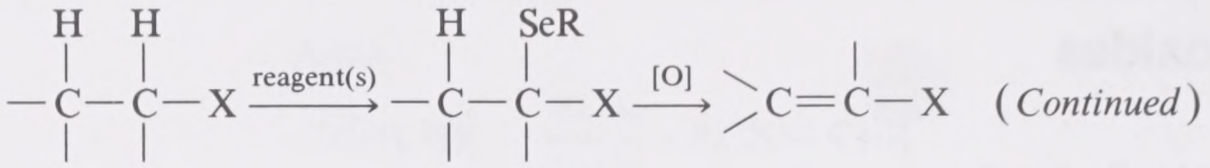


X = OR, O_2CCF_3

JOC *39* 428, 429 (1974)

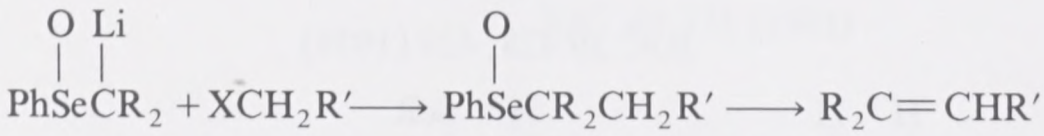


X	Reagent(s)	
CHO	$(PhSe)_2$, SeO_2, H_2SO_4	TL *23* 4813 (1982)
	PhSeCl (on enamine)	TL *21* 4417 (1980)
COR	PhSeX (X = Cl, Br)	JACS *95* 6137 (1973) JOC *50* 2981 (1985) TL *28* 5755 (1987)

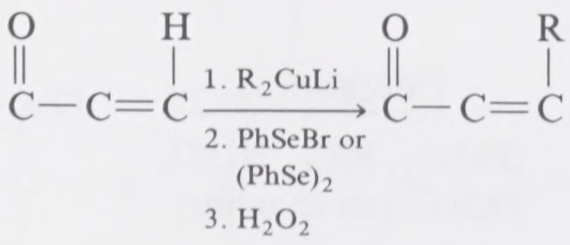


(*Continued*)

X	Reagent(s)	
COR (*continued*)	$(PhSe)_2$, SeO_2, H_2SO_4	TL *23* 4813 (1982)
	$LiNR_2$/PhSeX (X = Cl, Br)	JACS *95* 5813 (1973); *97* 5434 (1975); *107* 7745 (1985); *108* 3443 (1986)
		JOC *39* 2133 (1974); *47* 1598 (1982); *51* 2416, 5232 (1986)
		Tetr *37* 3981 (1981)
		TL *28* 6021 (1987)
	$PhSeO_2CCF_3$ (on enol acetate)	CC 695 (1973)
		JACS *97* 5434 (1975)
	MeLi/PhSeBr (on enol acetate)	JOC *39* 2133 (1974)
	PhSeCl, *n*-Bu_4NF (on enol silane)	CC 880 (1987)
CO_2R	LDA/PhSeX (X = Cl, Br)	JACS *95* 5813, 6137 (1973); *97* 5434 (1975)
		JOC *39* 2133 (1974); *52* 2639 (1987)
lactone	LDA/PhSeX (X = Cl, Br)	JACS *97* 5434 (1975)
		JOC *51* 4836 (1986)
	LDA/$(PhSe)_2$	JOC *39* 120 (1974); *43* 3693 (1978); *52* 4792 (1987)
CN	$LiNR_2$/PhSeX (X = Br, OAc) or $(PhSe)_2$	TL 2279 (1974)
$PhSO_2$	*n*-BuLi/PhSeCl	TL *28* 5763 (1987)
β-dicarbonyl compounds	PhSeCl, py	JOC *46* 2920 (1981)
	$(PhSe)_2$, SeO_2, H_2SO_4	TL *23* 4813 (1982)
	amide base/PhSeX (X = Cl, Br)	JOC *39* 2133 (1974)
		JACS *97* 5434 (1975)
		TL *27* 2691 (1986)
	NaH/Se/MeI	TL *22* 3043 (1981)



JACS *97* 3250 (1975)



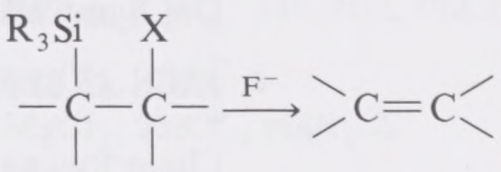
JOC *39* 2133 (1974); *50* 2539 (1985)
JACS *97* 5434 (1975); *108* 6276 (1986)

31. Tellurides

$$RCH_2X \xrightarrow{PhTeCH_2Li} RCH_2CH_2TePh \xrightarrow{\text{chloramine-T}} RCH{=}CH_2$$

CL 447 (1981)

32. β-Halosilanes

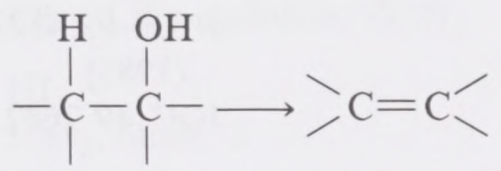


TL *23* 3455 (1982)

33. β-Oxysilanes

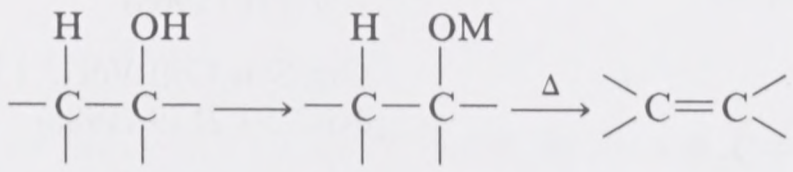
See page 178, Section 12.

34. Dehydration of Alcohols



DMSO	JOC *27* 2377 (1962); *29* 123, 221 (1964) TL *28* 1175 (1987)
HMPA	TL 567 (1971) BCSJ *47* 1693 (1974)
HBr	Org Syn Coll Vol *3* 312 (1955)
H_2SO_4	Org Syn Coll Vol *1* 183, 430 (1941); *2* 606 (1943); *4* 771 (1963)
H_3PO_4	Org Syn Coll Vol *2* 151 (1943) JOC *50* 2179 (1985)
P_2O_5	JACS *69* 2022 (1947) JCS 2154 (1954)
$(CO_2H)_2$	JACS *69* 50 (1947) JCS 2154 (1954)
TsOH	JOC *52* 5574 (1987)
$NaHSO_4$	JACS *69* 2022 (1947)
$KHSO_4$	JACS *69* 2022 (1947); *109* 7122 (1987)
$BF_3 \cdot OEt_2$	JACS *108* 3835 (1986)

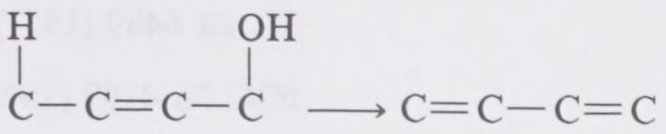
$CuSO_4$	Acta Chem Scand B *31* 721 (1977) JOC *45* 917 (1980); *47* 2590 (1982)
$CuSO_4$-silica gel	TL *28* 4565 (1987)
I_2	JCS 588 (1947)
$FeCl_3$, SiO_2	JOC *43* 1020 (1978)
KOH	JACS *69* 2022 (1947); *70* 1646 (1948) Ber *93* 2591 (1960)
Al_2O_3, Δ	Org Syn Coll Vol *3* 312 (1955)
ThO_2, Δ	JACS *85* 2180 (1963)
NBS, py	Chem Rev *63* 21 (1963)
$(PhO)_3PBr_2/K_2CO_3$	JCS Perkin I 1136 (1980)
$[(PhO)_3PMe]I$, HMPA	JOC *37* 4190 (1972); *52* 2644 (1987)
$POCl_3$, py	JACS *83* 5003 (1961); *106* 6690 (1984); *107* 4964 (1985); *108* 3443 (1986)
$POCl_3$, HMPA	JACS *102* 7910 (1980)
$SOCl_2$, py	JACS *77* 1028 (1955) JCS Perkin I 1136 (1980) JOC *51* 5463 (1986)
$Ph_2S[OC(CF_3)_2Ph]_2$	JACS *93* 4327 (1971); *94* 5003 (1972); *107* 4964 (1985) JOC *49* 2682 (1984); *51* 3098 (1986)
$MeO_2C\bar{N}SO_2\overset{+}{N}Et_3$	JACS *92* 5224 (1970); *106* 1518 (1984); *107* 1421 (1985); *108* 2343, 3731 (1986) JOC *35* 2594 (1970); *38* 26 (1973); *39* 2124 (1974); *52* 3614 (1987) TL *28* 31, 4965, 5643 (1987)
p-MeC_6H_5OCSCl/Δ	CC 1215 (1972) JOC *45* 3149 (1980)



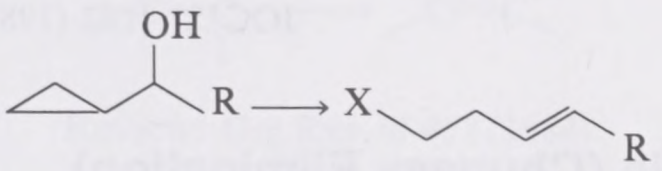
M	
Mg, Zn	JOC *44* 1221 (1979)
Al	JOC *44* 1221, 1340 (1979)

$$RCH_2CH_2OH \longrightarrow RCH_2CH_2SeAr \xrightarrow{[O]} RCH{=}CH_2$$

See page 149, Section 30.

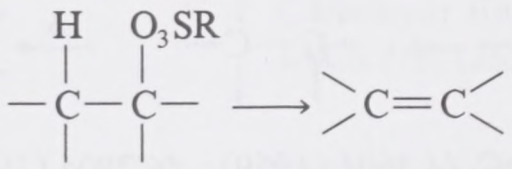


See page 242, Section 2.



X	Reagent(s)	
F	HF-py, KHF_2, *i*-Pr_2NH, PhCl	TL *28* 663 (1987)
Cl	$MgCl_2$, ether, Δ	JOC *45* 2566 (1980)
	$MgCl_2$, $ZnCl_2$, ether, Δ	JOC *45* 2566 (1980)
	Me_3SiCl	TL *27* 1907 (1986)
Br	HBr	Compt Rend *248* 820 (1959) BSCF 1072 (1960); 1805 (1970) JACS *90* 2882 (1968) Syn 37 (1979) JOC *50* 2719 (1985)
	HBr, $ZnBr_2$	JACS *90* 2882 (1968) TL 1281 (1973)
	$MgBr_2$, ether, Δ	CC 303 (1975) JOC *45* 2566 (1980)
	$MgBr_2$, $ZnBr_2$, ether, Δ	JOC *45* 2566 (1980)
	Me_3SiCl, LiBr	TL *27* 1907 (1986)
	PBr_3, LiBr, collidine/$ZnBr_2$	JACS *90* 2882, 6225 (1968)
I	HI	Syn 37 (1979)
	MgI_2, ether, Δ	CC 303 (1975) JOC *45* 2566 (1980)
	MgI_2, ZnI_2, ether, Δ	JOC *45* 2566 (1980)
	Me_3SiCl, LiI	TL *27* 1907 (1986)

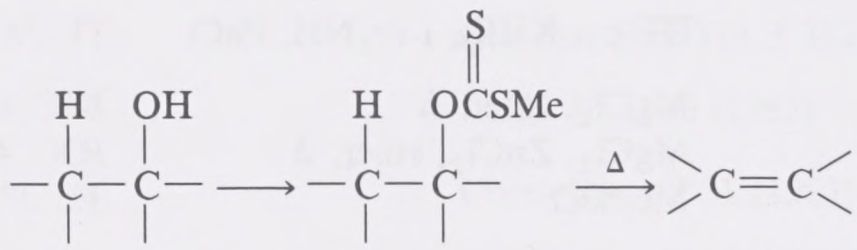
35. Sulfonate Ester Eliminations



NaI, HMPA, Δ	JACS *109* 2212 (1987)
Al_2O_3	JOC *42* 3173 (1977)
MOMe (M = Li, Na, K)	JOC *26* 4199 (1961)
KO-*t*-Bu	TL *28* 6489 (1987)
KO-*t*-Bu, DMSO	JOC *29* 742 (1964); *30* 2054 (1965) Org Syn *64* 50 (1985)
DBN	JOC *52* 2644 (1987)
DBU	JOC *52* 4044 (1987)

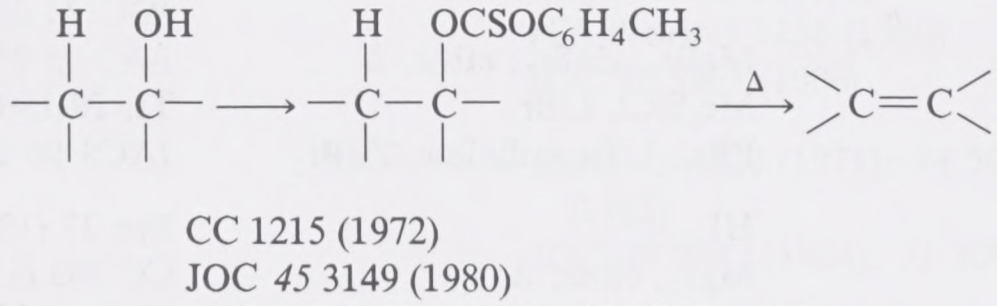
$PhCH(Me)NMe_2$ (chiral)	TL *28* 6489 (1987)
MNH_2 (M = Li, K), NH_3	JOC *26* 4199 (1961)
Et_2NMgBr	JOC *26* 4199 (1961)
o-$NO_2C_6H_4SeNa/H_2O_2$	JOC *52* 4142 (1987)

36. Xanthate Pyrolysis (Chugaev Elimination)



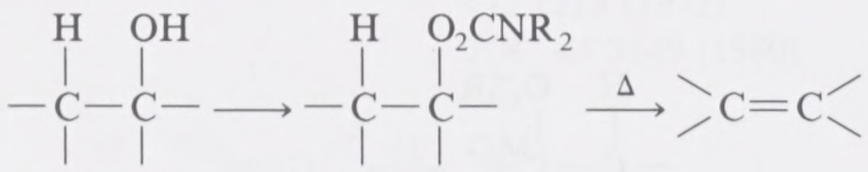
Org Rxs *12* 57 (1962) (review)
TL *28* 2795 (1987)

37. *p*-Tolylthiocarbonate Pyrolysis



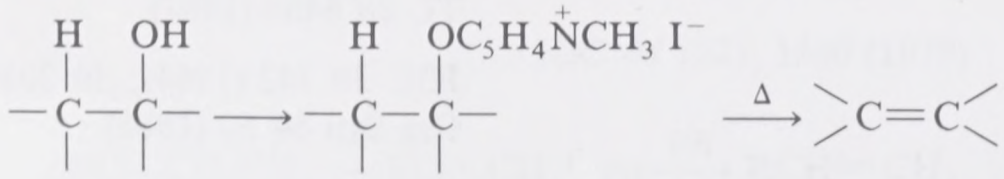
CC 1215 (1972)
JOC *45* 3149 (1980)
JACS *105* 7352 (1983); *108* 800 (1986)

38. Carbamate Pyrolysis



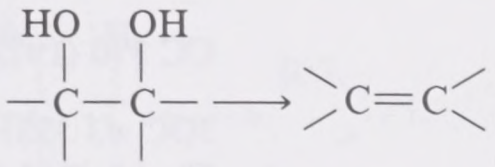
JOC *34* 3604 (1969); *46* 2804 (1981)

39. *N*-Methyl-4-Alkoxypyridinium Iodide Pyrolysis



Can J Chem *50* 1181 (1972)

40. 1,2-Diols

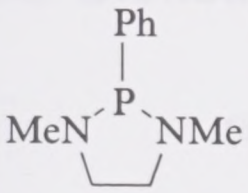


Review: Org Rxs *30* 457 (1984)

40.1. Stereospecific cis Elimination

thionocarbonate

$P(OR)_3$, Δ — JACS *85* 2677 (1963); *87* 934 (1965); *93* 4516 (1971); *94* 8627 (1972)
Carbohydr Res *1* 214 (1965); *1* 444 (1966)
TL 4645 (1967); 3655 (1978); 853 (1972)
JOC *35* 3558 (1970)
Can J Chem *48* 383 (1970)



TL *23* 1979 (1982)
JACS *108* 512 (1986)

Raney Ni — JACS *105* 1988 (1983)

$Ni(COD)_2$ — TL 2667 (1973)

benzylidene acetal, *n*-BuLi — CC 1593 (1968)
Tetr *26* 4339 (1970)
JCS C 886 (1971)
JCS Perkin I 2332 (1973)
JOC *45* 261 (1980)

2-alkoxy-1,3-dioxolane

Δ — TL *22* 1471 (1981)
Tetr *38* 2395 (1982)
JCS Perkin I 2279 (1986)
JACS *109* 7495 (1987)

H^+, Δ — Austral J Chem *17* 1392 (1964); *21* 2013 (1968)
Carbohydr Res *7* 161 (1968)
JACS *108* 1265 (1986)

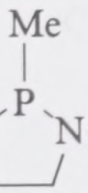
2-dialkylamino-1,3-dioxolane

MeI, Δ — TL 737 (1978)
Rec Trav Chim *104* 266 (1985)

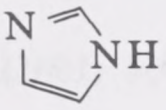
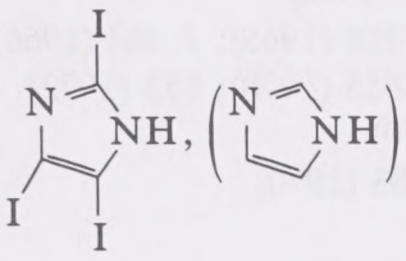
Ac_2O, Δ — TL 5223 (1970); *27* 2575 (1986)
JACS *96* 5254 (1974)

40.2. Non-stereospecific or Unknown Stereochemistry

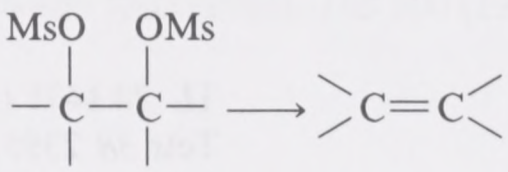
thionocarbonate, MeI or *i*-PrI, Δ/(Zn) — JOC *39* 3641 (1974)



thionocarbonate, $PhCH_2N$ P NCH_2Ph, Δ — JOC *39* 3641 (1974)

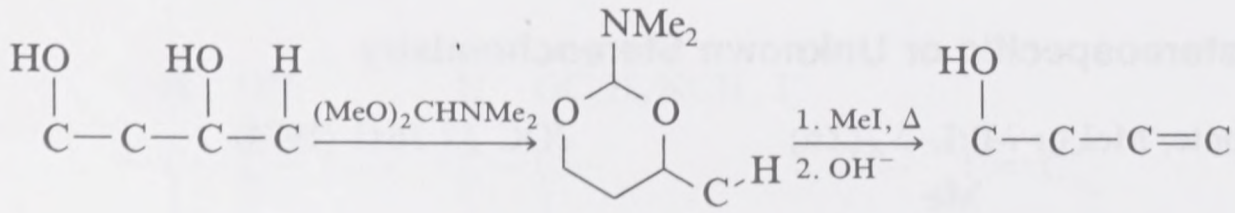
thionocarbonate, $Fe(CO)_5$, Δ	TL 4435 (1972)
carbonate tosylhydrazone pyrolysis	TL 3161 (1973)
2 MeLi/K_2WCl_6	CC 370 (1972)
$TiCl_3$, K	JOC *43* 3255 (1978) TL *28* 4965 (1987)
Me_3SiCl, NaI	TL *23* 1365 (1982)
PBr_3/CuBr, Zn	BCSJ *52* 1752 (1979)
Ph_3P, I_2, 	Syn 469 (1979)
Ph_3P, 	Syn 813 (1979)
NaOH or NaH/CS_2/MeI/*n*-Bu_3SnH	CC 866 (1977) Chem Pharm Bull *26* 1786 (1978) JCS Perkin I 2378 (1979)
Cl_2POX (X = OEt, NMe_2)/Li-NH_3 or Ti-THF	JOC *42* 1311 (1977)

41. 1,2-Dimesylates



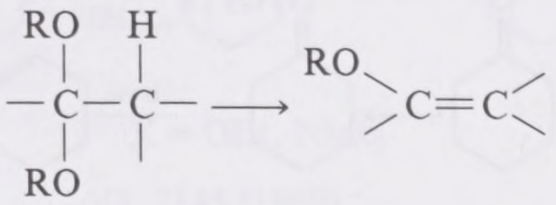
Na naphthalenide	TL 3447 (1972) JACS *109* 5524 (1987)
NaI, Zn	TL *28* 2183 (1987) JACS *109* 6403 (1987)

42. 1,3-Diols



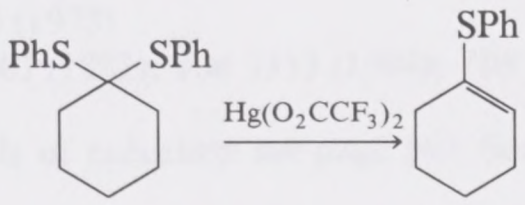
CC 1756 (1987)

43. Acetals

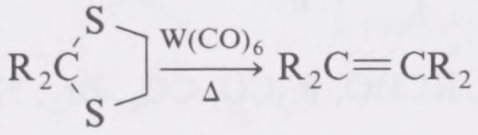


cat TsOH	Syn 38 (1974)
$AlCl_3$ or $MgBr_2$, Et_3N	Helv *62* 1451 (1979)
Me_3SiI, $(Me_3Si)_2NH$	TL *23* 323 (1982)
$Me_3SiMn(CO)_5$	Organomet *1* 1467 (1982)
$TiCl_4$/DBU	Tl *27* 3053 (1986)

44. Dithioacetals



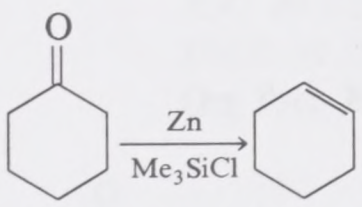
JACS *105* 5075 (1983)



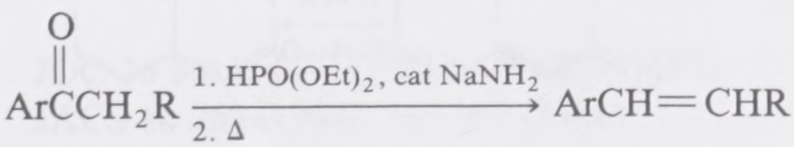
CC 981 (1987)

45. Aldehydes and Ketones

45.1. Direct Elimination

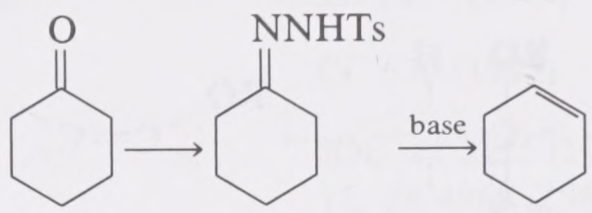


CC 935 (1973)
JCS Perkin I 809 (1975)



Angew Int *2* 98 (1963)

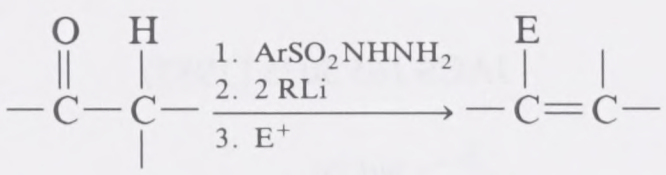
45.2. Tosylhydrazone Elimination (Bamford-Stevens)



Review: Org Rxs *23* 405 (1976)

JCS 4735 (1952)
Tetr *12* 168 (1961); *31* 1035 (1975)
Ann *691* 41 (1966)
JACS *89* 5734, 5736, 7112 (1967); *90* 4762 (1968); *106* 6006 (1984); *107* 3971, 7352, 7724 (1985)
TL 345 (1968), 2947 (1976)
Syn 595 (1970)
Austral J Chem *23* 857 (1970)
JOC *43* 147, 1404 (1978); *44* 3976 (1979); *50* 5460 (1985); *52* 3346 (1987)
Chem Pharm Bull *28* 984 (1980)

45.3. Shapiro Reaction

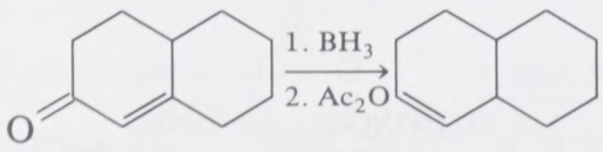


$E^+ = H_2O$, D_2O, RX, DMF, CH_2O, RCHO, R_2CO, CO_2, Br_2, NCBr, $BrCF_2CF_2Br$, Me_3SiCl, n-Bu_3SnCl

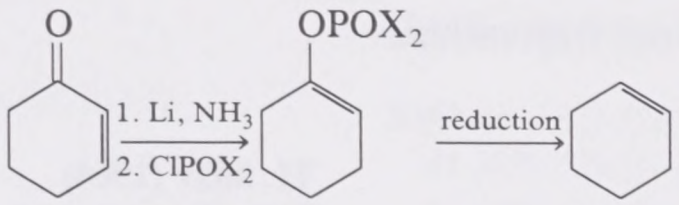
Reviews: Org Rxs *23* 405 (1976)
Acct Chem Res *16* 55 (1983)

JACS *89* 5734 (1967); *90* 4762 (1968); *106* 3539 (1984); *107* 256, 1293, 3971, 4964 (1985); *108* 4586 (1986); *109* 3174, 5731, 7838 (1987)
TL 1811, 1815 (1975); 2287 (1976); *21* 945, 3849 (1980); *23* 3733 (1982); *27* 2761, 5467 (1986); *28* 1985, 4629, 6159 (1987)
JOC *43* 147, 1404, 1409 (1978); *46* 1315 (1981); *50* 2438 (1985); *52* 569, 2644, 3541 (1987)
Syn 44 (1979)
CC 65, 1121 (1981)
JCS Perkin I 2848 (1981)
Tetr *37* 3935 (1981)

45.4. Enone Conversions



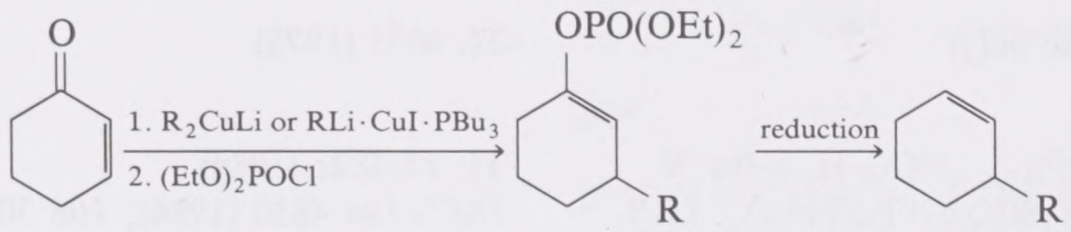
Tetr *20* 957 (1964)



$X = OEt, NMe_2$

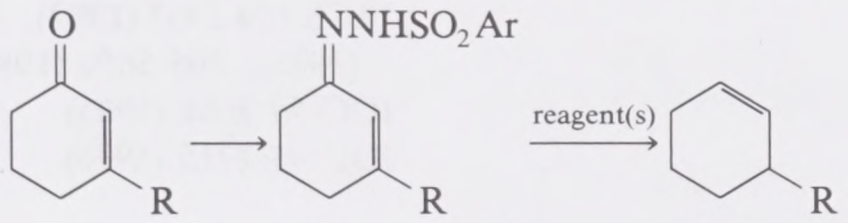
TL 2145 (1969)
JACS *94* 5098 (1972)
JOC *43* 2715 (1978)

For methods of reduction see page 160, Section 45.5.

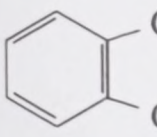


TL 2145 (1969)
Org Syn *52* 109 (1972)
JOC *43* 2715 (1978)
JACS *104* 1907 (1982); *106* 3353 (1984); *108* 5650 (1986)

For methods of reduction see page 160, Section 45.5.



Reagent(s)



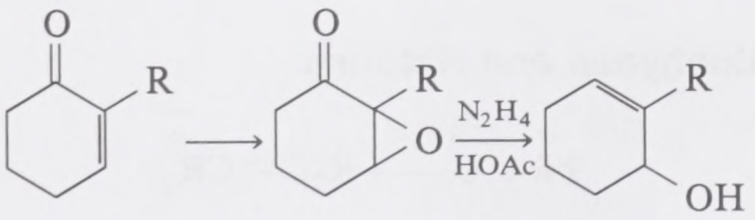
JOC *41* 574 (1976)
Org Syn *59* 42 (1980)
JACS *108* 6276, 7686 (1986)

$NaBH_4$, HOAc

JOC *43* 2299 (1978)

$NaBH_3CN$

JOC *40* 923 (1975); *50* 2798 (1985)
JACS *98* 2275 (1976); *106* 3353 (1984)
Org Prep Proc Int *11* 201 (1979) (review)



JOC *26* 3615, 4781 (1961); *27* 2205 (1962)
JACS *86* 269 (1964); *102* 862 (1980)
TL *28* 2099 (1987)

45.5. Reduction of Carbonyl Derivatives

enamine	
BH_3	TL 2039 (1964)
$LiAlH_4$, $AlCl_3$	Proc Chem Soc 19 (1963) Tetr *24* 4489 (1968)
enol ether	
i-Bu_2AlH	JOC *31* 329 (1966)
enol acetate	
BH_3	Gazz Chim Ital *92* 309 (1962)
enol silane	
BH_3/HCl (cyclic only)	TL 4005 (1975)
enol triflate	
cat $Pd(OAc)_2(PPh_3)_2$, HCO_2H, *n*-Bu_3N	TL *25* 4821 (1984)
n-Bu_3SnH or Et_3SiH, cat $Pd(PPh_3)_4$, LiCl	JACS *106* 4630 (1984); *108* 3033 (1986)
enol phosphate	
Li, *t*-BuOH, NH_3	CC 112 (1969) JACS *106* 3353, 5025 (1984)
Li, *t*-BuOH, $MeNH_2$	Helv *66* 522 (1983) JACS *108* 3435 (1986)
Li, *t*-BuOH, $EtNH_2$	TL 2145 (1969) Org Syn *52* 109 (1972) JACS *104* 1907 (1982); *106* 721 (1984); *107* 1308 (1985); *108* 5650 (1986) JOC *50* 2668 (1985)
K, $TiCl_3$/EtOH	JOC *43* 2715 (1978)
enol *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidates	
Li, NH_3	JACS *94* 5098 (1972)
Li, $EtNH_2$	TL *28* 31 (1987)
Li, $EtNH_2$, *t*-BuOH	JACS *94* 5098 (1972)
α-halocarbonyl compounds	
$LiAlH_4$/Zn, HOAc	JCS 1370 (1955)
N_2H_4	JOC *29* 958 (1964)
dithioketal	
Raney Ni	JOC *28* 1443 (1963) Tetr *25* 2823 (1969)

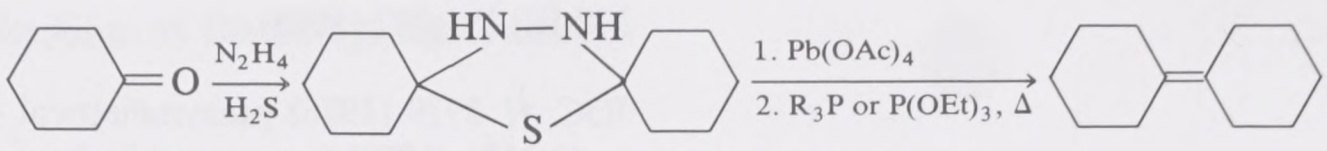
45.6. Dimerization of Aldehydes and Ketones

$$2\,R_2CO \longrightarrow R_2C{=}CR_2$$

Reviews:

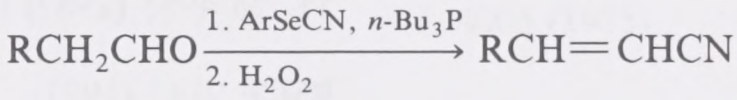
Org Prep Proc Int *12* 361 (1980)
JOC *47* 248 (1982)
Acct Chem Res *16* 405 (1983) (Ti reagents)

Ti-graphite	JOMC *280* 307 (1985)
$TiCl_3$, Li	JOC *41* 3929 (1976) (unsymmetrical coupling); *43* 3255 (1978) (unsymmetrical coupling); *51* 5446 (1986) Syn Commun *11* 895 (1981) Org Syn *60* 113 (1981) TL *23* 3227 (1982) (unsymmetrical coupling) JACS *106* 723, 6006 (1984) (both intramolecular)
$TiCl_3$, K	JOC *41* 896 (1976) (inter- and intramolecular); *43* 3255 (1978); *51* 2969 (1986); *52* 2905 (1987) (intramolecular) TL *28* 4965 (1987) (intramolecular)
$TiCl_3$, Mg	BSCF 2147 (1973)
$TiCl_3$, Zn-Cu	JOC *42* 2655 (1977); *43* 3255 (1978) (intramolecular); *46* 4293 (1981) TL *23* 1777 (intramolecular), 2723 (intramolecular), 3227 (unsymmetrical coupling) (1982); *28* 3091, 3209 (1987) (both intramolecular) JACS *106* 5018 (1984); *108* 515, 2932, 3513 (intramolecular) (1986); *52* 4885 (1987) (intramolecular)
$TiCl_3$, Zn-Ag	JOC *47* 5229 (1982) JACS *108* 1239 (1986) (intramolecular)
$TiCl_3$, $LiAlH_4$	JACS *96* 4708 (1974) Acct Chem Res *7* 281 (1974) TL 3265 (1976); *22* 3965 (1981) (enones) JOC *43* 3609 (1978); *52* 5636 (1987) Ber *115* 1234 (1982) Rec Trav Chim *101* 112 (1982)
$TiCl_4$, Mg	TL *22* 3965 (1981) (enones)
$TiCl_4$, Zn	CL 1041 (1973) JACS *106* 7514 (1984) (intramolecular); *108* 3460 (1986) TL *26* 1981 (1985) (intramolecular) CC 1072 (1987) (intramolecular)
$TiCl_4$, Zn, py	Syn 553 (1977) Ber *115* 3697 (1982)
$TiCl_4$, $LiAlH_4$	JACS *96* 4708 (1974)
$NbCl_5$, $NaAlH_4$	CL 158 (1982)
$Mo(CO)_6$ or $W(CO)_6$ or WCl_6, $LiAlH_4$	JOC *43* 2477 (1978)
WCl_6, 2 *n*-BuLi	JACS *94* 6538 (1972)
Zn, Me_3SiCl	CC 1803 (1986)

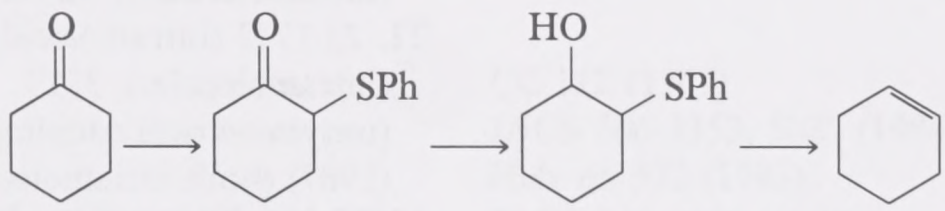


CC 1226 (1970)
JCS Perkin I 305 (1972)
JOC *38* 3061 (1973)
JACS *106* 5018, 8174 (1984); *108* 515, 2932 (1986)

45.7. Miscellaneous Reactions

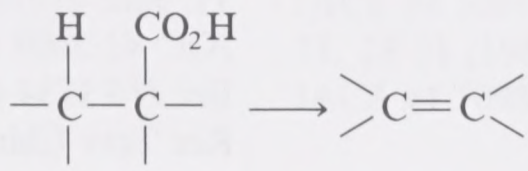


JACS *99* 5210 (1977)

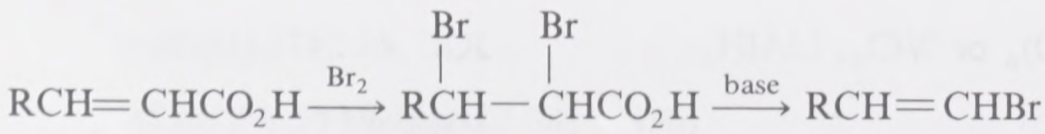


TL 4223 (1977)

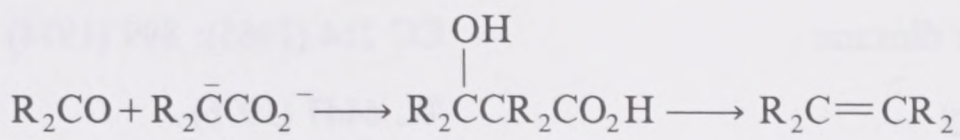
46. Carboxylic Acids



$PhI(OAc)_2$, $Cu(OAc)_2$	JOC *51* 402 (1986)
$Pb(OAc)_4$	JACS *83* 927 (1961)
$Pb(OAc)_4$, cat $Cu(OAc)_2 \cdot H_2O$, py	JACS *87* 1811, 3609 (1965); *107* 2149 (1985); *108* 4603 (1986) JOC *32* 2045 (1967); *39* 2217 (1974) TL 405, 5173 (1968); 399 (1974); *26* 6397 (1985) Tetr *24* 2215 (1968) JCS C 1047 (1969) Org Rxs *19* 279 (1972) (review) Syn 541 (1973); 889 (1974)



See page 319, Section 3.



syn elimination

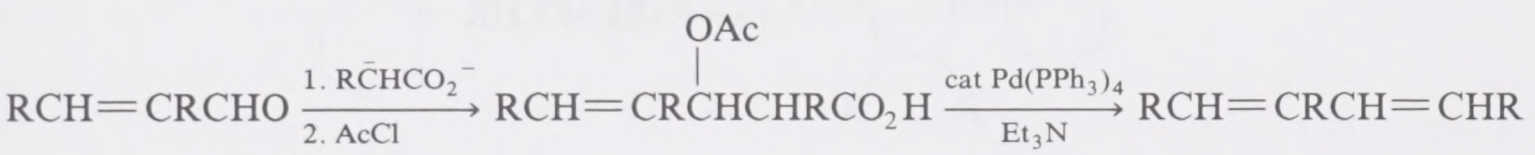
MsCl, Na_2CO_3/Δ	TL 4569 (1968)
$ArSO_2Cl$, py/Δ	JACS *94* 2000 (1972)
	Can J Chem *51* 981 (1973) (vinyl ethers)
	JOC *39* 1322, 1650 (1974); *43* 4574 (1978) (vinyl ethers); *46* 3359 (1981); *52* 3143 (1987)
	CC 52 (1979) (alkenes, vinyl ethers); 1199 (1986) (allylic silanes)
	Syn 388 (1979) (vinyl ethers)
	Helv *62* 2825 (1979)
	TL *28* 2753, 3103, 5921 (allylic silane) (1987)

anti elimination

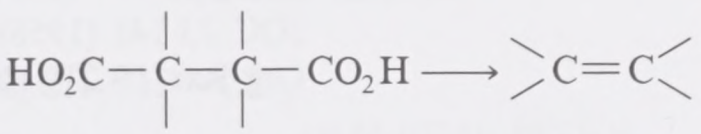
$EtO_2CN{=}NCO_2Et$, PPh_3	CC 52 (1979) (alkenes and vinyl ethers)
$(CH_3O)_2CHN(CH_3)_2$, Δ	TL 1545 (1975); 2953 (1978) (dienes); 1909 (1979) (mechanism); *27* 5417 (1986)
	Helv *62* 2825 (1979)
	Ber *115* 3453 (1982) (dienes)
	CC 1199 (1986) (allylic silanes)

unknown stereochemistry

Δ	TL *23* 5271 (1982)



JACS *102* 2841 (1980)

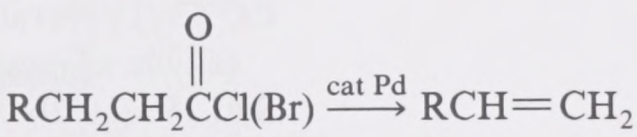


Review: Tetr *40* 2585 (1984)

electrolysis	JACS *85* 165 (1963); *89* 3922 (1967)
	Ber *100* 2427 (1967)
	TL 5117, 5123 (1968)
PbO_2	JACS *74* 4370 (1952)
$Pb(OAc)_4$, py	Helv *41* 1191 (1958)
	Angew *70* 343 (1958)
	JACS *83* 1705 (1961); *85* 165 (1963); *90* 113 (1968); *98* 628 (1976)
	JOC *30* 1431 (1965); *42* 1654 (1977)
	CC 214 (1965); 899 (1974)
	Ber *100* 2427 (1967)
	Org Rxs *19* 279 (1972) (review)

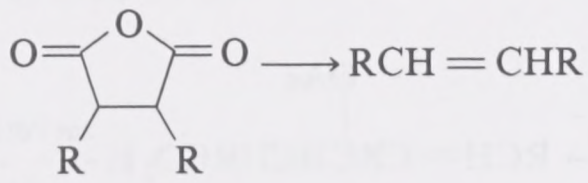
$Pb(OAc)_2$, DMSO or dioxane	CC 214 (1965); 899 (1974)
Cu_2O, quinoline, bipy	TL 4447 (1976) JACS *109* 4626 (1987)

47. Acid Halides



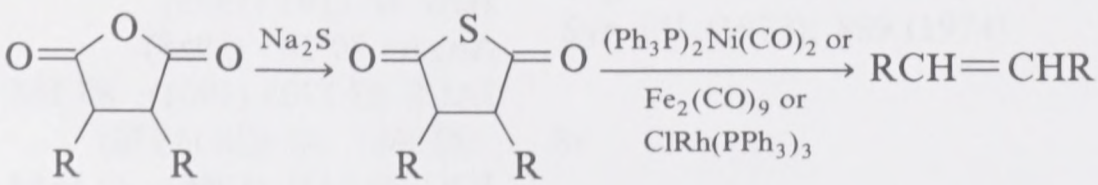
JACS *90* 94 (1968)
Syn 157 (1969)
Tetr *30* 11 (1974)
JOC *41* 3452 (1976)
TL *27* 4615 (1986)

48. Acid Anhydrides



Review: Tetr *40* 2585 (1984)

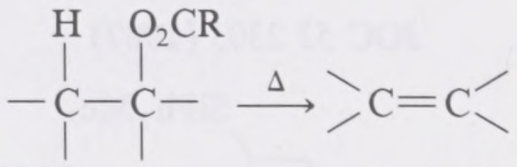
PbO_2	JACS *74* 4370 (1952) Ann *585* 154 (1954) JOC *23* 141 (1958) Org Rxs *19* 279 (1972) (review)
$Pb(OAc)_4$, py	Helv *41* 1191 (1958) JACS *83* 1705 (1961); *85* 3297 (1963); *90* 113 (1968); *93* 6092 (1971) Org Rxs *19* 279 (1972) (review)
Cu_2O, bipy, quinoline, H_2O	JACS *109* 4626 (1987)
$Ni(CO)_2(PPh_3)_2$	TL 2603 (1971) JOC *41* 887 (1976)



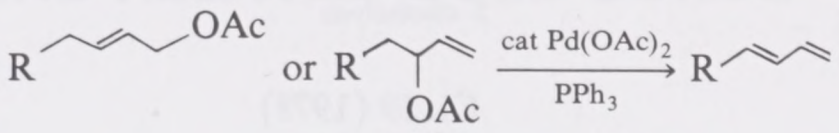
TL 2603 (1971)

49. Esters

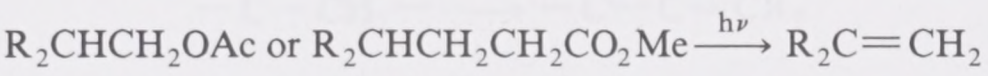
See page 162, Section 46, for elimination of β-hydroxy acids via β-lactones.



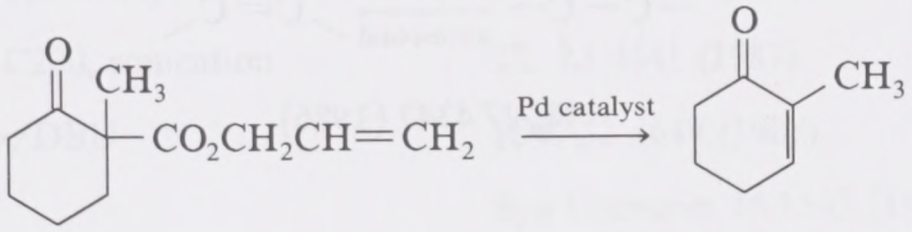
Chem Rev *60* 431 (1960) (review)
Org Syn Coll Vol *4* 746 (1963)
JOC *52* 5034 (1987)
TL *28* 1519 (1987)



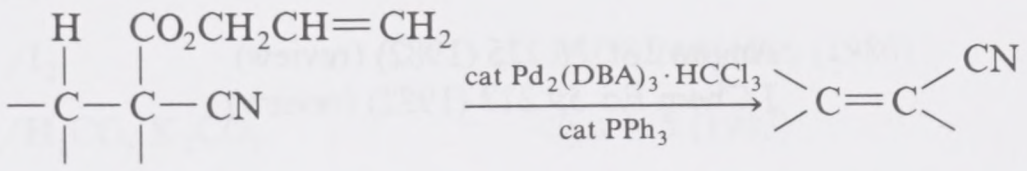
TL 2075 (1978)



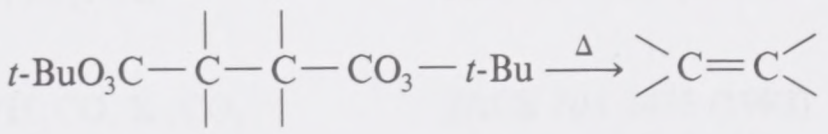
TL *22* 1441 (1981)



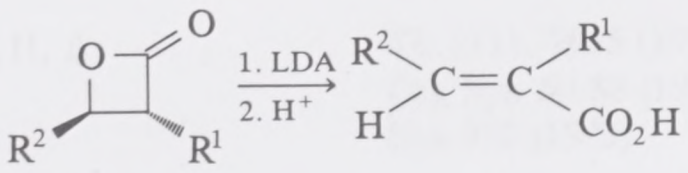
JACS *104* 5844 (1982)
TL *24* 1797 (1983)
CL 1133 (1984)
Syn 1009 (1984)



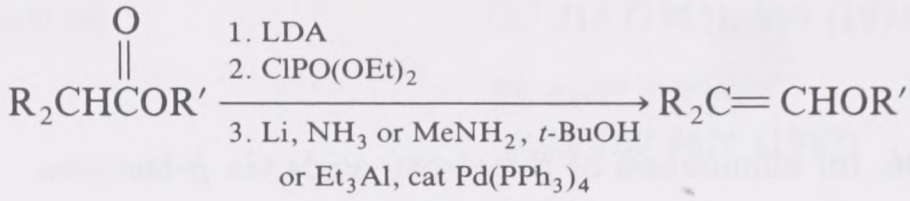
CC 118 (1986)



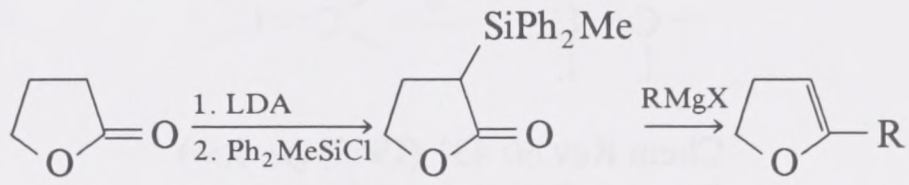
CC 98 (1969)



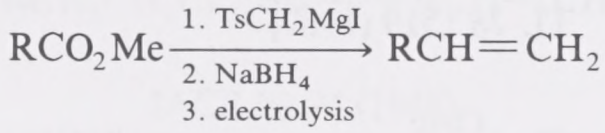
JACS *102* 3620 (1980)



JOC *52* 2303 (1987)

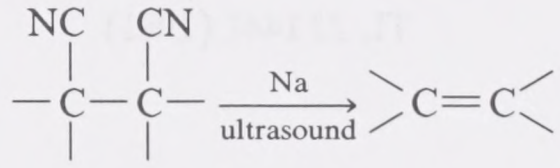


TL *23* 271 (1982)



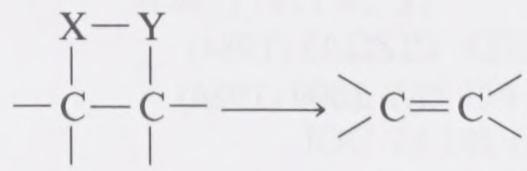
CL 69 (1978)

50. Nitriles



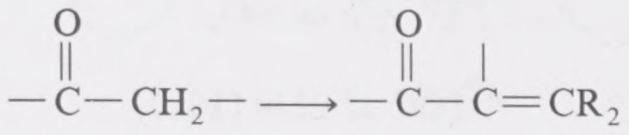
TL *27* 4347 (1986)

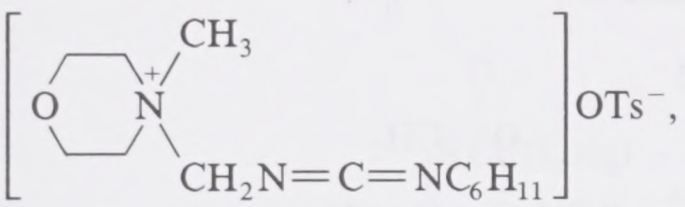
51. Miscellaneous Reactions



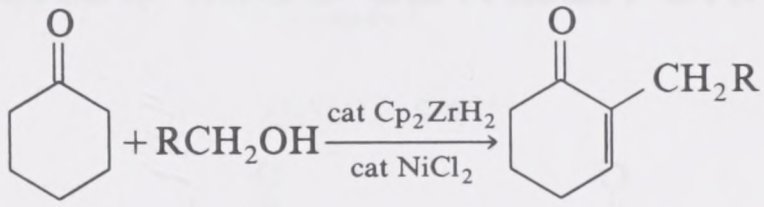
Angew Int *21* 225 (1982) (review)
J Chem Ed *59* 313 (1982) (review)

3. ALKYLIDENATION OF CARBONYL AND RELATED COMPOUNDS

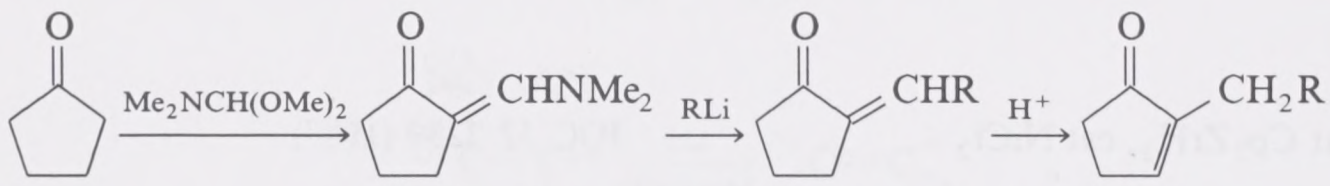


$RCHO$, cat Cp_2ZrH_2, cat $NiCl_2$	JOC *52* 2239 (1987)
$ArCHO$, cat $Ba(OH)_2$-C200, sonication	TL *28* 4541 (1987)
$LDA/H_2CO/TsCl$, py/DBU	JOC *52* 4647 (1987)
$LDA/H_2CO/$ 	Syn Commun *16* 1593 (1986) JOC *52* 2378 (1987) TL *28* 5081 (1987)
$CuCl_2$ (on lactone)	
$LDA/CH_3COCH_3/I_2$	JACS *108* 4556 (1986)
$NaOMe$, HCO_2Me/H_2CO, K_2CO_3	Syn 665 (1983)
base, HCO_2R/H_2CO; py, Et_3N or K_2CO_3	JOC *32* 3434 (1967)
$MeOCO_2MgOMe/H_2CO$, Et_2NH, NaOAc, HOAc	JOC *38* 2489 (1973)
$LiN(SiMe_3)_2/HCO_2Me/H_2CO$, K_2CO_3	JACS *105* 2435 (1983) JOC *50* 3957 (1985)
H_2CO, $(R_2\overset{+}{N}H_2)Cl^-$	JACS *95* 4873 (1973)
$(CH_2O)_3$, PhNHMe, CF_3CO_2H, Δ	TL 2111, 2955 (1978) Org Syn *60* 88 (1981) Syn 952 (1983)
$LDA/(Me_2\overset{+}{N}{=}CH_2)I^-/NaOH$	JACS *98* 6715 (1976); *99* 944 (1977) TL 1621 (1977) JOC *44* 1391 (1979); *45* 524 (1980)

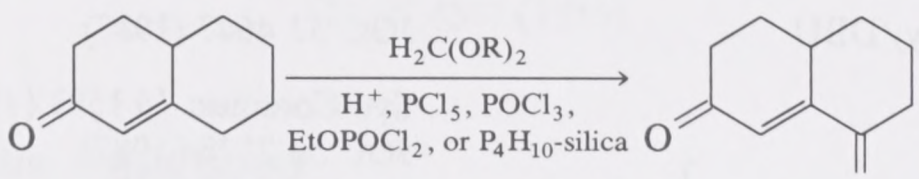
$BrCH_2SO_2Br$, hν (on enol silane)/DBN	JOC *49* 3664 (1984)
$RCHISO_2Br$, hν (on enol silane)/DBN	JACS *108* 4568 (1986)
LDA/$PhCH_2SCH_2Br$/$NaIO_4$/Δ (on acids and ketones)	JOC *51* 2981 (1986)
LDA or Et_3N, Me_3SiCl/$PhSCH_2Cl$, $TiCl_4$/$NaIO_4$/Δ	TL 993, 995 (1979)
LDA/$(PhSe)_2$/LDA/RCHO/$SOCl_2$, Et_3N (on amide)	JOC *51* 3108 (1986)
$H_2C{=}C(OAc)CH_3{-}H^+$ or $Me_3SiCl{-}Et_3N$/RCHClOMe, Zn(Cu), CH_2I_2/$KHSO_4$	JACS *101* 984 (1979)



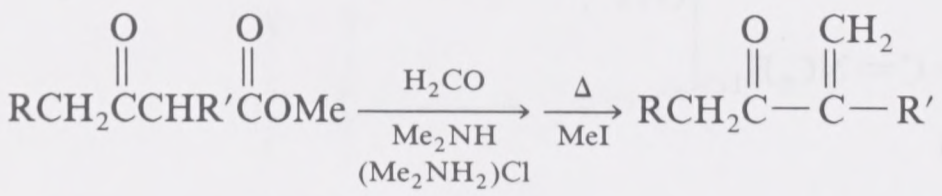
JOC *52* 2239 (1987)



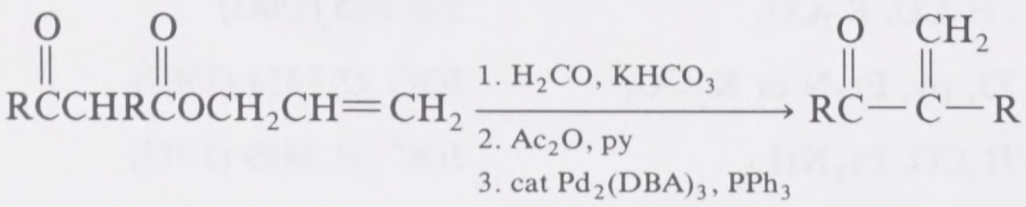
JOC *43* 4248 (1978)



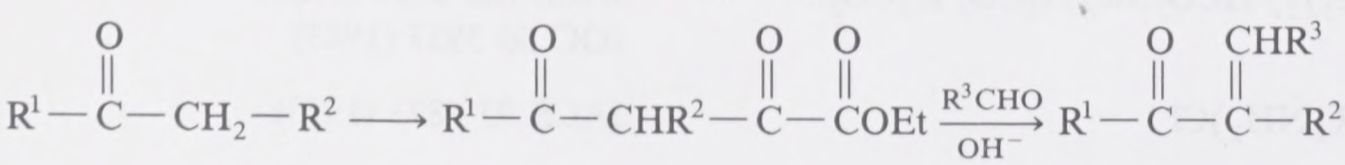
Syn 34 (1982)



TL 5037 (1973)



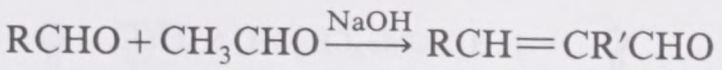
TL *27* 2483 (1986)



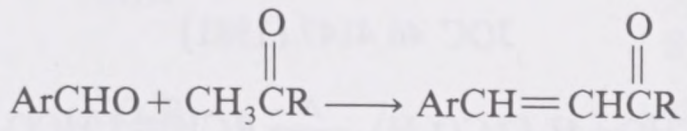
JOC *42* 1180 (1977)



See page 647, Section 7.

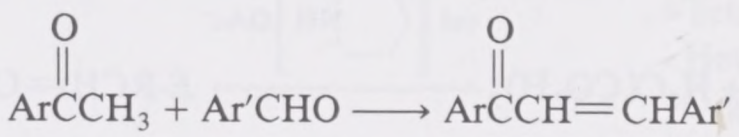


Ber *76* 676 (1943)



NaOH — Org Syn Coll Vol *1* 77 (1941); Ber *76* 676 (1943); Syn 647 (1980)

$M(OAc)_2$ (M = Co, Ni, Cu, Zn), bipy — BCSJ *53* 1366 (1980)

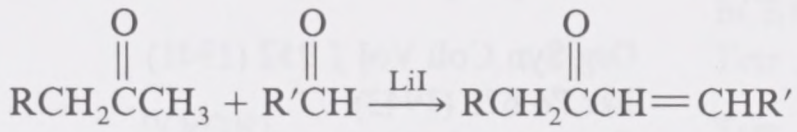


NaOH — Syn 647 (1980); JOC *52* 5560 (1987)

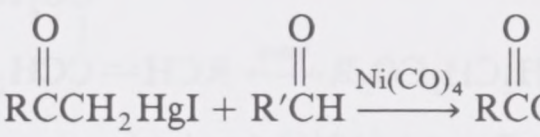
cat $Ba(OH)_2$-C200 — TL *28* 4541 (1987)

$TiCl_4$, Et_3N — TL *28* 4135 (1987)

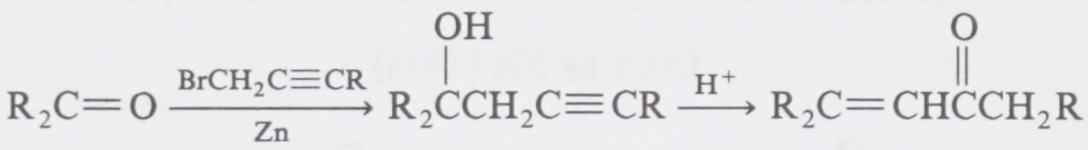
cat Co(II)-polymer — CL 1401 (1979); BCSJ *55* 3208 (1982)



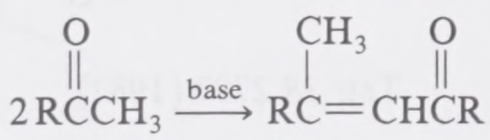
CC 486 (1980)



CL 1435 (1979)



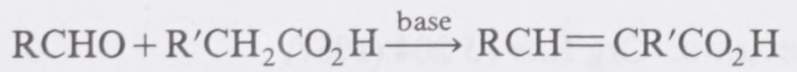
Syn Commun *10* 637 (1980)



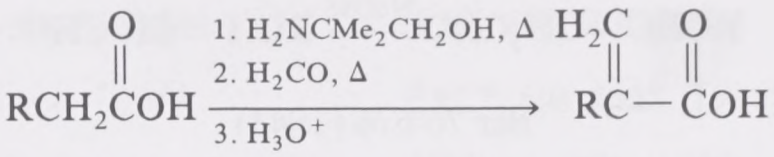
Base

$Al(O\text{-}t\text{-}Bu)_3$ — Org Syn Coll Vol *3* 367 (1955)

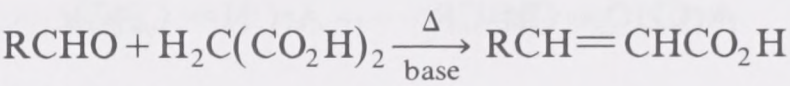
Al_2O_3 — Syn 60 (1982)



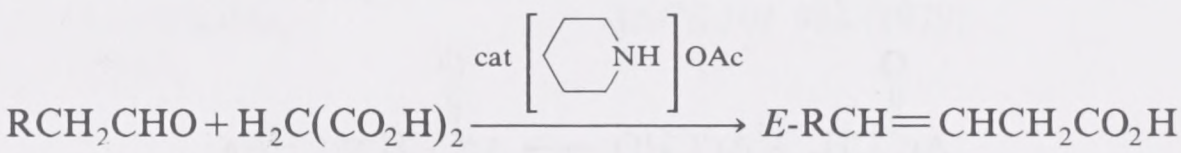
Org Syn Coll Vol *4* 777 (1963)



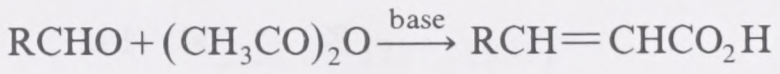
JOC *46* 4147 (1981)



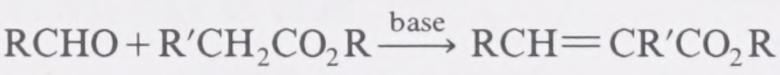
Org Syn Coll Vol *3* 425 (1955)
Org Rxs *15* 204 (1967) (review)
Heterocycles *20* 1541 (1983) (mechanism)



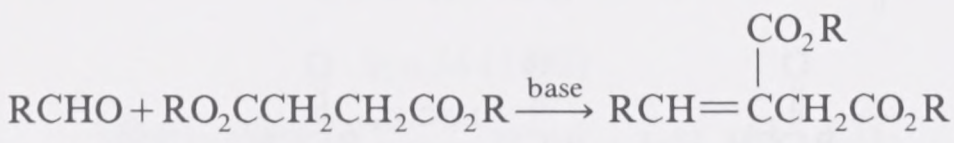
JCS 740 (1931); 557 (1933)
TL *28* 93 (1987)



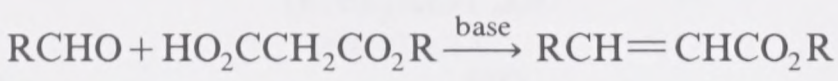
Org Rxs *1* 210 (1942) (review)
Org Syn Coll Vol *3* 426 (1955)



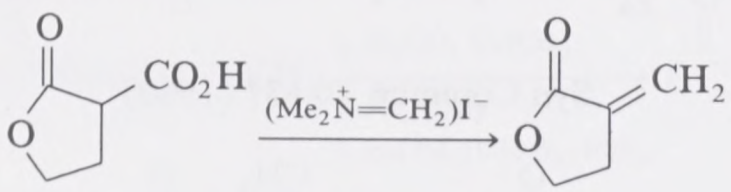
Org Syn Coll Vol *1* 252 (1941)
Ber *76* 676 (1943)
Org Rxs *6* 1 (1951)



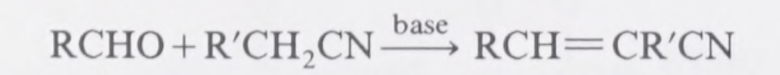
Org Rxs *6* 1 (1951) (review)



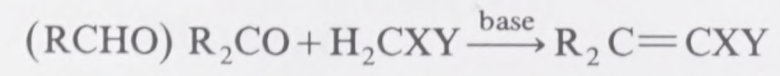
JACS *68* 376 (1946)



Tetr *38* 2797 (1982)



Org Syn Coll Vol *3* 715 (1955)



Reviews: Org Rxs *15* 204 (1967)
Can J Chem *45* 1001 (1967); *47* 3137 (1969)

X	Y	
Ph	CN	BCSJ *56* 1885 (1983)
COR	COR	Syn 667 (1974) Syn Commun *13* 1203 (1983)
COR	CO_2R	Tetr *28* 663 (1972)
CO_2R	CO_2R	JOC *4* 493 (1939); *48* 3603 (1983) Ber *76* 676 (1943) Org Syn Coll Vol *3* 377 (1955) TL 4723 (1970) Tetr *29* 635 (1973) Heterocycles *20* 1541 (1983) Org Syn *64* 63 (1985)
CO_2R	NO_2	Tetr *28* 663 (1972)
CO_2R	$PO(OR)_2$	Tetr *30* 301 (1974)
CO_2R	CN	JACS *95* 4873 (1973)
CN	CN	Chem Rev *69* 591 (1969) (review) Syn 165 (1978) (review) JOC *48* 1366, 3852 (1983) BCSJ *56* 1885 (1983) Tetr *39* 1161, 1167 (1983)
$PO(OR)_2$	$PO(OR)_2$	Tetr *30* 301 (1974)

4. WITTIG AND RELATED REACTIONS

See also page 167, Section 3.

1. Wittig Reaction

1.1. General

Quart Rev *17* 406 (1963) (general)
Angew Int *3* 250 (1964) (unsaturated fatty acids); *16* 423 (1977) (industrial practice); *21* 545 (1982) (synthesis of $R^1R^2C{=}PPh_3$)
Pure Appl Chem *9* 255 (general), 271 (stereochemistry) (1964); *51* 515 (1979) (polyenes)
Org Rxs *14* 270 (1965) (general); *25* 73 (1977) (phosphoryl-stabilized anions)
A. W. Johnson, "Ylid Chemistry," Academic Press, New York (1966)
Topics Stereochem *5* 1 (1970) (stereochemistry)
Syn 765 (1975) (bis-Wittig reaction)
I. Gosney, A. G. Rowley in "Organophosphorus Reagents in Organic Synthesis," Ed. J. I. G. Cadogan, Academic Press, New York (1979), Chpt 2
JCS Perkin I 1 (1979) (polymer-supported reagents)
Ann 1705, 2117 (1981) (pheromones and dienes)
Syn Commun *11* 125 (1981) (phase transfer); *12* 107 (phase transfer), 469 (preparation of ylid via decarboxylation) (1982)
J Chem Res (S) 142 (1981) (phase transfer); 188 (1982) (D labelling in vinylic positions)
JACS *104* 5821 (1982) (stereochemistry); *106* 7514 (1984) (bis-Wittig reaction); *107* 1068 (1985) (stereochemistry)
Chimia *36* 396 (1982) (preparation of ylid)
Russ Chem Rev *51* 1 (1982) (fluorine-containing ylids)
Topics Curr Chem *109* 85 (natural products), 165 (industrial applications) (1983)
Phosphorus and Sulfur *18* 171 (1983) (general)
Ann 2135 (1983) (promotion by high pressure)
JOC *49* 4293 (1984) (preparation of phosphonium salts); *51* 3302 (1986) (concentration effects on stereochemistry)
TL *28* 2191, 4377 (1987) (both promotion by high pressure)

1.2. Intramolecular Wittig

Helv *60* 68, 81 (1977)
Tetr *36* 1717 (1980)
CC 14 (1981) (indole synthesis)
TL *23* 3543 (1982) (bicycloalkenones)
JOC *47* 5372 (1982) (bicycloalkenes)

1.3. Mechanism

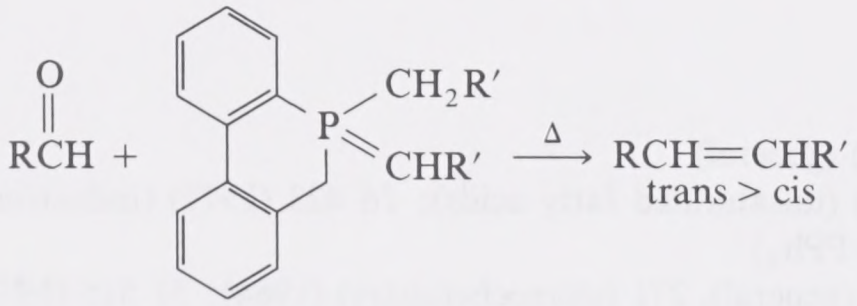
Angew Int *7* 650 (1968)
JACS *95* 5778 (1973); *103* 2823 (1981); *104* 5821 (1982); *106* 1873 (1984); *107* 1068 (1985); *108* 7664 (1986)
TL 2707 (1979)
CC 1072 (1979)
Pure Appl Chem *52* 771 (1980)
JOC *52* 4637 (1987)

1.4. Miscellaneous Reactions

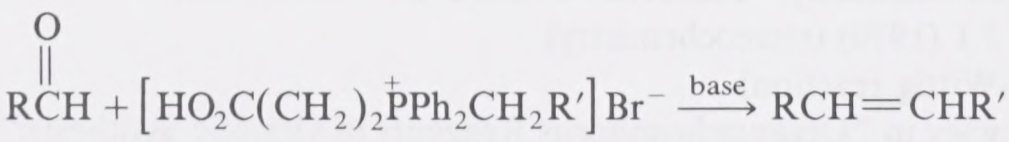
$$R_2CuLi + (H_2C{=}CH\overset{+}{P}Ph_3)Br^- \xrightarrow{R'CHO} RCH_2CH{=}CHR'$$

R = alkyl, aryl, vinylic — cis > trans

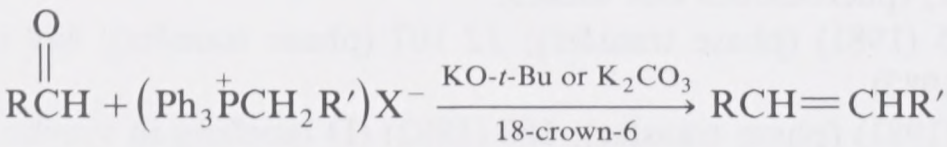
TL *26* 1799 (1985)



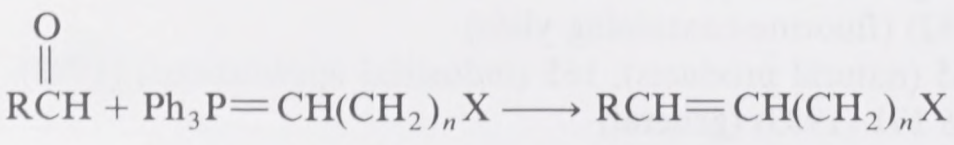
TL *28* 3445 (1987)



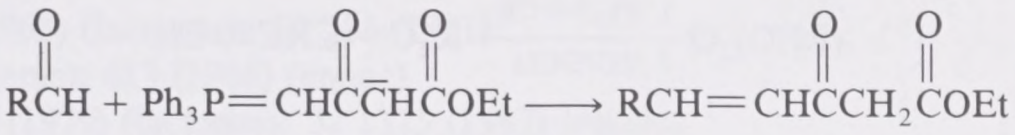
TL *28* 1165 (1987)



Syn 784 (1975)

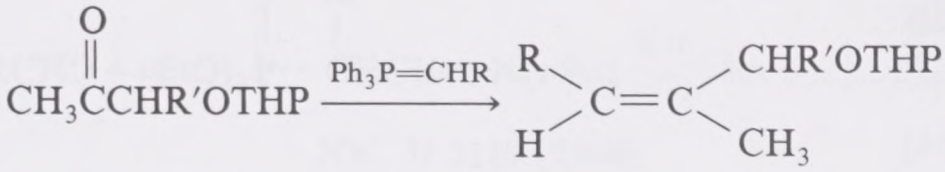


TL *22* 4185 (1981); *26* 311 (1985)
JACS *107* 217 (1985)

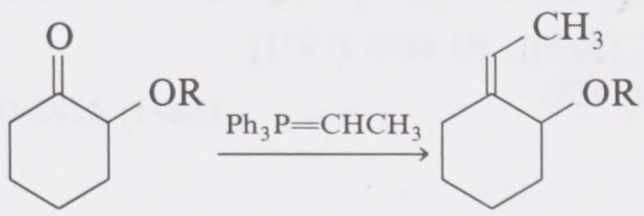


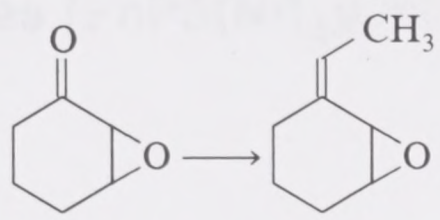
cis > trans

TL *27* 739 (1986)

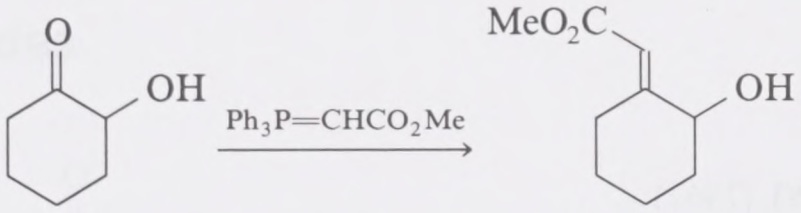


JOC *45* 4260 (1980)
CL 1711 (1981)

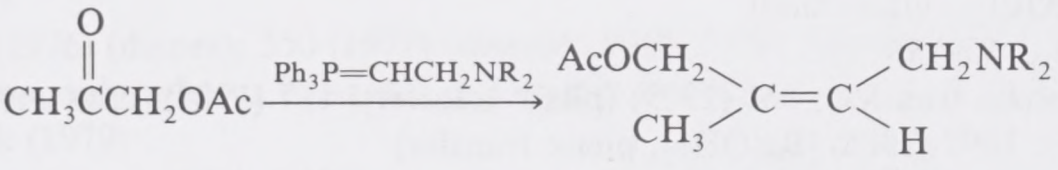




JOC *50* 5910 (1985)

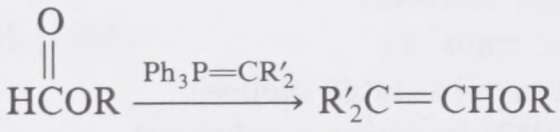


JOC *52* 2629 (1987)

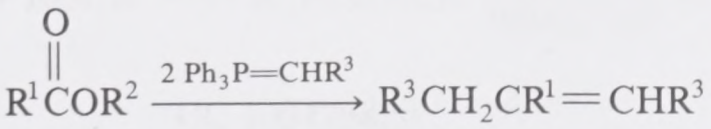


> 99% Z

TL *23* 2219 (1982)



CL 967 (1981)
TL *23* 427 (1982)
JOC *49* 3595 (1984)



TL 1439 (1975)
JOC *43* 3306 (1978); *44* 3157 (1979)

$$(RCO)_2O \xrightarrow[2.\ RC{\equiv}CLi]{1.\ Ph_3P{=}CR_2} R_2C{=}CRC{\equiv}CR$$

CC 703 (1987)

2. β-Oxido Ylids

Angew Int *5* 126 (1966)
Ann *708* 1 (1967)
Syn 38 (1969)
Ber *103* 2814 (1970)
TL 447 (1970); 3231 (1977)
JACS *92* 226, 6635, 6636, 6637 (1970); *93* 4835 (1971)
JOC *45* 3350 (1980); *50* 3111 (1985)

3. $Ph_3P{=}CHLi$

JACS *104* 4724 (1982)
TL *26* 555 (1985)

4. Phosphonates

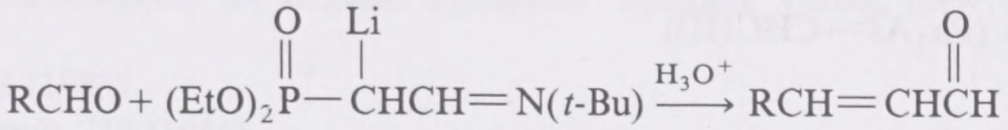
4.1. General

Ber *92* 2499 (1959); *95* 581 (1962)
JACS *83* 1733 (1964); *89* 5292 (1967)
TL 1821 (1971); *21* 2161 (1980) ($KF \cdot 2\ H_2O$ as base); *28* 2951 (1987) [cat $Ba(OH)_2$, $EtO_2CCH_2PO(OEt)_2$, ultrasound]
Org Syn Coll Vol *5* 509 (1973)
Syn 869 (1974) (phase transfer); 884 (1979) (phase transfer); 117 (1981) (crown ether use); 300 (1983) (heterogeneous); 1097 (1985) [$Ba(OH)_2$, phase transfer]
Chem Rev *74* 87 (1974) (review)
Org Rxs *25* 73 (1977) (review)
JCS Perkin I 2516 (1980) (polymer-supported phosphonates)
Syn Commun *14* 701 (1980) (phase transfer)
J Chem Res (S) 143 (1981) (phase transfer)
Z Chem *22* 117 (1982) (heteroatom-substituted olefins)
Phosphorus and Sulfur *14* 385 (1983) (reaction conditions)
Tetr *40* 5153 (1984) (stereochemistry); *41* 1259 (1985) (alumina)
JOC *50* 2624 (1985) (α,β-unsaturated esters); *52* 3875 (1987) (ultrasound, phase transfer)
CC 1509 (1987) (enone synthesis)

4.2. Intramolecular

JACS *90* 5926 (1968) (enones); *100* 7069 (1978) (lactone); *103* 1222 (1981); *104* 2027, 2030 (1982); *106* 260, 1148 (1984); *107* 7967 (1985) (enone); *108* 1035, 3110, 3112, 6389 (1986); *109* 2208 (1987) (enone)

Angew Int *7* 300 (1968) (lactones); *20* 286 (1981)
CC 445 (1970) (lactams); 413 (1986) (enone)
JOC *44* 4010, 4011 (1979) (lactones); *52* 1375 (1987) (enone)
Helv *62* 2661 (1979) (enones)
TL *27* 2157, 4873 (1986); *28* 2727 (1987) (lactone)



JOC *51* 5111 (1986)

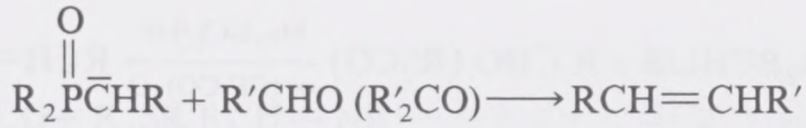
5. Phosphonic Acid bis Amides [$(R_2N)_2POCHLiR$]

JACS *88* 5652, 5653 (1966); *90* 6816 (1968)

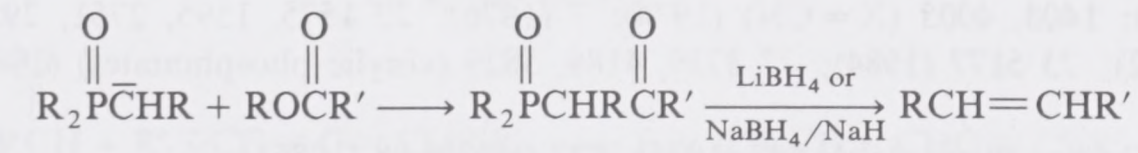
6. Phosphinothioic Amides [$PhPS(NR_2)CHLiR$]

JACS *104* 7041 (1982)
TL *23* 5005 (1982)
JOC *52* 34 (1987)

7. Phosphine Oxides



Ber *92* 2499 (1959)
JCS Perkin I 639 (1976) (dienes); 550 (1977) (dienes); 3099 (1979) (vinyl ethers); 2893 (1983)
B. J. Walker, "Organophosphorus Reagents in Organic Synthesis," Ed. J. I. G. Cadogan, Academic Press, New York (1979)
TL 2433 (1979) (enamines); 2671 (1980) (enamines); *23* 4505 (1982) (allylic amines); *24* 111 (1983); *28* 5559 (1987) (alkylidene cyclopropanes)
CC 100 (1981); 1196 (1987)
Tetr *37* 3911 (1981)
JOC *46* 459 (1981); *51* 1264, 1269 (1986)
Ann 99 (1981)
CL 1143 (1982)
JACS *108* 2662 (1986)



CC 100 (1981)
TL *24* 111, 5293 (1983)
JOC *52* 4303 (1987)

8. Arsenic Ylids

Org Prep Proc Int *14* 373 (1982) ($Ph_3As{=}CHCOCH_3$)
TL *26* 6447 (1985) ($Ph_3As{=}CHCHO$); *28* 2155 ($Ph_3As{=}CHCH{=}CHCOR$, R = H, Me), 2159 ($Ph_3As{=}CHCONR_2$, $Ph_3As{=}CHCHO$, $Ph_3As{=}CHCH{=}CHCHO$) (1987)
JOC *52* 3558 (1987) ($Ph_3As{=}CHCHO$)

9. Sulfinamides

JACS *88* 5656 (1966); *90* 5548, 5553 (1968)

10. Tellurium Compounds

$$ArCHO + BrCH_2X \xrightarrow[\Delta]{n\text{-}Bu_2Te} ArCH{=}CHX$$

$$X = CO_2R, COR, CN$$

TL *28* 801 (1987)

$$RCHO\ (R_2CO) + R_2Te{=}CHCO_2Et \longrightarrow RCH{=}CHCO_2Et$$

TL *24* 2599 (1983)

11. Boron Anions

$$Mes_2BCHLiR + R'CHO\ (R'_2CO) \xrightarrow[\text{or } (CF_3CO)_2O]{Me_3SiCl/HF} RCH{=}CHR'$$

$$E > Z$$

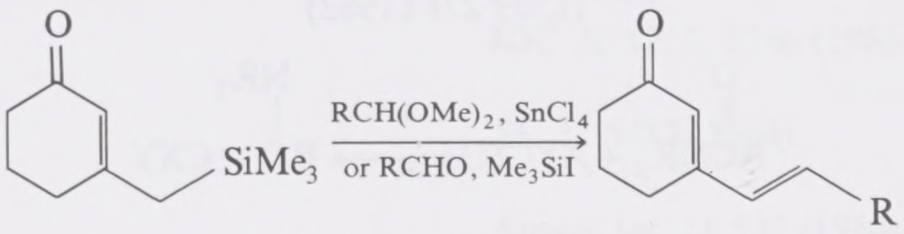
TL *24* 635 (1983)
CC 297 (1987)

12. Peterson Reaction (Oxysilane Elimination)

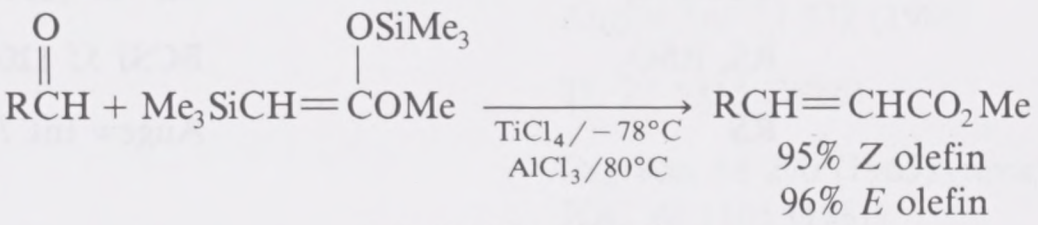
$$RCHO + R'_3Si\bar{C}HX \longrightarrow RCH{=}CHX$$

JOC *33* 780 (1968) (alkenes, vinylic sulfides and phosphines); *37* 939 (vinylic sulfides and phosphonates), 1926 (ketene thioacetals) (1972); *39* 3264 (1974); *43* 1947 (1978); *45* 2013, 2713, 3451 (1980); *51* 2863, 5111 (1986); *52* 2314 (1987) (vinyltriazoles)
TL 1137 (1970); 1403, 4005 (X = CN) (1974); 7 (1976); *22* 1575, 1595, 2751, 2923, 4705 (1981); *23* 1279 (1982); *25* 5177 (1984); *27* 3729, 4189, 5829 (vinylic phosphonates) (1986); *28* 259, 803 (1987)
CC 526 (1972) (ketene thioacetals); 537 (1975); 877 (1981); 98 (1986)
Angew Int *11* 443 (1972) (ketene thioacetals); *15* 161 (1976)
Ber *106* 2277 (1973) (ketene thioacetals)
JACS *96* 1620 (1974); *102* 3964 (1980); *103* 474 (1981); *104* 5708 (1982); *106* 3245, 3252 (1984); *107* 2474 (1985) (X = OMe)

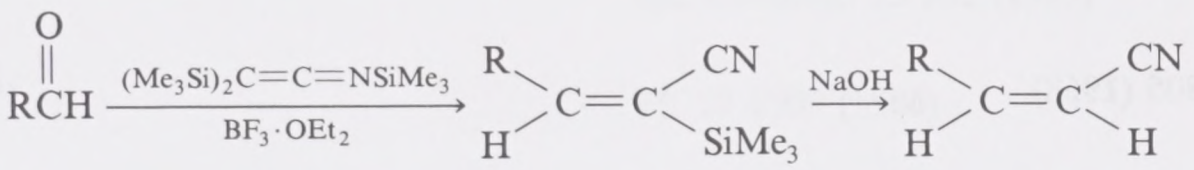
CL 853 (1975) (X = SR); 1093 (1982) (X = CN)
Acct Chem Res *10* 442 (1977) (review)
Chem Soc Rev *7* 15 (1978)
JCS Perkin I 26 (1979)
E. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), Chpt 12 (review)
W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer Verlag, New York (1983), Chpt 6 (review)
Syn Commun *13* 833 (1983)
Syn 384 (1984) (review); 734 (1986)



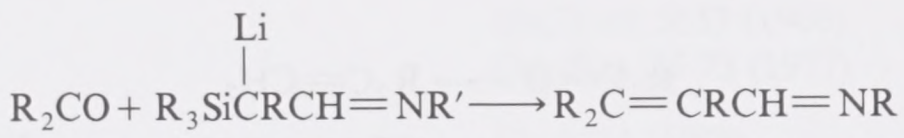
JOC *51* 1932 (1986)



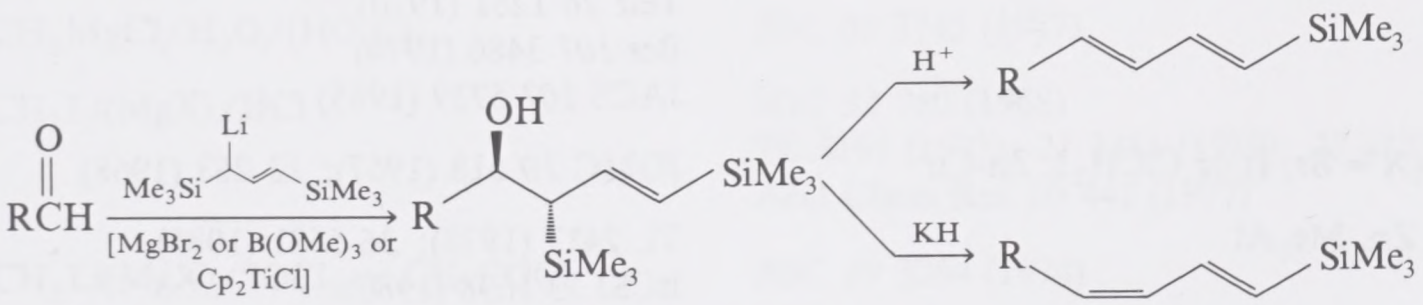
TL *22* 1805 (1981)



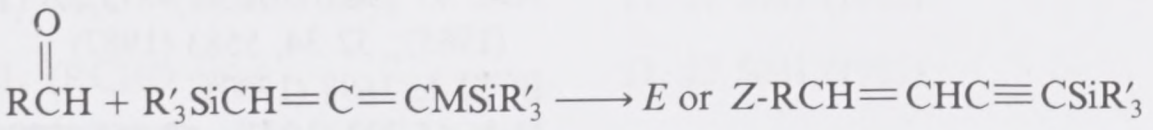
CC 56 (1982)



TL 7 (1976); *24* 2481 (1983); *26* 2391 (1985); *27* 6177 (1986); *28* 259 (1987)
JOC *45* 2013 (1980); *50* 2798 (1985)

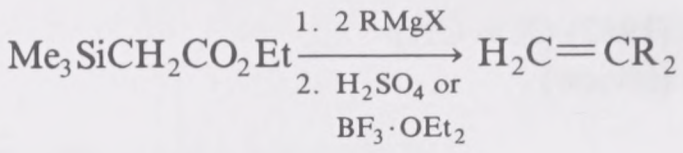


CC 969 (1982); 921 (1983)
JOMC *264* 207 (1984)
TL *28* 211 (1987)

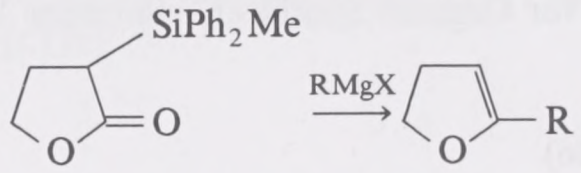


M = Li, MgBr

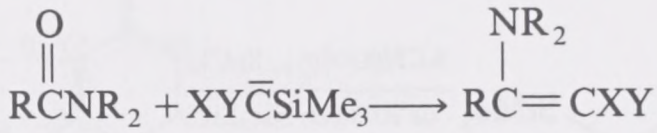
JACS *103* 5568 (1981)
TL *23* 719 (1982)



TL *23* 1035 (1982)



TL *23* 271 (1982)

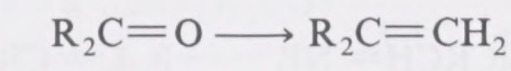


X	Y	
H	$CONMe_2$	TL 709 (1978)
H	RS, RSO_2	BCSJ *55* 1205 (1982)
RS	RS	Angew Int *11* 443 (1972)

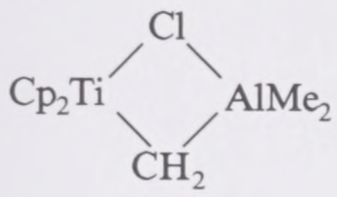
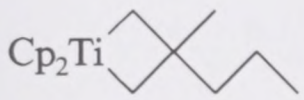
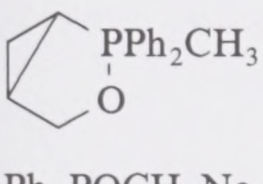
13. Isonitriles

Angew Int *7* 805 (1968)

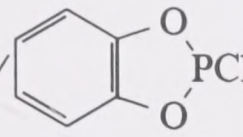
14. Miscellaneous Reactions



$ClCH_2I$, CH_3Li/Li	CC 1665 (1986)
H_2CI_2, Mg(Hg)	TL 5153 (1967) Tetr *26* 1281 (1970) Ber *107* 3486 (1974) JACS *107* 5739 (1985)
H_2CX_2(X = Br, I) or $ClCH_2I$, Zn-Cu	JOMC *10* 518 (1967); *12* 263 (1968)
H_2CI_2, Zn, Me_3Al	TL 2417 (1978); *26* 5581 (1985) BCSJ *53* 1698 (1980) JACS *107* 4964 (1985)
H_2CBr_2, Zn, $TiCl_4$	TL 2417 (1978); *23* 4293 (1982); *27* 5467 (1986); *28* 1893 (1987) JOC *45* 2005 (1980); *48* 2298 (1983); *50* 5898 (1985); *52* 34, 5583 (1987) BCSJ *53* 1698 (1980) Helv *65* 293 (1982); *69* 865 (1986) JACS *108* 3513, 7791 (1986); *109* 3147, 6937 (1987) Org Syn *65* 81 (1987) CC 1008 (1987)

H_2CI_2, Zn, $TiCl_4$	TL *26* 5579 (1985)
H_2CI_2, Zn, Ti(O-*i*-Pr)$_4$	TL *26* 5581 (1985)
$Cp_2TiCH_2 \cdot ZnX_2$	TL *24* 2043 (1983)
	JACS *100* 3611 (1978); *102* 3270 (1980) TL *23* 3143 (1982); *25* 5733 (1984); *27* 6189 (1986); *28* 3209 (1987) Pure Appl Chem *55* 1733 (1983) (review) JOC *50* 1212, 2386 (1985); *52* 1780 (1987)
	TL *25* 5733 (1984)
$Cl_2Mo(Me)=CH_2$	Angew Int *23* 532 (1984) TL *27* 5355 (1986)
$ClMo(Me)_2=CH_2$	Angew Int *23* 532 (1984)
$ClMo(O)=CH_2$	TL *27* 5355 (1986)
$H_2C=PPh_3$	Org Rxs *14* 270 (1965) (review) JOC *46* 1105 (1981) Org Syn *64* 164 (1985) Syn Commun *15* 855 (1985)
	TL *27* 1909 (1986)
Ph_2POCH_2Na	Ber *91* 61 (1958)
$(Me_2N)_2POCH_2Li$	JACS *88* 5653 (1966) Org Rxs *25* 73 (1977)
$Me_3SiCH_2PO(OMe)_2/\Delta$	CL 1385 (1978)
$Me_3SiCH_2MgCl/H_2O/NaH$	JOC *51* 5311 (1986)
$Me_3SiCH_2MgCl/H_2O/(HO_2C)_2$	JOC *52* 3745 (1987)
$Me_3SiCH_2Li(MgX)/HCl$	JOC *33* 780 (1968) TL 4193 (1973); *21* 3451 (1980); *27* 4873 (1986) Acct Chem Res *10* 442 (1977)
$Me_3SiCH_2Li(MgX)/SOCl_2$ or CH_3COCl	JOC *39* 3264 (1974)
Me_3SiCH_2Li, $CeCl_3$/HF or KH	JOC *52* 281 (1987)
$Me_3SiCH_2TiCl_3$ (RCHO only)	TL *22* 5031 (1981)
$Me_3SiCH_2CrCl_2/H_3O^+$ (RCHO only)	TL *22* 5031 (1981)
$Me_3GeCH_2TiCl_3$ (RCHO only)	TL *22* 5031 (1981)
$[(Me_3Si)_2N]_2\overline{UCH_2SiMe_2N}SiMe_3$	JOC *52* 688 (1987)
XCH_2Li (X = Ph_3Pb, Ph_3Sn, Ph_2Sb)/Δ or H^+	TL 4399 (1978)

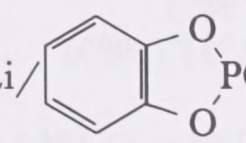
$PhSCH_2Li/TiCl_4$-$LiAlH_4$-3°amine — CL 871 (1975)



TL 737 (1972)

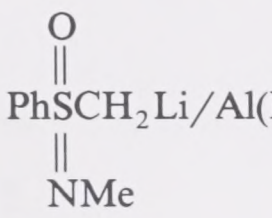
$PhSCH_2Li/(PhCO)_2O/Li, NH_3$ — JACS *94* 4728 (1972)

$PhSCH_2Li/(PhCO)_2O/TiCl_4$, Zn — CL 1523 (1974)

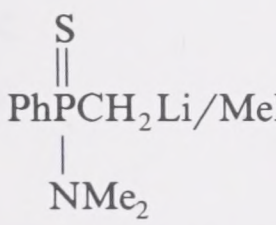


TL 649 (1972)

p-$MeC_6H_4SO_2CH_2MgI/NaBH_4$/electrolysis — CL 69 (1978)

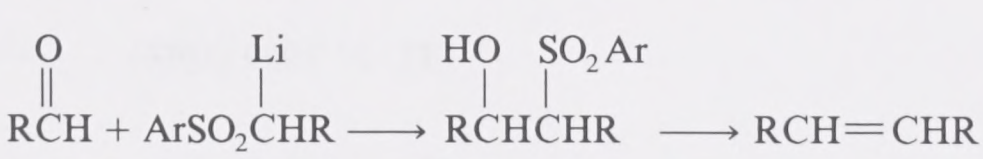


JACS *95* 6462 (1973); *101* 3602 (1979); *103* 7667 (1981); *106* 4547 (1984)

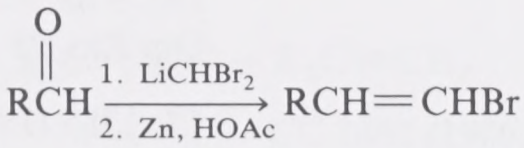


JACS *104* 7041 (1982); *106* 8217 (1984)

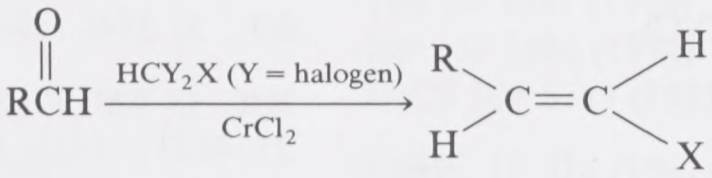
m-$CF_3C_6H_4SeCHLi(OMe)/MsCl, Et_3N$ — JACS *101* 6638 (1979)



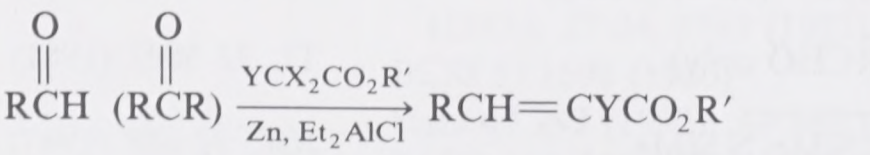
See page 146, Section 23.



TL *22* 3745 (1981)

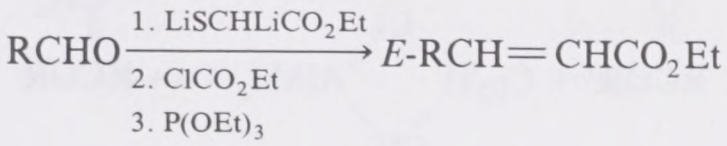


X	
alkyl	JACS *109* 951 (1987)
Cl, Br, I	JACS *108* 7408 (1986)
PhS, Me_3Si	TL *28* 1443 (1987)

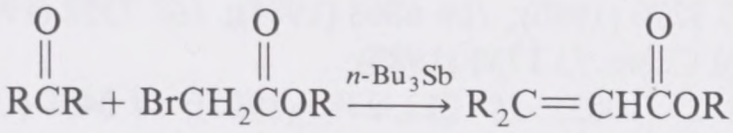


X = Cl, Br; Y = H, Cl

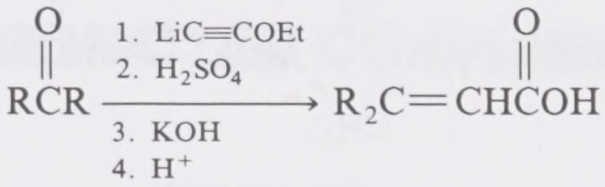
BCSJ *53* 1698 (1980)



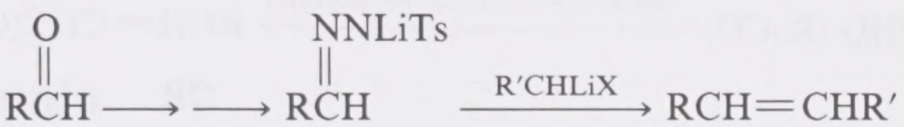
Syn 127 (1983)



TL *27* 2903 (1986)

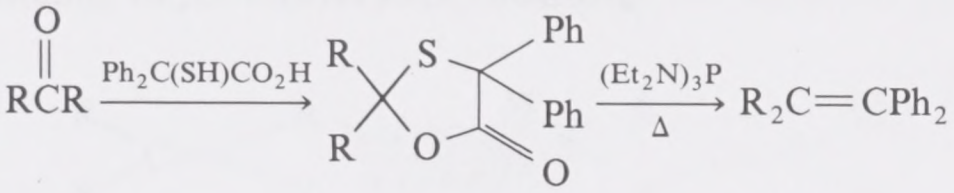


JACS *108* 2690 (1986)

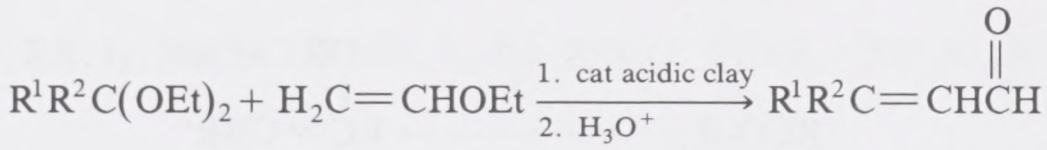


X = CN, SPh, SO_2R

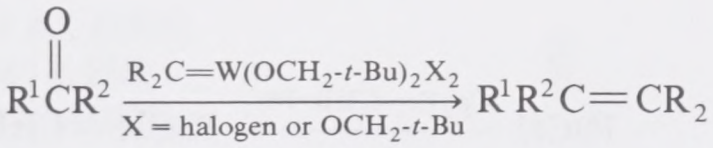
JACS *101* 249 (1979)



CC 1225 (1970)

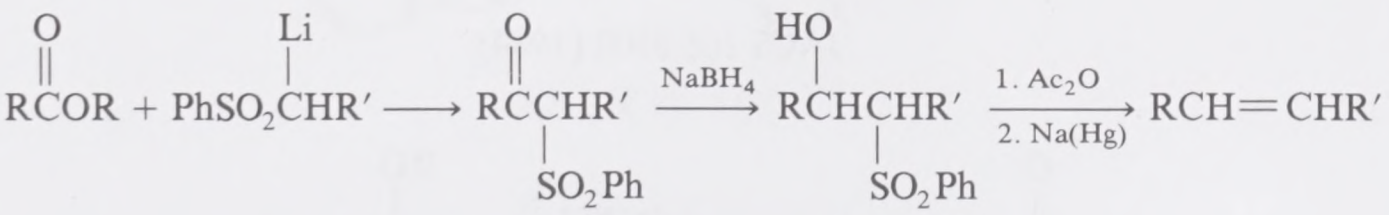


Syn 137 (1981)



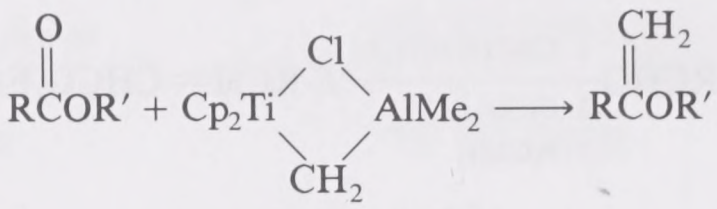
R^1, R^2 = H, Ph; Me, Me; H, OMe; R, OR; Me, NMe_2

CC 531 (1986)

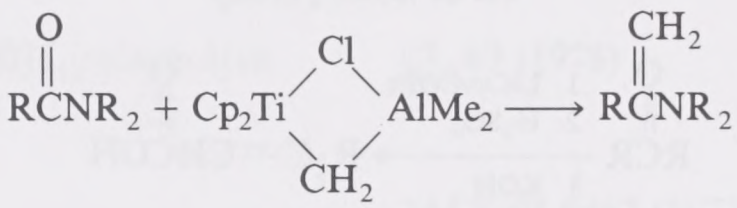


JACS *108* 284 (1986)

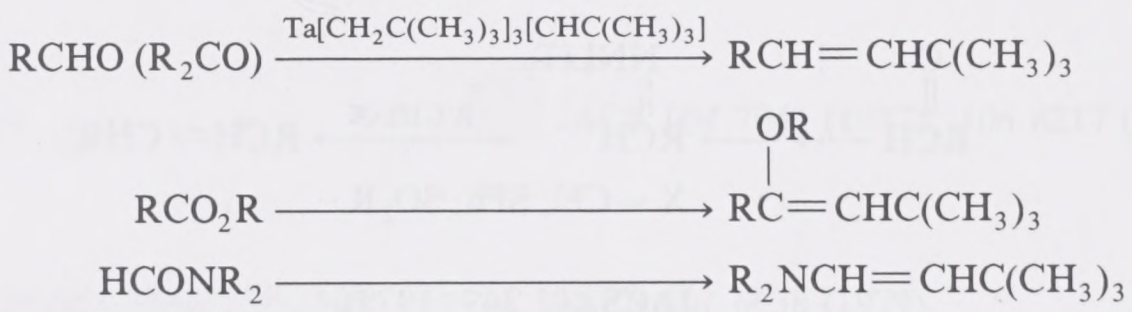
See page 146, Section 23, for other reagents to effect elimination.



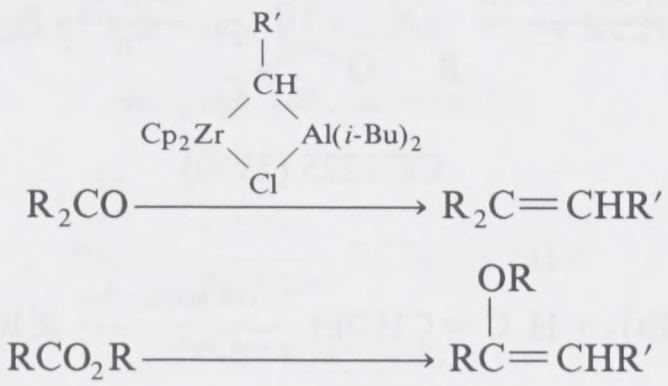
TL 1439 (1975); *23* 3143 (1982); *25* 395 (1984); *28* 4773 (1987)
JACS *102* 3270 (1980); *106* 6868 (1984); *107* 7352 (1985)
Pure Appl Chem *55* 1733 (1983)
JOC *48* 1829 (1983); *50* 1212, 2386 (1985); *51* 5458 (1986)



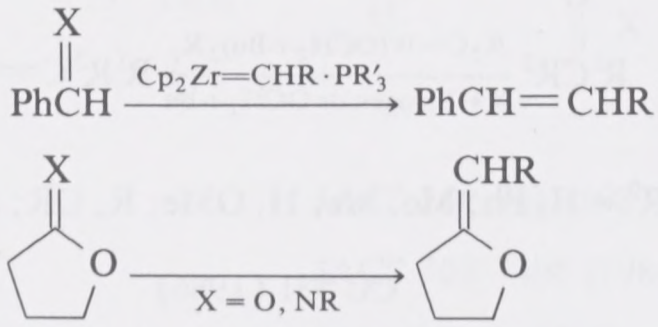
JOC *50* 1212 (1985)



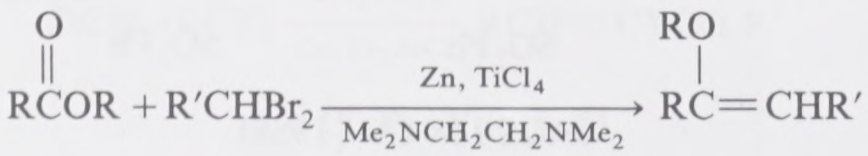
JACS *98* 5399 (1976)



JACS *105* 640 (1983)



JACS *106* 8300 (1984)



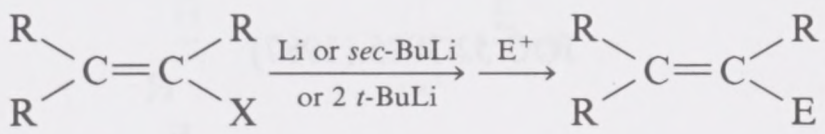
JOC *52* 4410 (1987)

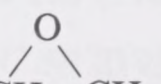
5. METAL-PROMOTED COUPLING REACTIONS

See also page 109, Section 6; and page 211, Section 6.

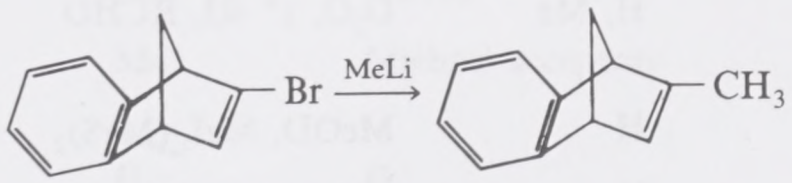
1. Lithium Reagents

For transition metal-catalyzed cross-coupling of organolithium compounds see the appropriate transition metal.
For other ways of generating vinylic lithium reagents see page 193, Section 6; and page 197, Section 7.

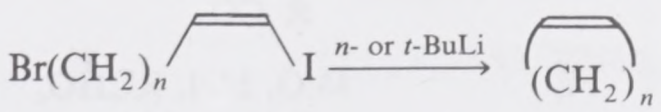


$E^+ = D_2O, RX, I_2, Me_3SiCl, RSSR, R_2CO, RCHO, ROOR, ClCO_2R,$ 

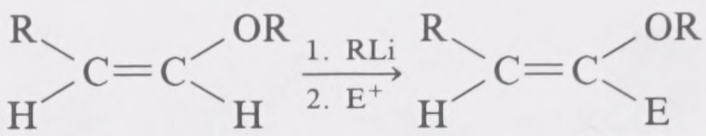
TL 3809 (1974); 4839 (1976); 4661 (1978); *22* 3745 (1981); *28* 5145 (1987)
Syn 434 (1975)
Ber *111* 2785 (1978)
Syn Commun *9* 831 (1979)
Organomet *1* 667 (1982)
JOC *52* 3860, 4495 (1987)



JOC *52* 2674 (1987)

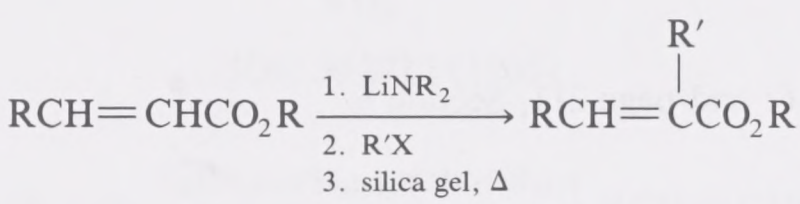


JACS *105* 6344 (1983); *106* 6105 (1984)
TL *26* 5671 (1985) (cyclopropenes); *28* 5793 (1987)

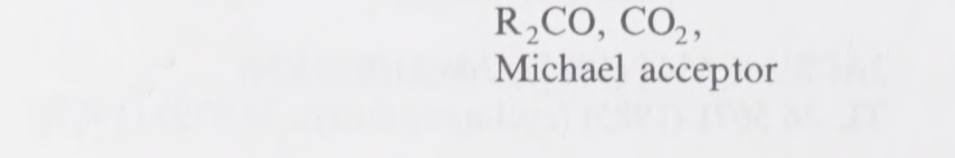


$E^+ = RX, RCHO, R_2CO, RCO_2R, RCN, CO_2$

Ann *763* 208 (1972)
Syn 888 (1974); 748 (1982)
JACS *96* 7125 (1974); *97* 3822 (1975) (cuprate); *103* 5259 (1981)
TL 4187 (1977); *24* 3905 (1983) (cuprate); *27* 5975, 6201 (1986)
Compt Rend C *284* 281 (1977)
Tetr *37* 3997 (1981)
Syn Commun *12* 579 (1982)
JOC *51* 4492 (1986)

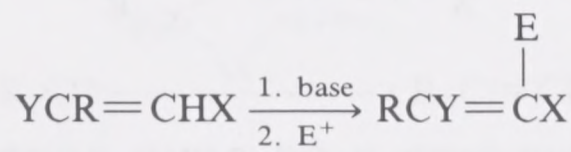


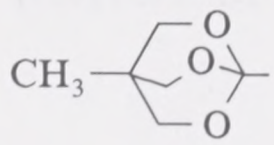
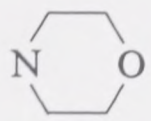
CC 1410 (1987)



$E^+ = MeOD, RX, RCHO, (MeS)_2$

JOC *52* 3825 (1987)



X	Y	R	E^+	
Cl		H	RX, RCHO, R_2CO, lactone	JOC *52* 2335 (1987)
SR	RS	H	D^+, CH_3OSO_2F, RCHO, $(RS)_2$	TL 3583 (1977)
SPh		H, Me	D_2O, 1° RI, RCHO	J Chem Res (S) 48 (1982)
SOR	RS	H	MeOD, MeI, $(MeS)_2$	TL 4277 (1979)
SO_2Ph	MeO	H	CH_3OD, MeI, R_2CO	JOC *52* 4760 (1987)
SO_2Ph	RO	H, Me	D_2O, RX, RCHO, R_2CO	TL *28* 4127 (1987)
CO_2R	Ph	Ph	D_2O, MeI, RCHO, R_2CO, CO_2, Michael acceptor	JCS Perkin I 1329 (1981)

CO_2R	OMe	R	D^+, RCHO, R_2CO, RCOX, $(RCO)_2O$, RCO_2R, $(MeS)_2$	TL *23* 1793 (1982) Tetr *39* 2043 (1983)
CO_2R	OMe	CO_2R	D^+, RCHO, Ac_2O, $(MeS)_2$	Tetr *39* 2043 (1983)
CO_2R	RNCOR	H	D_2O	TL *22* 4259 (1981)
CN	EtO	H	D_2O	TL *22* 4259 (1981)
CN	R_2N	H	MeOD, RI, RCHO	Angew Int *16* 853 (1977)
CN	RS	H	MeOD, MeI, RCHO, $(RS)_2$	TL 4277 (1979)
CN	Ph	H	D^+ D^+, MeI, RCHO, R_2CO, enone (1,4-addition)	TL 4273 (1979) Syn 797 (1979) Tetr *37* 2143 (1981)
CN	Ar	H	D^+, MeI, $(MeS)_2$	Tetr *39* 2043 (1983)
CN	Ph	Ph	RI, R_2CO, CO_2, Michael acceptor	JCS Perkin I 1228, 1232 (1978)

$$HCY{=}CRX \xrightarrow[2.\ E^+]{1.\ \text{base}} ECY{=}CRX$$

Review: Bull Soc Chim Belg *92* 825 (1983)

X	Y	R	E^+	
COR	R_2N	H	D^+	TL 4273 (1979)
CO_2H	H	OMe	D^+, RCHO	Syn 160 (1985)
CO_2H	Br	*n*-Bu	Ac_2O, RCHO	JOC *50* 2195 (1985)
CO_2R	Ph	H	R_2CO	JCS Perkin I 1329 (1981)
CO_2R	RO	H	D^+, RCHO, R_2CO, RCO_2R, $(RS)_2$	TL 4273 (1979); *22* 4259 (1981); *23* 1793 (1982) Tetr *39* 2043 (1983)
CO_2R	RO	OMe	PhNCO, PhNCS	Ber *115* 2674 (1982)
CO_2R	RO	OR	RCHO	Syn 748 (1982)
CO_2R	PhS	Me	Michael acceptors	CL 815 (1982) CC 496 (1982)
CO_2R	R_2N	H	D^+	TL 4273 (1979)
CO_2R	R_2N	H	RCHO, R_2CO, Michael acceptor	Angew Int *15* 171 (1976)
CO_2R	R_2N	H	CO_2, RNCO, RNCS	Ber *115* 2674 (1982)
CO_2R	R_2N	OMe	RCHO, PhNCO, PhNCS	Ber *115* 2674 (1982) Syn 748 (1982)

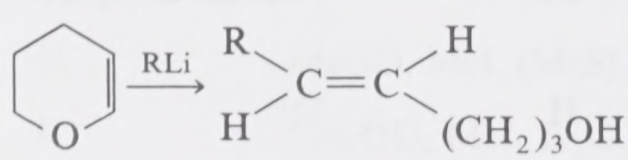
$$HCY{=}CRX \xrightarrow[2.\ E^+]{1.\ base} ECY{=}CRX \quad (\textit{Continued})$$

X	Y	R	E^+	
CO_2R	R_2N	SMe	D^+, RCHO	TL *22* 4259 (1981) Syn 748 (1982)
CO_2R	CO_2R	OMe	D^+, RCHO, Ac_2O, $(MeS)_2$	Tetr *39* 2043 (1983)
CONHR	H	OMe	D^+, RX, RCHO, Me_3SiCl, RSSR	Syn 160 (1985)
CONHR	PhS	OCH_2Ph	RCHO	TL *27* 5591 (1986)
$CONR_2$	Ar	H	D^+, MeI, RCHO	Tetr *39* 2043 (1983)
$CONR_2$	RO	H	D^+	TL *22* 4259 (1981)
$CONR_2$	R_2N	H	D^+	TL 4273 (1979); *22* 4259 (1981)
$CONR_2$	R_2N	H	D^+, MeI, RCO_2R	Angew Int *17* 204 (1978)
$CONR_2$	R_2N	H	$Ar\overset{\overset{X}{\|}}{C}R$ (X = O, NPh)	Syn 869 (1977)
$CONR_2$	R_2N	H	CO_2, RNCO, RNCS	Ber *115* 2674 (1982)
CN	RO	Me	D^+	TL *22* 4259 (1981)
CN	R_2N	H	D^+	TL 4273 (1979)
CN	R_2N	H	D^+, RI, RCHO	Angew Int *16* 853 (1977)
CN	R_2N	SMe	D^+	TL *22* 4259 (1981)

$$\overset{R_2N}{\overset{|}{RC}}{=}CH\overset{\overset{O}{\|}}{C}R(H) \xrightarrow[2.\ H_2O]{1.\ R'Li} \overset{R'}{\overset{|}{RC}}{=}CH\overset{\overset{O}{\|}}{C}R(H)$$

JOC *43* 4248 (1978)
CC 75 (1986)

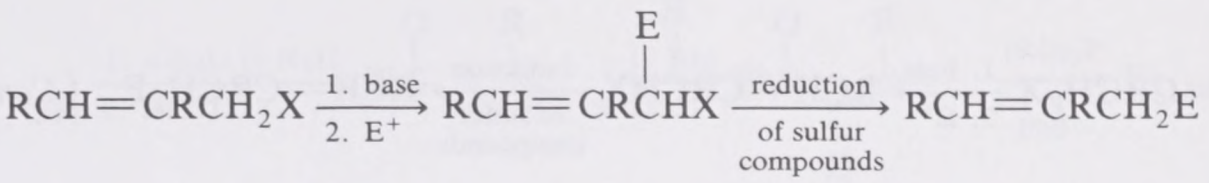
See also page 191, Section 2, for analogous reactions.



Can J Chem *41* 2600 (1963)

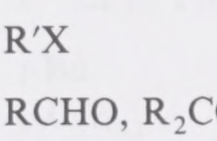
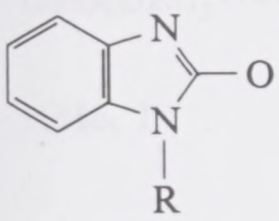
$$RLi + (H_2C{=}CR'CH_2\overset{+}{N}Me_3)I^- \longrightarrow RCH_2CR'{=}CH_2$$

JOC *52* 3683 (1987)

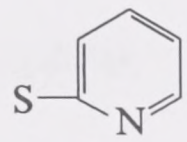


Review: Org Rxs *27* 1 (1982)

See also page 253, Section 3.6.

X	E^+	
H	H_2O, Me_3SiCl	TL 669 (1973)
	MeI	Helv *57* 1567 (1974)
	3° RBr	JACS *109* 3391 (1987)
	R′X, RCHO, R_2CO	TL 4115 (1973)
	D_2O, RX, R_2CO, Me_3SiCl	JACS *105* 6350 (1983)
	D_2O, R′X, RCHO, R_2CO, CO_2, Me_3SiX, Me_3SnCl	TL 3047 (1975) JACS *101* 3340 (1979)
	R′X, RCHO, R_2CO, O_2, $(RS)_2$	Chem Pharm Bull *32* 4632 (1984)
		Helv *57* 1567, 2261 (1974) JACS *108* 3385 (1986)
Cl	R′X	JOC *46* 1504 (1981)
OR	RCHO, R_2CO	JACS *96* 5560 (1974) (via Zn compounds) TL 833 (1979)
$OSiR_3$	RCHO, R_2CO R_3SiCl	JOC *41* 3620 (1976) JOC *43* 2551 (1978)
	RCHO	CL 1279 (1979)
SH	RCHO, R_2CO	Ber *112* 1420 (1979) (via Mg compounds)
SAr	R′X	TL 5629 (1968); 3707 (1969); *24* 5531 (1983); *27* 2157 (1986) Proc Natl Acad Sci USA *68* 1294 (1971) Tetr *27* 5861 (1971) CC 1311 (1972) JACS *95* 4444 (1973); *103* 4615 (1981) Helv *57* 2261 (1974) Syn 129 (1974) JOC *45* 4097 (1980)

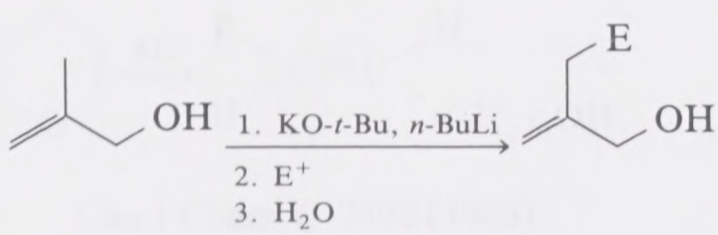
$$RCH{=}CRCH_2X \xrightarrow[2.\ E^+]{1.\ \text{base}} RCH{=}CR\overset{\overset{\displaystyle E}{|}}{C}HX \xrightarrow[\text{of sulfur compounds}]{\text{reduction}} RCH{=}CRCH_2E \quad (\textit{Continued})$$

X	E^+	
	epoxide $H_2C{=}CHCONR_2$, $PhN{=}NPh$	TL *28* 5665 (1987) JOC *52* 218 (1987)
	R′X	BCSJ *44* 2285 (1971)
SO_2Ar	R′X	BSCF 746 (1973) JOC *39* 2135 (1974); *51* 5100 (1986) JCS Perkin I 761 (1981) CL 25 (1981); 725 (1983) JACS *107* 396 (1985) TL *27* 2683 (1986); *28* 187, 3193, 6045 (1987) CC 1761 (1986); 1036 (1987)
	$H_2C\overset{\overset{\displaystyle O}{/\ \backslash}}{-}CHR$ enone (1,4-addition)	BSCF 513 (1976) TL *28* 6045 (1987)
$\overset{\overset{\displaystyle S}{\|}}{S}CNR_2$	RX	JACS *105* 2909 (1983) Syn 100 (1975) CL 249 (1975)
	RX, RCHO, R_2CO, epoxide	TL 4027 (1975)
SePh	R′X	JOC *52* 3759 (1987)
$SiMe_2N(i\text{-}Pr)_2$	RCHO, $ZnCl_2$	JOC *52* 957 (1987)

$$H_2C{=}C\overset{\overset{\displaystyle CH_3}{|}}{C}{\equiv}CH \xrightarrow[\substack{2.\ E^+\\ 3.\ H_2O}]{1.\ n\text{-BuLi, KO-}t\text{-Bu}} H_2C{=}C\overset{\overset{\displaystyle CH_2E}{|}}{C}{\equiv}CH$$

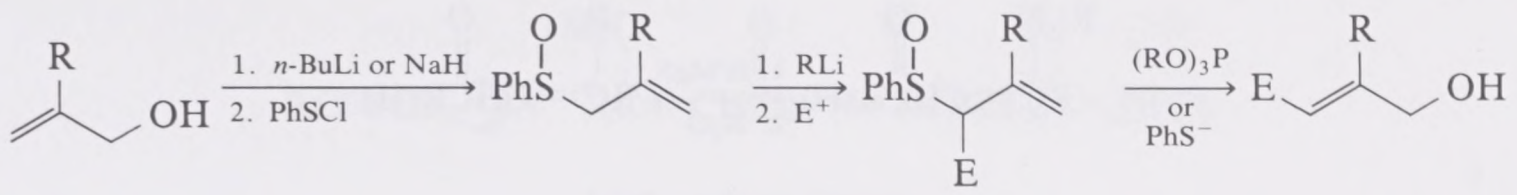
$$E^+ = RX,\ RC\overset{\overset{\displaystyle O}{/\ \backslash}}{H-CH_2},\ RCHO,\ R_2CO,\ RCONR_2,\ CO_2,\ (MeS)_2,\ RSCN$$

JOC *52* 5261 (1987)



$$E^+ = RCHO,\ R_2CO,\ H_2C\overset{\overset{\displaystyle O}{/\ \backslash}}{-}CHR$$

TL 111 (1978)
Syn Commun *13* 237 (1983)



Electrophile

RX	JACS *93* 4956 (1971); *94* 3672 (1972) CC 702 (1972) TL 1385, 1389 (1973) JOC *38* 2245 (1973) Acct Chem Res *7* 147 (1974)
epoxide	Syn Commun *11* 723 (1981)

2. Grignard Reagents

For transition metal-catalyzed cross-coupling reactions of Grignard reagents see the appropriate transition metal.

$$RMgY + H_2C{=}CHCH_2X \longrightarrow RCH_2CH{=}CH_2$$

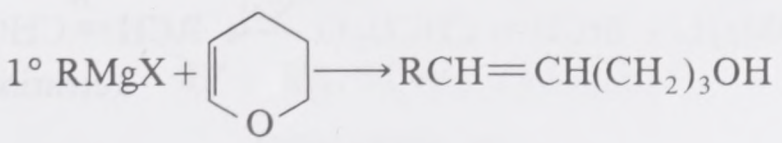
X	R	
Cl	1° alkyl	Org Mag Res *10* 192 (1977)
	1° alkyl, Ph	Ind Eng Chem *33* 115 (1941)
Br	*t*-Bu	JACS *55* 4555 (1933)
	c-C_5H_{11}	JACS *68* 1101 (1946)
	n-Bu, Ph	Helv *17* 351 (1934)
	Me	JOC *14* 505 (1949)
OR	1° alkyl, aryl	JACS *75* 5408 (1953)
$OPO(OEt)_2$	1° alkyl, allyl, benzyl, aryl, alkynyl	CC 285 (1982)
$\overset{+}{N}Me_3\ I^-$	Me, Ph	JOC *52* 3683 (1987)

$$RMgX \xrightarrow[\text{2. KH (cis) or } BF_3\cdot OEt_2 \text{ (trans)}]{\text{1. } R'\overset{t\text{-BuSiMe}_2}{\overset{|}{C}}HCHO} \underset{\text{cis or trans}}{R'CH{=}CHR}$$

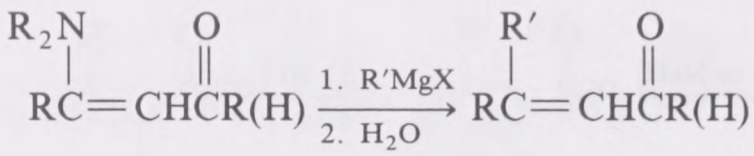
JACS *103* 6251 (1981)

$$ArMgX + RCH{=}\overset{OEt}{\overset{|}{C}}C_6H_5 \longrightarrow RCH{=}\overset{Ar}{\overset{|}{C}}C_6H_5$$

JACS *73* 1663 (1951)

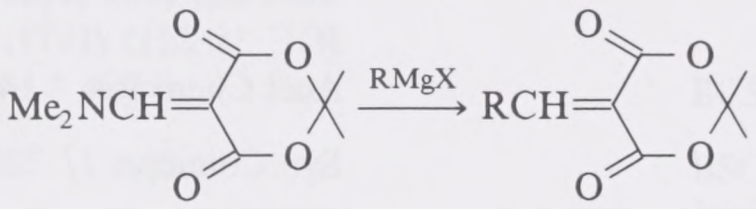


JACS *76* 4538 (1954)

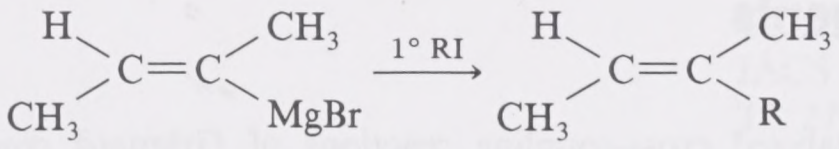


Ber *64* 2543 (1931)
BSCF 515 (1960); 1294 (1964)

See also page 185, Section 1, for analogous reactions.



Syn Commun *10* 661 (1980)



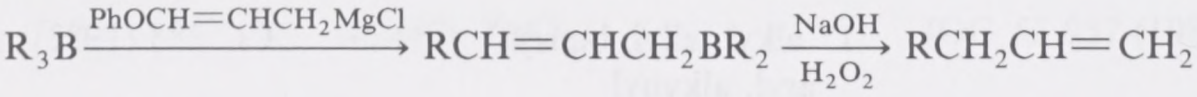
TL 3225 (1976)

$$H_2C{=}CHCH_2MgBr + ROTs \longrightarrow H_2C{=}CHCH_2R$$

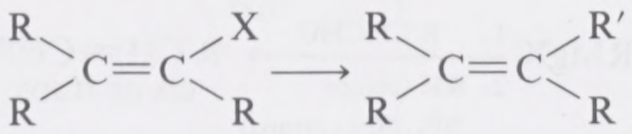
TL 1181 (1977)
JACS *109* 7488 (1987)

3. Boron Reagents

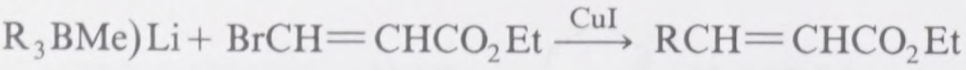
See also page 206, Section 14.



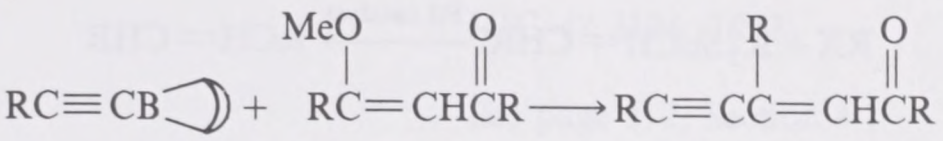
Syn Commun *12* 813 (1982)



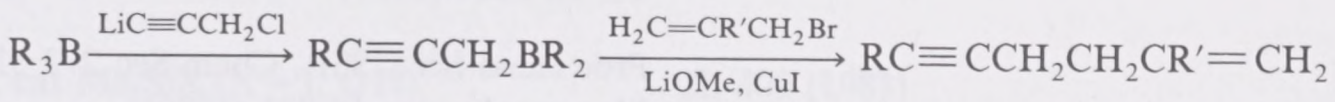
n-BuLi/R'_3B/I_2	JOC *43* 1279 (1978) Syn 945 (1980)
R'_3B or R′B  (R′ = 1° alkyl), cat $PdCl_2$[bis(diphenylphosphino)ferrocene], NaOH or NaOMe	TL *27* 6379 (1986)



TL 3369 (1977)



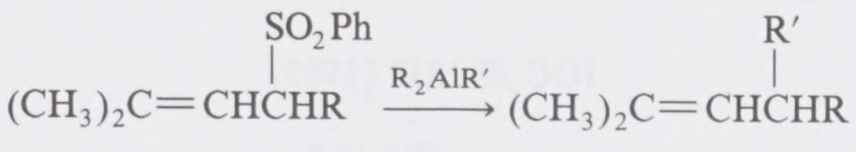
JOC *42* 3106 (1977)



CL 1289 (1982)

4. Aluminum Reagents

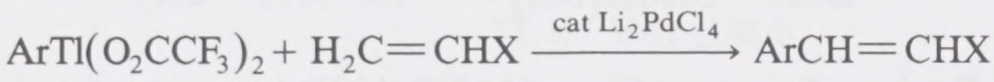
See also page 197, Section 8; page 198, Section 12; and page 201, Section 13.



R′ = vinyl, alkynyl

JACS *108* 1098 (1986)

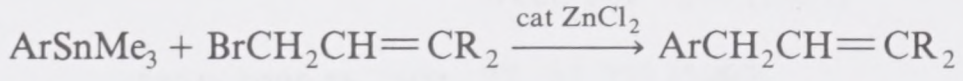
5. Thallium Reagents



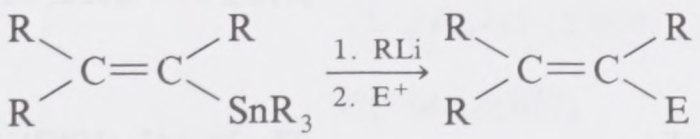
JOMC *99* C8 (1975)
BCSJ *53* 553 (1980)
JOC *51* 3708 (1986)

6. Silicon, Germanium and Tin Reagents

For other reactions of allylic silanes and stannanes look under the functional group introduced; for silicon and tin reagents, see also page 201, Section 13.



TL *24* 1905 (1983)



$E^+ = RX, RCHO, Me_3SiCl$

CC 926 (1986)

$$RX + R''_3SnCH{=}CHR' \xrightarrow{\text{Pd catalyst}} RCH{=}CHR'$$

RX	
R_fI	TL *28* 5857 (1987)
ArX	Proc Acad Sci USSR, Chem Sec *272* 333 (1983) Macromolecules *18* 321 (1985) JOC *52* 422 (1987) JACS *109* 7223 (1987)
$ArCl \cdot Cr(CO)_3$	CC 1755 (1987)
ArOTf	JACS *109* 5478 (1987)

$$(ArN_2)BF_4 + n\text{-}Bu_3SnCH{=}CH_2 \xrightarrow{\text{Pd catalyst}} ArCH{=}CH_2$$

JOC *48* 1333 (1983)

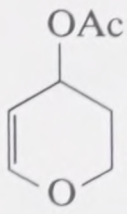
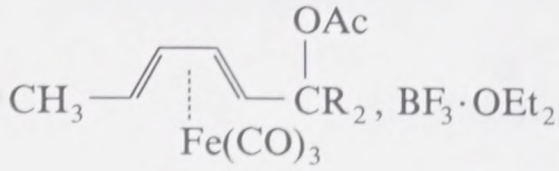
$$ArH + H_2C{=}CHCH_2MR_3 \xrightarrow{Tl(O_2CCF_3)_3} ArCH_2CH{=}CH_2$$

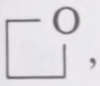
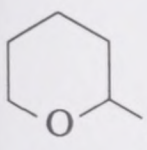
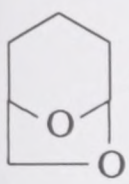
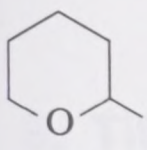
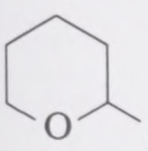
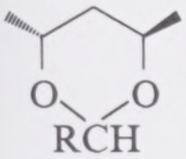
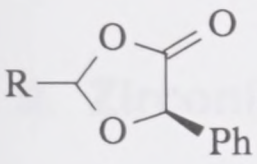
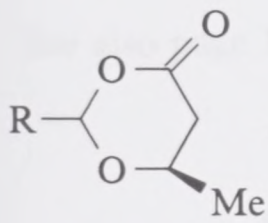
$R_3M = Me_3Si, Me_3Ge, n\text{-}Bu_3Sn$

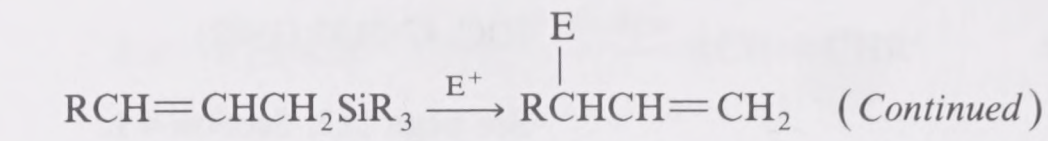
TL *22* 4491 (1981)

$$RCH{=}CHCH_2SiR_3 \xrightarrow{E^+} \underset{\displaystyle E}{\underset{|}{R}}CHCH{=}CH_2$$

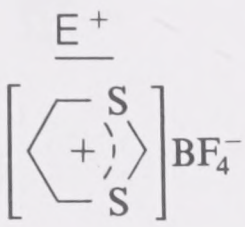
Review: Pure Appl Chem *55* 1707 (1983) (stereochemistry)

E^+	
$R_3CCl, TiCl_4$	TL 4925 (1978) Syn 446 (1979) JOC *45* 3559 (1980) JACS *104* 4962 (1982)
R_3CX (X = OTf, $OSiMe_3$, OAc), Lewis acid	JOC *47* 3219 (1982)
RX (R = allylic, benzylic; X = halogen, OR), $TiCl_4$	TL *23* 2953 (1982)
 , Lewis acid	JOC *47* 3803 (1982) TL *28* 4951 (1987) JACS *109* 2082, 8117 (1987)
	TL *28* 641 (1987)
RNO_2 (R = allylic, benzylic), $SnCl_4$	CC 1285 (1986)

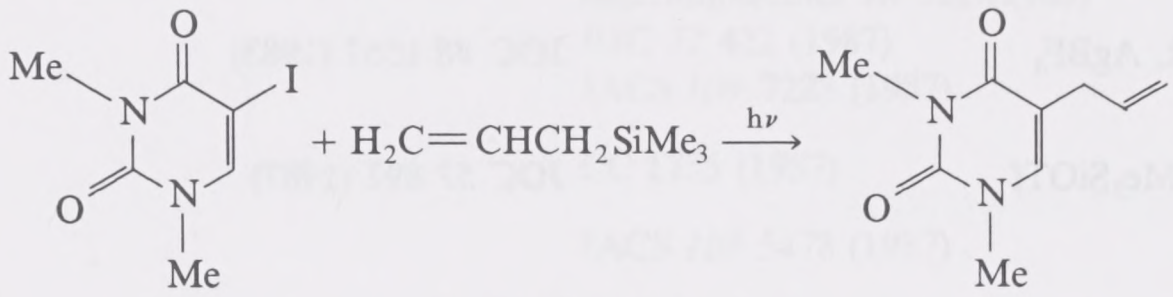
$ArCR_2OH$, $BF_3 \cdot OEt_2$	JOC *47* 2125 (1982)
epoxides, Lewis acid	See page 512, Section 4.1.
 , $TiCl_4$	JOC *50* 2782 (1985)
$ROCHClR$, cat Me_3SiX (X = I, OTf)	CL 409 (1983)
$ROCHRCHBrR$, $AgBF_4$	JOC *48* 1557 (1983)
 , Me_3SiOTf	JOC *52* 892 (1987)
 , $BF_3 \cdot OEt_2$	JOC *52* 2335 (1987)
 , Lewis acid	TL *24* 1563 (1983) JOC *50* 3017 (1985)
 , $BF_3 \cdot OEt_2$	CC 1245 (1987)
 , Lewis acid	JACS *104* 7371 (1982); *105* 2088 (1983) TL *25* 3951 (1984)
 , $ZnBr_2$	JOC *49* 2513 (1984)
 , $TiCl_4$	Angew Int *25* 178 (1986)
$PhCH(OMe)_2$, $BF_3 \cdot OEt_2$	JOC *48* 3351 (1983)
$RCH(SAr)_2$, $SnCl_4$	JACS *109* 7199 (1987)
$PhSCH_2Cl$, $TiCl_4$	TL *23* 723 (1982) CL 961 (1982)
$PhSCHClR$, Lewis acid	TL *24* 1711 (1983)
$PhSCH(NO_2)R$, $SnCl_4$	CC 947 (1987)
$PhSCHRCHRNO_2$, $TiCl_4$ (E = PhSCHRCHR)	JOC *52* 4133 (1987)
$PhX-C-C-Cl$ (X = S, Se), $ZnBr_2$	TL *24* 5911 (1983)



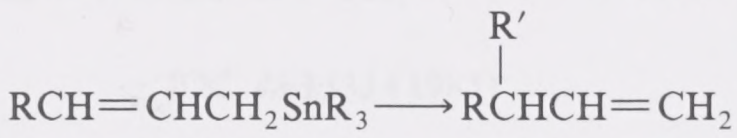
$$RCH{=}CHCH_2SiR_3 \xrightarrow{E^+} \underset{\displaystyle E}{\underset{|}{R}}CHCH{=}CH_2 \quad (\textit{Continued})$$



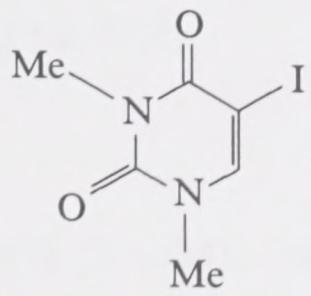
TL *23* 4835 (1982)



JOC *51* 5148 (1986)

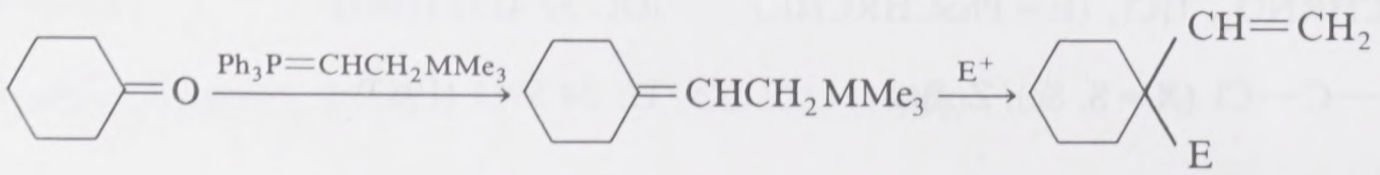


$$RCH{=}CHCH_2SnR_3 \longrightarrow \underset{\displaystyle R'}{\underset{|}{R}}CHCH{=}CH_2$$

R′X [R′ = 1°, 2°, 3° alkyl; X = Cl, Br, I, OC(= S)OPh, SPh, SePh], free radical initiation or hν	JOMC *26* C4 (1971); *56* C11 (1973); *61* C33 (1973); *96* 225 (1975) JACS *104* 5829 (1982) JOC *47* 3590 (1982); *49* 1462 (1984); *52* 3659 (1987) TL *24* 1357 (1983); *25* 1867 (1984); *26* 3311 (1985) (intramolecular); *27* 4857 (1986) BCSJ *56* 2480 (1983) CC 1339 (1986)
R_fI, cat $Pd(PPh_3)_4$	TL *28* 5857 (1987)
$RCOCH_2X$, AIBN (R′ = $RCOCH_2$)	CL 795 (1978)
 , hν	JOC *51* 5148 (1986)
ArX, cat $Pd(PPh_3)_4$ (R′ = Ar)	CL 301 (1977) TL *28* 3935 (1987)
$R_2C(SMe)_2$, $(Me_2SSMe)BF_4$ (R′ = R_2CSMe)	JACS *107* 719 (1985)
immonium salts (R′ = CH_2NR_2)	JOC *52* 1378 (1987)

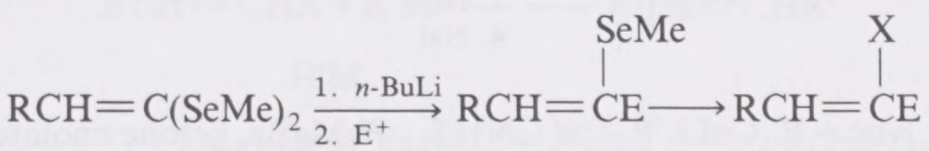
$$R_2C{=}O\ (RCHO) \xrightarrow[2.\ BF_3\cdot HOAc]{1.\ Me_3SiCH_2CH_2M\ (M = Li,\ MgX)} R_2CHCH{=}CH_2$$

JOC *47* 1983 (1982)



M	E^+	
Si	BF_3-HOAc; $TiCl_4$ + RX, RCOCl, enone, or epoxide	Syn 446 (1979)
Sn	H^+	CC 630 (1975)

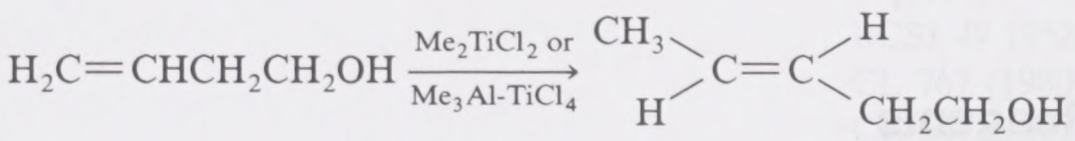
7. Selenium Reagents



$E^+ = H_2O$, D_2O, MeI, RCHO, R_2CO, Me_2NCHO, $ClCO_2Me$, CO_2
X = H (*n*-Bu_3SnH), Br (Br_2)

TL *23* 3411 (1982)

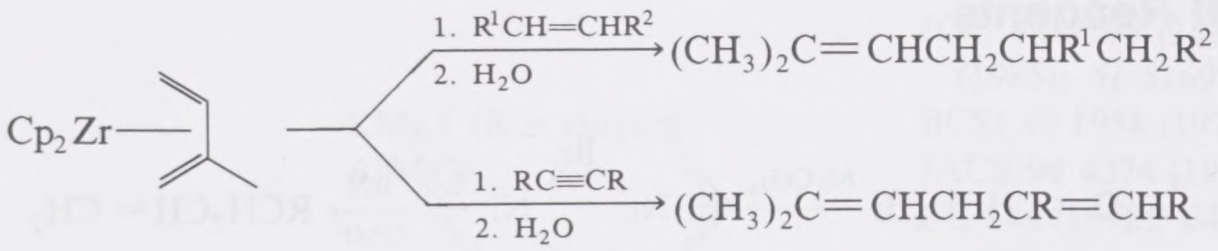
8. Titanium Reagents



CL 1819 (1982)
Angew Int *21* 309 (1982)

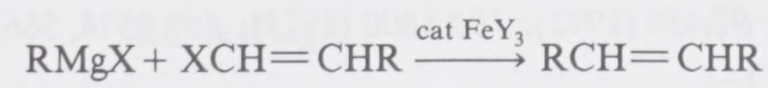
9. Zirconium Reagents

See also page 198, Section 12.

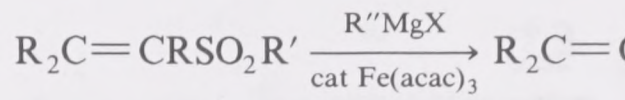


CL 719 (1981)

10. Iron Reagents

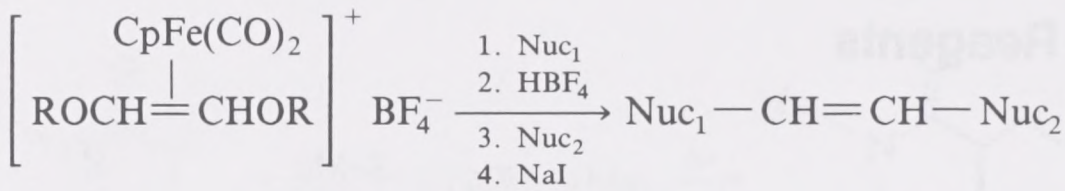


JACS *93* 1487 (1971) (Y = Cl)
Syn 303 (1971) (Y = Cl)
JOC *40* 599 (1975); *41* 502 (1976) (both Y = PhCOCHCOPh)



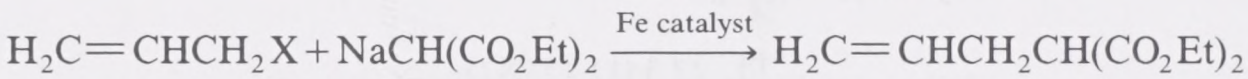
$R' = t\text{-Bu, Ph}$ $\quad$ $R'' = 1°$ alkyl, Ph

TL *23* 2469 (1982)



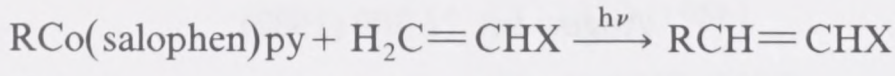
Nuc = R_2CuLi, $R_2Cu(CN)Li_2$, PhMgBr, ketone enolate

JACS *106* 7264 (1984)



X	Catalyst	
OAc	$Fe_2(CO)_9$	JOMC *285* C13 (1985)
OCO_2Et	*n*-$Bu_4N[Fe(CO)_3NO]$	JOC *52* 974 (1987)

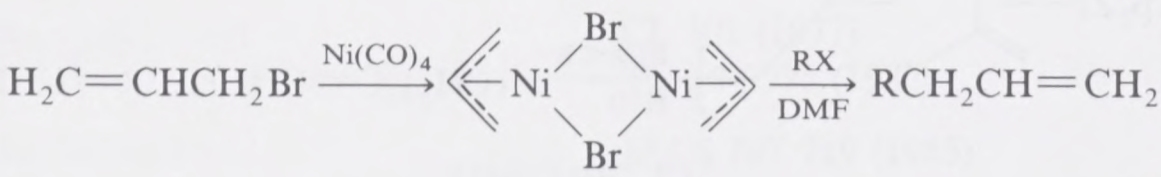
11. Cobalt Reagents



$R = 1°, 2°$ alkyl $\quad$ X = Ph, COR, CO_2R, CN

CC 871 (1987)

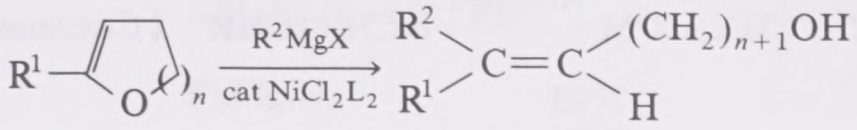
12. Nickel Reagents



R = alkyl, aryl, vinyl

Review: Org Rxs *19* 115 (1972)

JACS *89* 2755 (1967); *97* 459 (1975); *100* 5800 (1978); *107* 5574, 5663 (mechanism) (1985)
CC 235, 2289 (1973)
BCSJ *47* 3098 (1974); *49* 3351 (1976)
JCS Perkin I 2411 (1981)
Organomet *1* 259 (1982)



$n = 1, 2$

JACS *101* 2246 (1979)
JOC *49* 4894 (1984); *50* 719 (1985)
CC 241, 429 (1987)

$$RCH{=}CHX + R'M \xrightarrow{\text{Ni catalyst}} RCH{=}CHR'$$

X	R′M	
halogen	RO_2CCH_2Li	JACS *99* 4833 (1977)
	RMgX	Pure Appl Chem *52* 669 (1980) (review)
	RMgX (R = 1°, 2°, 3° alkyl)	JACS *94* 4374 (1972); *104* 180 (1982)
		JOMC *55* C91 (1973); *168* 227 (1979)
		Helv *56* 460 (1973)
		TL 3 (1974); *22* 137, 315 (1981); *24* 3209 (1983); *28* 6351 (1987)
		BCSJ *49* 1958 (1976)
		CL 767 (1980)
		CC 647 (1982)
		JOC *48* 2195 (1983); *50* 3261 (1985); *52* 678 (1987)
	RMgX (R = benzylic)	Helv *56* 460 (1973)
		TL 3 (1974); *21* 79, 4623 (1980); *27* 2049 (1986)
		JACS *98* 3718 (1976); *104* 180 (1982)
		BCSJ *49* 1958 (1976)
		JOMC *209* Cl (1981)
		CC 647 (1982); 1746 (1987)
		JOC *48* 2195 (1983); *50* 3261 (1985); *51* 5169 (1986)
	RMgX (R = vinylic)	BCSJ *49* 1958 (1976)
	ArMgX	JACS *94* 4374 (1972)
		CC 144 (1972); 647 (1982); 883 (1986)
		JOMC *55* C91 (1973); *168* 227 (1979)
		BCSJ *49* 1958 (1976)
		JOC *52* 678 (1987)
		TL *28* 6351 (1987)
	Me_3SiCH_2MgCl	TL *23* 27 (1982); *28* 6351 (1987)
	$RC{\equiv}CMgX$	JOC *49* 4733 (1984)
		JACS *108* 4685 (1986)
	RZnX (R = 1° alkyl)	Bull Acad Sci USSR, Div Chem Sci 620 (1986)
	EtO_2CCH_2ZnBr	JOMC *209* 109 (1981)

$$RCH{=}CHX + R'M \xrightarrow{\text{Ni catalyst}} RCH{=}CHR' \quad (\textit{Continued})$$

X	R′M	
$OSiMe_3$	RMgX (R = 1° alkyl, aryl, benzylic)	TL *21* 3915 (1980)
$OPO(OEt)_2$	$Me_3SiCHRMgCl$	Syn 1001 (1981)
OR	RMgX (R = Ph, 1° alkyl)	JACS *101* 2246 (1979) JOC *49* 4894 (1984); *50* 719 (1985) CC 241, 429 (1987)
SR	RMgX (R = 1° alkyl, aryl)	TL 43 (1979); *25* 5177 (1984); *27* 6301 (1986) CC 637 (1979); 647, 840 (1982) CL 1209 (1980)
O_2SR	RMgX (R = Me, Ph)	TL *23* 2469 (1982)
SePh	RMgX (R = *n*-Bu, Ph)	TL *21* 87 (1980)

$$RC(OPO(OR'')_2){=}CHCO_2R \xrightarrow{R'M} RCH(R'){=}CHCO_2R$$

R′M	
Me_3SiCH_2MgCl, cat $Ni(acac)_2$	Can J Chem *60* 673 (1982) TL *28* 2753 (1987)
Me_2Zn, cat $Ni(acac)_2$	JACS *109* 1564 (1987) (lactone)

See also page 206, Section 14, for related reactions.

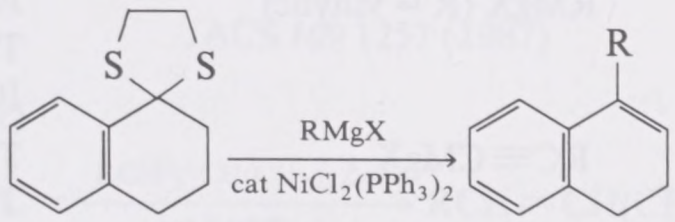
$$RCH{=}CHM + R'X \xrightarrow{\text{Ni catalyst}} RCH{=}CHR'$$

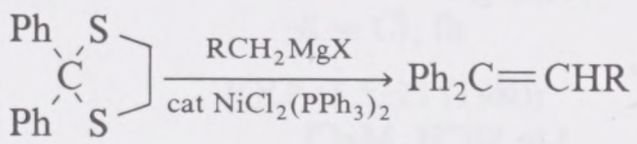
M	R′X	
MgX	ArX	BCSJ *49* 1958 (1976) JOC *50* 5370 (1985)
$Al(i\text{-}Bu)_2$	ArX	CC 596 (1976) JACS *109* 2393 (1987)
	$ArOPO(OEt)_2$	TL *22* 4449 (1981)
Cp_2ZrCl	ArX	JACS *103* 4466 (1981); *109* 2393 (1987)

$$RM + H_2C{=}CHCH_2X \xrightarrow{\text{Ni catalyst}} RCH_2CH{=}CH_2$$

X	RM	
Cl	$(i\text{-}PrO_2CCH_2CH_2)_2Zn$	JACS *109* 8056 (1987)
OH	RMgX (R = 1° alkyl, benzylic, aryl)	JOMC *127* 371 (1977); *134* 265 (1977) Helv *63* 987 (1980) CC 313, 681 (chiral) (1981) TL *28* 4547 (1987)

OPh	RMgBr (R = Et, Ph)	CC 112 (1983)
Cl, OR, $OSiR_3$	PhMgBr	CC 313 (1981)
Br, OH, OPh, S-*t*-Bu	RMgX (R = Me, Et)	Tetr *42* 2043 (1986)





CC 1515 (1987)

13. Palladium Reagents

See also page 193, Sections 5 and 6; and page 210, Section 17.

$$R_fI + RCH{=}CHBr \xrightarrow[\text{Pd catalyst}]{\text{Zn}} RCH{=}CHR_f$$

ultrasound

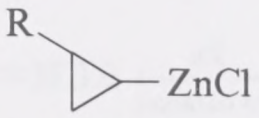
$$R_fI + RCH{=}CHCH_2Br \longrightarrow \underset{\displaystyle R_f}{\underset{|}{R}}CHCH{=}CH_2$$

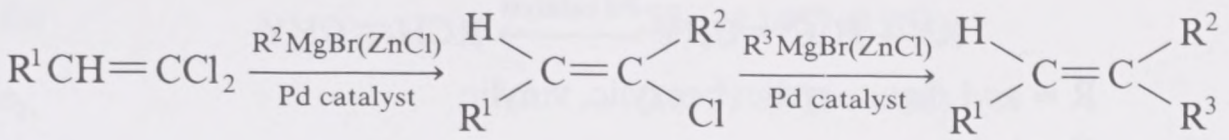
CL 137 (1982)
JACS *107* 5186 (1985)

$$RCH{=}CHX + R'M \xrightarrow{\text{Pd catalyst}} RCH{=}CHR'$$

X	R′M	
halogen	RLi (R = 1° alkyl, aryl)	JOMC *91* C39 (1975) JOC *44* 2408 (1979)
	RMgX (R = 1°, 2° alkyl)	JOMC *91* C39 (1975) TL 191 (1978); 1073, 1871 (1979); *27* 2529 (1986) JOC *44* 2408 (1979); *48* 2195 (1983); *51* 3772 (1986) CC 647 (1982) JACS *104* 180 (1982); *106* 158 (1984)
	RMgX (R = benzylic)	CC 647 (1982); 1746 (1987) JOC *51* 3772 (1986)

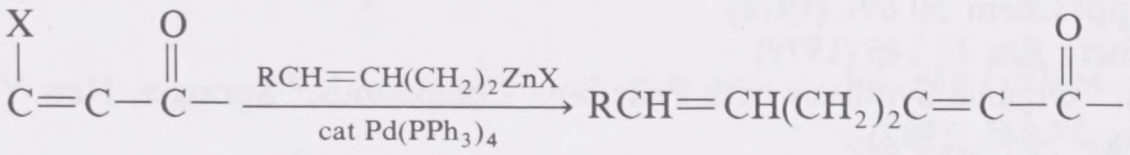
$$RCH{=}CHX + R'M \xrightarrow{\text{Pd catalyst}} RCH{=}CHR' \quad (\textit{Continued})$$

X	R′M	
	RMgX (R = vinylic)	JOMC *91* C39 (1975) TL 191 (1978) JOC *44* 2408 (1979)
	$RC{\equiv}CMgX$	TL 191 (1978) Tetr *37* 2617 (1981)
	ArMgX	TL 191 (1978) CC 647 (1982) JACS *109* 1257 (1987)
	Me_3SiCH_2MgCl	TL *23* 27 (1982)
	Ph$SnMe_3$	Proc Acad Sci USSR, Chem Sec *272* 333 (1983)
	RC$\equiv$**C**SnR_3	JACS *109* 2138 (1987)
	RZnX (R = 1° alkyl)	JACS *102* 3298 (1980); *109* 1257 (1987) JOC *46* 4093 (1981); *51* 4080 (1986); *52* 4885 (1987) JOMC *285* 109 (1985) Bull Acad Sci USSR, Div Chem Sci 620 (1986)
		TL *28* 5075 (1987)
	EtO_2CCH_2ZnBr	JOMC *209* 109 (1981)
	$EtO_2C(CH_2)_nZnI$ (n = 2, 3)	TL *27* 955 (1986)
	$(RO_2CCHRCH_2)_2Zn$	JACS *109* 8056 (1987)
	$ArCH_2ZnX$	TL *22* 2715 (1981)
	ArZnCl	JOC *50* 2121 (1985) J Med Chem *29* 2053 (1986)
	$RC{\equiv}CZnX$	CC 683 (1977) TL *27* 4351, 5533 (1986) JACS *108* 4685 (1986)
$OPO(OPh)_2$	Me_3SiCH_2MgCl	Syn 1001 (1981)
	R_3Al (R = 1° alkyl, vinylic, alkynyl)	TL *21* 2531 (1980); *22* 1609 (1981)
O_3SCF_3	$R'SnR_3$ (R′ = alkyl, allyl, alkynyl, vinylic), LiCl	JACS *106* 4630 (1984); *108* 3033 (1986) CC 809 (1985) (intramolecular) TL *27* 1523 (1986)
	$EtO_2C(CH_2)_nZnI$ (*n* = 2, 3)	TL *27* 955 (1986)
	$(RO_2CCH_2CH_2)_2Zn$	JACS *109* 8056 (1987)
	ArZnX	TL *28* 701 (1987)



R^1, R^2 or R^3 = aryl, 1° alkyl

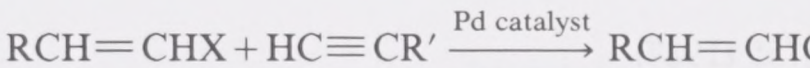
JACS *109* 1257 (1987)



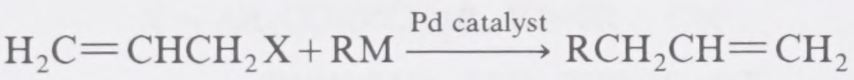
X = Cl, Br

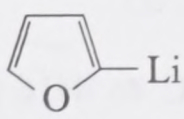
JOC *45* 5223 (1980)

See also page 206, Section 14, for related reactions.



X	
O_3SCF_3	JOC *50* 2302 (1985) TL *27* 1523 (1986) Heterocycles *26* 355 (1987)
halogen	TL 4467 (1975); *22* 421 (1981); *27* 2033, 3589, 5857 (1986); *28* 1127, 1649, 3857, 3859, 4875, 4879, 5751, 5849 (1987) JOMC *93* 253, 259 (1975) Syn Commun *11* 917 (1981) J Chem Res (S) 93 (1982) Tetr *38* 631 (1982) JACS *106* 3548, 5734 (1984); *107* 7515 (1985); *108* 5589 (1986); *109* 1879 (1987) CC 1816 (1986)



X	RM	
OH	RMgX	JOMC *186* C1 (1980) CC 313 (1981)
Cl	*n*-Bu_3SnR (R = heterocyclic)	TL *28* 1191 (1987)
Br		Syn 51 (1987)
Cl, Br	$RSnR'_3$ (R = aryl, vinylic)	JACS *105* 7173 (1983); *106* 4833 (1984)
Cl, OR, $OSiR_3$	RMgX	CC 313 (1981)
RCO_2 (lactone)	PhZnCl	CC 160 (1982)

$$RX + H_2C{=}CHY \xrightarrow{\text{Pd catalyst}} RCH{=}CHY$$

R = aryl, heterocyclic, benzylic, vinylic

X = halogen

Y = H, CO_2R, CO_2H, $CONH_2$, CN, Ar, alkyl, alkenyl, OR

Reviews:

Pure Appl Chem *50* 691 (1978)
Acct Chem Res *12* 146 (1979)
J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980)
Org Rxs *27* 345 (1982)
R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)

JOC *37* 2320 (1972); *40* 1083 (1975); *43* 2454, 2941, 2947, 2949, 5018 (1978); *44* 4078 (1979); *46* 1067, 2767, 5414 (1981); *52* 3319 (1987)
JACS *96* 1133 (1974); *101* 4743 (1979); *109* 4335 (1987)
Syn 365 (1981)
CC 541 (1981); 1287 (1984); 1755 (1987)
CL 1993 (1982) ($H_2C{=}CHSiMe_3 \longrightarrow ArCH{=}CH_2$)
JOMC *258* 101 (1983)
TL *26* 2667 (1985); *28* 3039 (1987)

$$ArI + H_2C{=}CR^1CHR^2OSiMe_3 \xrightarrow[LiCl]{Pd(OAc)_2} ArCH{=}CR^1\overset{O}{\overset{\|}{C}}R^2$$

CL 403 (1981)

$$ArO_3SR_f + H_2C{=}CHX \xrightarrow[Et_3N]{\text{cat } PdCl_2(PPh_3)_2,\ \Delta} ArCH{=}CHX$$

X = CN, CO_2Et

TL *27* 1171 (1986)

$$ArH + H_2C{=}CHX \xrightarrow[[Cu(OAc)_2]]{Pd(OAc)_2} ArCH{=}CHX$$

X = R, Ar, CN, CO_2R

Tetr *25* 4809, 4815, 4819 (1969)
Syn 524 (1973) (review)
CL 1230 (1979); 239 (1986) (ArH = uracil)
CC 859 (1981) (olefin = quinone)
JOC *46* 851 (1981) (ArH = heterocycles)

$$o\text{-}X{-}Ar{-}H \longrightarrow o\text{-}X{-}Ar{-}PdOAc(Cl) \xrightarrow{H_2C{=}CHR} o\text{-}X{-}Ar{-}CH{=}CHR$$

X	
NHCOR	JOC *46* 4416 (1981)
$CHRNR'_2$	Acct Chem Res *2* 144 (1969) JOMC *102* 239 (1975); *179* 301 (1979); *182* 537 (1979) TL 355 (1977); *21* 2757 (1980); *27* 2169 (1986) BCSJ *51* 663 (1978); *52* 142, 957 (1979) Tetr *37* 173 (1981)

$CH{=}N{-}t\text{-Bu}$	TL *23* 1957 (1982)
$CH_2CH_2NMe_2$	TL *27* 1971 (1986)

$$RM + H_2C{=}CHX \xrightarrow{\text{Pd(II) salts}} RCH{=}CHX$$

RM	X	
ArMgX	Ar	CC 918 (1978)
$ArTl(O_2CCF_3)_2$	—	See page 193, Section 5.
$K_2(PhSiF_5)$	CHO, CO_2R	Organomet *1* 542 (1982)
Ph_2CuM (M = Li, MgX)	Ph, CO_2R	TL 4657 (1979)
RHgX (R = Me, CO_2R', Ar)	—	See page 210, Section 17.

$$ArN_2^+ + H_2C{=}CHR \xrightarrow{\text{Pd catalyst}} ArCH{=}CHR$$

CL 159 (1977)
Tetr *37* 31 (1981)

$$ArNH_2 + H_2C{=}CHX \xrightarrow[\text{Pd(O) or Pd(II)}]{t\text{-BuONO}} ArCH{=}CHX$$

X = R, Ar, CO_2R

CL 551 (1980)
JOC *45* 2359 (1980); *46* 4885 (1981)

$$ArCOCl + H_2C{=}CHX \xrightarrow[R_3N]{\text{cat } Pd(OAc)_2} ArCH{=}CHX$$

X = Ar, COR, CO_2R, $CONR_2$, CN

JOMC *233* 267 (1982); *240* 209 (1982)

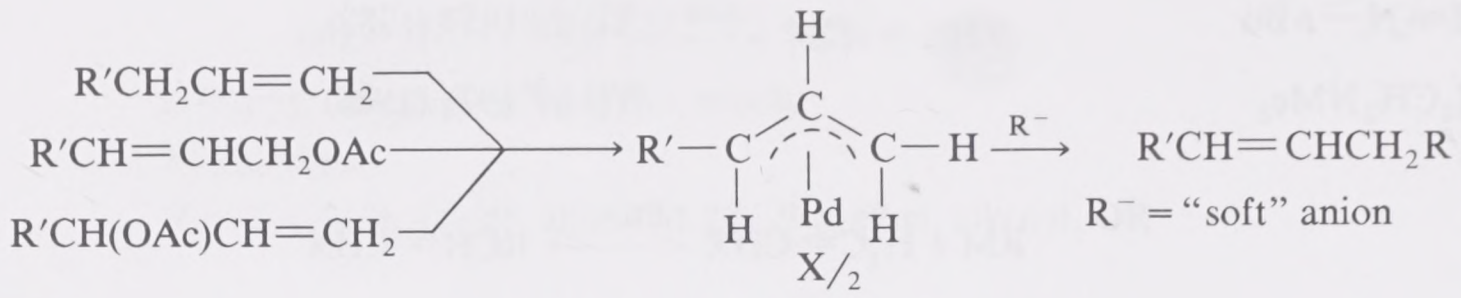
$$ArC(=O)Cl + H_2C{=}CHOR \xrightarrow[Et_3N]{\text{cat } \overset{\Delta}{Pd}(OAc)_2} ArC(=O)CH{=}CHOR$$

TL *28* 4215 (1987)

$$RCH{=}CH_2 + {}^-CRX_2 \xrightarrow[2\ Et_3N]{PdCl_2} \xrightarrow{25°C} RC(CRX_2){=}CH_2$$

X = CO_2R, COR

JACS *99* 7093 (1977)



Reviews:

Tetr *33* 2615 (1977)
Acct Chem Res *13* 385 (1980)
J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer Verlag, New York (1980)
R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)

14. Copper Reagents

See also page 197, Section 10; and page 201, Section 13.

$$R'X \xrightarrow[\text{reagent}]{\text{organocopper}} R'CH{=}CHR$$

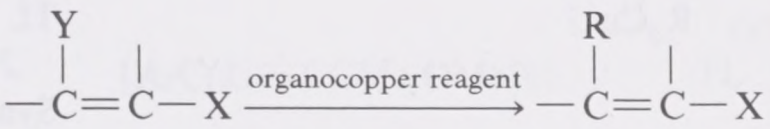
RCH=CHMgX, cat CuI	TL 1073 (1979) BCSJ *54* 2831 (1981) JOC *51* 4726 (1986)
RCH=CHLi, CuI	Organomet *1* 667 (1982) CC 925 (1986)
R_fCF=CFCu	JACS *108* 4229 (1986)
$(H_2C{=}CH)_2CuLi$	J Ind Chem Soc *45* 1026 (1968) Helv *54* 1939 (1971) JACS *93* 7016 (1971)
$[(H_2C{=}CH)_2CuCN]Li_2$	JACS *109* 1186 (1987)
[**RCH=CH**CuC≡CC$(CH_3)_3$]Li	TL *23* 739 (1982)

$$R'CH{=}CHX \xrightarrow[\text{reagent}]{\text{organocopper}} R'CH{=}CHR$$

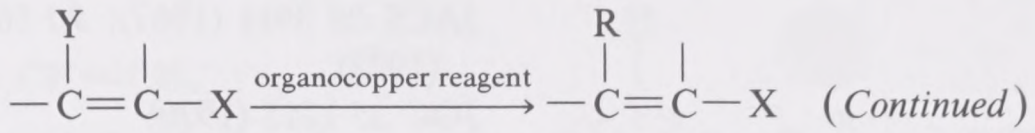
X = halogen

RLi or RMgX, cat CuBr	Compt Rend C *278* 967 (1974)
RMgX, cat Li_2CuCl_4	JOMC *128* 1 (1977) JACS *109* 1856 (1987)
RCu (R = Ph, C≡CR, $CH_2C{\equiv}CSiMe_3$, CH_2CMe_3)	JOMC *93* 415 (1975)

R_2CuLi			JACS *89* 3911 (1967); *90* 5615 (1968); *94* 2520 (1972) JOC *35* 1715 (1970) Org Rxs *19* 1 (1972) (review)



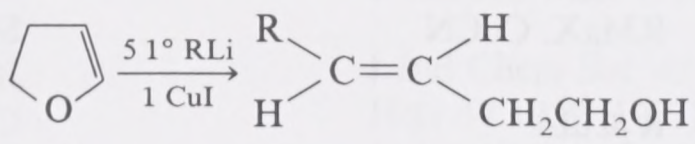
X	Y	Reagent	
H or R	O_3SCF_3	$R_2CuLi(MgX)$	TL *21* 4313 (1980)
		$(R_2CuCN)Li_2$	Heterocycles *26* 355 (1987)
	$OPO(OPh)_2$	R_2CuLi	TL 4405 (1976)
COR	halogen	RMgX, CuX	JCS Perkin I 593, 599 (1981) CC 671 (1986)
		R_2CuLi	JOC *41* 636, 3629 (1976); *46* 2089 (1981) Can J Chem *60* 1256 (1982)
		(RCuSPh)Li	JOC *40* 2694 (1975) TL 3233, 3237 (1976) CC 1033 (1978) ($R = Me_3Sn$) JCS Perkin I 593 (1981) Can J Chem *60* 1256, 2965 (1982)
	OAc	R_2CuLi	TL 2071 (1973) JOC *41* 3629 (1976)
	OCO_2R	R_2CuLi	Ind J Chem *12* 325 (1974)
	$OPO(OEt)_2$	R_2CuLi	Can J Chem *57* 1431 (1979)
	OR	R_2CuLi	Ind J Chem *12* 325 (1974)
	SR	RMgX, CuBr	Syn 320 (1976)
		RMgX, CuCN	Syn Commun *6* 209 (1976) JOC *51* 4807 (1986)
		R_2CuLi	CC 907 (1973) TL 3817 (1973) Acta Chem Scand B *33* 460 (1979) CL 815 (1982) JOC *48* 2786 (1983); *51* 4687 (1986); *52* 110 (1987) JACS *107* 4679 (1985)
		(RCuSPh)Li	TL *23* 3751 (1982) JACS *107* 4679 (1985)
		$(RCuC{\equiv}CCMe_2OMe)Li$	JOC *48* 2786 (1983) JACS *107* 4679 (1985)
		$(R_2CuSCN)Li_2$	JOC *51* 4687 (1986)
		$(R_2CuCN)Li_2$	JOC *51* 4687 (1986)
CO_2R	Cl	R_2CuLi	JOC *43* 3974 (1978); *46* 2089 (1981)
	Br	$(R_3BMe)Li$, CuI	TL 3369 (1977)



(*Continued*)

X	Y	Reagent	
	O_2CR	R_2CuLi	TL 2071 (1973); *27* 959 (1986) Syn Commun *3* 321 (1973) JOC *43* 3974 (1978) Ann 1173 (1982)
		$R_2CuLi \cdot n\text{-}Bu_3P$	TL 925 (1974)
	OCO_2R	R_2CuLi	JOC *43* 3974 (1978)
	$OPO(OEt)_2$	MeMgCl, MeCu	TL *25* 1333, 1643 (1984); *28* 731 (1987)
		R_2CuLi	Can J Chem *57* 1431 (1979); *59* 2239 (1981) Ann 1173 (1982) CC 421 (1982); 24 (1987) JOC *49* 1707 (1984); *52* 1106 (1987) JACS *107* 2712 (1985) TL *27* 5555 (1986)
	O_3SCF_3	R_2CuLi	JOC *51* 3247 (1986)
	SR	RMgX, CuX	CL 1097 (1973); 705 (1974) Syn 320 (1976)
		R_2CuLi	CC 907 (1973) JOC *50* 2730 (1985)
		(RCuSPh)Li	JACS *107* 4679 (1985)

For related reactions see page 198, Section 12; and page 201, Section 13.

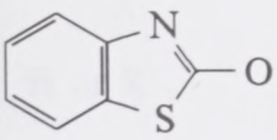


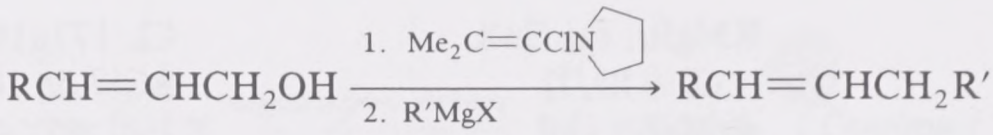
CL 1641 (1982)

$$R'CH{=}CHCH_2X \xrightarrow{RM} R'CH{=}CHCH_2R$$

For allylic rearrangements see page 119, Section 8.

X	RM	
Cl	RMgBr, cat CuX (X = Cl, I)	Helv *65* 684 (1982)
	RMgBr, cat $Cu(acac)_2$	Tetr *39* 3283 (1983)
	RMgX (X = Cl, Br), cat Li_2CuCl_4	TL *23* 3115 (1982) Helv *65* 684 (1982) CC 590 (1986)
	R_2CuLi (R = 1° alkyl)	TL 4439 (1976)
	$R_2CuLi \cdot SMe_2$ (R = 1° alkyl, vinyl)	TL 2705 (1978)

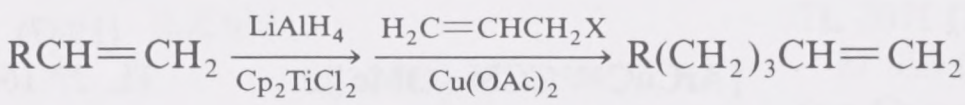
Br	RMgBr, cat CuX (X = Br, I)	CL 177 (1982)
		BCSJ *56* 1446 (1983)
	ArMgBr, CuI	JOC *50* 2427 (1985)
	RCu (R = *sec*-Bu, *t*-Bu)	JOC *49* 1840 (1984)
	Ar_2CuLi	JCS Perkin I 2909 (1982)
		JOC *49* 1840 (1984); *52* 3394 (1987)
	[**Ar**$CuC{\equiv}CCMe_2OMe$]Li	TL *27* 1607 (1986)
OTs	RMgBr, cat Li_2CuCl_4	Helv *65* 684 (1982)
OAc	RMgBr, cat CuBr	Syn 804 (1983)
	RMgBr, cat CuI	Helv *65* 684 (1982)
	RMgBr, cat $Cu(acac)_2$	Tetr *39* 3283 (1983)
	RMgX, cat Li_2CuCl_4 (R = 1° alkyl, aryl)	Angew Int *13* 82 (1979)
		Helv *65* 684 (1982)
		TL *24* 5103 (1983); *28* 1175 (1987)
		Syn 804 (1983)
		CC 827 (1987)
	R_2CuLi (R = Me, *n*-Bu)	JOMC *136* 103 (1977)
		JOC *46* 5304 (1981); *48* 721, 3986 (1983)
		TL *23* 3093 (1981)
	R_2CuLi (R = Ph)	JACS *101* 4413 (1979)
	$Li_2Cu_3Me_5$	TL *23* 3093 (1982)
OAc (R′ = CO_2R)	$RCu{\cdot}(AlCl_3)_n$ (R = *n*-Bu)	Syn Commun *10* 119 (1980)
O_2CCMe_3	R_2CuLi	Can J Chem *61* 632 (1983)
		JOC *52* 897 (1987)
OCO_2Et	RMgBr, cat CuBr	Syn 804 (1983)
$OCONMe_2$	RMgX, cat CuI	JOC *51* 5456 (1986)
$OPO(OEt)_2$	RMgBr, cat CuX (X = Br, I)	CL 177 (1982)
		BCSJ *56* 1446 (1983)
	1° RMgX, CuBr	JOMC *231* 179 (1982)
		JCS Perkin I 2953 (1983)
SO_2Ph	RMgX (R = 1° alkyl), cat $Cu(acac)_2$	TL 2393 (1979)
		Tetr *39* 3283, 3289 (1983)
	R_2CuLi	Tetr *39* 3283 (1983)
$\overset{+}{S}Me_2\ Br^-$	RMgBr, cat CuBr	Syn 804 (1983)
$\overset{+}{N}R'_3\ X^-$	RMgBr, cat CuBr	Syn 804 (1983)
	RMgX, cat Li_2CuCl_4	JOC *52* 2947 (1987)
	R_2CuLi	TL *21* 67 (1980)
		JOC *52* 3683 (1987)



$$RCH{=}CHCH_2OH \xrightarrow[2.\ R'MgX]{1.\ Me_2C{=}CClN} RCH{=}CHCH_2R'$$

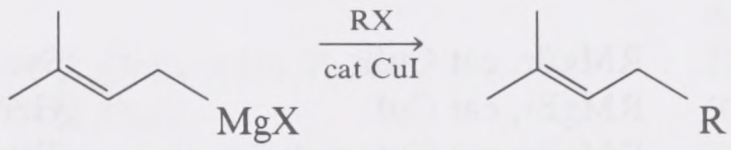
$R' = Ph,\ CH{=}CH_2,\ Et\ (R = Ph)$

TL *24* 5745 (1983)



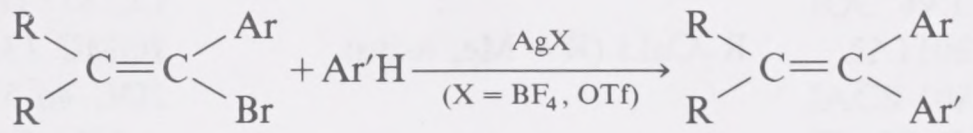
$$RCH{=}CH_2 \xrightarrow[Cp_2TiCl_2]{LiAlH_4} \xrightarrow[Cu(OAc)_2]{H_2C{=}CHCH_2X} R(CH_2)_3CH{=}CH_2$$

CL 1155 (1978)



TL 1181 (1977)
Syn Commun *11* 859 (1981)

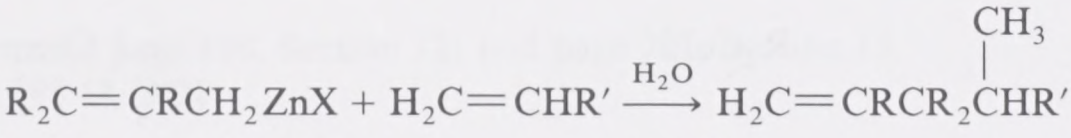
15. Silver Reagents



JOC *47* 5003 (1982)

16. Zinc Reagents

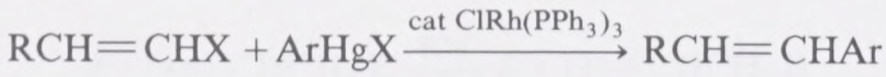
For transition metal-catalyzed cross-coupling of organozinc compounds see the appropriate transition metal.



JOMC *221* 123, 131 (1981)

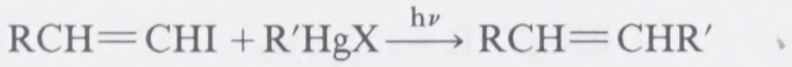
17. Mercury Reagents

See also page 201, Section 13.

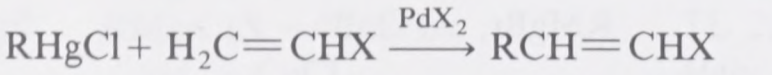


X = halogen

JOC *48* 4377 (1983)



JACS *106* 4622 (1984)
TL *26* 4975 (1985); *28* 6113 (1987)



R = Me, CO_2R', Ar

X = CHO, COR, CO_2R, CN, Ar

R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer Verlag, New York (1985), Chpt 7 (review)

6. ALKYNE AND DIENE ADDITION REACTIONS

See also page 241, Section 7.

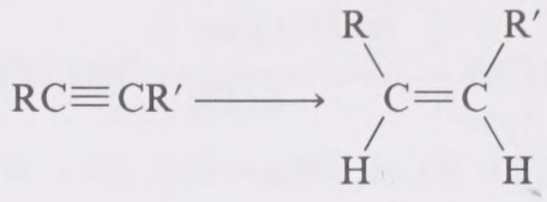
1. Hydrogen Addition

diene ⟶ monoene

H_2, cat $K_3[Co(CN)_5H]$	TL 115 (1979) JOC *45* 3860 (1980)
H_2, cat $ClRh(PPh_3)_3$	Discuss Faraday Soc *46* 60 (1968)
H_2, cat $Ni(acac)_2$-$Al_2Et_3Cl_3$-PPh_3	BCSJ *55* 343 (1982)
H_2, cat Pd(O)-polymer	Israel J Chem *17* 269 (1978)

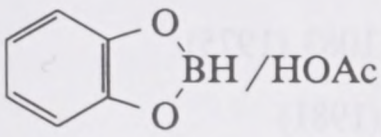
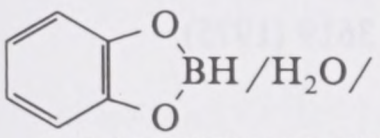
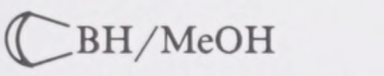
$$RCH{=}CHCH{=}CHX \longrightarrow RCH_2CH{=}CHCH_2X$$

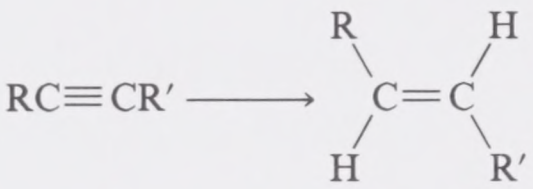
X	Reagent(s)	
H or R′	H_2, cat $C_6H_5CO_2CH_3 \cdot Cr(CO)_3$	TL 1919 (1968) JOC *34* 3930, 3936 (1969); *49* 4096 (1984)
	H_2, cat naphthalene$\cdot Cr(CO)_3$	TL *28* 1893 (1987)
COR	H_2, cat $C_6H_5CO_2CH_3 \cdot Cr(CO)_3$	JACS *106* 3875 (1984) (cis product)
COR, CO_2R	*i*-Bu_2AlH, cat MeCu, HMPA/H_2O	JOC *51* 537 (1986)
CO_2R	H_2, cat $C_6H_5CO_2CH_3 \cdot Cr(CO)_3$	TL 1919 (1968); *28* 5841 (1987) JACS *90* 2446 (1968)
	Et_3SiH, cat $ClRh(PPh_3)_3$	Syn Commun *15* 965 (1985)
	$Na_2S_2O_4$	CL 715 (1982) (trans product)



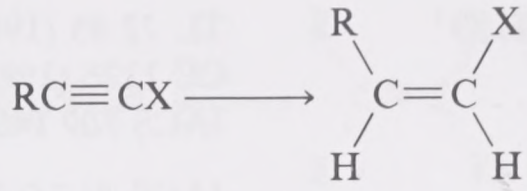
Review: Syn 457 (1973) (hydrogenation)

Li/H_2O	JACS *92* 2268 (1970) (R, R′ = Ph) JOC *35* 1702 (1970) (R, R′ = Ph) Angew Int *25* 167 (1986) [R, R′ = $(CH_2)_6$]
Zn(Cu), MeOH	TL *21* 1069 (1980)
Zn, KCN, H_2O, ROH	Helv *58* 1016 (1975) JACS *109* 8051 (1987)
Zn, HOAc, MeOH	TL *28* 5395 (1987)
H_2, cat $[Rh(NBD)(PR_3)_n]PF_6$	JACS *98* 2143 (1976)
H_2, cat nickel boride P-2	JACS *85* 1005 (1963) CC 553 (1973) JOC *38* 2226 (1973); *46* 1263 (1981)
H_2, cat Ni graphite, EDA	JOC *46* 5340, 5344 (1981)
H_2, cat $Ni_4[CNC(CH_3)_3]_7$	Pure Appl Chem *50* 941 (1978)
H_2, cat NaH-$Ni(OAc)_2$-*t*-AmOH	TL 3965 (1977) JOC *45* 1937, 1946 (1980)
H_2, cat Pd polymer	J Catalysis *57* 315 (1979)
H_2, cat Pd graphite, EDA	CC 540 (1981)
H_2, cat Pd on tungsten film	JOC *52* 3132 (1987)
H_2, cat Pd-$CaCO_3$, $Pb(OAc)_2$, quinoline (Lindlar)	Helv *35* 446 (1952) JACS *78* 2518 (1956); *107* 1028 (1985) Org Syn Coll Vol *5* 880 (1973) JOC *41* 3497 (1976); *43* 3435 (1978); *52* 3126 (1987)
H_2, cat Pd-$CaCO_3$, cat $MnCl_2$, $Pb(OAc)_2$, quinoline	Tetr *39* 2315 (1983)
H_2, cat Pd-$BaSO_4$, py	JOC *50* 2309 (1985)
H_2, cat Pd-$BaSO_4$, quinoline	JACS *78* 2518 (1956) Org Syn *64* 108 (1985) JOC *51* 4158 (1986)
H_2, cat $PdCl_2$, DMF	Ber *109* 531 (1976)
H_2, cat NaH-$Pd(OAc)_2$-*t*-AmOH, quinoline	JOC *49* 4058 (1984)
$(Et_3NH)O_2CH$, cat Pd-C (R = aryl, vinyl)	JOC *45* 4926 (1980)
MgH_2, CuI or CuO-*t*-Bu	JOC *43* 757 (1978)
2 *n*-BuMgX, CuI/H_2O	JOC *41* 4089 (1976)

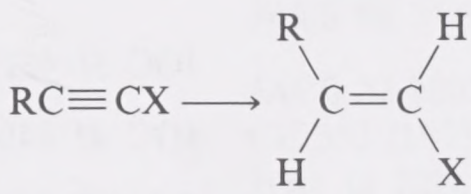
i-BuMgX (X = Cl, Br), Cp_2TiCl_2/H_3O^+	TL *22* 85 (1981) CC 1126 (1982) JACS *109* 1469 (1987)
BH_3 or R_2BH/HOAc	JACS *81* 1512 (1959); *83* 3834 (1961); *93* 3395 (1971); *109* 2138 (1987) Tetra *37* 2617 (1981) JOC *51* 4512, 4514 (1986)
$ClBH_2$/HOAc	JOC *38* 1617 (1973)
	JACS *94* 4370 (1972)
 $HOCH_2CH_2OH$/HOAc	JACS *107* 3626 (1985)
	JOC *51* 4512 (1986)
R_2BH/*n*-BuLi/NaOH	JOC *41* 3484 (1976)
R_2BH/cat $Pd(OAc)_2$	CC 702 (1978) BCSJ *53* 1670 (1980)
$NaBH_4$, cat $PdCl_2$	CC 515 (1983)
i-Bu_2AlH/H_2O	Ann *629* 222 (1960) JOC *43* 2739 (1978)
$LiAlH_4$, $TiCl_4$	TL 15 (1976)
$LiAlH_4$, $NiCl_2$	TL 4481 (1977)
$NaAlH_4$, $NbCl_5$	CL 157 (1982)
$Cl_3SiH/KF/CuF_2 \cdot 2\ H_2O$	TL 1141 (1979)
$LaNi_5H_6$	JOC *52* 5695 (1987)



Li/H_2O	Angew Int *25* 167 (1986)
Li, CH_3NH_2	CC 634 (1968)
Na, NH_3	JACS *63* 216, 2683 (1941); *65* 2020 (1943); *74* 3643 (1952) JCS 3558 (1955) Syn 567 (1972); 616 (1973); 114 (1979)
Yb, NH_3	JOC *43* 4555 (1978)
i-Bu_2AlH/H_2O	TL 3145 (1979) (3° propargylic amines)
$LiHAlMe(i\text{-}Bu)_2/H_2O$	JACS *89* 5085 (1967)
$CrSO_4$, H_2O	JACS *86* 4358 (1964) JOC *51* 253 (1986)



X	Reagent(s)	
I	$\left(\bigcirc\right)_2$BH/HOAc	JACS *107* 713 (1985)
	$KO_2CN{=}NCO_2K$, HOAc	JOC *40* 1083 (1975)
CR_2OH	*i*-BuMgX, cat Cp_2TiCl_2/H_2O	CC 718 (1981)
CO_2R	$NaH_2Al(OCH_2CH_2OCH_3)_2$, CuBr	JOC *40* 3619 (1975)

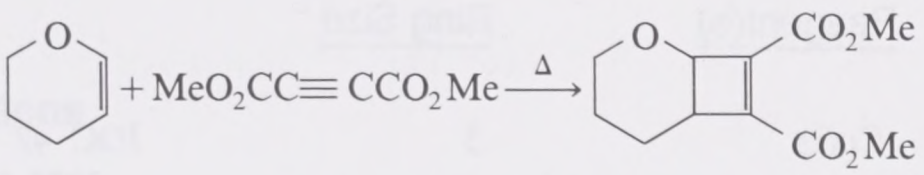


X	Reagent(s)	
Cl	$LiAlH_4$	JACS *101* 5101 (1979)
OR	$LiAlH_4$	JOC *52* 2919 (1987)
CH_2NH_2, CH_2NHR	$LiAlH_4$	JOC *52* 5044 (1987)
CH_2OH	Na, NH_3	JOC *41* 3497 (1976)
	$LiAlH_4$	JACS *71* 4140 (1949); *89* 4245 (1967); *92* 4898 (1970); *106* 7614 (1984); *107* 1028 (1985)
		JCS 1094 (1952); 1584 (1953); 1854 (1954); 2754 (1957)
		JOC *31* 528 (1966); *39* 968 (1974); *47* 4595 (1982); *51* 4158 (1986); *52* 3798 (1987)
		CC 1017 (1968)
		TL *27* 5857 (1986)
	$NaAlH_2(OCH_2CH_2OMe)_2$	JOC *41* 3497 (1976); *43* 3435 (1978); *47* 4595 (1982); *51* 1155 (1986)
		Org Syn *64* 182 (1985)
		JACS *109* 1186, 1469, 2205 (1987)
		TL *28* 527, 803, 2041 (1987)
	$NaAlH_2(OCH_2CH_2OEt)_2$(?)	JOC *51* 863 (1986)
$(CH_2)_nOH$	$LiAlH_4$	Syn 561 (1977) ($n = 2, 6, 7$)
		Ber *114* 292 (1981) ($n = 7$)
COR, CO_2Me	*i*-Bu_2AlH, HMPA, (cat MeCu)	JOC *52* 1624 (1987)
CN	$LiAlH_4$	Syn 430 (1979)

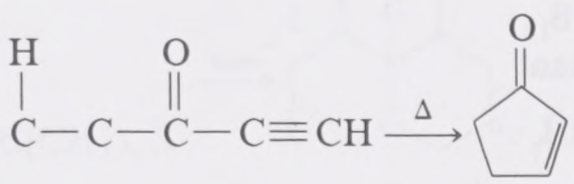
2. Alkylation and Functionalization

See also page 333, Section 4, for the synthesis of vinylic halides; and page 273, Section 9.

2.1. Thermal

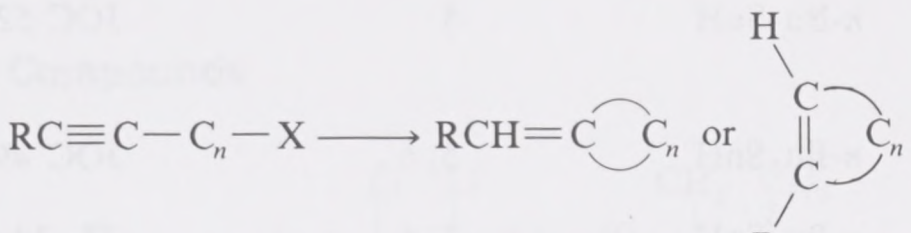


TL *28* 1501 (1987)

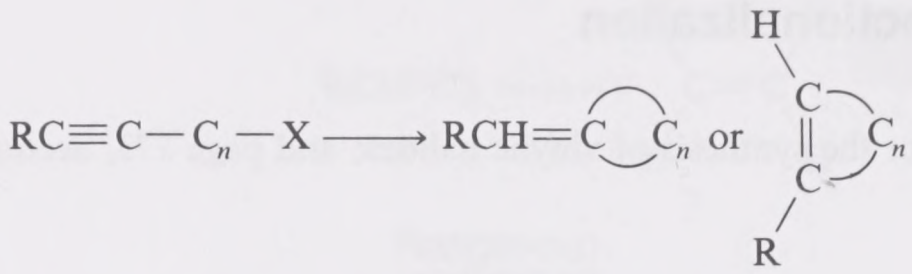


Helv *62* 852 (1979); *65* 13, 2413, 2517 (1982)

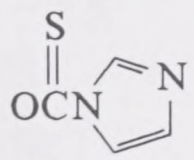
2.2. Free Radical

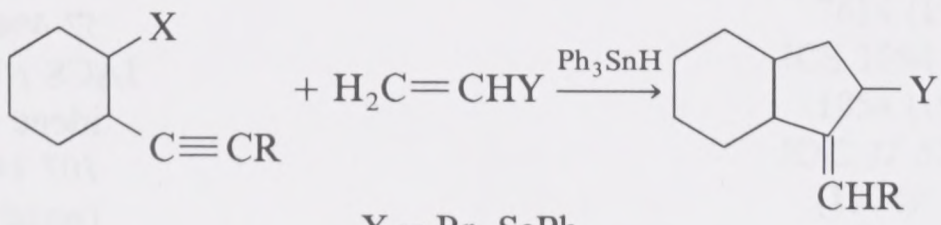


X	Reagent(s)	Ring Size	
halogen	*n*-Bu_3SnH	5	JOC *47* 5382 (1982) (3-methylene tetrahydrofurans); *52* 4943 (1987)
			JACS *105* 3720 (1983) (3-alkylidene tetrahydrofurans); *107* 1448 (1985) (serial cyclization)
			CL 1437 (1984) (3-methylene tetrahydrofurans)
			TL *26* 6001 (1985) (methylene dihydrobenzofuran); *27* 3715 (1986) (3-methylene tetrahydrofuran); *28* 2009 (3-methylene tetrahydrofurans), 2887 (carbapenam) (1987)
			CC 587 (1987) (3-methylene tetrahydrofurans)
		6	JOC *44* 546 (1979)
		6, 7	TL *23* 2505 (1982)
			JOC *48* 1841 (1983) (both bicyclic β-lactams)
	n-Bu_3SnCl, $NaBH_3CN$	5	TL *28* 5203, 6393 (1987) (both 3-methylene tetrahydrofurans)



(*Continued*)

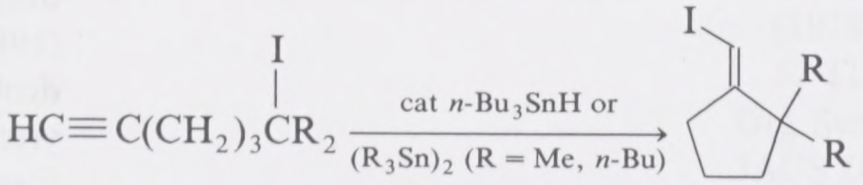
X	Reagent(s)	Ring Size	
	Co(I)	5	JOC *47* 1775, 5382 (1982); *50* 5875 (1985) (all 3-methylene tetrahydrofurans)
	vitamin B_{12}, reductant	5	Chimia *39* 203 (1985)
NO_2	*n*-Bu_3SnH	5	CL 635 (1985) (3-methylene tetrahydrofurans) Tetr *41* 4013 (1985) (3-methylene tetrahydrofurans)
$O_2CC_6H_4CF_3$	hν	5	JOC *52* 5583 (1987)
OCS_2CH_3	*n*-Bu_3SnH	5	JOC *52* 5583 (1987)
	*n*-Bu_3SnH	5, 6	JOC *49* 1313 (1984)
SPh	*n*-Bu_3SnH	5, 6	TL *23* 4765 (1982) Tetr *41* 3959 (1985) (pyrrolizidinones and indolizidinones)
SePh	Ph_3SnH	5	CC 941, 1205 (1985); 878 (1986) JOC *52* 4943 (1987)



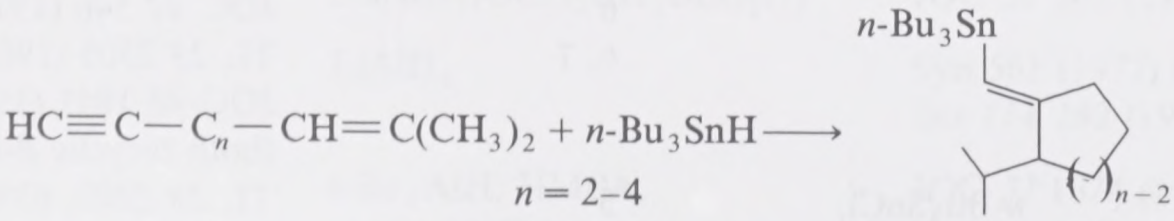
X = Br, SePh

Y = CO_2Me, CN, SO_2Ph

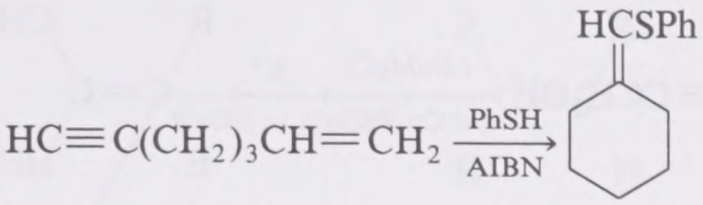
CC 980 (1985)



JACS *108* 2489 (1986)
TL *28* 2477 (1987)

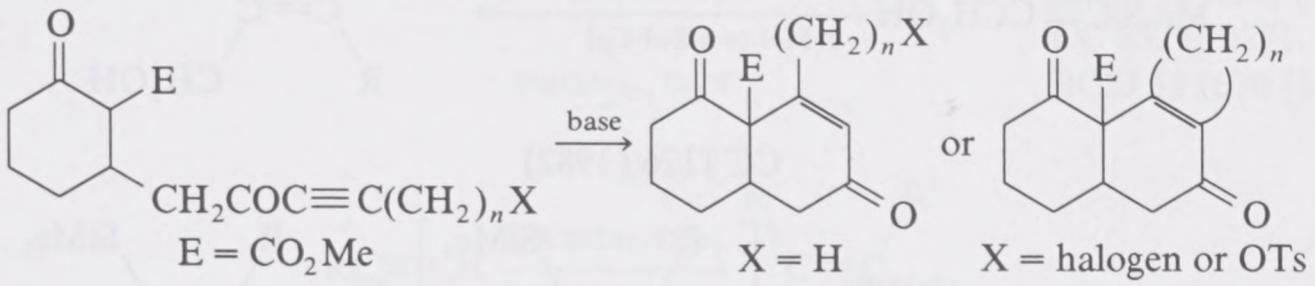


JACS *109* 2829 (1987)
TL *28* 1503 (1987)



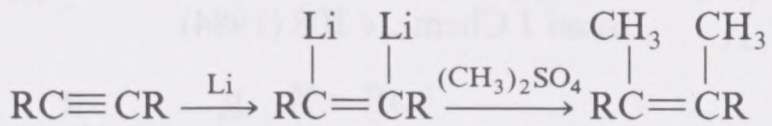
TL *28* 1503 (1987)

2.3. Michael Additions

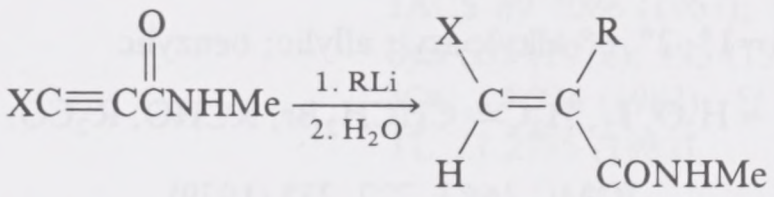


TL *27* 5455 (1986); *28* 3457 (1987)

2.4. Organolithium Compounds



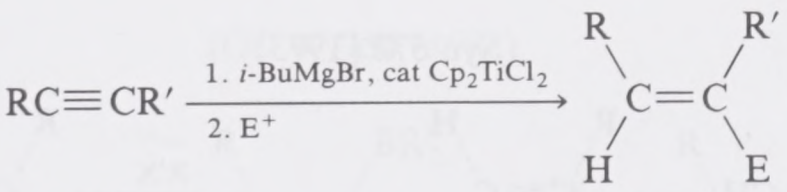
Angew Int *25* 167 (1986)



X = Ph, $SiMe_3$

JACS *107* 6740 (1985)

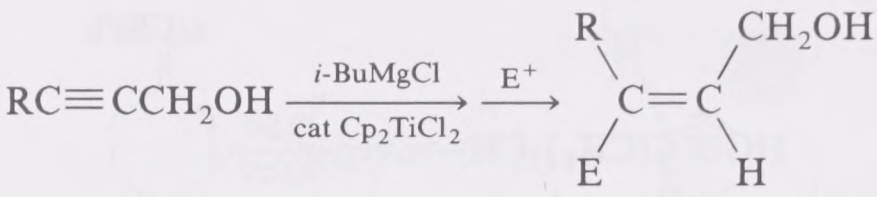
2.5. Organomagnesium Compounds



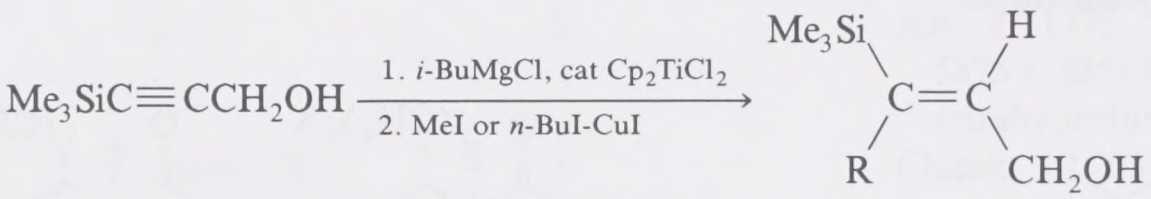
$E^+ = H_2O, D_2O, I_2$, MeI, RCHO

R, R′ = Me, Ph; *n*-Bu, Me_3Si; Me_3Si, Ph

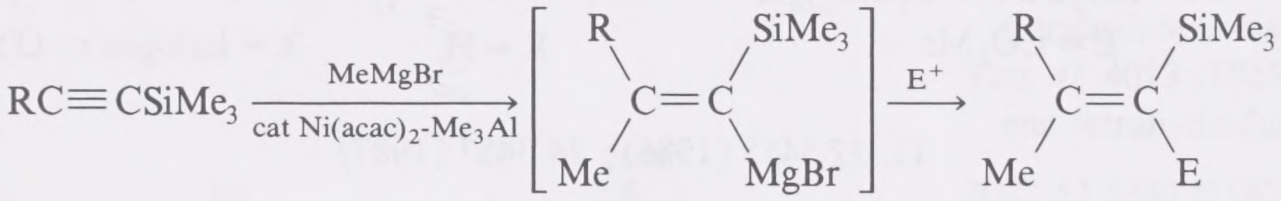
TL *22* 85 (1981)



E^+	
MeI	CC 718 (1981)
CO_2/H^+	JOC *52* 3860 (1987)

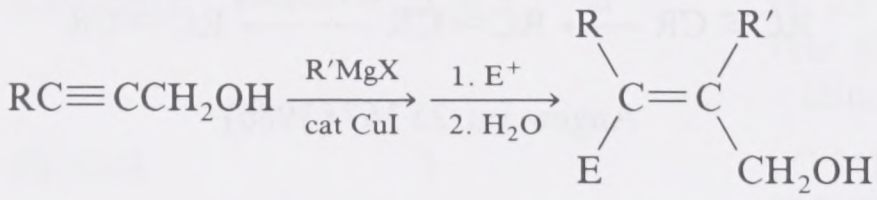


CC 1126 (1982)



$E^+ = D_2O, CO_2, RCHO, I_2, H_2C{=}CHBr, CH_3I, H_2C{=}CHCH_2Br$

JACS *100* 4624 (1978)
TL 1682 (1979)
Israel J Chem *24* 108 (1984)

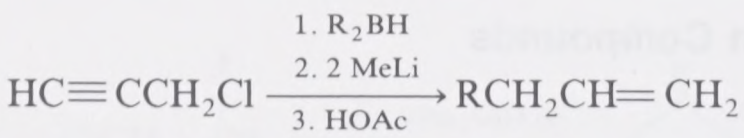


$R' = 1°, 2°, 3°$ alkyl; aryl; allylic; benzylic

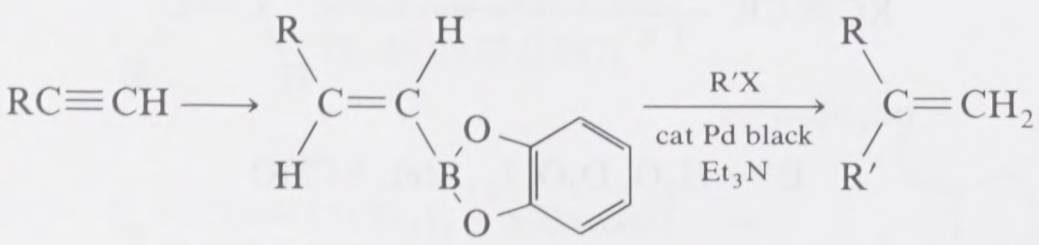
$E^+ = H_2O, I_2, H_2C{=}CHCH_2Br, RCHO, R_2CO, CO_2$

JOMC *168* 1, 227, 233 (1979)
JOC *51* 4080 (1986)

2.6. Organoboron Compounds

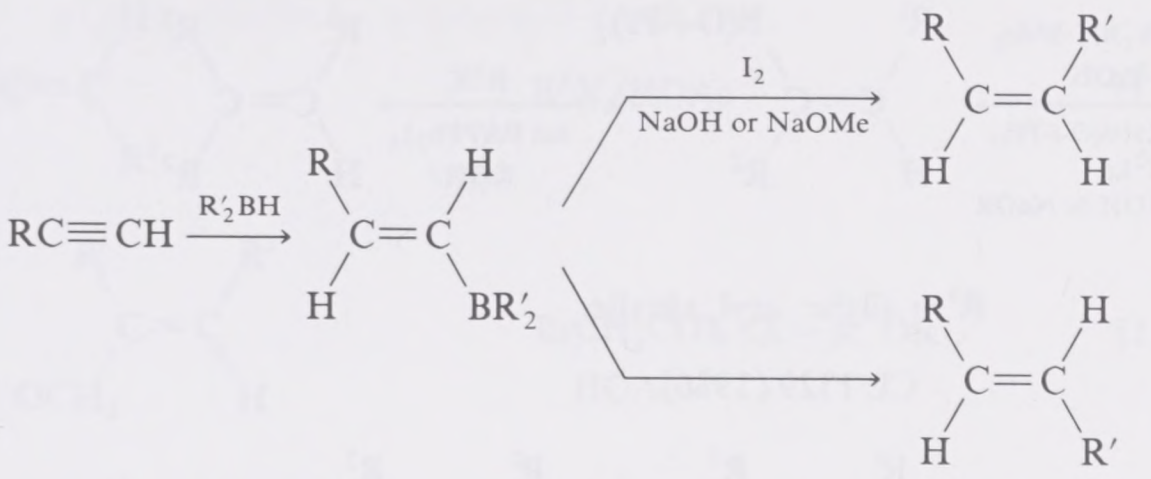


Syn 672 (1973)

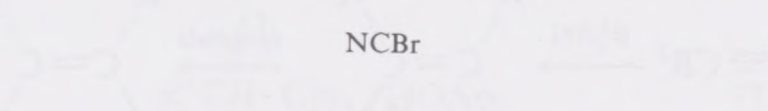


$R' =$ aryl, vinylic

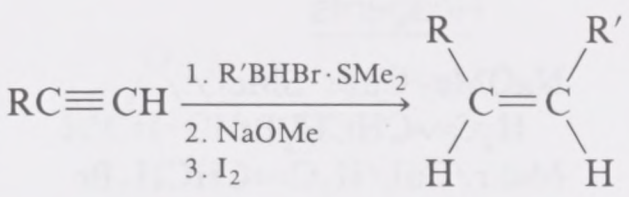
JOMC *213* C53 (1981)



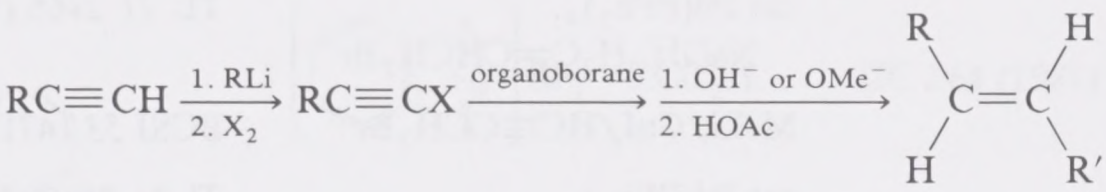
JACS *89* 3652 (1967); *93* 6309 (1971)
JOC *41* 3947 (1976); *47* 1792 (1982)
JOMC *225* C1 (1982)
Tetr *38* 2355 (1982)



JACS *94* 6560 (1972)
CC 852 (1977)
BCSJ *53* 1670 (1980)



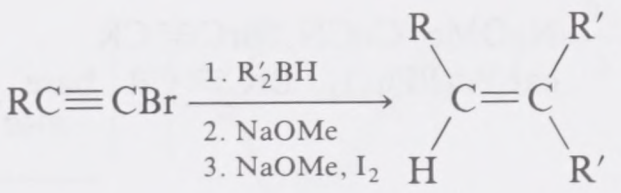
JOC *47* 171, 3806, 5407 (1982)



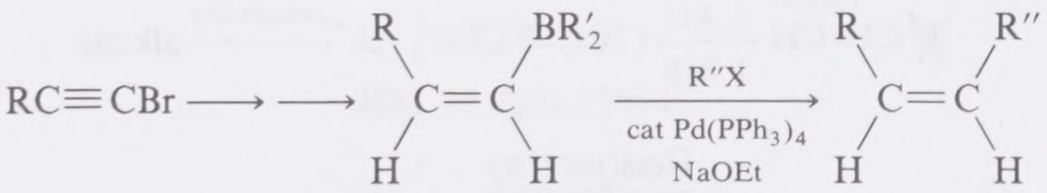
$X = Br, I$

Organoborane

R'_2BH	JACS *89* 5086 (1967); *94* 4013 (1972) Syn 555 (1972); 195 (1982) JOC *47* 754 (1982); *51* 5270 (1986) TL *23* 2785 (1982)
$R'BHBr \cdot SMe_2$	JOC *47* 3808 (1982); *51* 5270 (1986)
$(CH_3)_2CHC(CH_3)_2BHR'$	JOC *51* 5270 (1986)

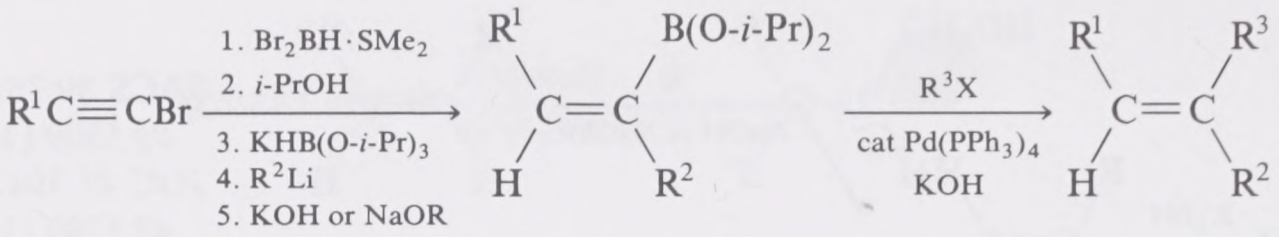


JOC *47* 754 (1982)



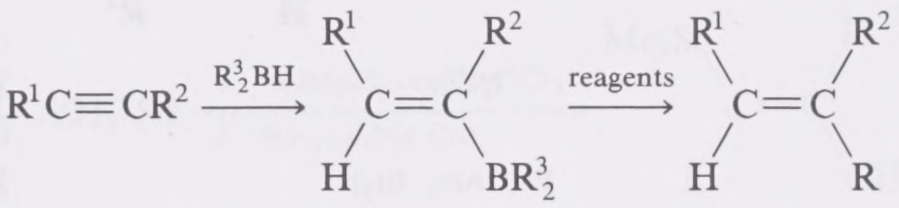
$R'' =$ aryl, vinylic

TL *27* 3745 (1986)

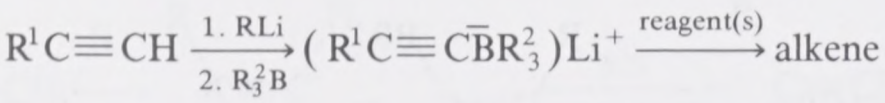


R^3 = allylic, aryl, vinylic

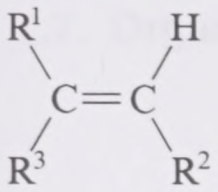
CL 1329 (1986)



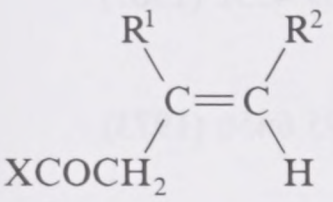
R	Reagents	
$CH_2CH{=}CH_2$	$NaOMe/CuBr \cdot SMe_2$ / $H_2C{=}CHCH_2Br$	JOC *45* 550 (1980)
	$MeLi/CuI/H_2C{=}CHCH_2Br$	BCSJ *53* 1471 (1980)
	$MeCu/H_2C{=}CHCH_2Br$	JOC *45* 1640 (1980)
	$Pd(OAc)_2$, $H_2C{=}CHCH_2Br$	BCSJ *53* 1670 (1980)
	cat $Pd(PPh_3)_4$, NaOH, $H_2C{=}CHCH_2Br$	TL *21* 2865 (1980)
$CH_2C{\equiv}CH$	$MeLi/CuI/HC{\equiv}CCH_2Br$	BCSJ *53* 1471 (1980)
CH_2Ar	cat $Pd(PPh_3)_4$, NaOH, $ArCH_2X$ (X = Cl, Br)	Tl *21* 2865 (1980) JOC *47* 2117 (1982)
Ar	cat $Pd(PPh_3)_4$, NaOH, ArI	JOC *47* 2117 (1982)
	cat $Pd(PPh_3)_4$, NaOEt, ArX (X = Br, I)	CC 866 (1979)
$CH{=}CHR'$	—	See page 248, Section 3.2.
$C{\equiv}CR$	$LiC{\equiv}CR/I_2$, OH^-	CC 874 (1973) TL *27* 539 (1986)
	$NaOMe/CuCN/BrC{\equiv}CR$	JACS *106* 462 (1984)
	cat $Pd(PPh_3)_4$, $BrC{\equiv}CR$, base	TL 3437 (1979); *22* 127 (1981) Tetr *37* 2617 (1981) JACS *107* 972 (1985) Pure Appl Chem *57* 1749 (1985)



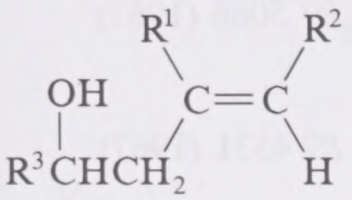
Alkene	Reagent(s)	
Z-$R^1CH{=}CHR^2$	RCO_2H	TL 2961 (1974); *28* 1007 (1987)
$R^1CH{=}CR_2^2$	HCl/I_2, OH^-	Syn 376 (1975)

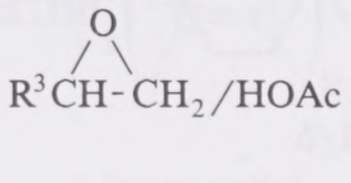


R^3X/HOAc — TL 1633 (1975); *28* 1003, 1007 (1987)

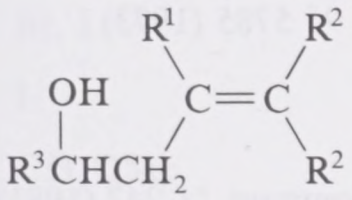


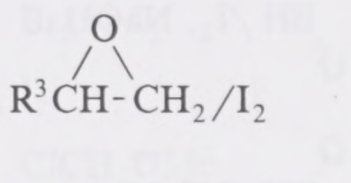
$BrCH_2COX$ (X = R, OR)/HOAc — TL 4491 (1973)



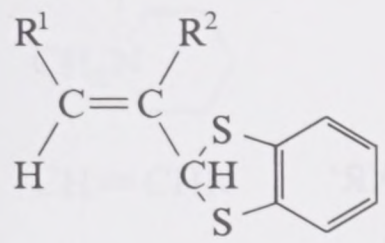


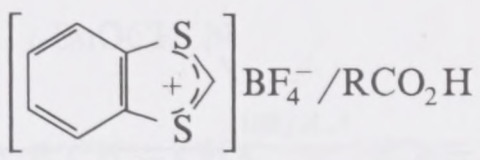
TL 2741 (1973)





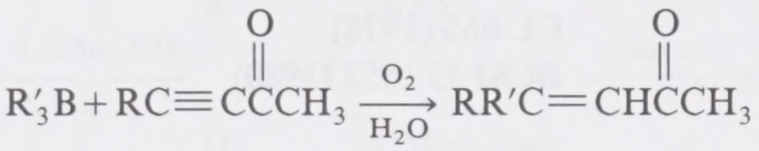
TL 2741 (1973)





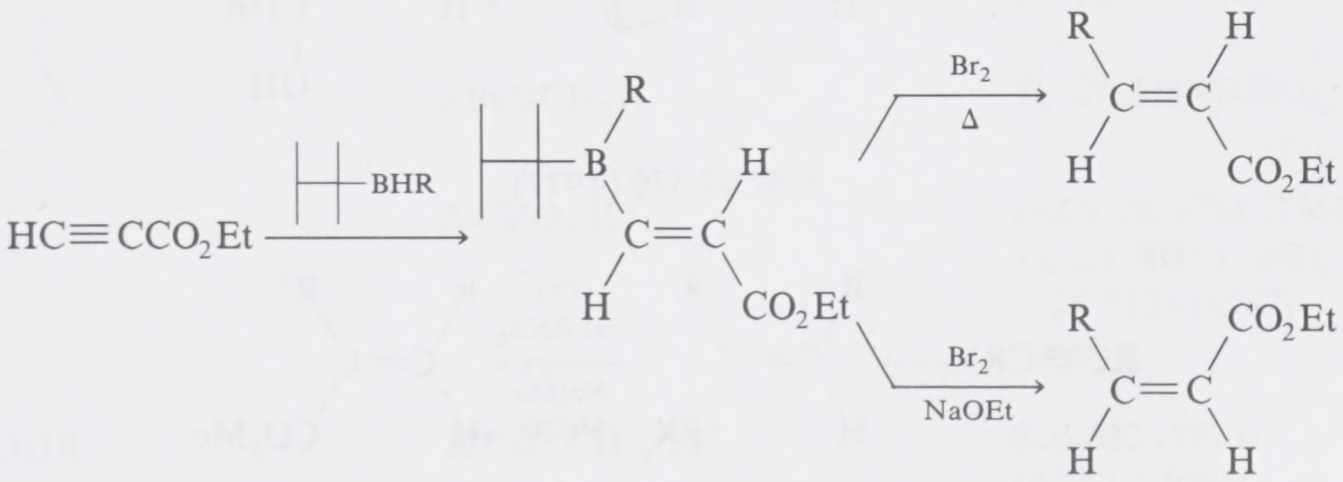
CC 164 (1981)

$R^2CH{=}CR'CHR^3CHXCO_2Et$ $R^3CH{=}CXCO_2Et$ (X = $COCH_3$, CO_2Et) — TL *22* 797 (1981)

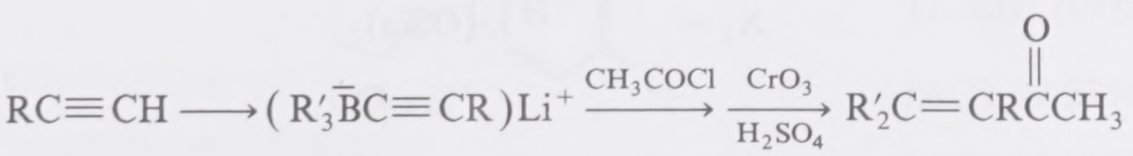


E + *Z*

JACS *92* 3503 (1970)

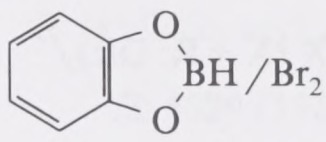
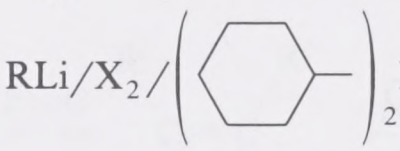
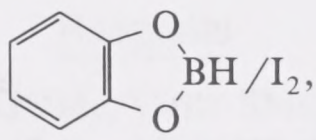
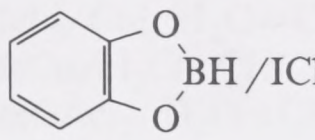


JOC *39* 2321 (1974)



TL 795 (1973)

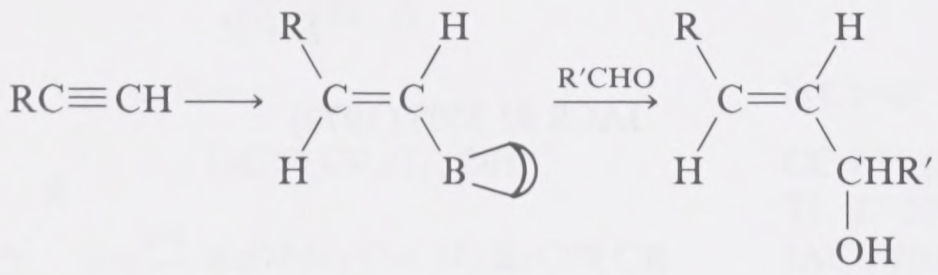
$$RC{\equiv}CH \longrightarrow RCH{=}CHX$$

Stereochemistry	X	Reagents	
cis	Br	$(Sia)_2BH/Br_2/H_2O$	JACS *89* 4531 (1967)
	Br		JACS *95* 6456 (1973)
	Br, I		JACS *89* 5086 (1967)
trans	Br	$(Sia)_2BH/\Delta$	JACS *89* 4531 (1967)
	I		JACS *95* 5785 (1973)
	I		Syn Commun *11* 247 (1981)

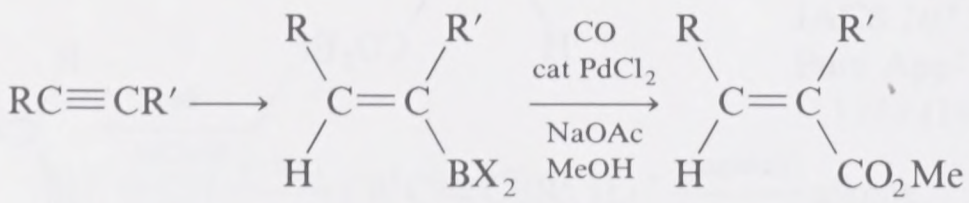
$$RC{\equiv}CH \longrightarrow RC{\equiv}CX \xrightarrow[2.\ Pb(OAc)_4 \text{ or } PhI(OAc)_2]{1.\ R'_2BH} RCH{=}CXR'$$

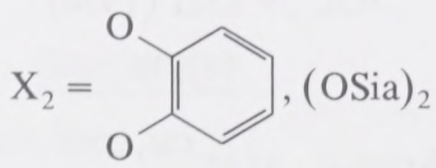
X = Cl (*Z*)
X = Br (*E* or *Z*)

CL 665 (1978)
BCSJ *53* 1652 (1980)



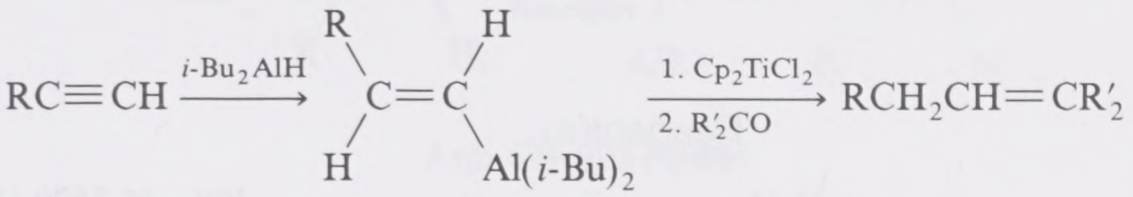
JOC *42* 579 (1977)



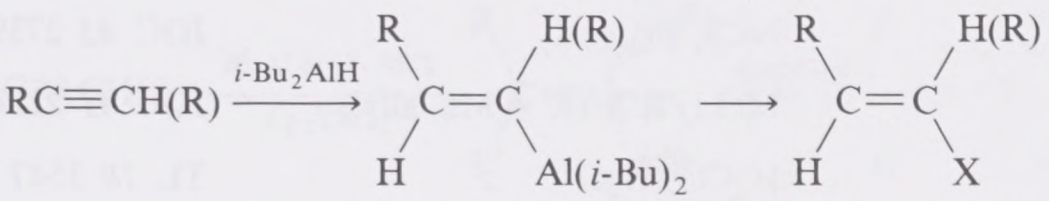


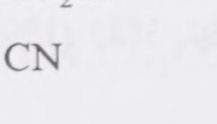
CL 879 (1981); 1329 (1986)

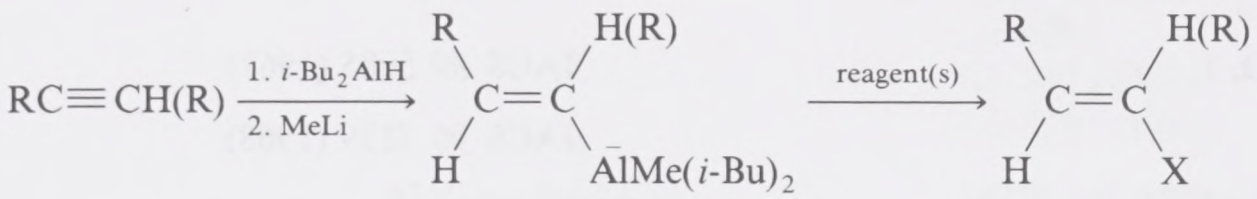
2.7. Organoaluminum Compounds



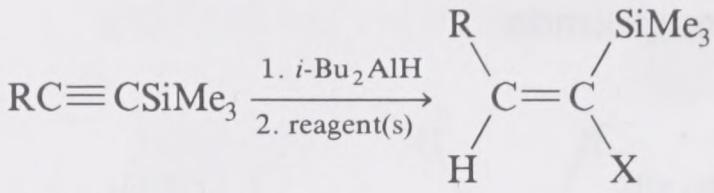
CL 429 (1982)

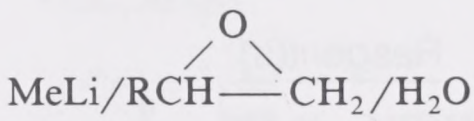


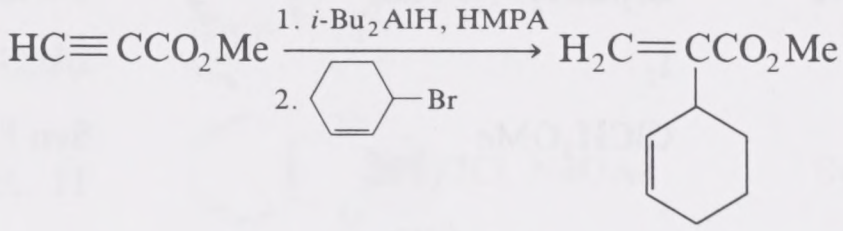
X	Reagent(s)	
Br, I	Br_2 or I_2	JACS *89* 2753 (1967)
I	I_2	JACS *108* 3403, 7791 (1986)
CH_2OMe	$ClCH_2OMe$	Syn 816 (1976) TL *23* 2087 (1982)
	*i*-BuOCH_2	TL *21* 3763 (1980)
CH=CHR′	R′CH=CHX, cat Ni(O) R′CH=CHX, cat Pd(O)	JACS *109* 2393 (1987) JACS *98* 6729 (1976); *109* 2393 (1987) TL *28* 1649, 4875 (1987)



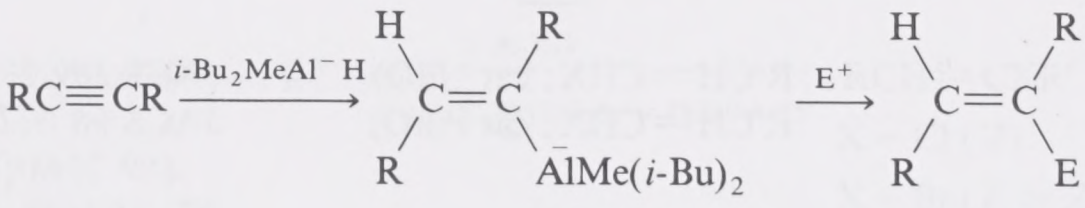
X	Reagent(s)	
R′	R′X	TL 1927 (1976)
	i-BuOCH_2	TL *21* 3763 (1980)
CHOHR′	R′CHO/H^+	JACS *89* 2754 (1967) TL *23* 2087 (1982); *28* 5129 (1987)
CH_2CHOHR'		Syn 632 (1975) CC 17 (1976)
		TL 4083 (1972)
CO_2H	CO_2/H^+	JACS *89* 2754 (1967)
CN	$(CN)_2$	JACS *90* 7139 (1968)



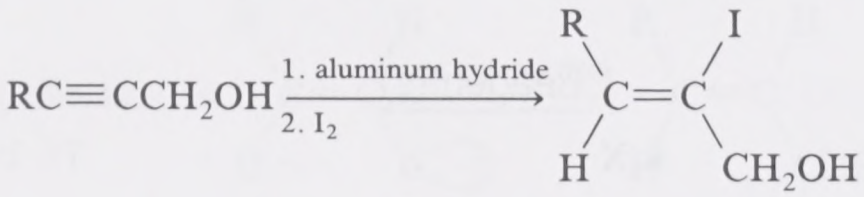
X	Reagent(s)	
H	H_2O	JOC *36* 3520 (1971) Syn 803 (1980)
Cl, Br, I	NCS, Br_2 or I_2	JOC *43* 2739 (1978)
R′	MeLi/R′X (R′ = Me, allyl)	JOC *41* 2214, 2215 (1976)
CH_2OH	H_2CO/H_2O	TL *28* 3547 (1987)
CH_2CHOHR		JACS *106* 4192 (1984)



JOC *52* 1624 (1987)

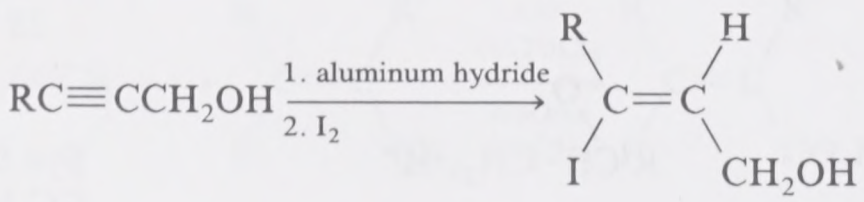


E^+	
CO_2, H_2CO, I_2	JACS *89* 5085 (1967)
$(CN)_2$	JACS *90* 7139 (1968)



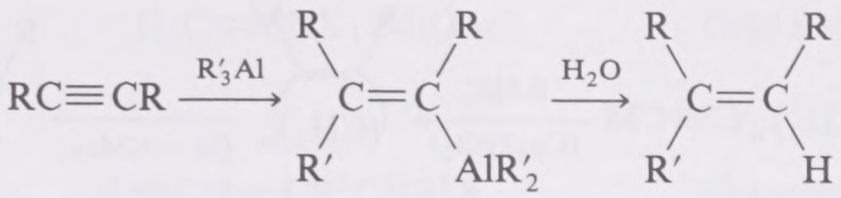
Aluminum hydride

$LiAlH_4$, cat $AlCl_3$	JACS *89* 4245 (1967); *91* 4318 (1969)
n-BuLi/*i*-Bu_2AlH	JACS *92* 6314 (1970)

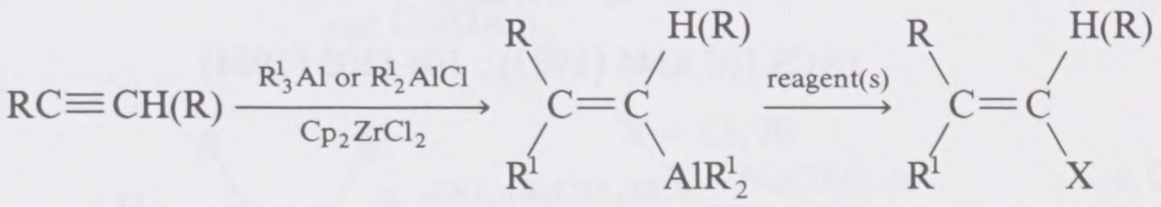


Aluminum hydride

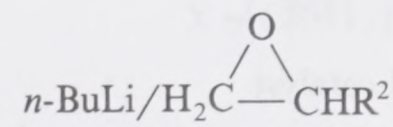
$LiAlH_4$, $NaOCH_3$	JACS *89* 4245 (1967); *90* 5618 (1968) TL 1821 (1971); *28* 5793 (1987)
$NaAlH_2(OCH_2CH_2OCH_3)_2$	JOC *51* 4316 (1986); *52* 1236, 3860, 3883 (1987) TL *28* 723 (1987)

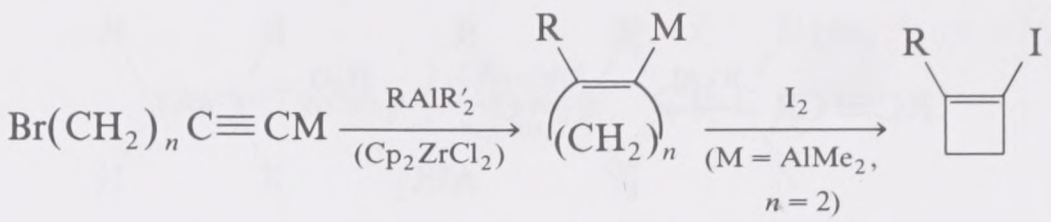


Ann *629* 222 (1960)



Review: Pure Appl Chem *53* 2333 (1981)

X	Reagent(s)	
H or D	H_2O or D_2O	JACS *100* 2252 (1978); *103* 4985 (1981); *107* 6639 (1985) JOC *46* 4093 (1981) TL *27* 3311 (1986)
I	I_2	JACS *100* 2252 (1978); *102* 3298 (1980); *104* 4708 (1984); *107* 6639 (1985); *108* 7791 (1986) Syn 501 (1979) TL *23* 27 (1982) JOC *46* 4094 (1981); *51* 2230 (1986) CL 293 (1982) CC 1237 (1986)
R^2	R^2X, cat Pd(O) or Ni(O), $ZnCl_2$ (R^2 = aryl, vinylic, alkynyl, allylic, benzylic)	JACS *100* 2254 (1978); *103* 2882 (1981) TL *22* 2715 (1981); *28* 2221 (1987) Acct Chem Res *15* 340 (1982) (review)
CH_2OH	*n*-BuLi/CH_2O	TL 2357 (1978)
CH_2OMe	*n*-BuLi/$ClCH_2OMe$	TL 2357 (1978)
CO_2H	*n*-BuLi/CO_2/H^+	TL 2357 (1978) JOC *46* 4094 (1981)
CO_2Et	$ClCO_2Et$	TL 2357 (1978); *23* 27 (1982) JOC *46* 4094 (1981)
CH_2CHOHR^2	*n*-BuLi/ 	Syn 1034 (1980) JOC *45* 5223 (1980)
$CH_2CH_2COCH_3$	$H_2C{=}CHCOCH_3$	Pure Appl Chem *53* 2333 (1981)

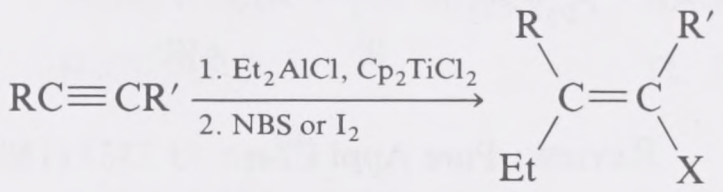


$n = 2, 4$

$M = AlMe_2, SiMe_3$

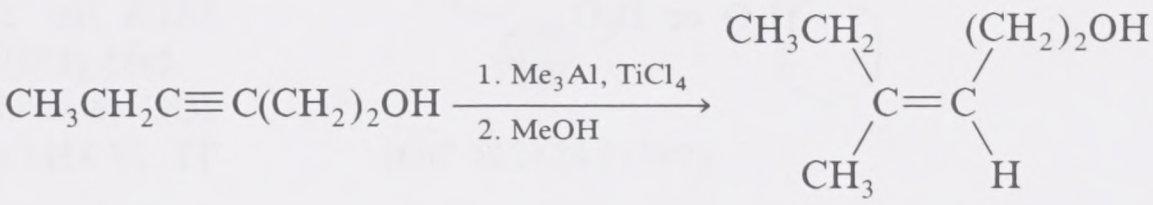
R = H, alkyl

JACS *105* 6344 (1983); *106* 6105 (1984)

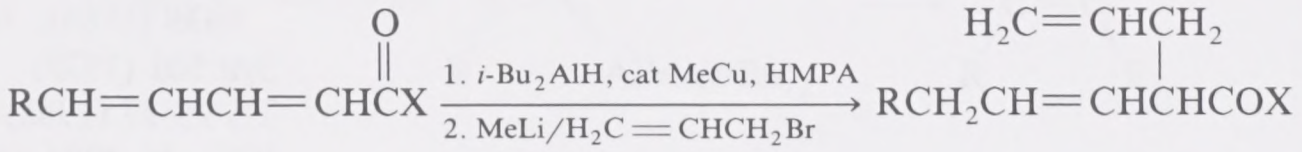


R′ = Ph, $SiMe_3$; X = Br, I

JOC *50* 2121 (1985)



JOC *46* 807 (1981); *50* 2124 (1985)

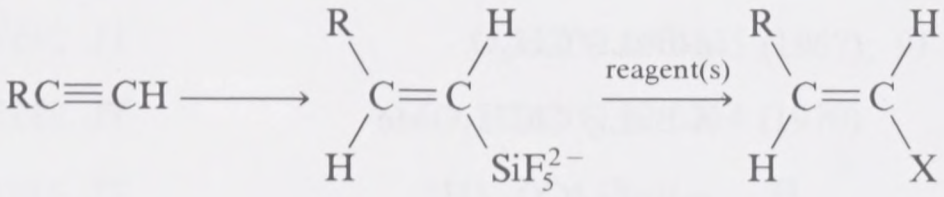


X = Me, OMe

JOC *52* 439 (1987)

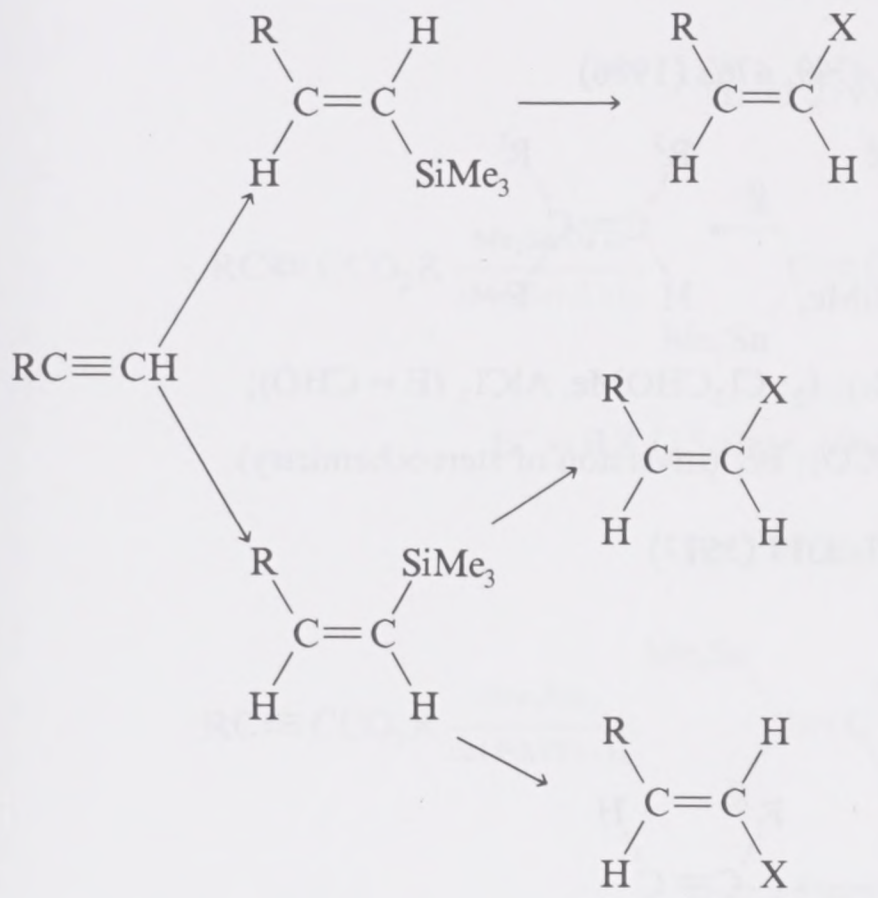
2.8. Organosilicon Compounds

Review: Syn 761 (1979) (electrophilic substitution of organosilicon compounds)



X	Reagent(s)	
Cl, Br	$CuCl_2$, $CuBr_2$	Organomet *1* 369 (1982)
Cl, Br, I	Cl_2, Br_2, NBS, I_2	Organomet *1* 355 (1982)
Ph	PhI, Pd catalyst	Organomet *1* 542 (1982)
CO_2R	CO, ROH, $PdCl_2$, NaOAc	Organomet *1* 542 (1982)
E-CH=CHR	$PdCl_2$	Organomet *1* 542 (1982)

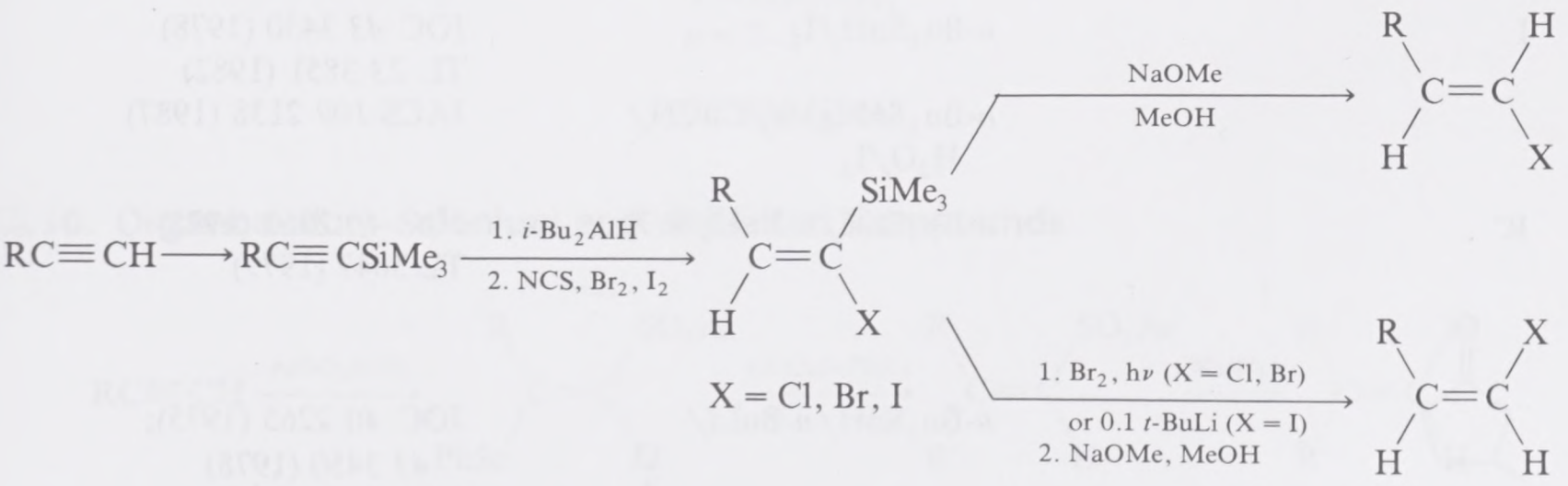
E-CH=CHX (X = CHO, CO_2R, CN)	$H_2C{=}CHX$, $Pd(OAc)_2$	Organomet *1* 542 (1982)
$CHR^1CR^2{=}CHR^3$	$R^1CH{=}CR^2CHR^3X$, $Pd(OAc)_2$ (X = Cl, Br, OTs)	Organomet *1* 542 (1982)
OR′	R′OH, O_2, cat $Cu(OAc)_2$	TL *21* 4105 (1980)



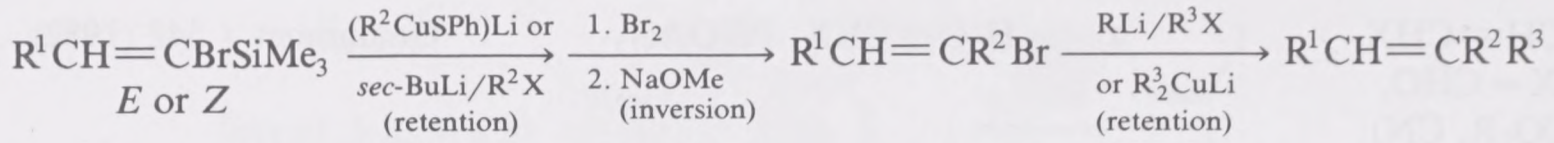
	X = Cl, Br X_2/NaOMe or KF or alumina	Syn Commun *7* 475 (1977); *8* 291 (1978) JOC *43* 4424 (1978)
	X = Br *m*-$ClC_6H_4CO_3H$/HBr, BF_3	JACS *99* 1993 (1977)
	X = I ICl/KF	JOMC *285* 109 (1985)
	X = I I_2 or I_2-AgO_2CCF_3/KF	TL 543 (1976); 3317 (1977)
	X = Cl, Br X_2/NaOMe or KF or alumina	Syn Commun *7* 475 (1977); *8* 291 (1978) JOC *43* 4424 (1978)
	X = Br *m*-$ClC_6H_4CO_3H$/HBr, BF_3	TL 1453 (1976) JACS *99* 1993 (1977)

Reviews:

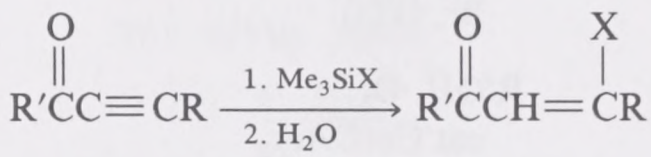
Syn 761 (1979) (halogenation of organosilanes)
TL *27* 883 (1986) (I_2, $AlCl_3$ or $SnCl_4$- variable stereochemistry)
JOC *52* 1100 (1987) (stereochemistry of halogenation)



JOC *43* 2739 (1978)
Syn 999 (1981)

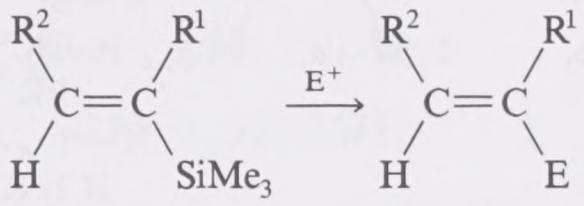


JOC *44* 4623 (1979)



R = H or alkyl
X = Br, I

TL *27* 4759, 4763 (1986)

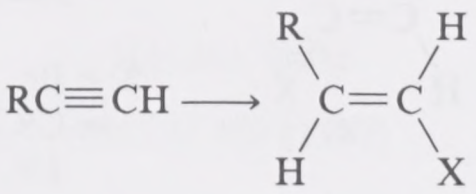


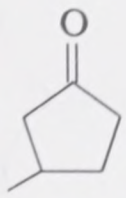
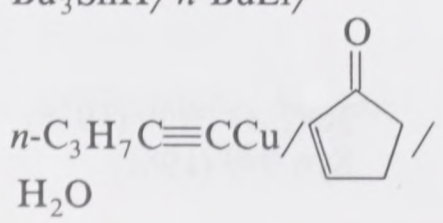
E^+ = HI; BrCN, $AlCl_3$ (E = Br); I_2; Cl_2CHOMe, $AlCl_3$ (E = CHO);

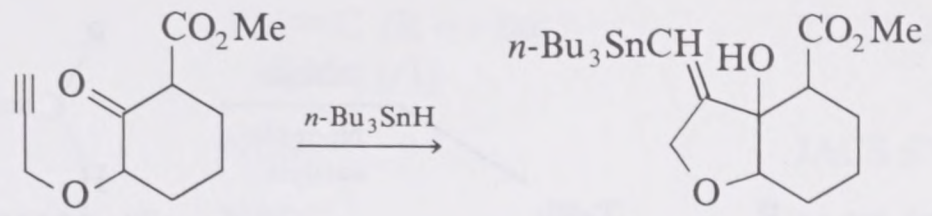
CH_3COCl, $AlCl_3$ (E = CH_3CO); Br_2 (inversion of stereochemistry)

TL 3317 (1977)

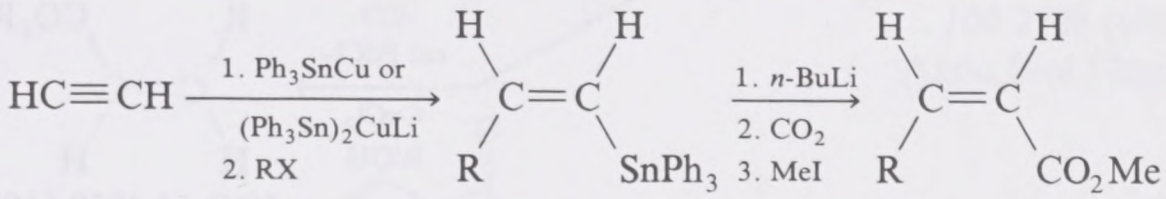
2.9. Organotin Compounds



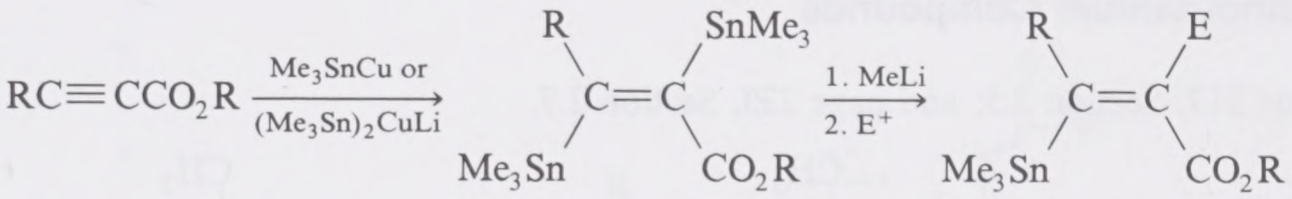
X	Reagents	
Br	*n*-Bu_3SnH/Br_2	JOC *43* 3450 (1978) JACS *106* 5734 (1984); *107* 7515 (1985)
I	*n*-Bu_3SnH/I_2	JOC *43* 3450 (1978) TL *23* 3851 (1982)
	n-$Bu_3SnMgMe/CuCN/H_2O/I_2$	JACS *109* 2138 (1987)
R′	*n*-Bu_3SnH/*n*-BuLi/R′X	JOC *40* 2265 (1975) TL 3847 (1977)
	*n*-Bu_3SnH/*n*-BuLi/  H_2O	JOC *40* 2265 (1975); *43* 3450 (1978) TL 4705 (1976)



TL *28* 2001 (1987)

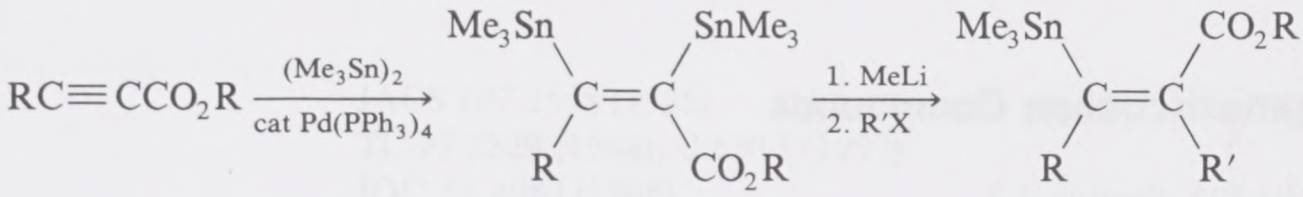


TL *23* 2797 (1982)

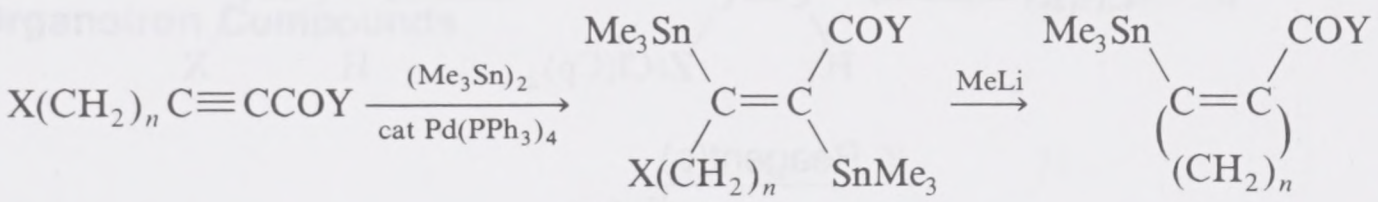


$E^+ = RX$ (1° alkyl, allylic, benzylic), R_2CO

JOC *47* 1602 (1982)



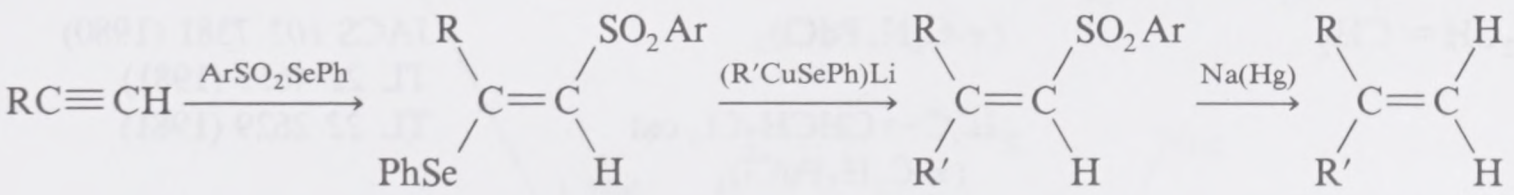
JOC *52* 4421 (1987)



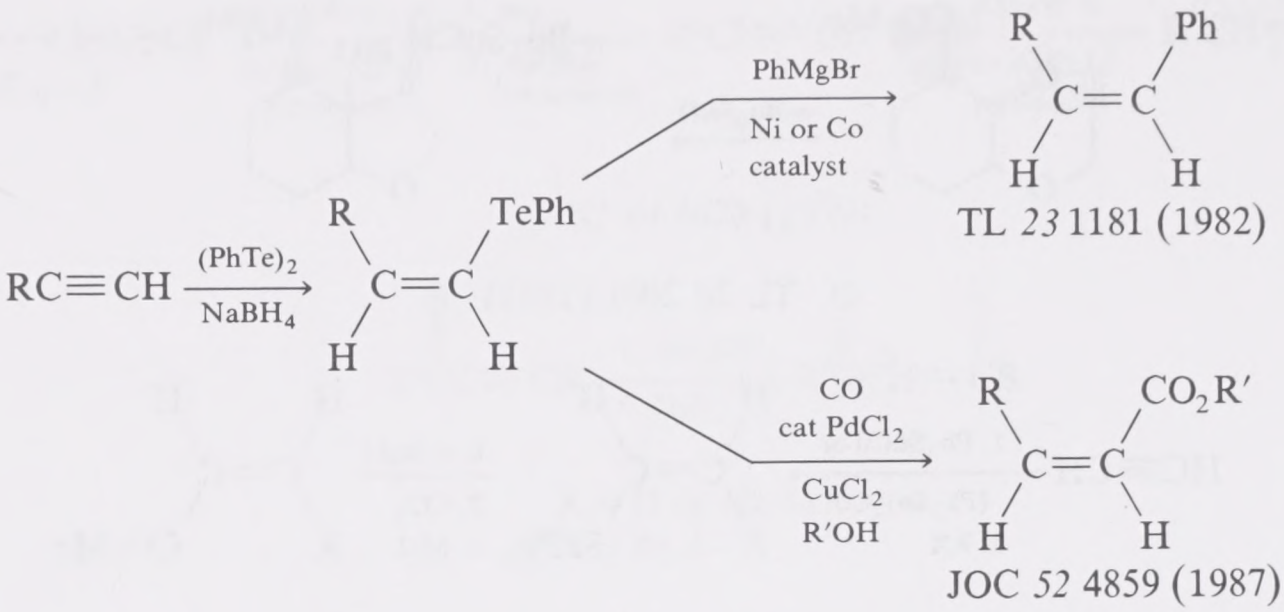
X = halogen
Y = OR, NR_2
n = 3–5

CC 626 (1986)

2.10. Organosulfur, -selenium and -tellurium Compounds

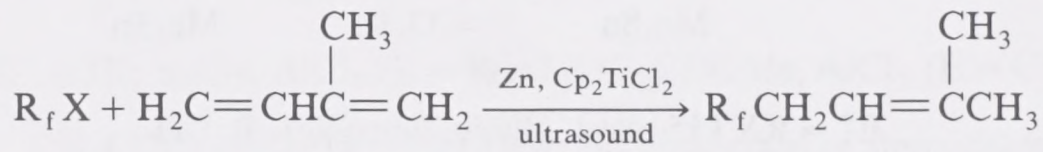


TL *27* 2187 (1986)
JOC *52* 4258 (1987)



2.11. Organotitanium Compounds

See also page 217, Section 2.5; and page 223, Section 2.7.

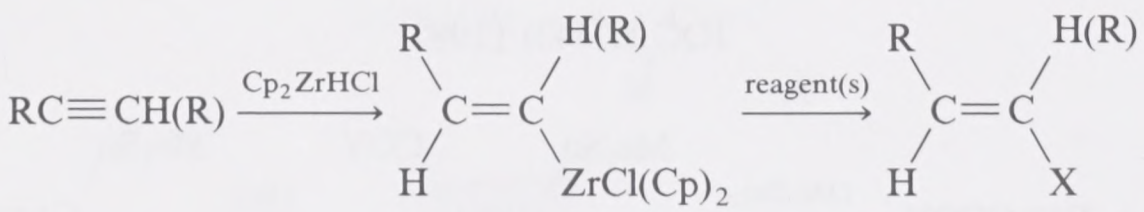


X = Br, I

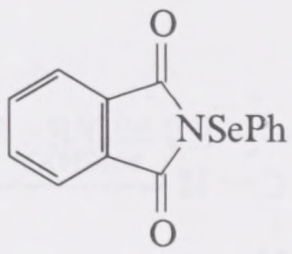
JACS *107* 5186 (1985)

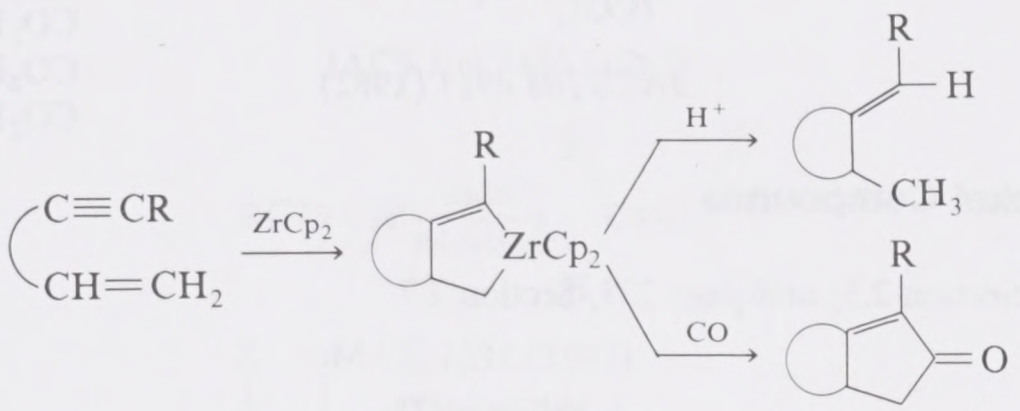
2.12. Organozirconium Compounds

See also page 223, Section 2.7.



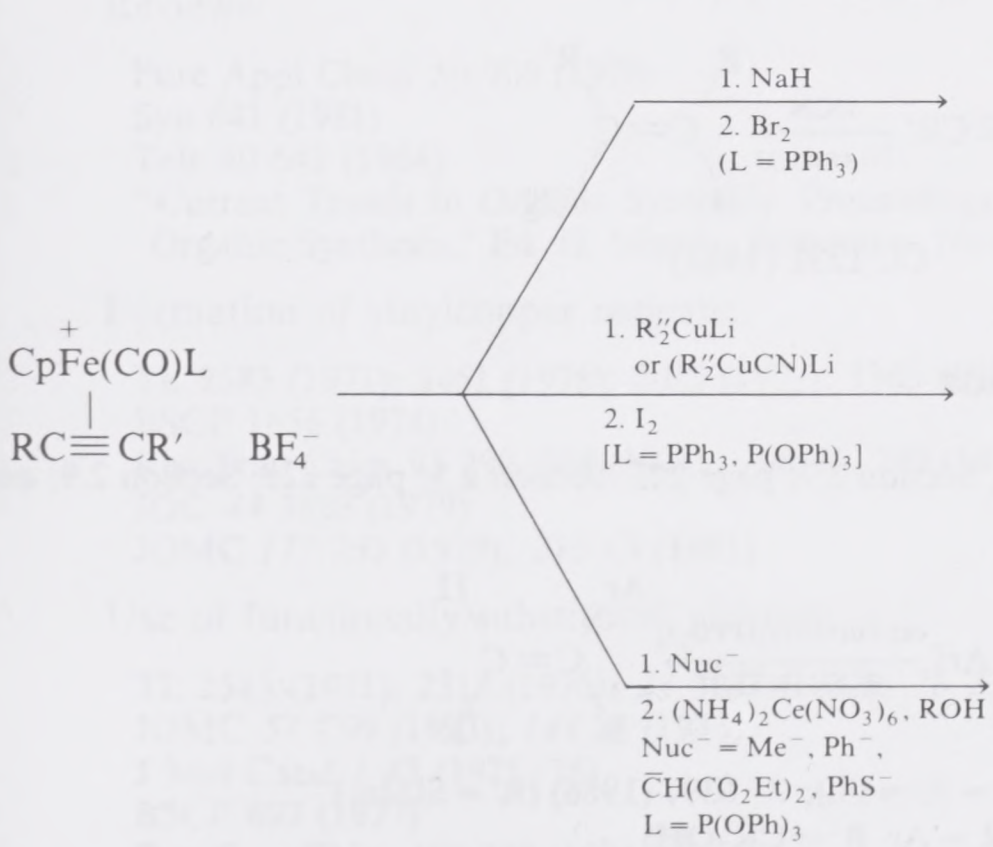
X	Reagent(s)	
Ar	ArI, cat $Ni(PPh_3)_4$	JACS *99* 3168 (1977) JOC *52* 3319 (1987)
$CH=CHR^1$	$R^1CH=CHX$, cat Pd(O)	TL 1027 (1978); *23* 62 (1982); *28* 4875, 4879 (1987) JACS *109* 2393 (1987)
$CH(R)=CHR$	$CuCl_2$	TL 1303 (1977)
$CH_2CH=CH_2$	$(\pi\text{-}C_3H_5PdCl)_2$	JACS *102* 7381 (1980) TL *22* 4655 (1981)
	$H_2C=CHCH_2Cl$, cat $(\pi\text{-}C_3H_5PdCl)_2$	TL *22* 2629 (1981)
$CH_2CH_2COR^1$	$H_2C=CHCOR^1$, cat $Ni(acac)_2$	JACS *99* 8045 (1977)
	$H_2C=CHCOR^1$, CuOTf, LiI	TL 1303 (1977)

CN	$RN{=}C$ (R = *t*-Bu, $SiMe_3$)/I_2	TL *28* 295 (1987)
Cl	NCS	JACS *97* 679 (1975)
Br	NBS	JACS *97* 679 (1975); *108* 5559 (1986)
I	I_2	JACS *97* 679 (1975); *109* 2138 (1987) Agric Biol Chem *46* 717 (1982)
SePh		JOC *52* 2334 (1987)



JACS *107* 2568 (1985)
TL *27* 2829 (1986); *28* 917 (1987)
JOC *51* 4080 (1986)

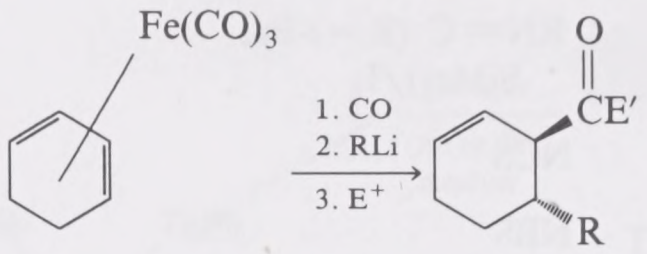
2.13. Organoiron Compounds



JACS *102* 5923 (1980)

JACS *102* 5923 (1980)
Organomet *1* 443 (1982); *2* 101 (1983); *3* 134 (1984)

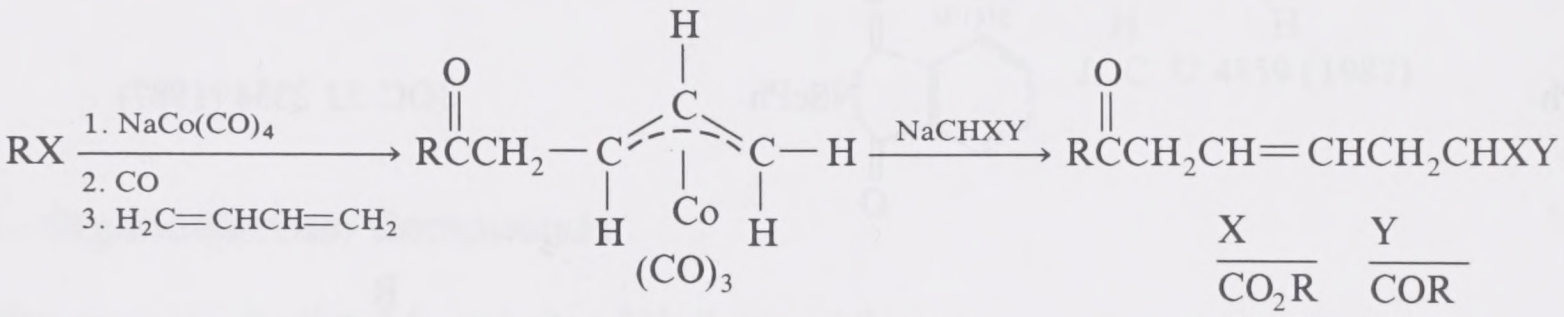
JACS *108* 1940 (1986)



R = stabilized anion; $E^+ = CF_3CO_2H$, MeI, $EtOSO_2F$ (E′ = OEt)

JACS *105* 2497 (1983)

2.14. Organocobalt Compounds

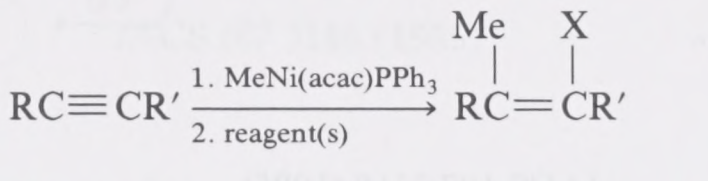


JACS *104* 4917 (1982)

X	Y
CO_2R	COR
CO_2R	CO_2R
CO_2R	CN

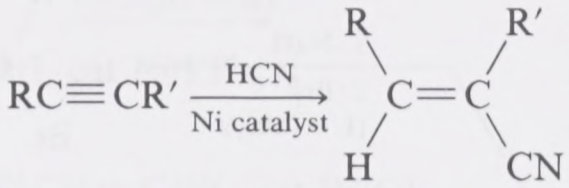
2.15. Organonickel Compounds

See also page 217, Section 2.5; and page 223, Section 2.7.



X	Reagent(s)
H	TsOH or $LiAlH_4$
Me	Me_3Al or MeLi
I	I_2
CO_2Me	CO, MeOH

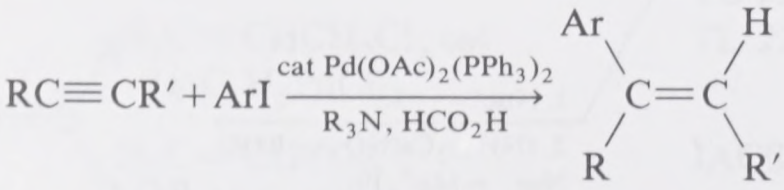
JACS *103* 3002 (1981)



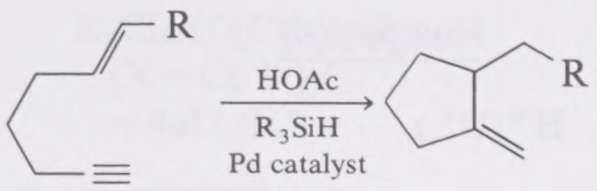
CC 1231 (1982)

2.16. Organopalladium Compounds

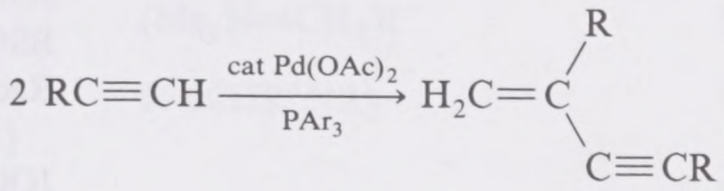
See also page 218, Section 2.6; page 223, Section 2.7; page 226, Section 2.8; page 228, Section 2.9; and page 239, Section 2.19.

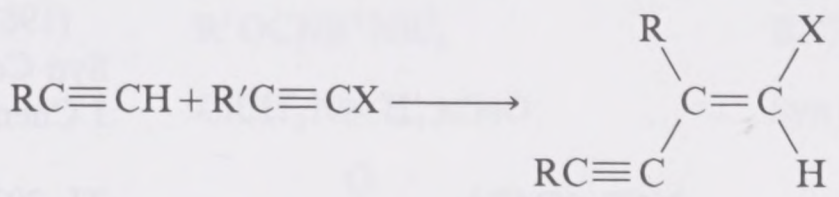


TL *25* 3137 (1984) (R = R′ = Ph); *27* 6397 (1986) ($R' = SiMe_3$)
Tetr *41* 5121 (1985) ($R = Ar, R' = CR_2OH$)



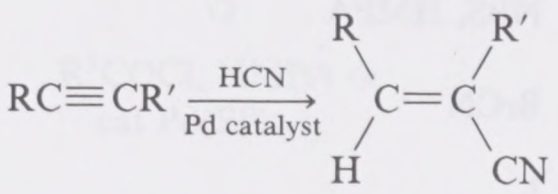
JACS *109* 3061 (1987)





X = CO_2Me, SO_2Ph

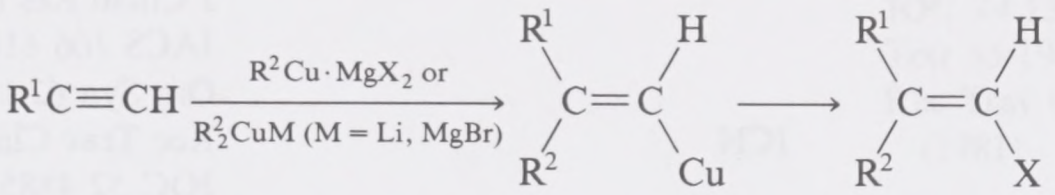
JACS *109* 3486 (1987)



CC 1231 (1982)

2.17. Organocopper Compounds

See also page 217, Section 2.5; page 218, Section 2.6; page 228, Section 2.9; and page 231, Section 2.13.



Reviews:

Pure Appl Chem *50* 709 (1978)
Syn 841 (1981)
Tetr *40* 641 (1984)
"Current Trends in Organic Synthesis. Proceedings of the 4th International Conference on Organic Synthesis," Ed. H. Nozaki, Pergamon, New York (1982), pp 291–302

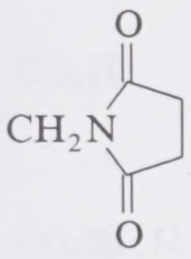
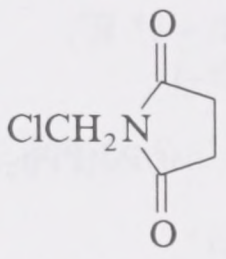
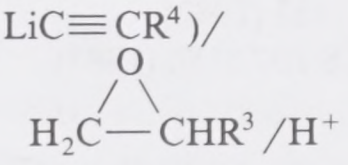
Formation of vinylcopper reagent:

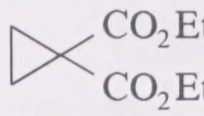
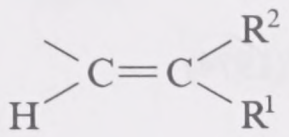
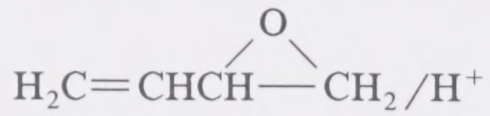
TL 2583 (1971); 3461 (1976); 2023 (1977); 1363 (1978)
BSCF 1656 (1974)
Rec Trav Chim *95* 299, 304 (1976); *100* 98, 249 (1981)
JOC *44* 3888 (1979)
JOMC *177* 293 (1979); *215* C1 (1981)

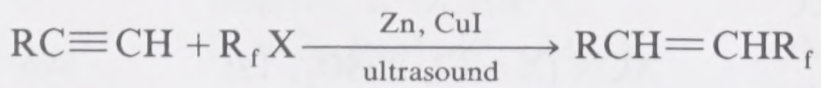
Use of functionally substituted alkynes:

TL 2583 (1971); 2313 (1976); *24* 5077 (1983); *28* 2363 (1987)
JOMC *57* C99 (1973); *144* 13 (1983)
J Mol Catal *1* 43 (1975/76)
BSCF 693 (1977)
Rec Trav Chim *100* 337 (1981)

X	Reagent(s)	
H(D)	H^+ (D^+)	TL 2583 (1971); 2023 (1977); 1363 (1978); *23* 5155 (1978); *24* 5077 (1983) JOMC *77* 269 (1974) BSCF 1656 (1974) Rec Trav Chim *95* 299, 304 (1976); *100* 98, 337 (1981) JOC *44* 3888 (1979); *52* 5419 (1987) Syn Commun *11* 157 (1981) J Chem Res (S) 354 (1981)
Cl	NCS, HMPA	TL 2023, 3545 (1977) Rec Trav Chim *96* 168 (1977)
Br	$HgBr_2/Br_2$, py	Syn 803 (1974)
	NBS, HMPA	TL 2023, 3545 (1977) Rec Trav Chim *96* 168 (1977)
	BrCN	Rec Trav Chim *96* 168 (1977)
I	I_2	TL 2583 (1971); 3461 (1976); *23* 5155 (1982) JOMC *77* 269 (1974); *177* 293 (1979) Rec Trav Chim *96* 168 (1977) JOC *43* 1279 (1978); *52* 1381 (1987) J Chem Res (S) 354 (1981) JACS *106* 6105 (1984) Org Syn *62* 1 (1984)
	ICN	Rec Trav Chim *96* 168 (1977) JOC *52* 4885 (1987)
R^3	R^3X, HMPA, $P(OR^4)_3$ R^3 = 1° alkyl, allylic, benzylic, R^5OCHR^6X; X = Cl, Br, I; R^4 = Me, Et	TL 2583 (1971); 1363, 3125 (1978); 1433 (1980); *23* 3587, 5155 (1982) JOMC *40* C49 (1972); *77* 269 (1974) Syn 826 (1979) JOC *44* 1345, 3888 (1979) Rec Trav Chim *100* 249 (1981) J Chem Res (S) 354 (1981) Org Syn *64* 1 (1986)
Ar	ArI, $ZnBr_2$, cat $Pd(PPh_3)_4$	TL *22* 3851 (1981) BSCF II 321 (1983)
$CH(OMe)R^3$	$R^3CH(OMe)_2$, $BF_3 \cdot OEt_2$	TL *25* 3075 (1984)
CH_2OH	H_2CO/H^+	Tetr *36* 1961 (1980)

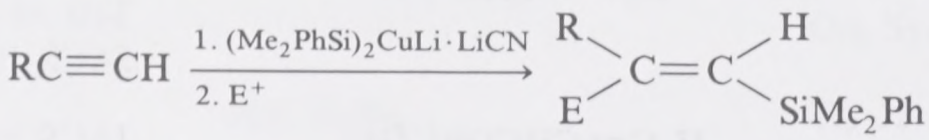
$CHOHR^3$	$R_3CHXO(CH_2)_2Cl$ (X = Cl, Br)/ *n*-BuLi/H^+	TL 2407 (1973) JOMC *77* 269 (1974)
CHR^3SR^4	$ClCHR^3SR^4$	JOMC *77* 269 (1974) Syn 43 (1984)
CH_2NMe_2	$(Me_2\overset{+}{N}{=}CH_2)I^-$	BSCF II 377 (1984)
$CHR^4NR^3_2$	$R^5SCHR^4NR^3_2$	TL *21* 3763 (1980); *23* 5155 (1982) BSCF II 377 (1984)
	$R^5OCHR^4NR^3_2$	BSCF II 377 (1984)
$CH_2N(CH_3)CHO$	$ClCH_2N(CH_3)CHO$	Syn 40 (1984)
		Syn 40 (1984)
COR^3	R^3COCl, HMPA or cat $Pd(PPh_3)_4$	TL 1363 (1978); *24* 5081 (1983) JOC *44* 3888 (1979) Pure Appl Chem *56* 91 (1984) Tetr *42* 1369 (1986)
CO_2H	CO_2, HMPA, cat $P(OEt)_3/H^+$	JOMC *54* C53 (1973); *77* 281 (1974); *144* 13 (1978) TL 3461 (1976); *23* 5155 (1982) JOC *44* 1345 (1979) Tetr *36* 1961 (1980) Rec Trav Chim *100* 249 (1981)
CS_2CH_3	CS_2/CH_3I	Syn 432 (1979)
CONHPh	$PhNCO/H^+$	JOMC *54* C53 (1973); *77* 281 (1974)
CN	XCN (X = Cl, $PhSO_2$, Ts)	Syn 784 (1977) JOMC *206* 257 (1981)
CH_2CHR^3OH	$(LiC{\equiv}CR^4)$/ 	TL 3461 (1976); 1363, 2465 (1978) JOC *44* 1345, 3888 (1979) Tetr *36* 1961 (1980) JACS *104* 1774 (1982)
$CH_2CH_2COR^3$	$H_2C{=}CHCOR^3/H^+$	JACS *99* 253 (1977) TL 1363 (1978) JOC *44* 3888 (1979) Tetr *36* 1961 (1980) Pure Appl Chem *56* 91 (1984)

$CH_2CH_2CH(CO_2Et)_2$		Tetr *36* 1961 (1980)
	O_2 or Δ	TL 2583 (1971) JOMC *77* 269 (1974) BSCF 1656 (1974) Rec Trav Chim *95* 299, 304 (1976)
$CH{=}CHR^3$	$XCH{=}CHR^3$ (X = Br, I), $ZnBr_2$, cat $Pd(PPh_3)_4$	TL *22* 959 (1981); *23* 1589, 5155 (1982) BSCF II 321, 332 (1983) Tetr *40* 2741 (1984)
Z-$CH{=}CHE$	$HC{\equiv}CH/E^+$ (E = 1° R^3, CO_2H, CH_2NEt_2)	BSCF 1656 (1974) TL *23* 5151 (1982)
E-$CH{=}CHCOR$	$XCH{=}CHCOR$, cat $Pd(PPh_3)_4$	Tetr *42* 1369 (1986)
E-$CH{=}CHCO_2Et$	$HC{\equiv}CCO_2Et/H^+$ (other alkynes also)	TL 3461 (1976); *23* 5151, 5155 (1982) Tetr *36* 1961 (1980)
Z,Z-$CH{=}CHCH{=}CHE$	2 $HC{\equiv}CH/E^+$ (E^+ = RX, I_2, RCHO, CO_2, enone, $HC{\equiv}CCO_2Et$)	JCS Perkin I 1809 (1986)
Z-$CH_2CH{=}CHR'$	$(H_2C{=}CHPPh_3)Br$/ R′CHO	TL *26* 1799 (1985) JOC *52* 1801 (1987)
E-$CH_2CH{=}CHCH_2OH$		Syn 528 (1978) TL 2027 (1978)
$C{\equiv}CR^3$	$XC{\equiv}CR^3$ (X = Br, I), TMEDA	TL 1465 (1975) Syn 826 (1979) Tetr *36* 1215 (1980)
	$TsO(Ph)IC{\equiv}CR^3$	JACS *109* 7561 (1987)



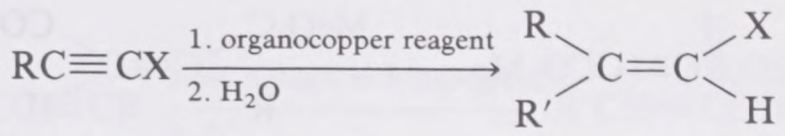
X = Br, I

CL 1453 (1982)
JACS *107* 5186 (1985)

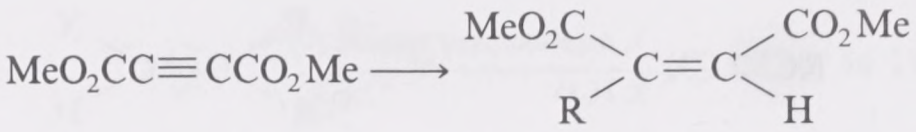


$E^+ = H^+, I_2$, RX, RCOCl, CO_2, enone, epoxide

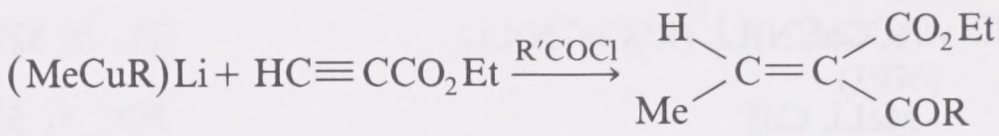
JCS Perkin I 2527 (1981)



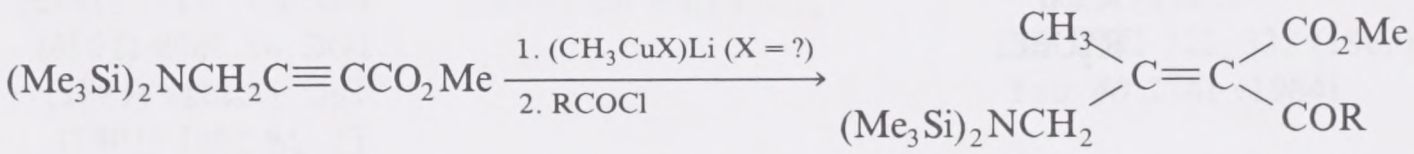
X	Reagent(s)	
$COCF_3$	$(R'CuCN)Li$, $(R'_2CuCN)Li_2$	TL *28* 5271 (1987)
COR	MeLi, CuI	JOC *51* 5320 (1986) (on HC≡CCOR)
	R′Cu	JACS *97* 1197 (1975)
	R'_2CuLi	JOC *41* 3629 (1976) Tetr *37* 4027 (1981) TL *28* 5081 (1987)
CO_2H	R′Cu	JACS *91* 6186 (1969) JCS C 1380 (1970)
	R'_2CuLi	JACS *91* 6186 (1969)
CO_2R	R′Cu	JCS C 1380 (1970) JACS *94* 4395, 5374 (1972); *97* 1197 (1975) TL 1811 (1979); *27* 5471 (1986); *28* 2964 (1987)
	R'_2CuLi	JACS *91* 1851, 1853 (1969); *94* 4395 (1972); *97* 1197 (1975); *103* 7007 (1981); *109* 6199 (1987) Helv *54* 1939 (1971) Acta Chem Scand *25* 1471 (1971) TL 1277, 1281 (1973); 1811 (1979); *21* 2057 (1980); *28* 2963, 5473 (1987) JOC *41* 3629 (1976); *51* 1077 (1986); *52* 398 (1987) CC 1220 (1987)
	$[\mathbf{R'}CuC{\equiv}C(CH_2)_3CH_3]Li$	JACS *94* 7210 (1972) TL *28* 2963 (1987)
	$(\mathbf{RC}(\mathbf{OSiMe_2}(t\text{-}\mathbf{Bu}))\mathbf{=CHCH_2}CuC{\equiv}CSiMe_3)Li$	JACS *107* 5495 (1985)
	$(\mathbf{RC}(\mathbf{OSiMe_2}(t\text{-}\mathbf{Bu}))\mathbf{=C=CH}CuC{\equiv}CSiMe_3)Li$	TL *28* 1299 (1987)
	$(\mathbf{RCH=CR}CuC{\equiv}CCMe_2OMe)Li$	JACS *108* 5559 (1986)
	$(Z\text{-}RCH{=}CHCuSPh)Li$	TL 3461 (1976)
CN	$R'Cu{\cdot}MgX_2$, R'_2CuLi	Syn 454 (1978)
	R'_2CuLi	JACS *106* 462 (1984)
CO_2H, CO_2R, CHO, COR	$R'Cu{\cdot}BR_3$	JOC *44* 1744 (1979)



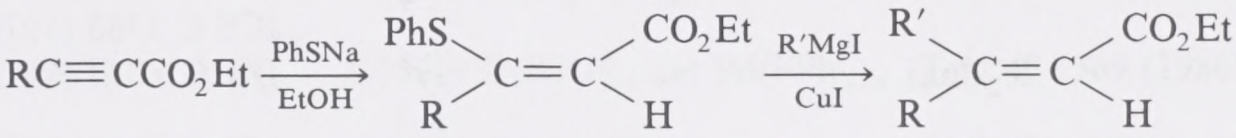
$MeCu/H_2O$ JACS *95* 6149 (1973)
$RCu \cdot MgX_2/H_2O$ CL 905 (1981)
$RCu \cdot BR'_3/H_2O$ JOC *44* 1744 (1979)



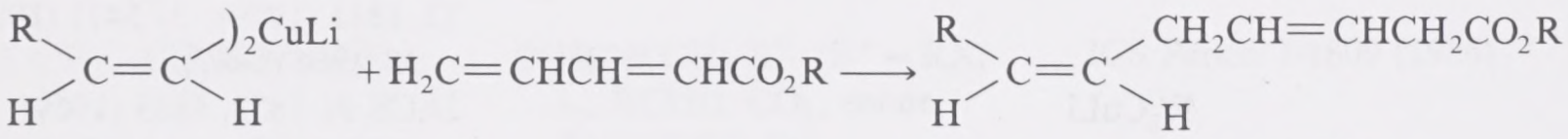
JOC *46* 3696 (1981)



TL *28* 2963 (1987)

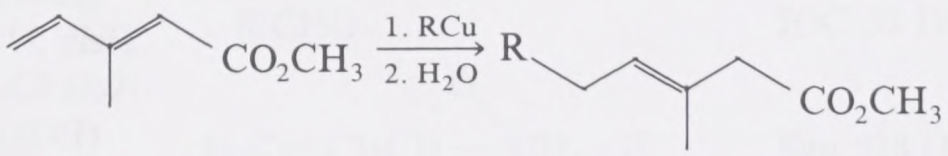


CL 705 (1974)
TL *28* 5473 (1987)

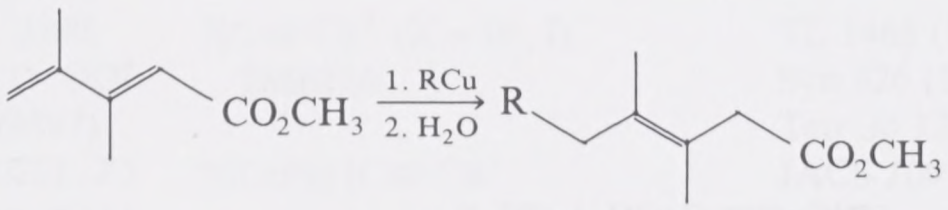


E + *Z*

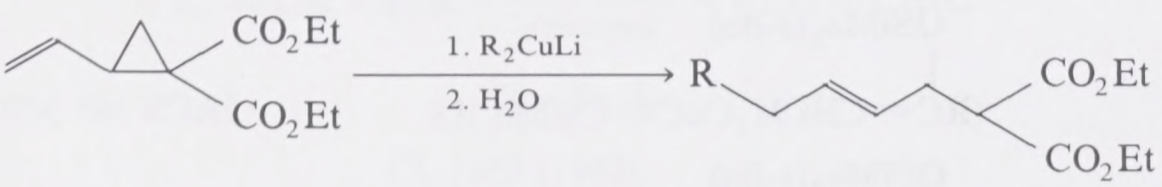
Helv *55* 82 (1972)



TL 1611 (1973)

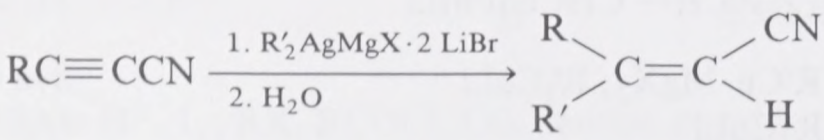


TL 1611 (1973)

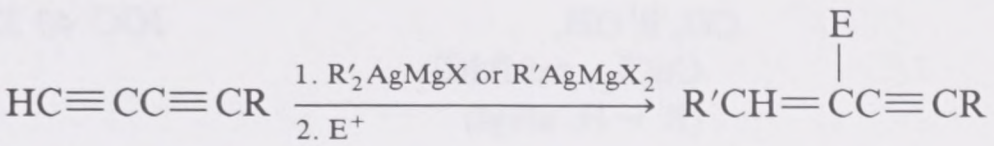


JOC *38* 2100 (1973)

2.18. Organosilver Compounds



TL 3327 (1979)
JOMC *206* 257 (1981)

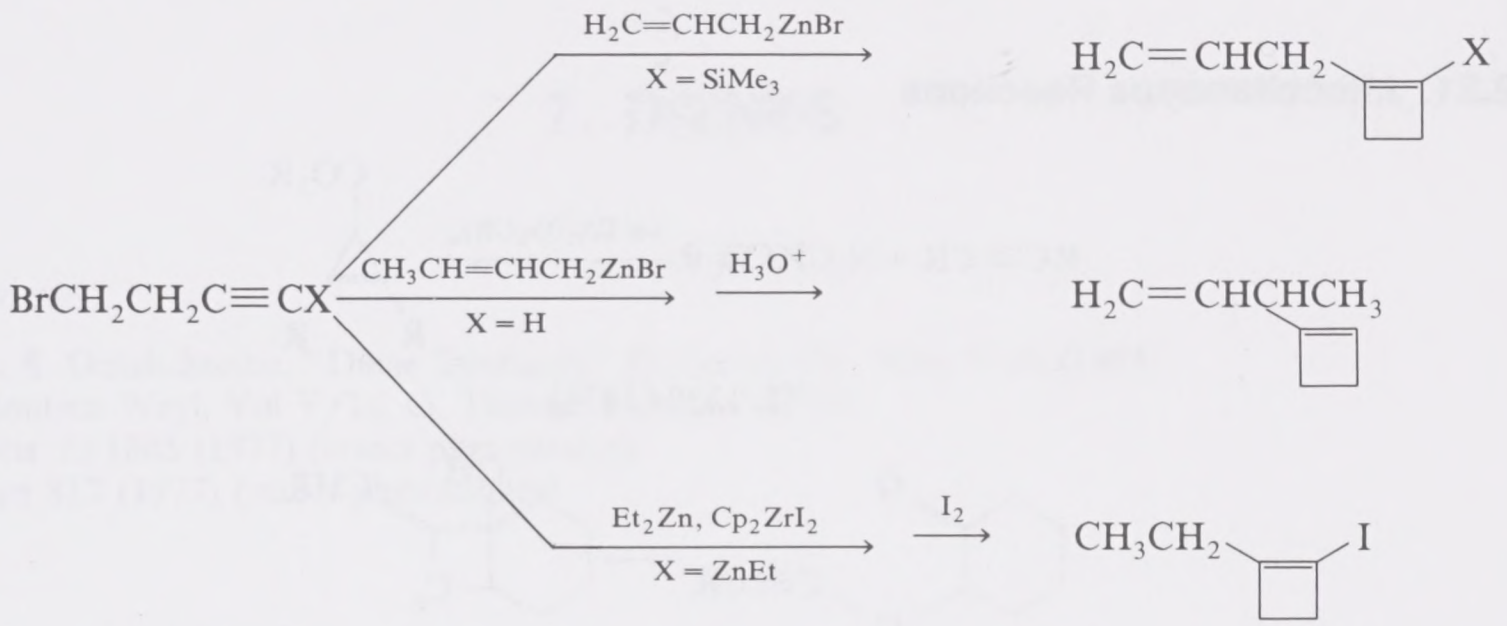


E^+ = NBS, I_2, $H_2C{=}CHCH_2Br$, CO_2

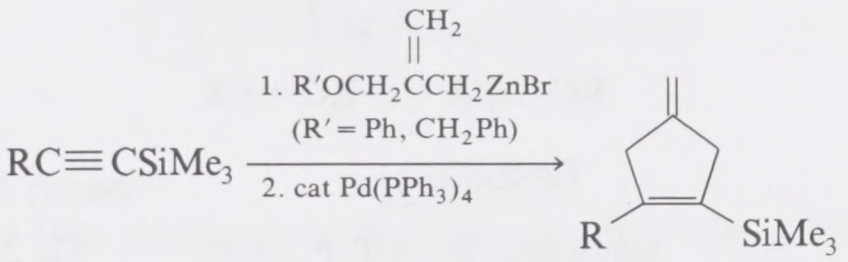
Rec Trav Chim *100* 337 (1981)

2.19. Organozinc Compounds

See also page 230, Section 2.11; and page 233, Section 2.17.



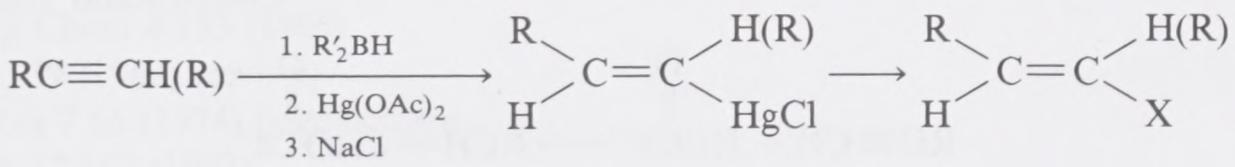
JACS *106* 6105 (1984)



TL *28* 2889 (1987)

2.20. Organomercury Compounds

See also page 260, Section 3.16.



X	Reagent(s)	
CH_3	$CH_3RhI_2(PPh_3)_2$	TL *22* 2443 (1981) JOMC *225* 31 (1982)
R^1	R^1_2CuLi (R^1 = alkyl, vinyl)	Organomet *1* 74 (1982)
COR^1	R^1COCl, $AlCl_3$	JOC *43* 710 (1978)

CO_2R^1	CO, R^1OH, $CuCl_2$, cat $PdCl_2$ (R^1 = H, alkyl)	JOC *40* 3237 (1975)
$COCH(R)=CHR$	CO, cat $[ClRh(CO)_2]_2$	JOC *45* 3840 (1980)
OAc	$Hg(OAc)_2$, cat $Pd(OAc)_2$	JACS *102* 1966 (1980)

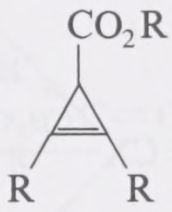
$$RHgCl + XC{\equiv}CCO_2R \xrightarrow{NaBH_4} RCX{=}CHCO_2R$$

X = H, CO_2R

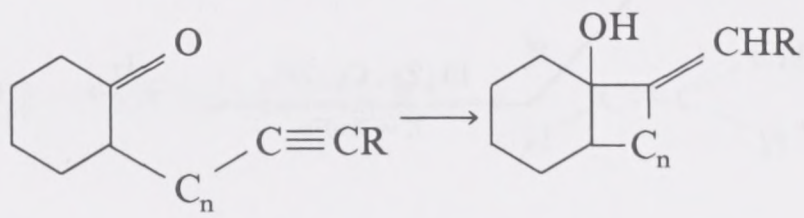
Angew Int *21* 768 (1982); *26* 479 (1987)

2.21. Miscellaneous Reactions

$$RC{\equiv}CR + N_2CHCO_2R \xrightarrow{\text{cat } Rh_2(O_2CR)_4}$$



TL 1239 (1978)



See page 574, Section 2.2.

$$RC{\equiv}CR \longrightarrow RC(I){=}C(X)R$$

X	Reagent(s)	
H, F, Cl, Br, I, OAc, SCN, pyridinium salt, Ar	$I(py)_2BF_4$; Et_3SiH, F^-, Cl^-, Br^-, I^-, HOAc, SCN^-, py or Ar-H	TL *27* 3303 (1986)
Br, SCN	I_2, CuO-HBF_4, LiBr or KSCN	CC 1491 (1987)
SCN	ISCN	BSCF 2569 (1964) Compt Rend *258* 3878 (1964)

$$RC{\equiv}CH + HOCR' \longrightarrow RCH{=}CHOCR'$$

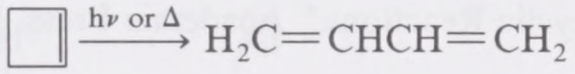
See page 830, Section 5.

7. DIENES

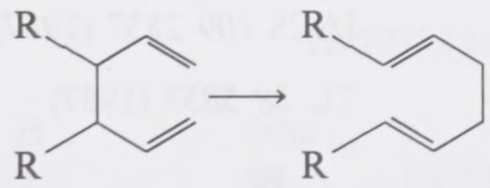
Reviews:

A. S. Onishchenko, "Diene Synthesis," D. Davey Co., New York (1964)
Houben-Weyl, Vol V/1c, G. Thieme, Stuttgart (1970)
Tetr *33* 1845 (1977) (insect pheromones)
Syn 817 (1977) (insect pheromones)

1. Rearrangement



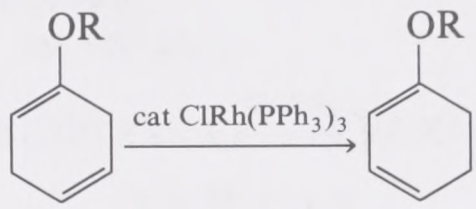
Angew *66* 640 (1954)
Ann *615* 14 (1958); *627* 1 (1959)
JACS *84* 4141 (1962); *87* 3996 (1965); *88* 1073 (1966); *90* 5310, 6896 (1968); *91* 5404, 7557 (1969); *93* 4616 (1971); *94* 4262 (1972); *101* 3340 (1979); *102* 3548, 6353 (1980); *103* 1256 (1981); *107* 2099, 3921 (1985); *109* 6086 (1987)
Proc Chem Soc 334 (1962)
Trans Faraday Soc *58* 957 (1962)
Ber *96* 2362 (1963); *97* 1811, 2934 (1964)
JOC *29* 257 (1964); *43* 2726, 4559 (1978); *52* 3708 (1987)
TL 1207 (1965); 3387 (1974); 3047 (1975); *21* 1997 (1980); *28* 1501 (1987)
Adv Phys Org Chem *4* 183 (1966)
Angew Int *7* 559 (1968) (review)
Acct Chem Res *7* 65 (1974) (mechanism)
Syn Commun *12* 167 (1982)



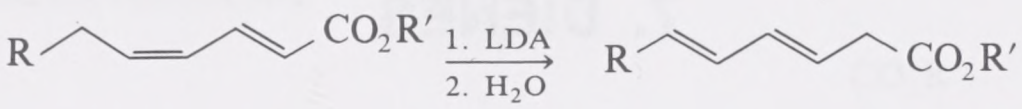
(Cope reaction)

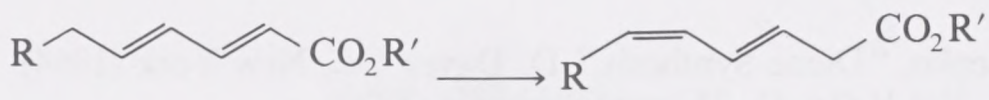
Org Rxs *22* 1 (1975) (review)
Helv *60* 978 (1977) (aza-Cope)
TL *22* 1583 (1981) (acid catalyzed 2-acyl-1,5-dienes); *23* 2733, 2737, 2741 (1982) (all aza-Cope)
JACS *104* 7225 (1982) ($PdCl_2$ catalyzed)

Ber *115* 2309 (1982) (heteroatom substituted)
Angew Int *21* 198 (1982) (aza-Cope)
R. K. Hill in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 8 (review)
Chem Rev *84* 205 (1984) (catalysis, review)

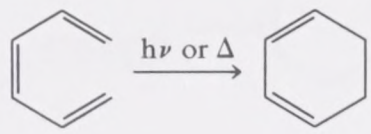


TL 3797 (1968)



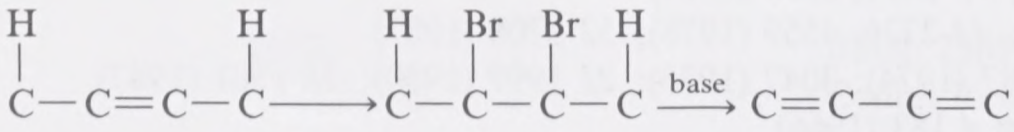


CL 1541 (1984)



CC 173 (1970)
E. N. Marvel, "Thermal Electrocyclic Reactions," Academic Press, New York (1980) (review)
JACS *107* 1034 (1985)
JOC *51* 4131 (1986)
JCS Perkin I 225 (1987)
TL *28* 1469 (1987)

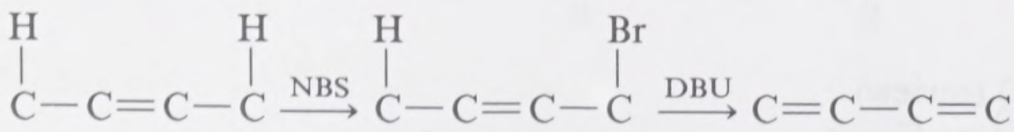
2. Elimination Reactions



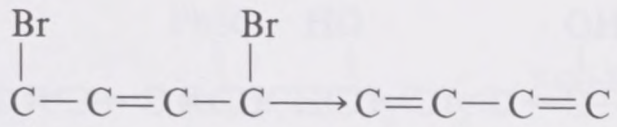
LiCl, Li_2CO_3, HMPA, Δ — JACS *99* 7899 (1977); Syn 449 (1977)

KO-*t*-Bu — TL *28* 4965 (1987); JACS *109* 2857 (1987)

DBN — TL *28* 5833 (1987)



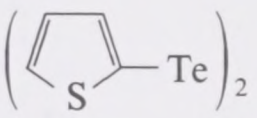
JACS *109* 2212 (1987)

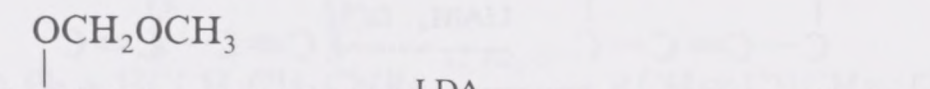


Zn — CC 508 (1966)

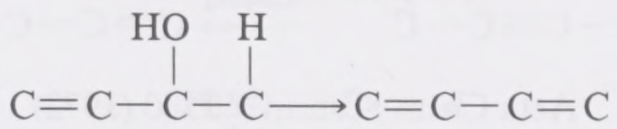
Zn(Hg) — Syn 742 (1982)

Zn-Cu, KI, I_2 — JACS *99* 8 (1977); *108* 512 (1986)

cat $NaBH_4$—  — JOC *50* 3170 (1985)

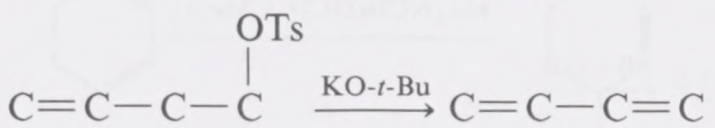


JOC *52* 4817 (1987)

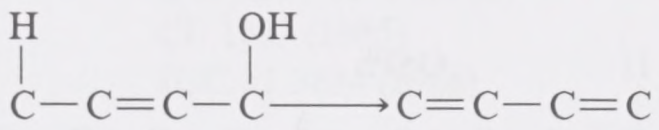


Al_2O_3, Δ — JOC *52* 3541 (1987)

Tf_2O, lutidine — JOC *52* 3956 (1987)



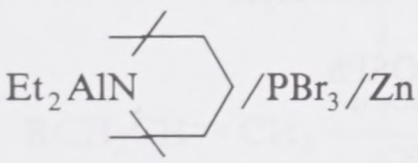
JOC *52* 4732 (1987)

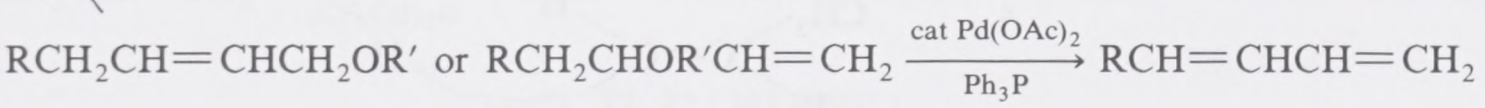


$(C_5H_5NH)OTs$ — TL *23* 4747 (1982); JOC *52* 3541 (1987)

2,4-$(NO_2)_2C_6H_3SCl$, Et_3N — JACS *100* 5981 (1978); *104* 7051 (1982); JOC *51* 5232 (1986)

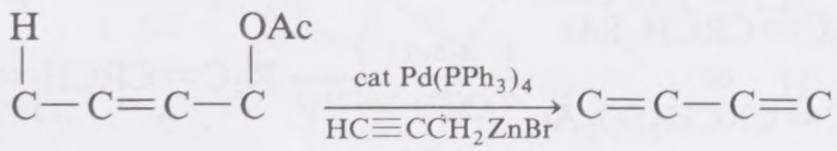
t-BuO_2H, $VO(acac)_2$/Me_3SiCl/ — JACS *97* 3252 (1975); BCSJ *52* 1752 (1979)



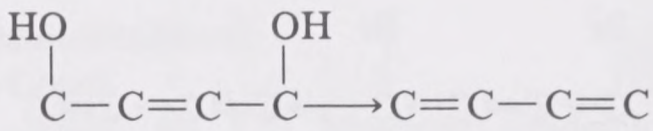


R′ = Ac, Ph

TL 2075 (1978)



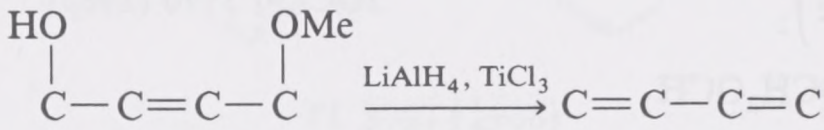
JOC *47* 4161 (1982)



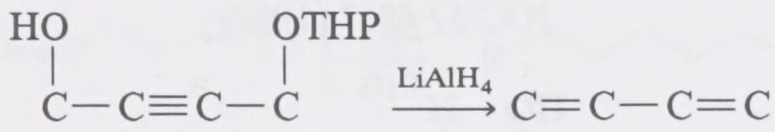
$LiAlH_4$ JCS 4006 (1954)

$TiCl_3$, $LiAlH_4$ JACS *104* 5807 (1982)

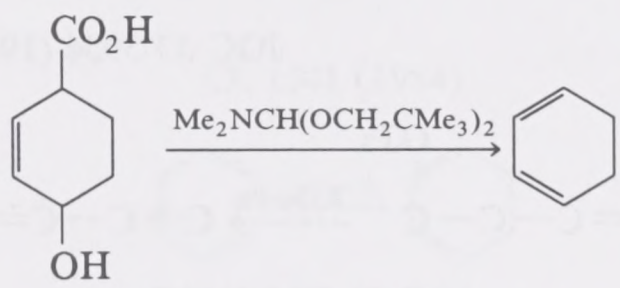
MsCl, py/NaI JCS C 15 (1967)
Syn 956 (1982)



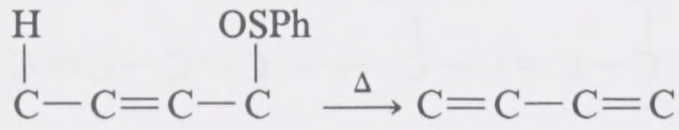
JOC *52* 3560 (1987)



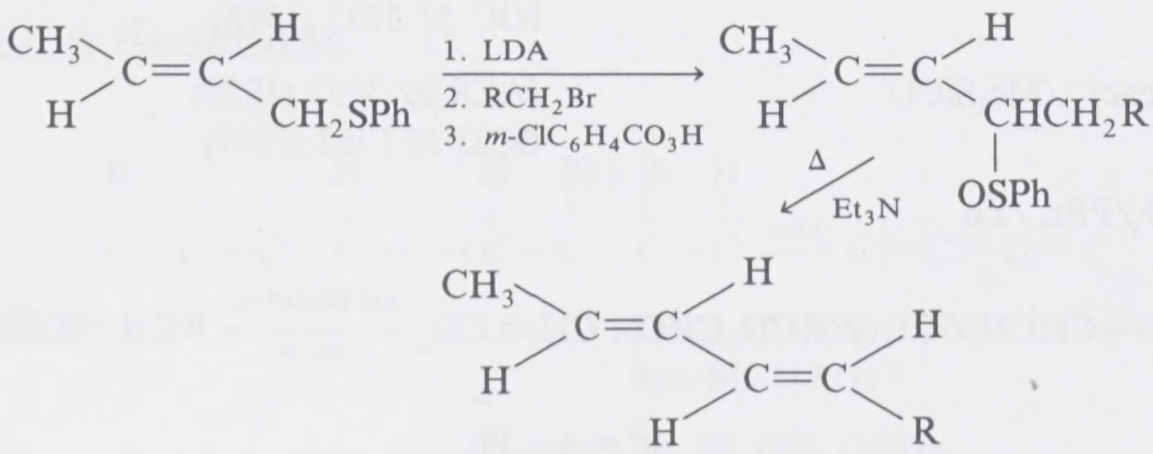
Acta Chem Scand *26* 2540 (1972)
JACS *108* 1338 (1986)



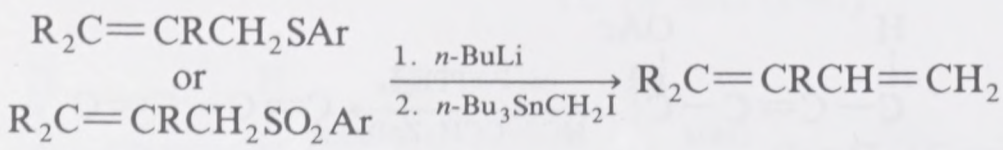
Helv *58* 1450 (1975)



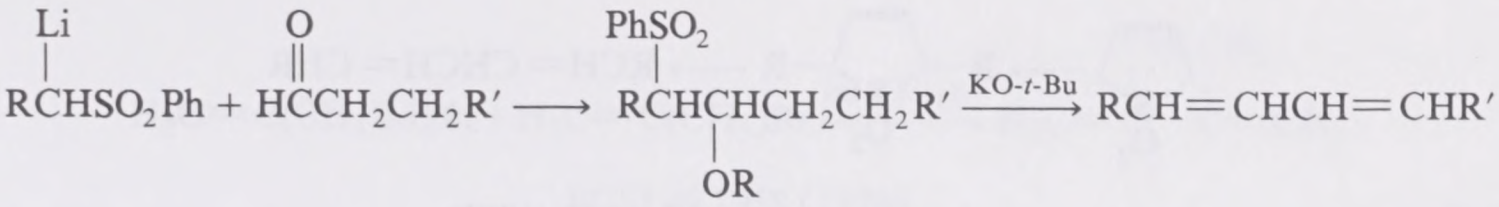
TL *22* 4137 (1981)
JOC *51* 4594 (1986)



JOC *47* 4801 (1982)

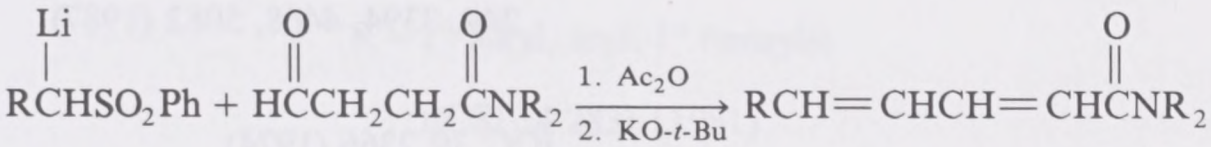


TL *23* 2205 (1982)

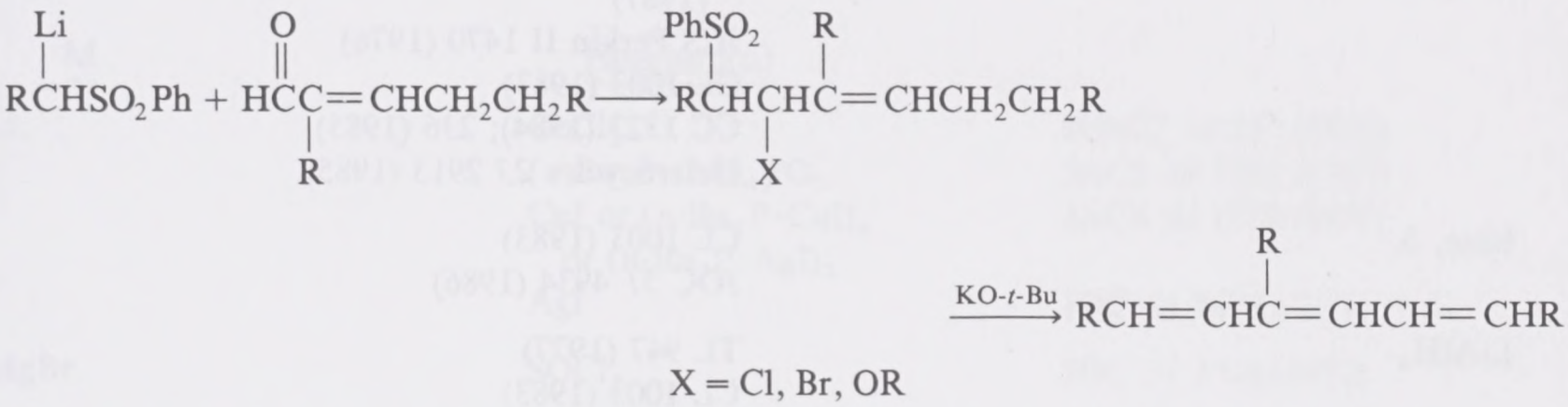


R = alkyl, Ac

JACS *106* 3670 (1984)
JOC *51* 3830 (1986)

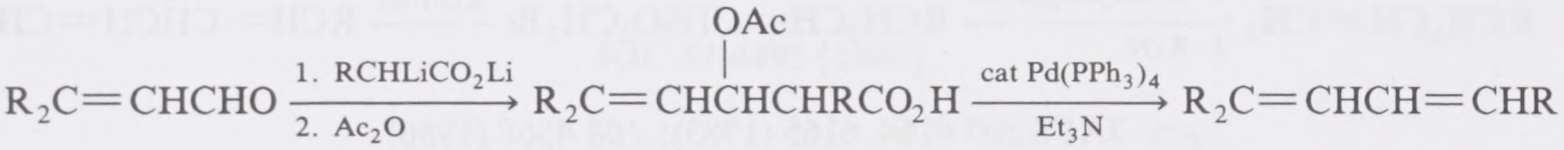


TL *27* 603 (1986)
JOC *51* 3896 (1986)

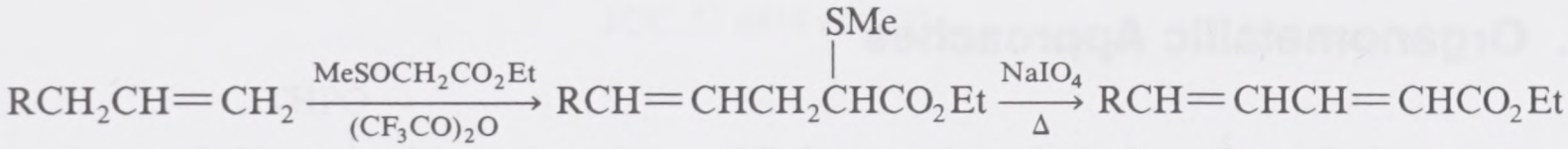


X = Cl, Br, OR

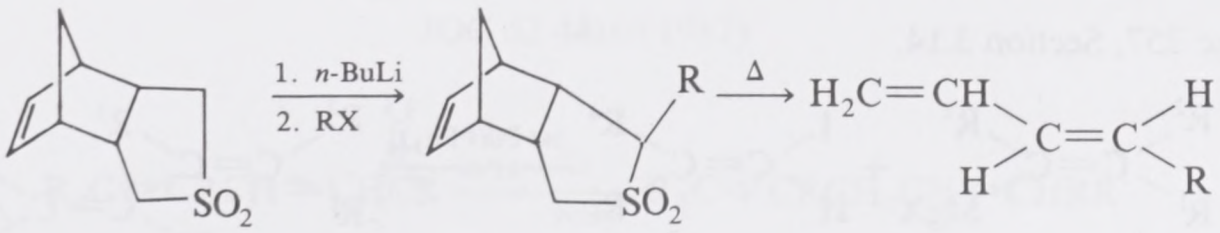
JACS *106* 3670 (1984)
CL 1883 (1985)
JOC *51* 3834 (1986)



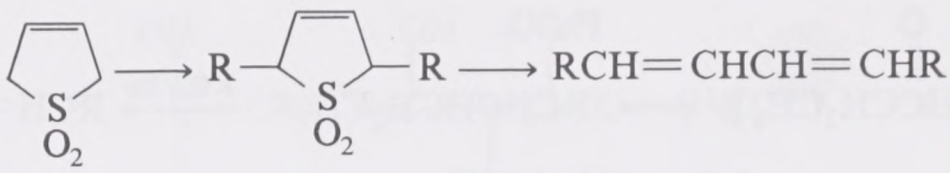
JACS *102* 2841 (1980)



TL *22* 1343 (1981)



TL *23* 3277 (1980)



alkylation

CL 1003 (1983)
CC 1323 (1984); 236 (1985); 934 (1987)
JCS Perkin I 515 (1985); 1039 (1986)
Heterocycles *23* 2913 (1985)
JOC *51* 1000, 4718, 4934 (1986); *52* 244, 3394, 4468, 5082 (1987)

elimination

hν

JOC *39* 2366 (1974)

Δ

JACS *88* 2857, 2858 (1966); *97* 3666 (1975)
JOC *39* 2366 (1974); *52* 244, 3394 (1987)
JCS Perkin II 1470 (1976)
CL 1003 (1983)
CC 1323 (1984); 236 (1985)
Heterocycles *23* 2913 (1985)

base, Δ

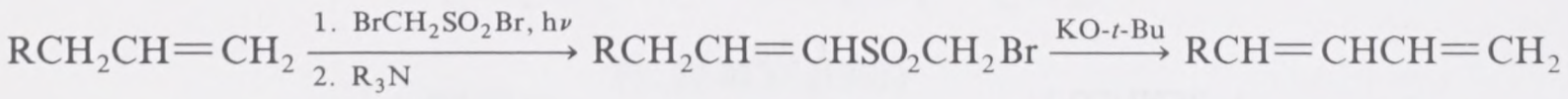
CL 1003 (1983)
JOC *51* 4934 (1986)

$LiAlH_4$

TL 947 (1977)
CL 1003 (1983)
JOC *51* 4934 (1986); *52* 4468, 5082 (1987)

K, ultrasound

JOC *52* 2224 (1987)



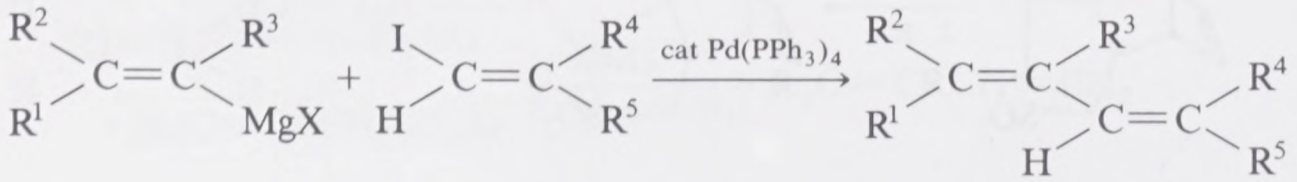
JACS *105* 6164, 6165 (1983); *108* 4568 (1986)
TL *25* 5469 (1984)
Org Syn *65* 90 (1987)

3. Organometallic Approaches

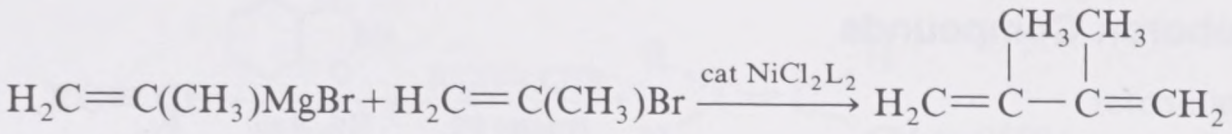
For symmetrical coupling of allylic and vinylic halides or alcohols see also page 45, Section 1.

3.1. Organolithium and -magnesium Compounds

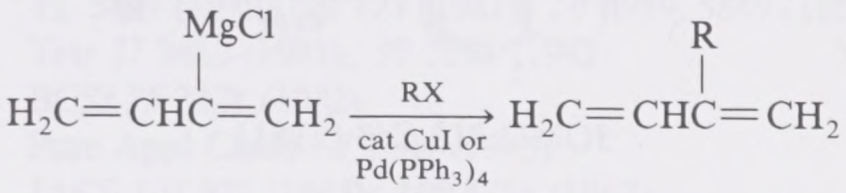
See also page 257, Section 3.14.



TL 191 (1978)

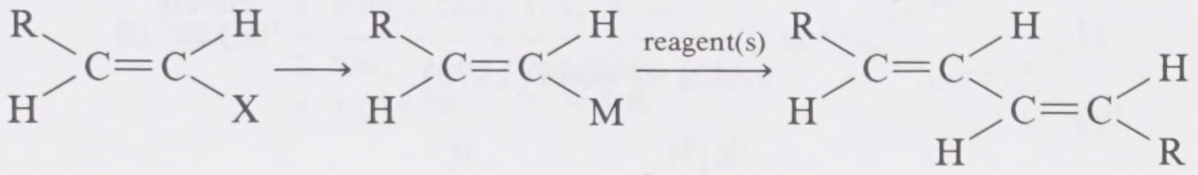


BCSJ *49* 1958 (1976)

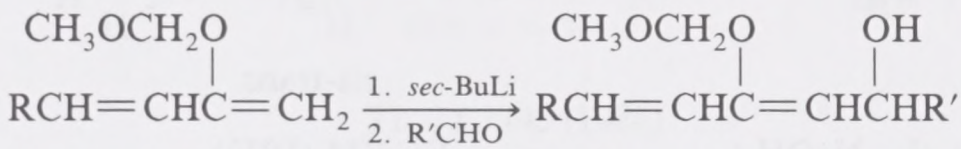


R = 1° alkyl, aryl, 1° benzylic

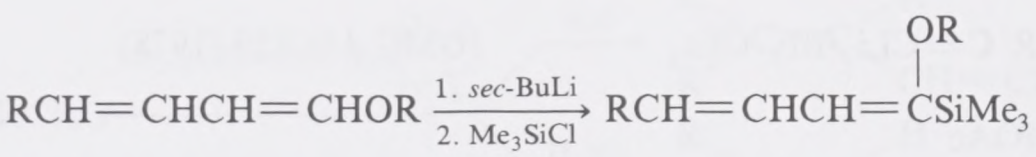
BCSJ *54* 2831 (1981)



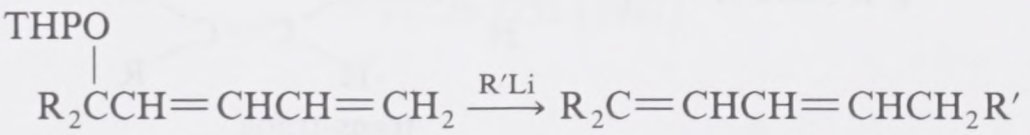
M	Reagent(s)	
Li	$CoCl_2$	JOMC *24* 537 (1970)
	$(n\text{-}Bu_3P\cdot CuI)_4/O_2$	JACS *89* 5302 (1967)
	CuI or $(n\text{-}Bu_3P\cdot CuI)_4$ or $(n\text{-}Bu_3P\cdot AgI)_4$	JACS *93* 1379 (1971)
	AgI	JOC *36* 1694 (1971)
MgBr	$SOCl_2$	JOC *37* 3749 (1972)
MgX (X = Cl, Br)	CuCl	Angew Int *6* 85 (1967)



JOC *51* 4492 (1986)

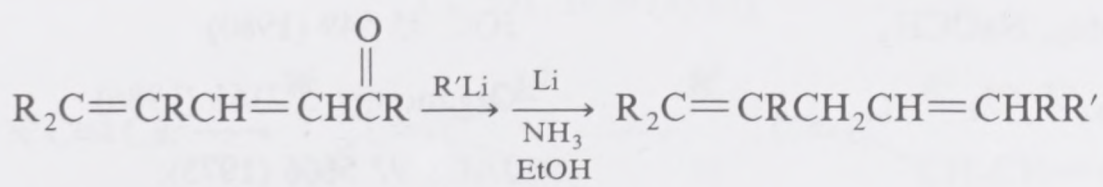


JOC *52* 4818 (1987)



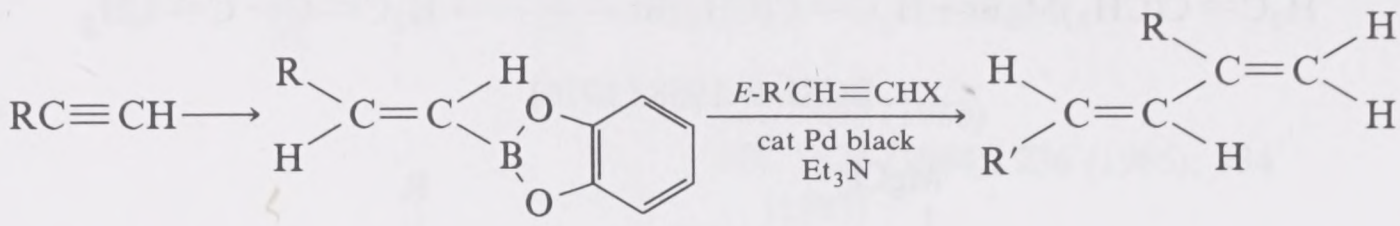
R′ = 1°, 2° alkyl; NEt_2; $SiMe_2Ph$; $SnMe_3$

JOC *52* 4416 (1987)

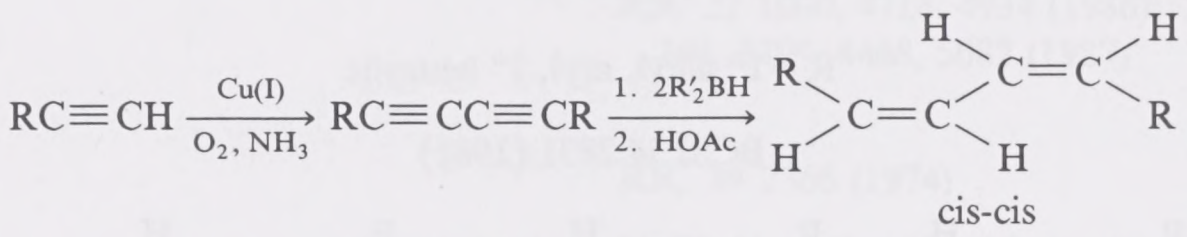


JOC *44* 1159 (1979)

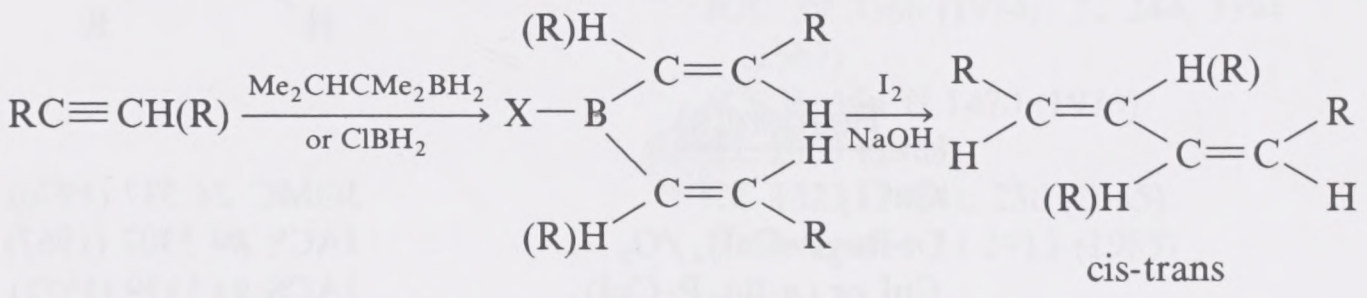
3.2. Organoboron Compounds



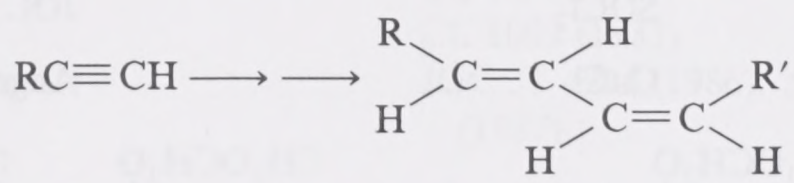
JOMC *213* C53 (1981)

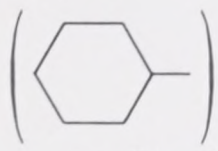


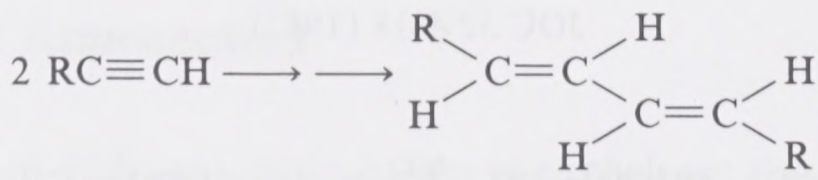
JACS *92* 4068 (1970)

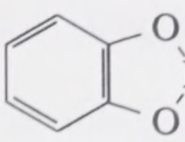


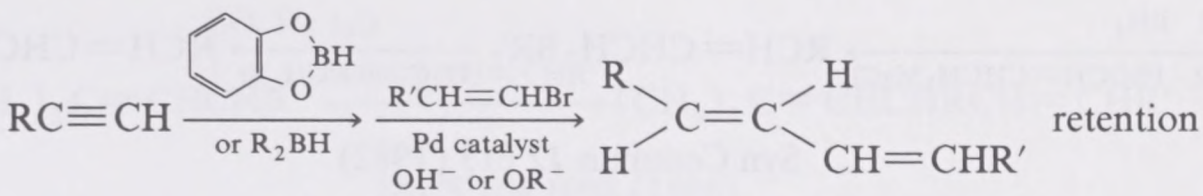
JACS *90* 6243 (1968)
JOC *38* 1617 (1973)



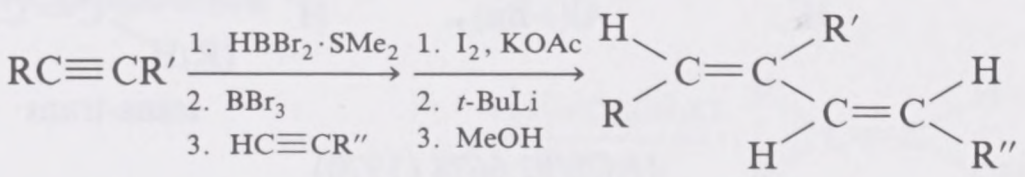
$(Sia)_2BH/R'C{\equiv}CLi/I_2$, NaOH/ $(Sia)_2BH$/HOAc	CC 874 (1973)
 $BH/R'C{\equiv}CLi/BF_3{\cdot}OEt_2$ or n-Bu_3SnCl/HOAc	JOMC *156* 159 (1978)



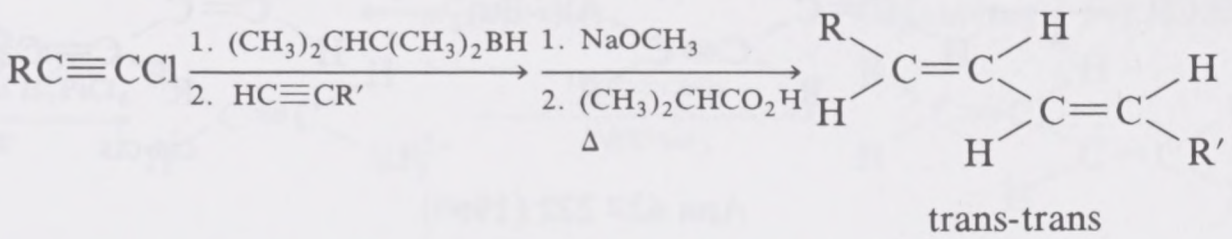
 BH/H_2O/cat $PdCl_2$, LiCl, Et_3N	JOMC *179* C7 (1979)
$R'_2BH/CuBr{\cdot}SMe_2$, $NaOCH_3$	JOC *45* 549 (1980)
$R'_2BH/NaOCH_3/ZnCl_2$	Organomet *5* 2161 (1986)
$ClBH_2/CH_3Cu$	JACS *97* 5606 (1975); *99* 5652 (1977) BCSJ *50* 3427 (1977)



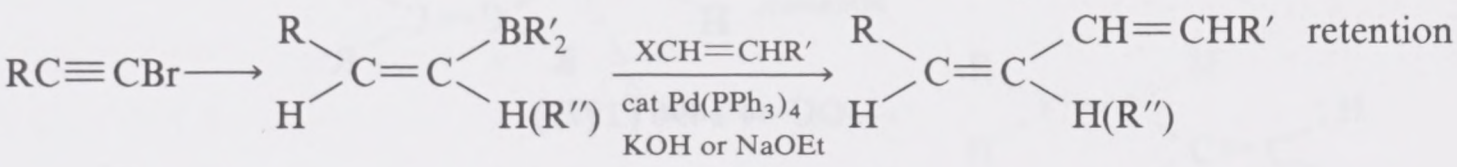
TL 3437 (1979); *22* 127 (1981); *28* 3959, 5849 (1987)
Tetr *37* 2617 (1981); *39* 3271 (1983)
BCSJ *55* 2221 (1982)
Pure Appl Chem *57* 1749 (1985)
JACS *107* 972 (1985); *109* 4756 (1987)
JOC *52* 292 (1987)
CL 27 (1987)



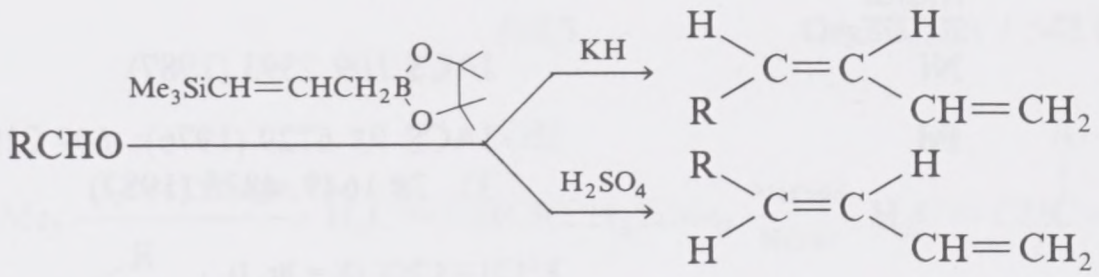
TL *27* 977 (1986)



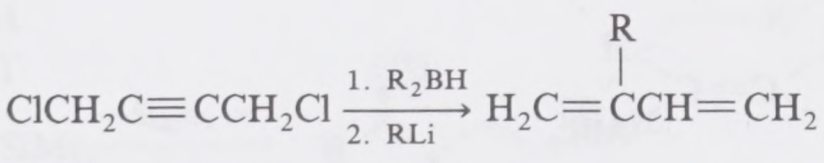
CC 606 (1973)



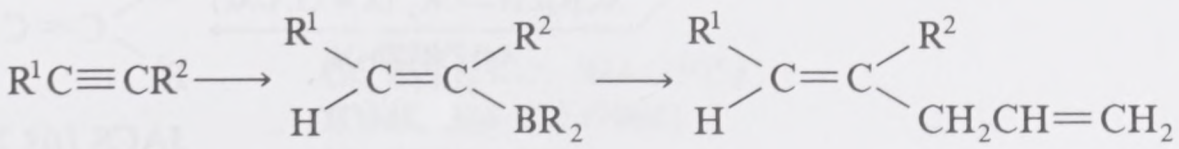
TL *27* 3745 (1986)
CL 1329 (1986)



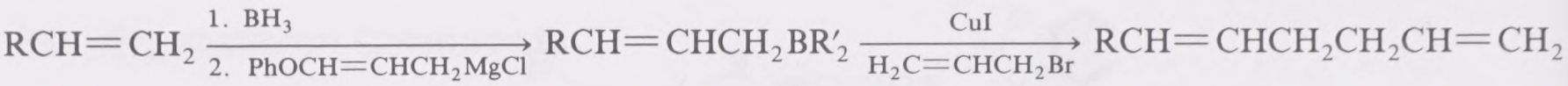
TL *22* 2751 (1981)



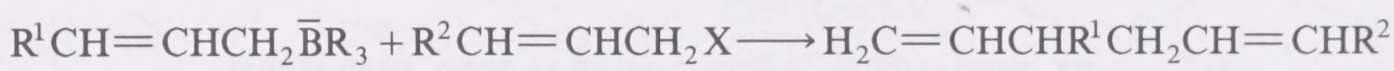
CC 531, 1629 (1987)



See page 218, Section 2.6.



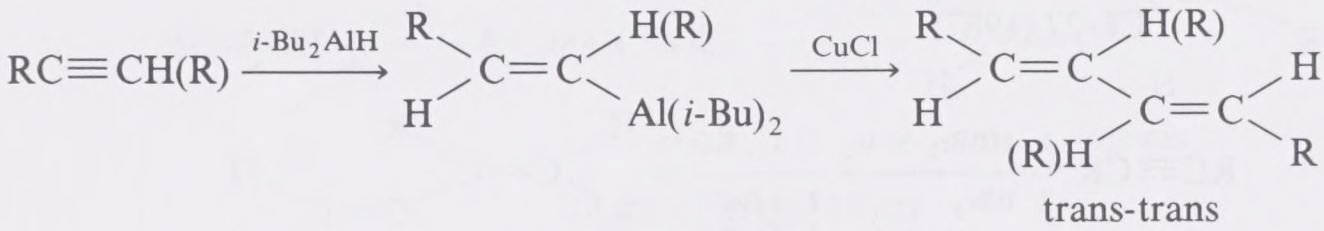
Syn Commun *12* 813 (1982)



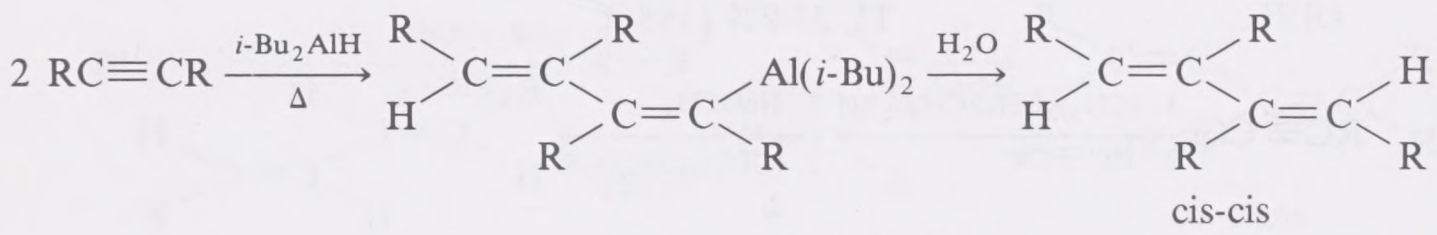
X = Cl, Br

JACS *100* 6282 (1978); *103* 1969 (1981)

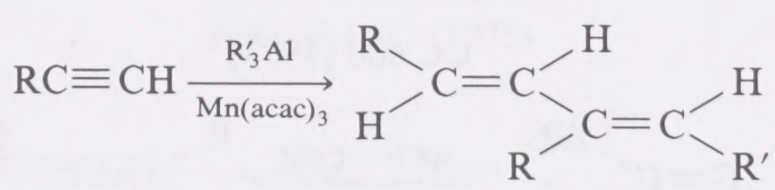
3.3. Organoaluminum Compounds



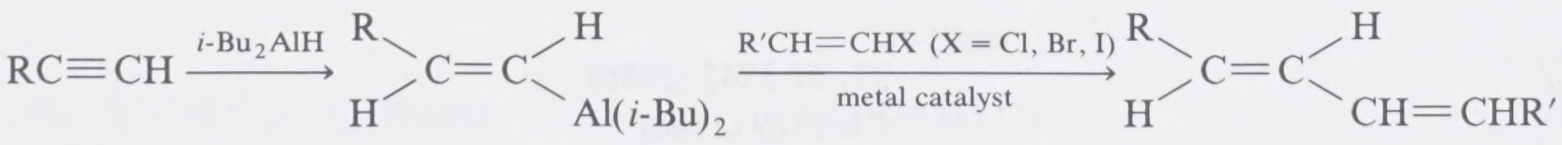
JACS *92* 6678 (1970)



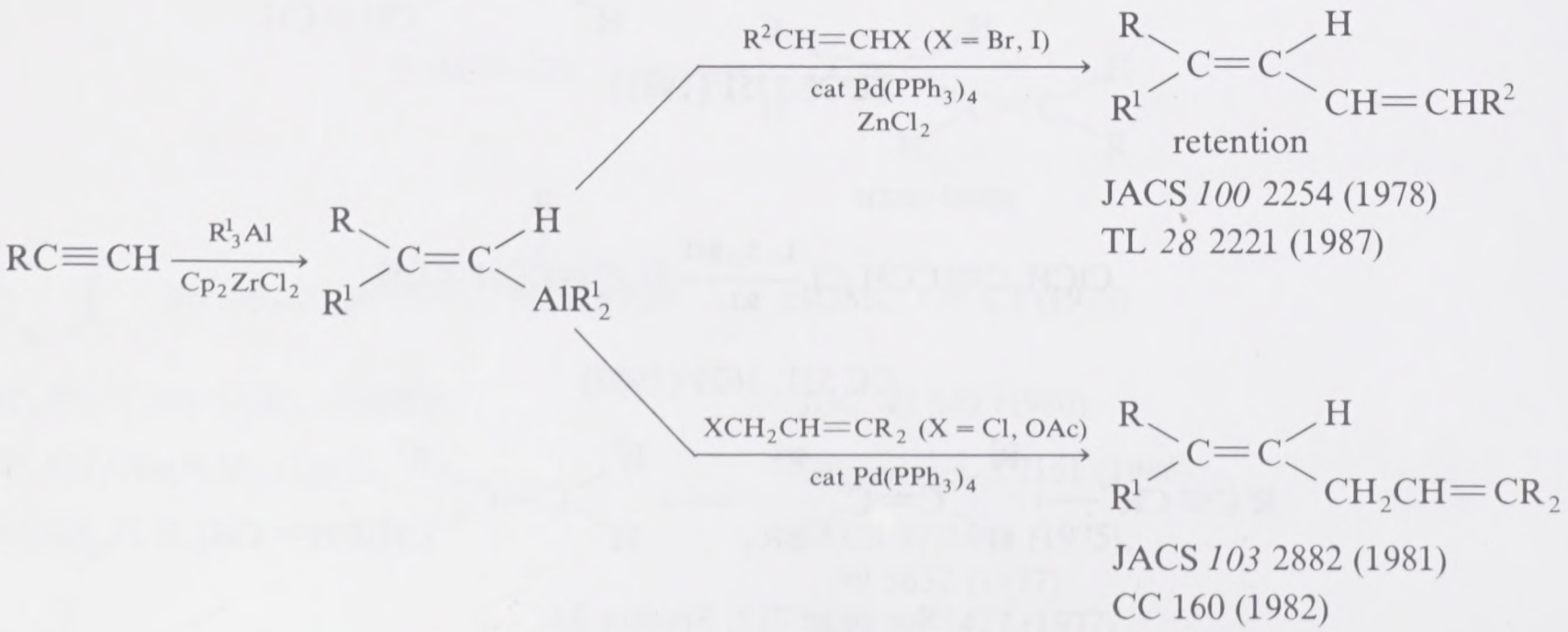
Ann *629* 222 (1960)



JOC *44* 1496 (1979)

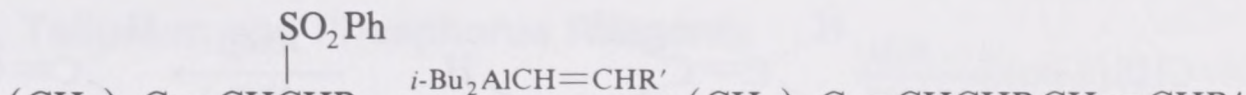


metal	
Ni	JACS *109* 2393 (1987)
Pd	JACS *98* 6729 (1976); *109* 2393 (1987) TL *28* 1649, 4875 (1987)

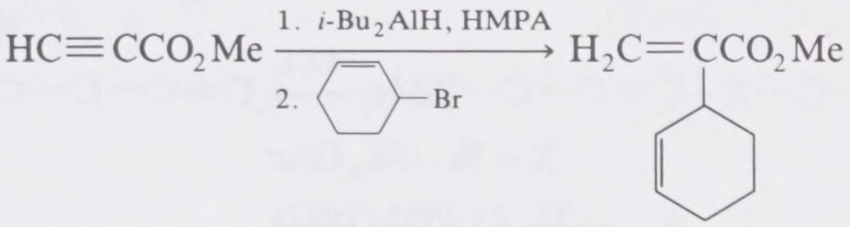


JACS *100* 2254 (1978)
TL *28* 2221 (1987)

JACS *103* 2882 (1981)
CC 160 (1982)

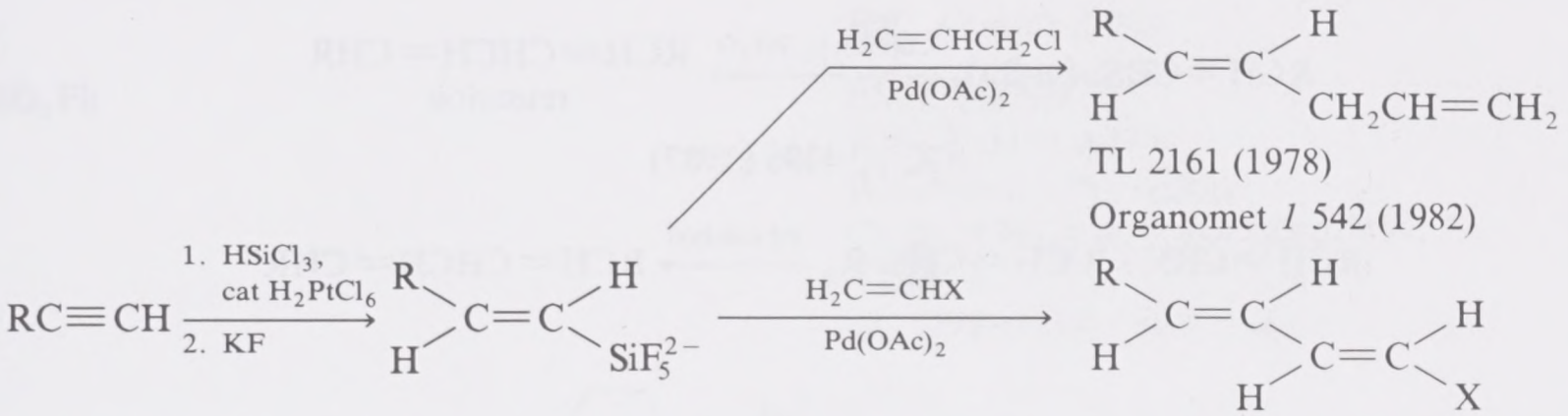


JACS *108* 1098 (1986)



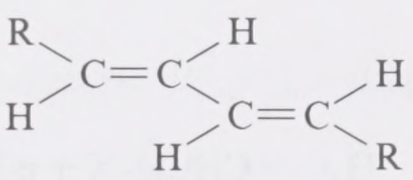
JOC *52* 1624 (1987)

3.4. Organosilicon Compounds

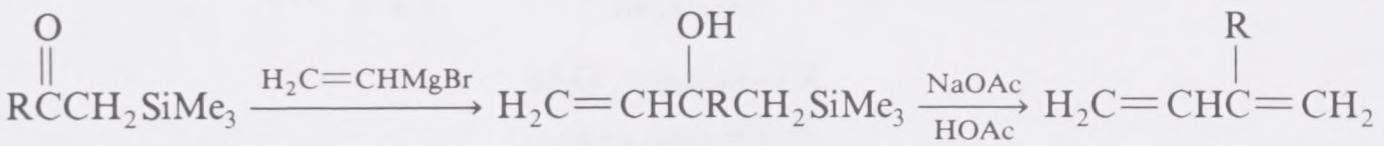


TL 2161 (1978)
Organomet *1* 542 (1982)

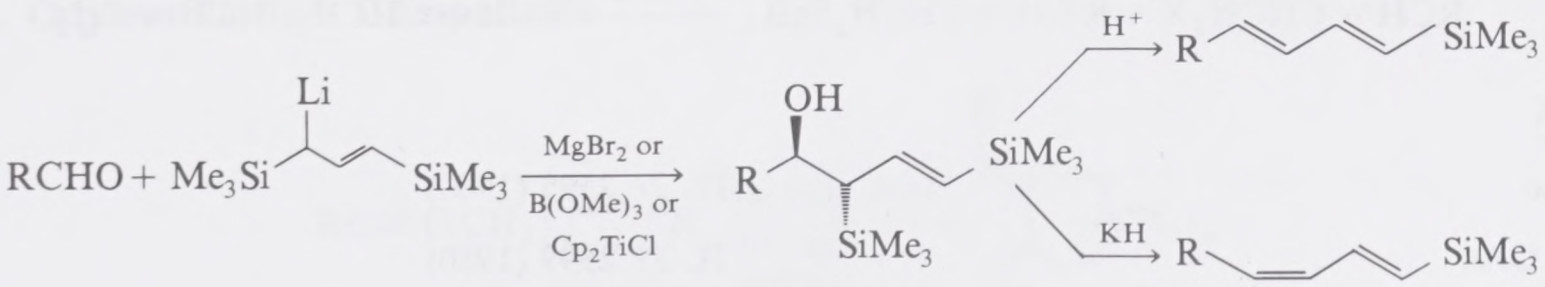
X = CHO, CO_2R, CN
Organomet *1* 542 (1982)



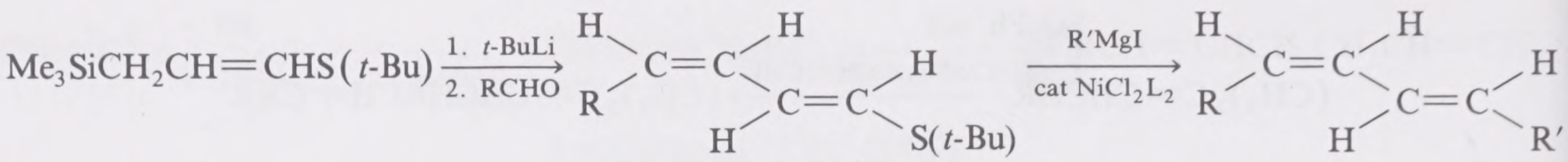
AgF or $AgNO_3$	TL 1137 (1979)
CuCl	TL 1141 (1979)
$PdCl_2$	Organomet *1* 542 (1982)



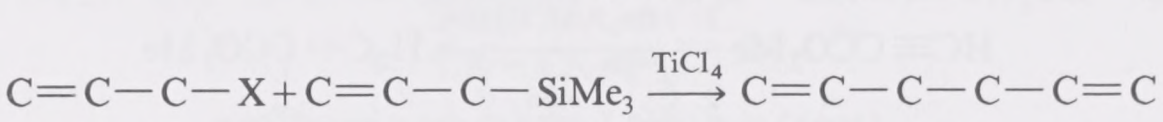
TL *28* 693, 697 (1987)



CC 969 (1982); 921 (1983)
JOMC *264* 207 (1984)
TL *28* 211 (1987)



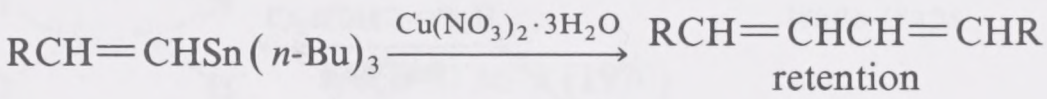
TL *25* 5177 (1984)



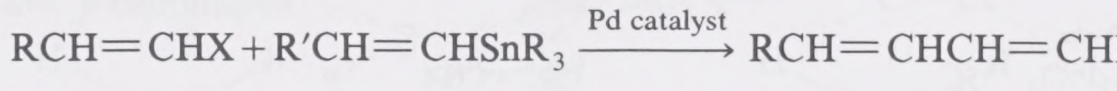
X = Br, OR, OAc

TL *23* 2953 (1982)
JOC *47* 3803 (1982)

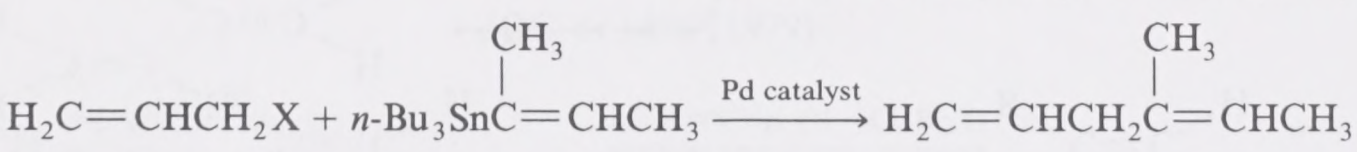
3.5. Organotin Compounds



JOC *52* 4296 (1987)

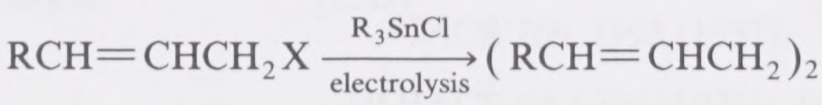


X	
OTf	JACS *108* 3033 (1986); *109* 3785 (1987) (intramolecular, macrocyclic lactones)
	TL *27* 5595 (1986)
Br, I	JACS *108* 1359 (1986); *109* 813 (1987)



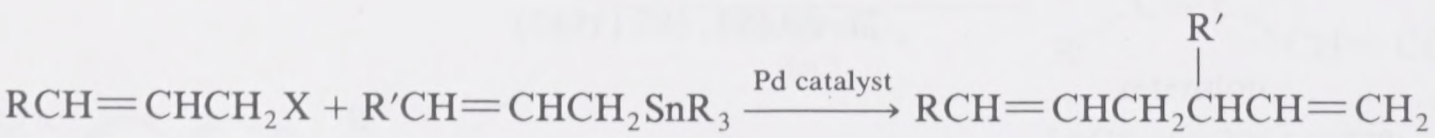
X = Cl, Br

JACS *105* 7173 (1983); *106* 4833 (1984)

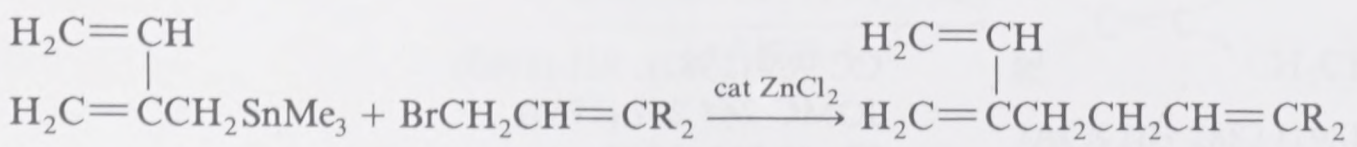


X = halogen, OAc

TL *27* 4469 (1986)

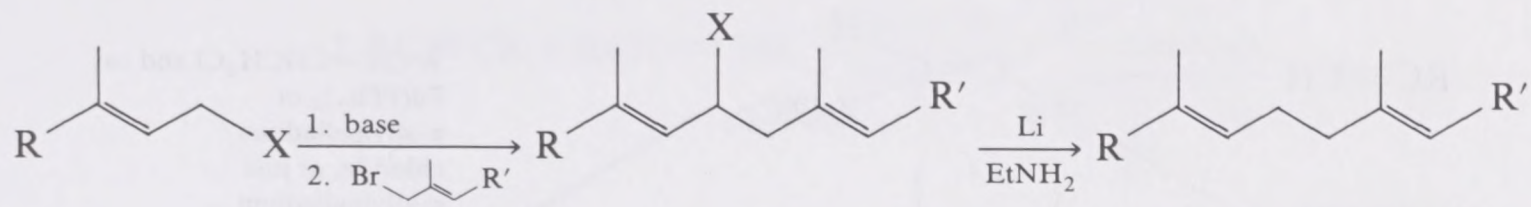


X	
OAc	TL *21* 2595 (1980)
Br, OAc	TL *21* 2599 (1980)

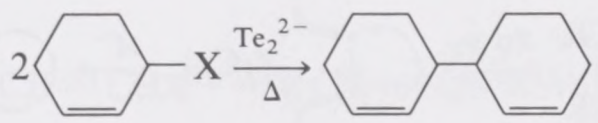


TL *24* 1905 (1983)

3.6. Sulfur, Tellurium and Phosphorus Reagents



X	
SPh	TL 3707 (1969); *27* 2157 (1986) Tetr *27* 5861 (1971) Proc Natl Acad Sci USA *68* 1294 (1971) JACS *95* 4444 (1973) Syn 129 (1974) JOC *45* 4097 (1980)
SO_2Ph	BSCF 746 (1973) JOC *39* 2135 (1974) JCS Perkin I 761 (1981) CL 25 (1981) (intramolecular); 725 (1983) CC 1761 (1986); 1036 (1987)



JOC *47* 1641 (1982)

$$RCH{=}CHCH{=}PPh_3 + R'CH{=}CHCH_2X \xrightarrow[EtNH_2]{Li} RCH{=}CHCH_2CH_2CH{=}CHR'$$

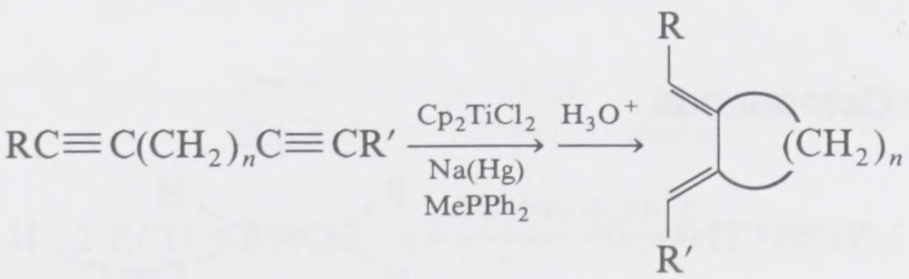
JACS *92* 2139 (1970)

$$RCH{=}CHCH{=}CHCH_2Br \xrightarrow[2.\ n\text{-BuLi}\ 3.\ R'X]{1.\ P(OEt)_3} RCH{=}CHCH{=}CHCHR' \xrightarrow{LiAlH_4} RCH{=}CHCH_2CH{=}CHR'$$

($OP(OEt)_2$ on the CHCHR′ carbon)

TL 245 (1979)
Ann 536 (1982)

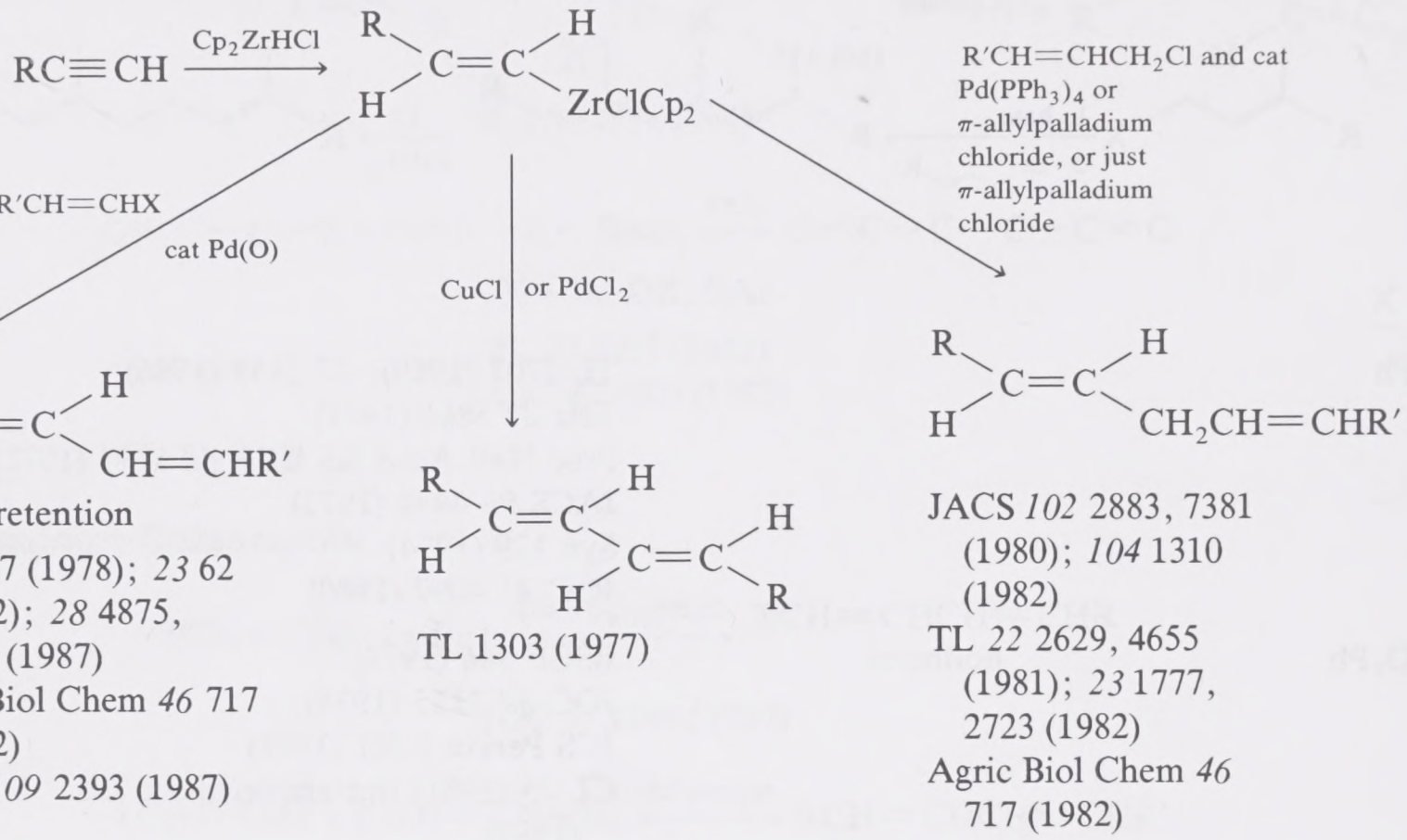
3.7. Organotitanium Compounds



$n = 3–5$

JACS *106* 6422 (1984); *109* 2788 (1987)

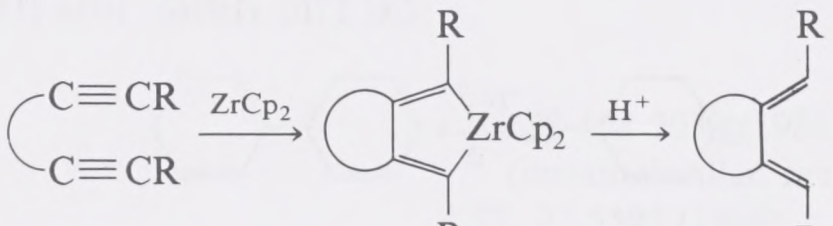
3.8. Organozirconium Compounds



TL 1027 (1978); *23* 62 (1982); *28* 4875, 4879 (1987)
Agric Biol Chem *46* 717 (1982)
JACS *109* 2393 (1987)

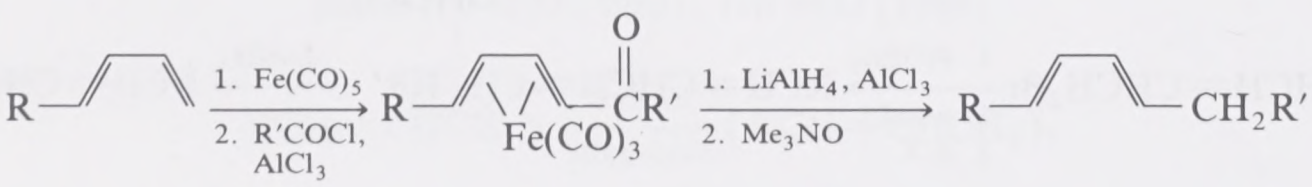
TL 1303 (1977)

JACS *102* 2883, 7381 (1980); *104* 1310 (1982)
TL *22* 2629, 4655 (1981); *23* 1777, 2723 (1982)
Agric Biol Chem *46* 717 (1982)

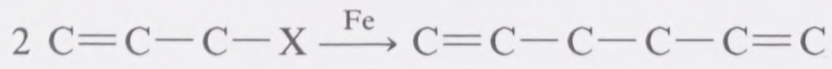


TL *27* 2829 (1986)
JACS *109* 2788 (1987)

3.9. Organoiron Compounds

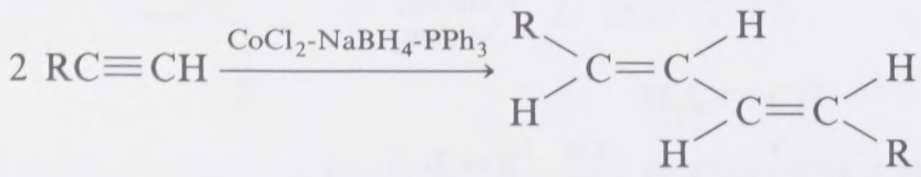


CC 373 (1981)

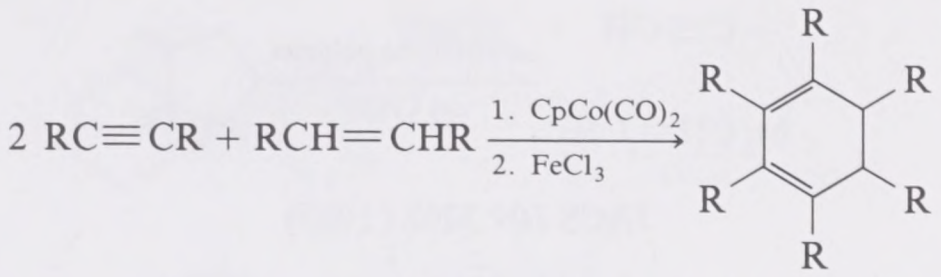


Can J Chem *47* 1238 (1969)
JOC *52* 5560 (1987)

3.10. Organocobalt Compounds



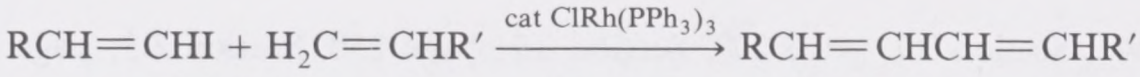
TL *27* 6253 (1986)



JACS *102* 4839 (1980) (intramolecular); *107* 1664 (1985) (intramolecular)
CC 53 (1981); 388 (1986) (intramolecular)
Angew Int *20* 802 (1981) (intramolecular); *23* 539 (1984) (review)
JOC *47* 3447 (1982) (intramolecular)

3.11. Organorhodium Compounds

See also page 260, Section 3.16.



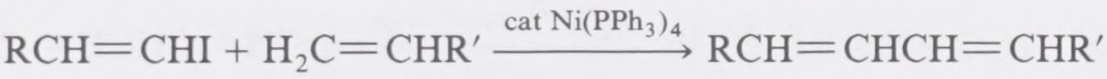
JOMC *219* C16 (1981)

3.12. Organonickel Compounds

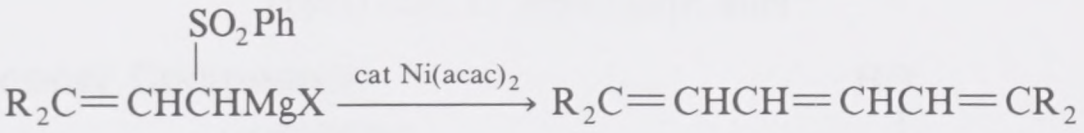
See also page 246, Section 3.1.

X = halogen

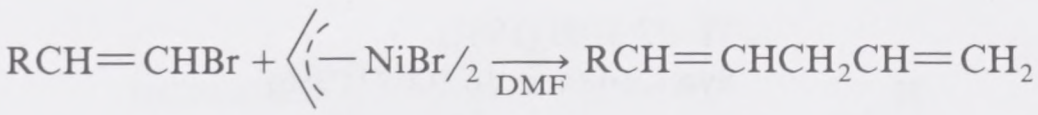
$Ni(COD)_2$, DMF	JACS *94* 9234 (1973); *103* 6460 (1981)
NaH, *t*-AmONa, $Ni(OAc)_2$, bipy	JOMC *264* 263 (1984) TL *27* 3517 (1986)
Zn, cat $NiCl_2(PEt_3)_2$, KI	BCSJ *57* 1887 (1984)



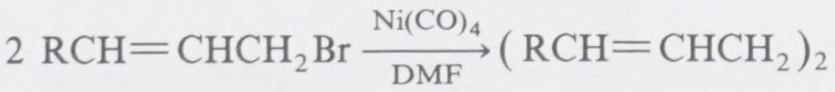
JOMC *219* C16 (1981)



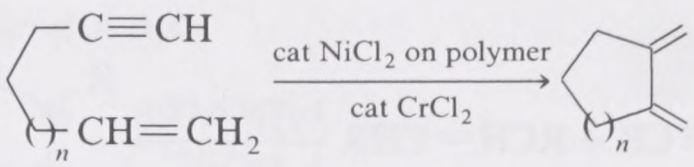
TL *23* 2457 (1982)



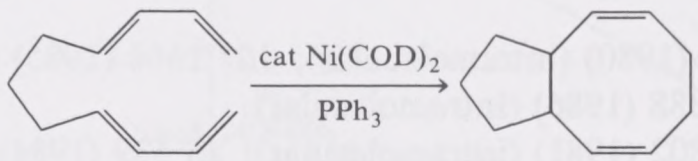
JACS *89* 2755 (1967)
Org Rxs *19* 115 (1972) (review)



Org Rxs *19* 115 (1972) (review)
TL *28* 2795 (1987)



JACS *109* 5268 (1987)



JACS *108* 4678 (1986)
TL *28* 2221, 2451 (1987)

3.13. Organopalladium Compounds

See also page 246, Section 3.1; page 248, Section 3.2; page 250, Section 3.3; page 251, Section 3.4; page 252, Section 3.5; page 254, Section 3.8; and page 260, Section 3.16.

$$RCH{=}CHX + H_2C{=}CHR' \xrightarrow{\text{Pd catalyst}} RCH{=}CHCH{=}CHR'$$

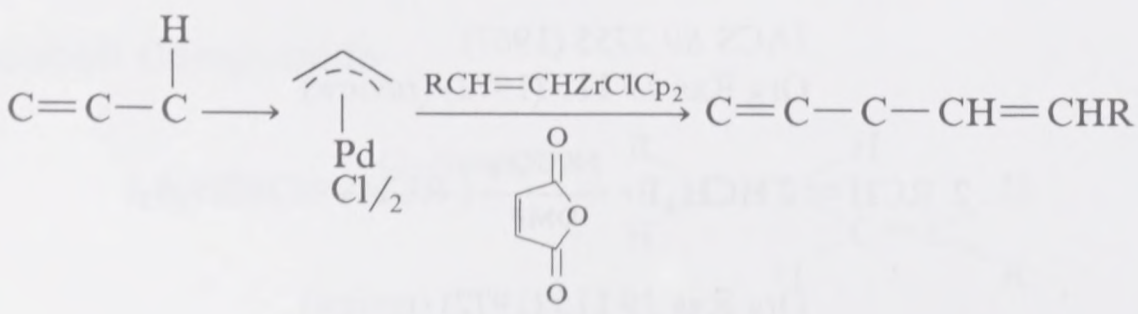
X	
halogen	JOC *37* 2320 (1972); *40* 1083 (1975); *46* 1061, 1067 (1981) JACS *96* 1133 (1974) Pure Appl Chem *53* 2323 (1981) Tetr *37* 4035 (1981) Syn 365 (1981) TL *26* 2667 (1985)
O_3SCF_3	JOC *50* 2302 (1985) Heterocycles *26* 355 (1987)

$$ArX + H_2C{=}CHCH{=}CHR \xrightarrow[\text{amine}]{\text{cat } Pd(OAc)_2(PAr_3)_2} ArCH{=}CHCH{=}CHR$$

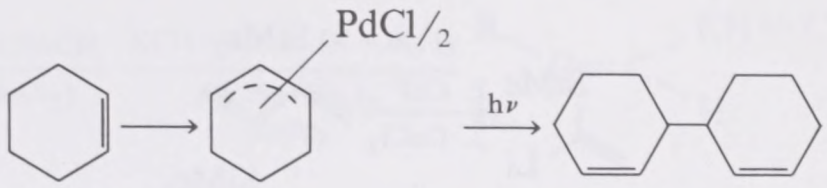
JOC *43* 5018 (1978)
Pure Appl Chem *53* 2323 (1981)

$$RCHO + H_2C{=}CHCHR' \text{ or } HOCH_2CH{=}CHR' \xrightarrow[PPh_3]{\overset{\Delta}{\text{cat } Pd(acac)_2}} RCH{=}CHCH{=}CHR'$$

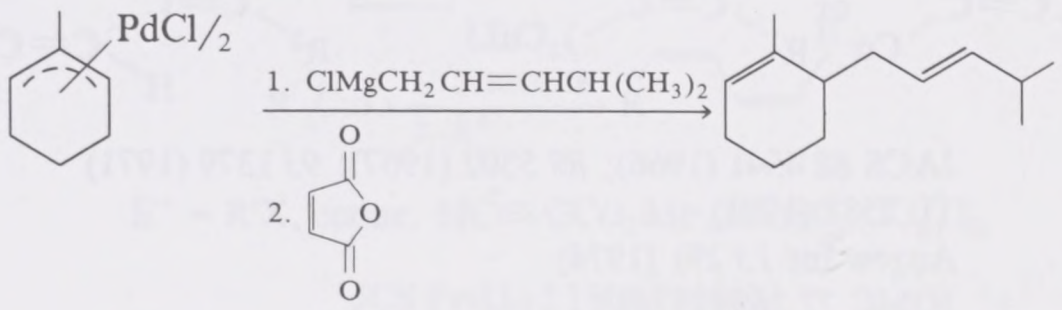
TL *22* 3109 (1981)
Syn Commun *16* 1003 (1986)



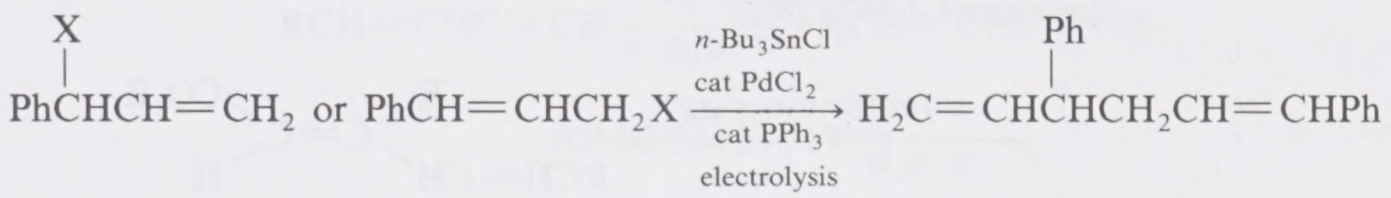
JACS *104* 1310 (1982)



CC 258 (1980)

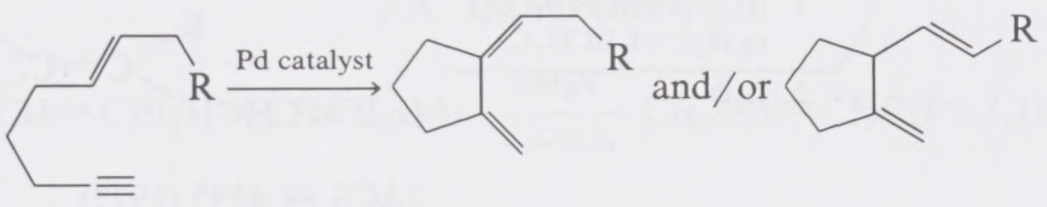


JACS *106* 5029 (1984)



X = Cl, OAc

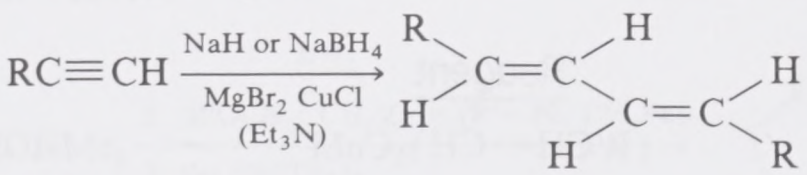
TL *27* 4469 (1986)



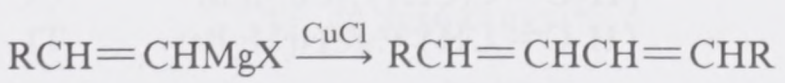
JACS *107* 1781, 4586 (1985); *108* 6053 (1986)
TL *26* 4887 (1985); *28* 1611 (1987)
See page 255, Section 3.12, for a similar reaction

3.14. Organocopper Compounds

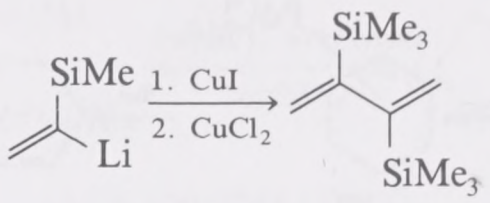
See also page 233, Section 2.17; page 246, Section 3.1; page 248, Section 3.2; page 250, Section 3.3; and page 251, Section 3.4.



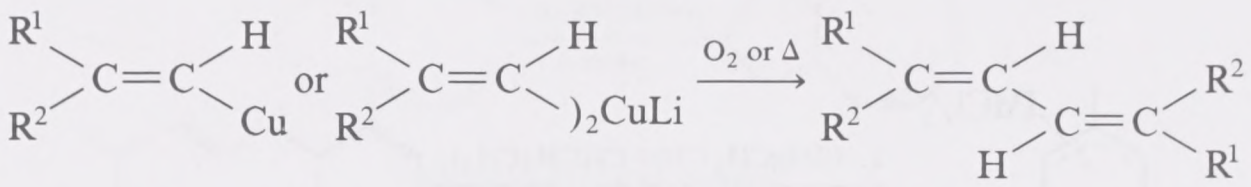
CC 495 (1987)



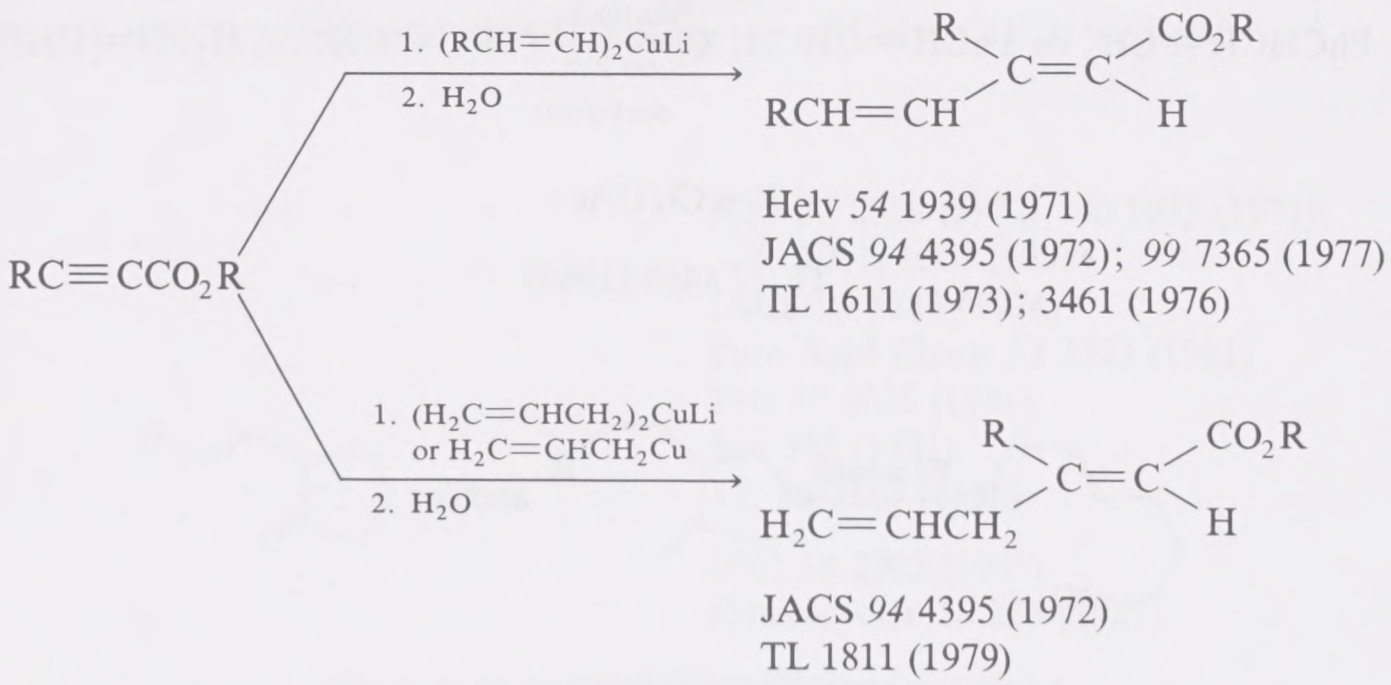
Angew Int *6* 85 (1967)
BCSJ *44* 3063 (1971)



TL *27* 2761 (1986)

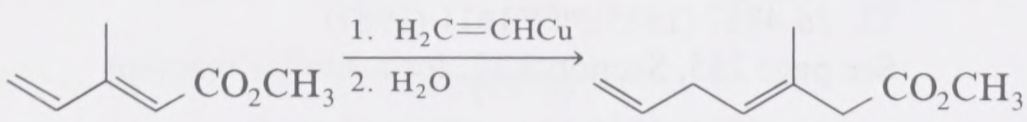


JACS *88* 4541 (1966); *89* 5302 (1967); *93* 1379 (1971)
TL 2583 (1971)
Angew Int *13* 291 (1974)
JOMC *77* 269 (1974)
BSCF 1656 (1974)
Rec Trav Chim *95* 299, 304 (1976)
Organomet *1* 667 (1982)

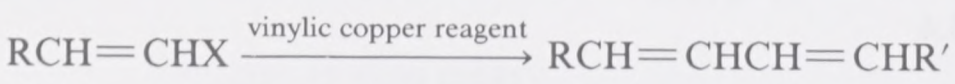


Helv *54* 1939 (1971)
JACS *94* 4395 (1972); *99* 7365 (1977)
TL 1611 (1973); 3461 (1976)

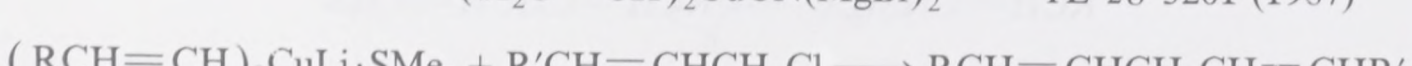
JACS *94* 4395 (1972)
TL 1811 (1979)



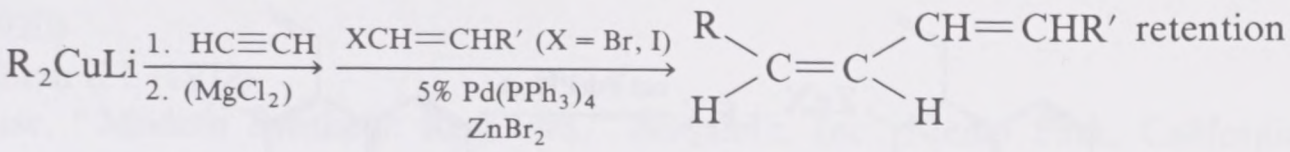
Helv *55* 82 (1972)
JACS *94* 4395 (1972)
TL 1611 (1973)



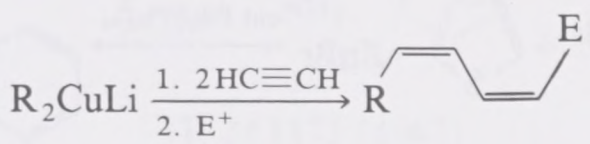
X	Reagent	
halogen	$(R'CH{=}CH)_2CuLi$	JACS *91* 6470 (1969) TL 191 (1978)
OTf	$[H_2C{=}C(CH_3)]_2CuMgBr$ $(H_2C{=}CH)_2CuCN(MgBr)_2$	CC 1452 (1985) TL *28* 3201 (1987)



TL 2705 (1978)

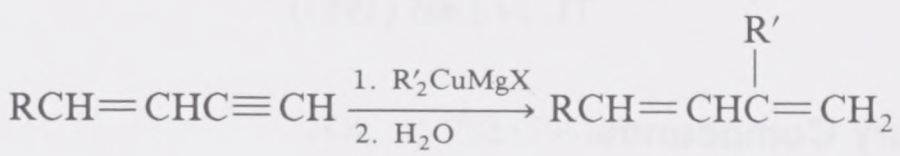


TL *22* 959 (1981); *23* 1589, 5155 (1982)
BSCF II 321, 332 (1983)
Tetr *40* 2741 (1984)

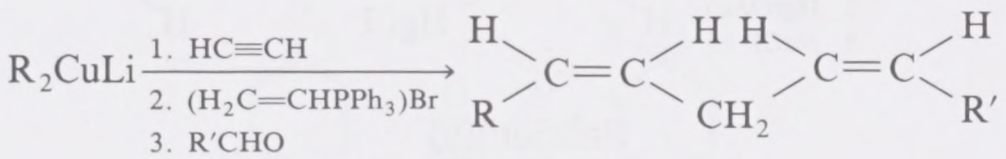


$E^+ = R'X$, enone, $HC{\equiv}CCO_2Me$, RCHO, CO_2, I_2

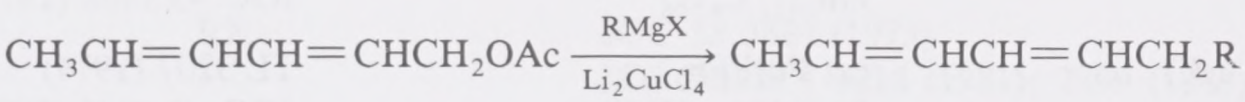
JCS Perkin I 1809 (1986)



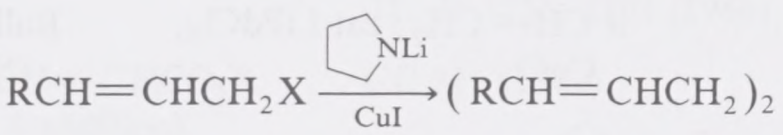
JOMC *144* 13 (1978)



TL *26* 1799 (1985)
JOC *52* 1801 (1987)



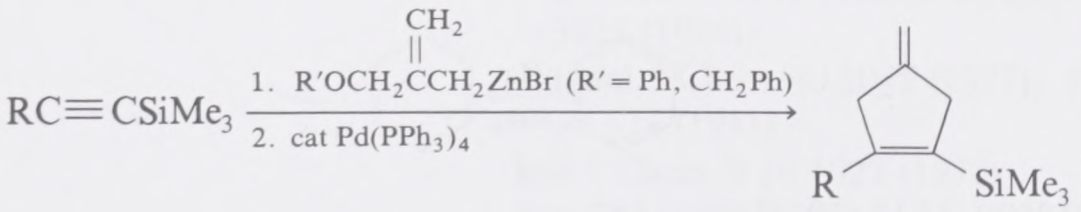
TL *28* 1175 (1987)



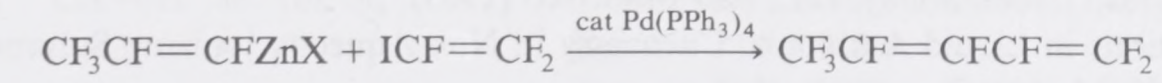
TL 783 (1979)

3.15. Organozinc Compounds

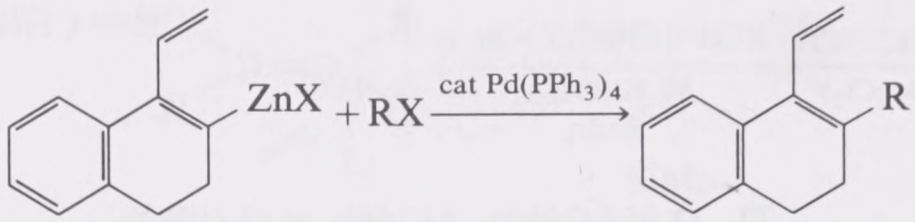
See also page 256, Section 3.13.



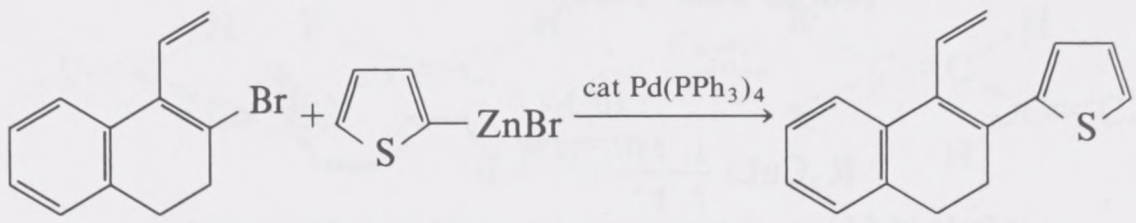
TL *28* 2889 (1987)



TL *27* 4387 (1986)



R = aryl, vinylic

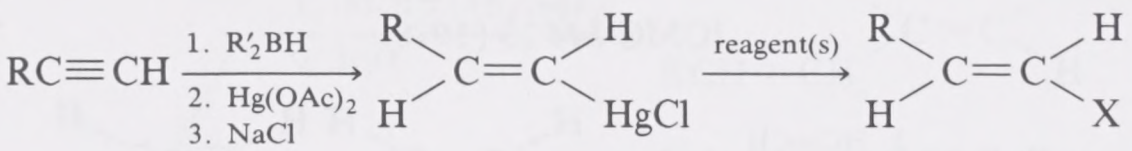


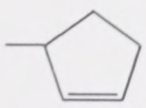
TL *28* 1469 (1987)

$$H_2C{=}CHCH_2ZnBr + BrCH_2CH{=}C(CH_3)_2 \longrightarrow H_2C{=}CHCH_2CH_2CH{=}C(CH_3)_2$$

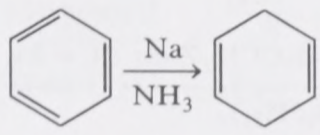
TL *24* 1905 (1983)

3.16. Organomercury Compounds



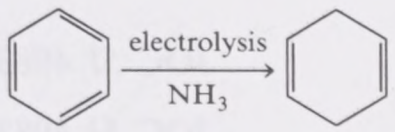
X	Reagent(s)	
$CH{=}CH_2$	$(H_2C{=}CH)_2CuLi$	TL *22* 3435 (1981) Organomet *1* 74 (1982)
$CR{=}CH_2$	$PdCl_2$, C_6H_6	JOC *43* 1468 (1978)
$CH{=}CHR$ (*E*)	cat $Pd(PPh_3)_4$ Li_2PdCl_4, HMPA cat $[ClRh(CO)_2]_2$	TL 3207 (1974) JOC *41* 2241 (1976) JOC *42* 1680 (1977)
$CH{=}CHR'$	$R'CH{=}CH_2$, cat $LiPdCl_3$, $CuCl_2$	Bull Korean Chem Soc *7* 142, 235, 472 (1986)
	 , Li_2PdCl_4	TL *22* 5231 (1981)
$CH_2CH{=}CH_2$	$H_2C{=}CHCH_2Cl$, Li_2PdCl_4	JOMC *156* 45 (1978)

4. Birch Reduction

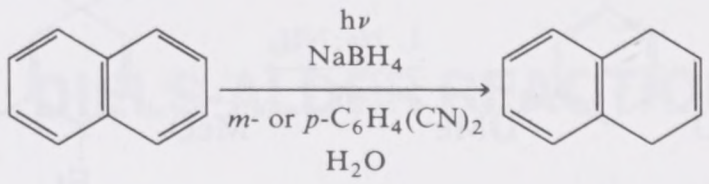


Quart Rev *4* 69 (1950); *12* 17 (1958)
Chem Rev *46* 317 (1950)
"Steroid Reactions," Holden-Day, Inc., San Francisco (1963), pp 267–88, 299–325
"Organic Reactions in Liquid Ammonia, Chemistry in Non-Aqueous Ionizing Solvents," Wiley, New York (1963), Vol 1, part 2
"Reduction," Marcel Dekker, New York (1968), pp 95–170, 186–194

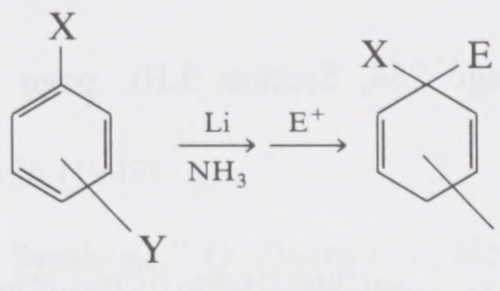
Syn 161 (1970)
Adv Org Chem *8* 1 (1972)
H. O. House, "Modern Synthetic Reactions," Benjamin, Inc., Menlo Park, California (1972), pp 190–205
Natl Prod Repts *3* 35 (1986)
JOC *51* 4983 (1986)



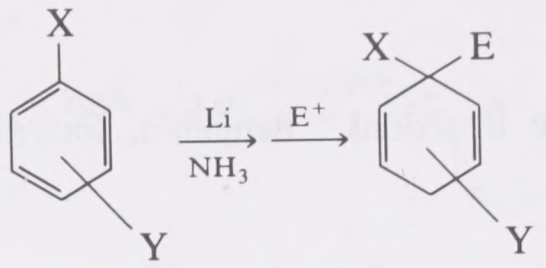
TL *28* 1173 (1987)



JOC *46* 788 (1981)
TL *27* 1469 (1986)

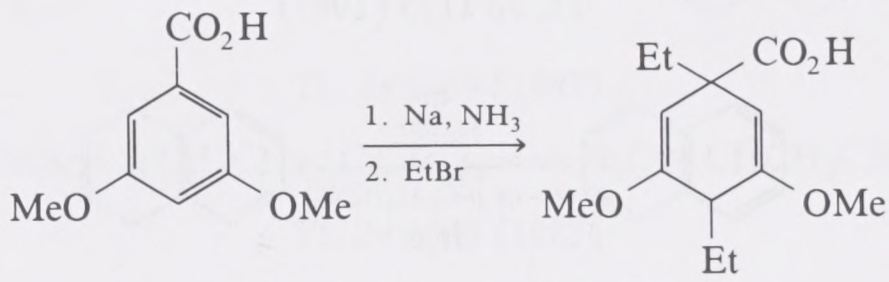


X	E^+	
COR	RX	JOC *38* 3887 (1973) JCS Perkin I 3214 (1981); 2399 (1983); 383, 735 (1985) CC 1292 (1986) TL *27* 5253, 5303 (1986)
CO_2H(R)	$RCH{=}CHCO_2R$ (1,4-addition)	CC 315 (1980)
	RX	JOC *34* 126 (1969); *41* 2649 (1976); *42* 1794 (1977); *45* 1722 (1980); *49* 4429 (1984); *50* 915, 3086 (1985); *51* 2844 (1986); *52* 5482 (1987) Rec Trav Chim *90* 137 (1971) JCS Perkin II 851 (1976) TL 2079 (1976); *21* 3309 (1980); *22* 3683, 4115 (1981); *23* 1095 (1982); *24* 1369 (1983); *27* 1481, 3923 (1986) Austral J Chem *30* 1045 (1977); *31* 1157 (1978); *34* 675 (1981) Ind J Chem B *16* 1027 (1978) Syn 374 (1979) JACS *102* 5085, 6628 (1980); *107* 5574 (1985); *108* 5893 (1986); *109* 3991 (1987) Ber *114* 214 (1981) Tetr *38* 2831 (1982); *39* 4221 (1983) (naphthalene) Natl Prod Repts *3* 35 (1986) (review)



(*Continued*)

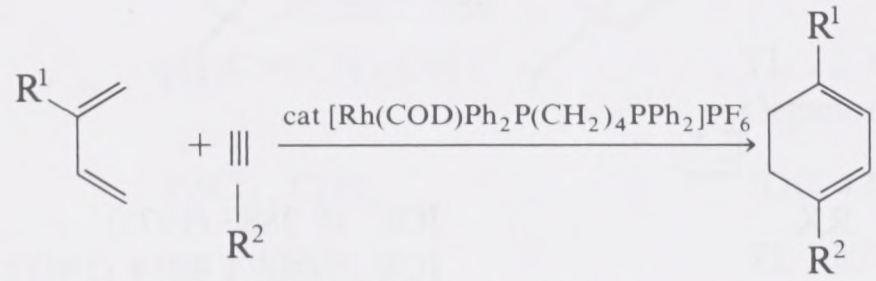
X	E^+	
$CONR_2$	RX	JOC *51* 4983 (1986)
CN	RX	JOC *51* 4983 (1986) JACS *109* 3991 (1987)



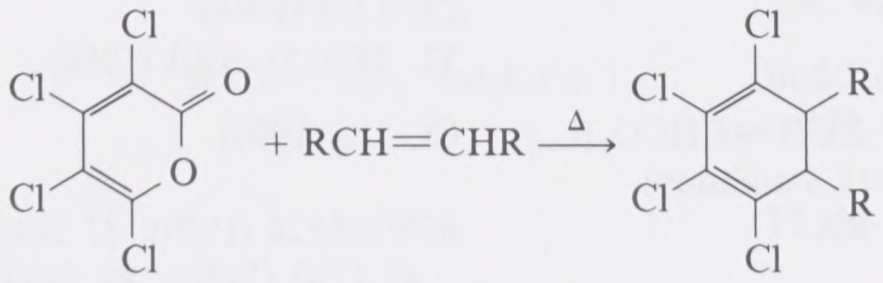
Syn Commun *11* 223 (1981)

5. Cyclization

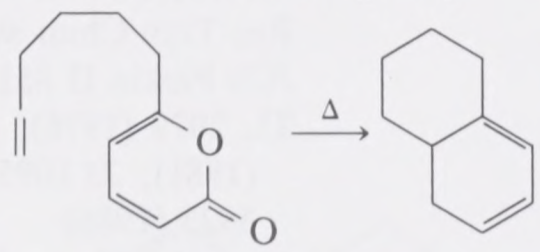
See also page 253, Section 3.7; page 254, Section 3.10; page 255, Section 3.12; and page 256, Section 3.13.



TL *28* 3361 (1987)

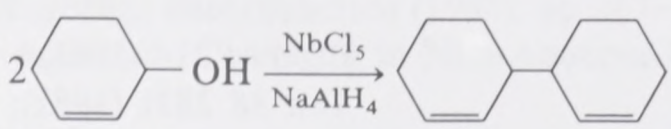


JACS *109* 7074 (1987)



JACS *109* 6124 (1987)

6. Miscellaneous Reactions



CL 157 (1982)

8. DIELS-ALDER REACTION

For Diels-Alder reactions affording arenes see page 101, Section 6.

1. General Reviews

Org Rxs *4* 1, 60 (1948); *5* 136 (1949)
Chem Rev *61* 537 (1961)
A. S. Onishchenko, "Diene Synthesis," D. Davey Co., New York (1964)
R. Huisgen, R. Grashey and J. Sauer, "The Chemistry of Alkenes," Ed. S. Patai, Interscience, New York (1964), Chpt 11
A. Wasserman, "Diels-Alder Reactions," Elsevier, New York (1965)
Angew Int *5* 211 (1966); *6* 16 (1967)
Houben-Weyl, "Methoden der Organischen Chemie," Vol 5/1c, G. Thieme, Stuttgart (1970), p 977

2. Regioselectivity

Facial selectivity	JACS *109* 663 (1987) JOC *52* 3050, 4726, 4732 (1987)
Frontier orbitals	JACS *95* 4092 (1973); *108* 7381 (1986) Acct Chem Res *8* 361 (1975) (review) JOC *43* 1864 (1978); *46* 2338 (1981) (quinones) Pure Appl Chem *55* 237 (1983)
Diene polarity	JACS *100* 7098 (1978) TL *22* 2043, 2047 (1981)
Dienophile substituents	JOC *47* 5009 (1982)
Lewis acids	JACS *86* 3899 (1964); *95* 4094 (1973) TL 5127 (1970) Can J Chem *50* 2377 (1972) JOC *45* 5012 (1980)

Cation-radical	JACS *103* 718 (1981); *104* 2665 (1982); *105* 2378 (theory), 3584 (1983) TL *28* 927 (1987)
Micelles	JOC *47* 3186 (1982); *48* 3137 (1983)

3. Endo Addition

Angew *50* 510 (1937) (review)
Chem Rev *61* 537 (1961) (review)
TL 731 (1966)
JACS *92* 6548 (1970); *93* 4606 (1971); *94* 3633 (1972)
JOC *48* 276 (1983)

4. Asymmetric Diels-Alder Reaction

Angew Int *4* 989 (1951); *23* 876 (1984) (review); *24* 112, 784 (intramolecular, heterodienophile) (1985)
JOC *26* 4778 (1961); *31* 2418 (1966); *48* 1137, 4441 (1983); *49* 1527 (1984); *51* 1457 (1986)
Tetr *19* 2333 (1963); *42* 4035, 5045 (heterodienophile), 5157 (review), 6477 (heterodienophile) (1986)
TL 6359 (1966); *23* 4875 (1982); *24* 3451 (1983) (heterodienophile); *26* 1631, 3095, 5437 (intramolecular) (1985); *27* 667, 4507, 4895 (chiral catalyst), 5509 (1986); *28* 107, 183, 777 (chiral catalysts), 2681, 4045, 5687 (chiral catalysts), 5481 (1987)
JACS *97* 6908 (1975); *102* 7595 (1980); *104* 2269 (1982); *106* 4261 (1984); *108* 3510 (chiral catalyst), 7373 (1986)
CC 437 (1979) (chiral catalysts); 540 (1983) (heterodienophile), 1786 (1985); 609 (1986); 423, 676 (chiral catalysts) (1987)
Helv *67* 1397 (1984)
L. A. Paquette in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Chpt 7 (review)
CL 1109, 1967 (1986) (both chiral catalysts)

5. Mechanism

Angew Int *6* 16 (1967); *19* 779 (1980) (both reviews)
JOC *37* 2181 (1972) (diradical)
JACS *95* 4092, 4094 (1973) (concerted); *106* 203 (1984) (unsymmetrical transition state)

6. Effect of High Pressure

JACS *96* 3664 (1974); *98* 1992 (1976); *102* 6893 (1980); *103* 7007 (1981); *108* 3040 (1986)
JOC *42* 282 (1977); *44* 3347 (1979); *50* 2576, 3239 (1985)
Chem Rev *78* 407 (1978) (review)
Heterocycles *16* 1287, 1367 (review) (1981)
Helv *65* 1021 (1982)
TL *23* 2611, 4875 (1982); *26* 2229 (1985); *27* 1015 (1986); *28* 4045, 5267 (1987)
Syn Commun *13* 537 (1983)
Tetr *42* 5045, 6477 (1986)

7. Use of Microwave Oven

TL *27* 4945 (1986)

8. Use of Ultracentrifuge

TL *28* 707 (1987)

9. Retro Diels-Alder Reaction

Angew Int *5* 211 (1966) (review); *25* 414 (1986) (review)
Chem Rev *68* 415 (1968) (review)
Tetr *34* 19 (1978)
TL *22* 4553, 4557 (1981); *23* 5463 (1982); *25* 3459, 3461 (1984); *26* 2103 (1985); *27* 3045 (1986); *28* 183, 357, 1329, 3027, 3147, 5819, 6503, 6507 (1987)
JOC *47* 598 (1982); *49* 1033, 4091 (1984); *51* 2851 (1986); *52* 4603, 5746 (aza) (1987)
JACS *106* 4862 (1984); *108* 1019 (1986); *109* 5859 (1987) (aza)
Can J Chem *62* 2019 (1984)
Syn 121 (1985) (review); 207 (1987) (review)
Austral J Chem *38* 1339 (1985)
Syn Commun *15* 959 (1985)

10. Intramolecular Diels-Alder Reaction

Angew Int *16* 10 (1977) (review); *21* 620 (1982) (allene + arene); *24* 784 (1985) (asymmetric, heterodienophile)
Syn 793 (1978) (*o*-quinodimethane review)
JACS *100* 6289, 8034 (1978); *102* 6353 (1980); *103* 2090, 4948, 5200, 6261, 6696 (1981); *104* 1033, 1140, 2269, 3216, 4725 (isobenzofuran as diene), 5708 (bridgehead alkene synthesis), 5715 (bridgehead enol lactone synthesis), 5719, 5728, 5853 (1982); *105* 3732 (1983); *106* 1133, 6085 (acid catalyzed), 6422, 6735, 7641, 8327 (1984); *107* 2149, 2573, 4072, 4791 (1985); *108* 4953 (1986); *109* 447, 1186, 4390, 6124 (1987)
JOC *45* 4264, 4267 (1980); *46* 1506, 1509, 2273, 3763 (1981); *47* 180, 337, 610 [via bis(orthoquinone)], 1789, 2682 (vinyl allene as diene), 4337 (pyrone as diene), 4611, 4786, 4825 (1982); *50* 725 (bridgehead dienes), 1770, 2626, 2719, 2807, 3086 (1985); *51* 1150, 1155, 1633, 2487, 3075 (ionic), 3553 (iminium ions), 3740, 4023 (1986); *52* 564, 1236, 1638, 2040, 4369, 4661, 5548, 5700 (1987)
Chem Rev *80* 63 (1980) (review)
Chem Soc Rev *9* 41 (1980) (review)
Helv *64* 478, 1387 (1981); *65* 2212 (1982)
TL *22* 97, 101, 361, 3929, 3933, 4877 (benzyne), 5141 (1981); *23* 303, 1523, 2361 (1982); *24* 3295, 3701 (1983); *25* 19 (1984); *26* 591, 1249, 2229, 2689, 3307, 5109, 5437 (asymmetric) (1985); *27* 1837, 3045, 3227, 4877, 6291 ($PhNMe_2$ as solvent) (1986); *28* 735, 927 (cation radical), 931, 1059, 1175, 2087, 2447, 2937, 2969, 3423, 3819 (photochemical), 5249, 5253, 5255, 5339, 5895 (allene), 6035, 6253 (1987)
CL 29 (1981)
Ann 973 (1982)
Can J Chem *62* 183 (1984) (review)

Org Rxs *32* 1 (1984) (review)
D. F. Taber, "Intramolecular Diels-Alder and Alder Ene Reactions," Springer, New York (1984) (review)
CC 1423 (1984); 421 (1985); 671, 724, 1447, 1449, 1797 (solvent effect) (1986); 418, 898, 1449 (allenic ester), 1540, 1786 (1987)
Acct Chem Res *18* 16 (1985) (imino review)

11. Inverse Electron Demand Diels-Alder Reaction

See also page 101, Section 6.

JOC *30* 3679 (1965); *51* 5328 (1986); *52* 4610 (1987)
TL 4651 (1972); *27* 667 (1986); *28* 2681 (1987)
JACS *94* 2891 (1972); *103* 6261 (1981); *107* 5745 (1985); *108* 7373 (1986) (asymmetric)
Ann 306 (1981)
Helv *64* 478 (1983)

12. Use of Heterodienophiles

JOC *44* 3347 (1979); *47* 1981, 3183, 3649 (1982); *51* 3553 (1986) (iminium ions)
Heterocycles *12* 949 (1979) (review)
JCS Perkin I 1795 (1979)
Tetr *37* 1825 (1981) (singlet oxygen review); *38* 1299, 3087 (review) (1982); *42* 5045, 6477 (1986) (both asymmetric aldehyde, high pressure)
TL *22* 4807 (1981); *23* 3739 (1982); *24* 3451 (1983) (aldehyde); *27* 1975, 2981 (imine), 6181 (1986); *28* 1059 (azo), 2103 (iminium ions), 4951 (aldehyde), 5103 (azetinone) (1987)
JACS *103* 6387 (1981); *106* 2453, 2455, 2456 (all aldehydes), 3240 (intramolecular acylimino), 4294 (aldehyde), 8217 (aldehyde, intramolecular) (1984); *107* 1246, 1256, 1269, 1274, 1280, 1285 (all aldehydes), 1768 (iminium ions), 6647, 7761, 7762 (all aldehydes) (1985); *108* 2486, 4145 (both aldehydes) (1986); *109* 1572, 2082, 4390 (1987) (all aldehydes)
CC 540 (1983) (asymmetric aldehyde)
Acct Chem Res *18* 16 (1985) (imino review)
D. L. Boger, S. M. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis," Academic Press, New York (1987) (review)
Adv Heterocyclic Chem *42* 245 (1987) (review)

13. Use of Heteroatom-Containing Dienes

JACS *72* 3079 (1950); *73* 913, 5267 (1951); *75* 1312 (1953) (all 1-oxa)
Chem Rev *62* 405 (1962) (general review); *75* 651 (1975) (general review)
TL 129 (1965) (1-oxa); 3417 (1977) (1-thia); *21* 1133 (1980) (1-oxa); *25* 721 (1984) (1-oxa); *26* 5273 (1985) (1-oxa); *27* 6181 (1986) (1-oxa); *28* 4045 (1987) (1-oxa)
JOC *42* 282 (1977) (1-oxa); *50* 2719 (1-aza), 5678 (2-aza) (1985); *52* 1638 (1987) (1-oxa)
Tetr *39* 2869 (1983) (aza review)
Angew Int *24* 784 (1985) (1-oxa, intramolecular, asymmetric)
Ann 2261 (1985) (1-oxa)

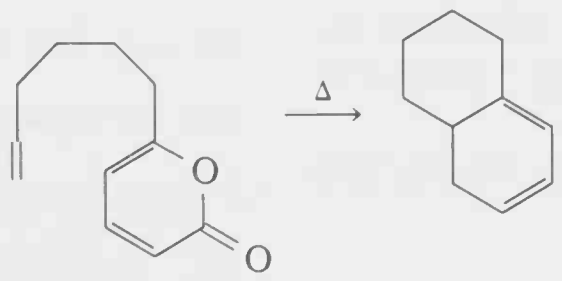
D. L. Boger, S. M. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis," Academic Press, New York (1987) (general review)
Adv Heterocyclic Chem *42* 245 (1987) (review)
CC 884 (1987) (1-oxa)

14. Use of 1,3-Dienes with Attached Heteroatom Substituents

Reviews:

Syn 753 (1981)
Acct Chem Res *14* 400 (1981) (R_3SiO)

Helv *58* 590, 593 (1975) (1-MeO_2CNR); *65* 2563 (1982) (1,1-MeO, 3-Me_3SiO); *66* 2769 (1983) (1-ArNH, 2-CO_2Me); *68* 1133 (1985) (1-EtO, 4,4-Me)
Chem Listy *70* 1266 (1976) (1-R_2N)
JACS *98* 3027 (1-MeO, 3-Me_3SiO), 5017 (2-MeO, 3-PhS) (1976); *101* 6996, 7001, 7008 (1979) (1-MeO, 3-Me_3SiO and derivatives); *102* 3554 (2-RO or RCO_2, 3-RS) (1980); *103* 2816 (1981) (1-RCONH); *104* 2059 (1-PhS, 2-MeO, 3-Me), 2308 (1-AcO, 4-Me_3Si), 2923 (1-PhS, 2-Me_3SiO, 3-H or Me), 3511 (1-Me, 3-Me_3SiO), 4299 (2,3-Me_3SiCH_2) (1982); *105* 6335 (1983) (1-RO_2CNH, 4-PhS or PhSO or $PhSO_2$) (1983); *109* 6396 (1987) (2-$PhSO_2$, 4-H or Me)
CC 681 (1976) (1-Me_3Si); 178 (1978) (1-Me_3Si; 1-Me_3Si, 3-Me_3SiO)
JOC *41* 2625 (1976) (1,4-AcO, 2-Me); *42* 282 (1-AcO); 1819 (1-PhSe, 2-Me_3SiO, 4-MeO) (1977); *43* 379 (1,1-MeO, 3-Me_3SiO), 2726 (2,3-Me_3SiO), 4559 (1-RCO_2, 4-Et) (1978); *46* 1810, 4161 (1980) (both various MeO, Me_3SiO); *47* 2051 (2-Me_3SiO; 2-Me_3SiCH_2; 1-MeO, 3-Me_3SiO), 3649 (various Me_3SiO), 4005 (1-PhS, 2-MeO), 4774 (1,3-MeO), 5009 (1-MeO, 3-Me), 5083 (1,4-MeO) (1982); *48* 3096 (1,4-*t*-BuO), 4986 (1-MeO, 3-Me_3SiO, 2-H or Me), 5051 (1-PhS, 2-MeO; 2-PhS, 3-MeO; 2-ArS, 3-AcO or MeO; 1-PhS, 4-AcO) (1983); *49* 1898 (1,4-*t*-$BuMe_2SiO$), 2954 (2-Cl or Br, 3-PhS or PhSe; 1,2-Cl, 3-PhS or PhSe; 1-Cl, 2-Br, 3-PhS or PhSe), 3595 (1-RO, 3-Me; 1-RO, 3-$RSCH_2$), 3628 (1-*t*-BuO, 3-Me_3SiO) (1984); *50* 141 (2-PhS, 3-Me), 1955 (1,3-AcO; 1-EtO_2CO, 3-AcO) (1985); *51* 2210 (2-Ph_2PO) (1986); *52* 2334 (1987) (1-PhSe, 4-MeO)
TL 2113 (1976) (1,4-OCH_2O), 3323 (1978) (2-Et_3Si); 4537 (1979) (1-RCONR); *22* 3381 (1981) (1-PhS, 2-RO, 3-Me); *23* 551 (2-Me_3SiCH_2), 775 (2-MeO), 2155 (1,3-MeO) (1982); *24* 1171 (1983) (1-RO, 3-$RSCH_2$); *25* 5715 (1984) (1-MeO, 4-CH_2CO_2Na); *26* 381 (1-EtO, 1-*t*-$BuMe_2SiO$), 2555, 2559 (both 1-Ar or 1,2-Ar), 5175 (1-RO, 3-Me_3SiCH_2; 1-MeO, 3-Me_3Si; 2-Me_3SiCH_2), 6519 (1-MeO, 1-Me_3SiO, 3-MeO or Me_3SiO) (1985); *27* 2761 (2,3-Me_3Si), 2913 (2-*n*-Bu_3Sn), 5075 (1-MeO, 3-Cl) (1986); *28* 4169 (1987) [1-$B(OR)_2$]
Org Syn *58* 163 (1978) (2-Me_3SiO); *61* 147 (1983) (1-MeO, 3-Me_3SiO)
JCS Perkin I 1582 (1,1-RO); 2415 (1-Me_3Si; 1-Me_3Si, 3-Me or 3-Me_3SiO or 4-Me or 4-Me_3Si) (1981)
Tetr *37* 4081 (1981) (1-MeO, 1-AcO, 3-Me_3SiO); *40* 5039 (1984) (1-Me_3SiO, 1,2-MeO, 4-Me)
Syn Commun *11* 481 (1981) (1,2-MeS); *14* 483 (2-COMe), 797 (1-$PhSeCH_2CH_2O$, 3-Me) (1984)
Syn 273 (1,4-EtO_2CNH), 380 (1,1,2,3-Me_3SiO); 958 (1-EtO_2CNH, 4-$PhCO_2$) (1982); 899 (1985) (3-*n*-Bu_3Sn; 3-$PhMe_2Si$)
CL 1057 (1982) [1-RO (R = *t*-Bu, Me_3Si, Ac), 3-Me_3SiO]
Can J Chem *62* 2676 (1984) [2-$OPO(OEt)_2$, 4-Me)]



JACS *109* 6124 (1987)

15. o-Quinodimethanes

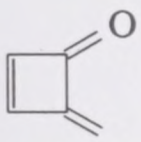
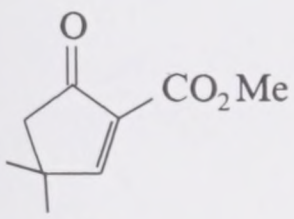
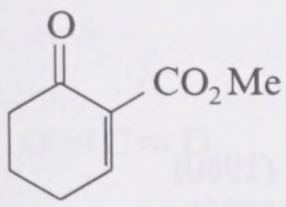
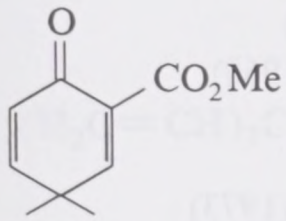
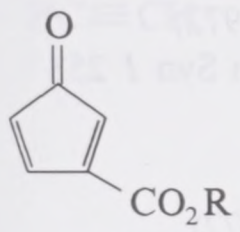
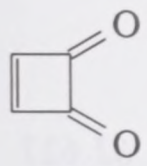
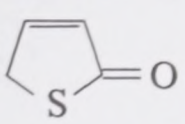
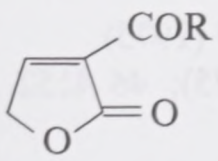
Syn 793 (1978) (review)
Helv *62* 2017 (1979)
CC 1119 (1979); 158, 430, 699 (1982)
Chem Soc Rev *9* 41 (1980) (review)
Acct Chem Res *13* 270 (1980) (review); *17* 35 (1984) (indole-2,3-quinodimethane review)
JACS *102* 863, 6885 (1980); *103* 476, 1992 (1981); *104* 1106, 1140 (indole-2,3-quinodimethane), 3511 (1982); *105* 1586 (1983)
Heterocycles *14* 1615 (1980) (review)
Tetr *37* 3, 2547, 2555, 3813 (1981)
TL *22* 1357 (1981); *23* 2973 (1982)
JCS Perkin I 1383, 1386 (1981); 2239, 2249 (1982)
Pure Appl Chem *53* 1181 (1981) (review)
JOC *47* 2331 (1982); *50* 2764 (1985) (intramolecular); *51* 3490, 4160, 4749 (intramolecular) (1986); *52* 28, 4833 (1987)
Ann 1999 (1982)
Can J Chem *62* 183 (1984) (review)

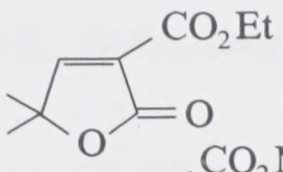
16. Arynes

R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York (1967)
BCSJ *50* 3338 (1977)
JACS *102* 6649 (1980) (bisaryne); *108* 4932 (1986)
JOC *46* 4874 (1981) (bisaryne); *51* 979 (1986) (bisaryne); *52* 792, 3835 (bisaryne) (1987)
TL *22* 4877 (1981) (intramolecular); *25* 2073 (1984) (bisaryne); *27* 5319 (1986)
Tetr *38* 427 (1982) (hetarynes review)

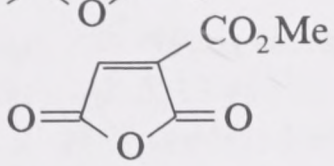
17. Some Other Dienophiles

$R^1CH{=}CR^2CR^3(OR')_2$ (R^1, R^2 or R^3 = H or Me) (as allyl cation)	JACS *109* 2182 (1987)
vinylic sulfoxides	TL *27* 6041 (1986)
$PhSOCH{=}CHCO_2R$	Austral J Chem *37* 1677 (1984)
vinylic sulfones	TL *21* 3339 (1980); *23* 5127 (1982) JACS *102* 853 (1980) JOC *48* 4976, 4986 (1983)
E- or *Z*-$PhSO_2CH{=}CHSO_2Ph$	See page 270, Section 18, $HC{\equiv}CH$.
$H_2C{=}C(SO_2Ph)_2$	Syn 757 (1984)
$H_2C{=}CHNO_2$	J Chem Res (S) 78 (1983)
$Me_3SiCH{=}CHNO_2$	JOC *49* 3235 (1984)
Z-$Me_3SiCH{=}CHCO_2H$	Angew Int *23* 233 (1984)

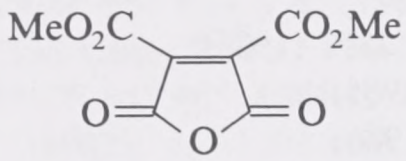
$H_2C{=}C(COR)CO_2R'$	JOC *47* 4152 (1982)
$H_2C{=}C(O_2CR)COCH_3$	Helv *64* 188 (1981) JOC *47* 409 (1982) TL *28* 865 (1987)
$(MeO)_2CHCH_2CH{=}CHCOCH_3$	Can J Chem *60* 2760 (1982)
cyclic enones	JOC *47* 5056 (1982); *48* 2802 (1983); *50* 4686, 4691, 4696 (1985); *51* 2642, 2649, 5177 (1986) Tetr *41* 349 (1985)
	TL *23* 841 (1982)
2,5-cyclohexadienones	Can J Chem *57* 377 (1979) JOC *48* 1810 (1983)
	TL *24* 1353 (1983)
	Syn Commun *12* 715 (1982)
	TL 2919 (1977) Can J Chem *59* 601 (1981)
	JOC *52* 5298 (1987)
	TL *23* 841 (1982)
quinones	CC 837 (1983)
butenolides	TL 5317 (1972); *25* 19 (1984) (intramolecular); *27* 1081 (1986); *28* 3405 (1987) CC 737 (1985) JCS Perkin I 2279 (1986)
	JOC *47* 4777 (1982)
	JOC *47* 4152 (1982)



Can J Chem *60* 921 (1982)



JOC *47* 1451 (1982)



JOC *47* 3647 (1982)

$H_2C{=}C{=}CHF$ JACS *107* 7183 (1985)

$H_2C{=}C{=}CHSO_2Ph$ JOC *50* 512 (1985)

allenic ketones J Chem Res (S) 300 (1982)

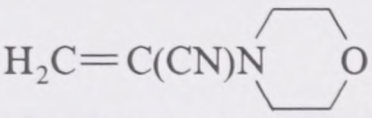
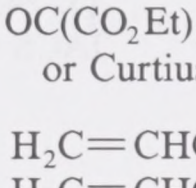
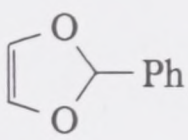
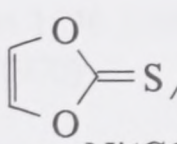
allenic esters Helv *65* 2563 (1982)

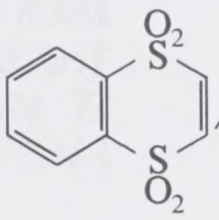
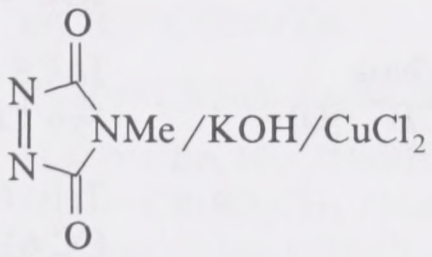
$n\text{-}Bu_3SnC{\equiv}CCO_2R(CN)$ CC 1452 (1984)

$ClCOC{\equiv}CCOCl$ Ber *115* 804 (1982)

18. Dienophile Equivalents

Equivalent	Reagent(s)	
$H_2C{=}CH_2$	$H_2C{=}CHSO_2Ph/Na(Hg)$	JACS *102* 853 (1980)
		JOC *48* 4976 (1983)
		CC 451 (1986)
	$BrCH{=}CHBr/Zn$	Ber *93* 1888 (1960)
$RCH{=}CHR$	$RCH{=}CRNO_2/n\text{-}Bu_3SnH$	CC 33 (1982)
$H_2C{=}C{=}CH_2$	$H_2C{=}CBrCHO/NaBH_4/Zn$	JOC *38* 3961 (1973)
	$H_2C{=}CBrSO_2CH_3/NaOMe$	JACS *94* 1012 (1972)
	$H_2C{=}C(SiMe_3)CH_2Cl/MeMgBr$	Organomet Chem Syn *1* 253 (1971)
$H_2C{=}C{=}CHR$	$(H_2C{=}CHPPh_3)Br/LDA/RCHO$	TL 2095 (1974)
		JOC *42* 4095 (1977)
$H_2C{=}C{=}O$	review	Syn 289 (1977)
	$H_2C{=}CClCOCl/NaN_3/\Delta/H_3O^+$	JACS *93* 4326 (1971)
	$H_2C{=}C(OAc)CN$ /base	JACS *78* 2473 (1956); *82* 627 (1960)
		JOC *31* 3787 (1966); *46* 4152 (1981)
		TL 121 (1972)
	$H_2C{=}CClCN/(S^{2-})$, KOH	CA *64* 4965g (1966); *71* 112496p (1969)
		JACS *91* 5675 (1969); *93* 1489 (1971)
		Ber *105* 1840 (1972)
		TL 121 (1972)
		CC 642 (1974); 39 (1975)
		JOC *40* 2565 (1975); *46* 4152 (1981)

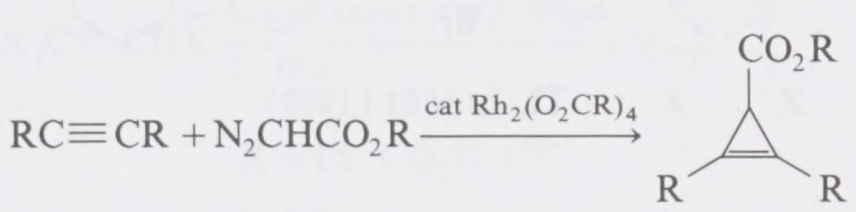
	 /hydrolysis	TL *23* 953 (1982)
	$H_2C{=}C(CN)SMe$ /hydrolysis	TL *23* 953 (1982)
	$H_2C{=}C(SMe)CO_2Me$ /hydrolysis	TL *23* 953 (1982)
	$H_2C{=}CHCN/PCl_5/OH^-$	JOC *33* 2111 (1968) CA *71* 112496p (1969)
	$H_2C{=}CHB(OBu)_2$ /[O]	TL 121 (1972)
	$H_2C{=}CHNO_2$ /NaOH/HCl	JACS *96* 5261 (1974) Tetr *32* 961 (1976)
	$H_2C{=}CHCO_2H$ /LDA/O_2	TL 4611 (1975)
	$H_2C{=}CHCO_2H$ /LDA/ $(MeS)_2$ /NCS	JACS *97* 3528 (1975)
	$H_2C{=}CHSO_2Ar$ /LDA/ $MoO_5 \cdot py \cdot HMPA$	TL *21* 3339 (1980)
$MeO_2CCH{=}C{=}O$	$MeOC{\equiv}CCO_2Me/H_3O^+$	CC 1227 (1982)
	$PhSC{\equiv}CCO_2Me/H_2O$, $HgCl_2$	CC 1227 (1982)
	$BrC{\equiv}CCO_2Me/NaOMe/H_3O^+$	TL 383 (1979)
	 /$NaHCO_3$,	JACS *99* 7079 (1977)
	MeOH/NCS/H_3O^+	
$O{=}C{=}O$	$(H_2C{=}CHPPh_3)Br/LDA/O_2$	TL 2095 (1974) JOC *42* 4095 (1977)
	$OC(CO_2Et)_2/OH^-/H^+/Pb(OAc)_4$ or Curtius	JACS *97* 6892 (1975) JOC *42* 4095 (1977)
$(H_2C{=}CH)_2CO$	$H_2C{=}CHCO(CH_2)_2Cl$ /base	JACS *91* 2806 (1969)
	$H_2C{=}CHCOCH(SePh)CH_3$ /[O]	Syn Commun *8* 211 (1978)
$HC{\equiv}CH$	review	Tetr *40* 2585 (1984)
	$TsC{\equiv}CH$ /Na(Hg)	CC 639 (1980) JACS *107* 686 (1985)
	$PhSOCH{=}CH_2/\Delta$	JACS *100* 1597 (1978)
	$ClCH{=}CHCl$ /Zn or Na	JACS *74* 2193 (1952) Tetr *28* 3031 (1972)
	 Ph /*n*-BuLi	CC 1593 (1968) JCS C 886 (1971) JACS *95* 7161 (1973) JCS Perkin I 2332 (1973)
	 /$P(OMe)_3$, $Fe(CO)_5$ or $Ni(COD)_2$	JACS *85* 2677 (1963); *95* 7161 (1973) TL 2667 (1973) JOMC *69* 423 (1974)
	Z-$PhSO_2CH{=}CHSO_2Ph$ /Na(Hg)	CC 914 (1982) JOC *49* 596 (1984); *52* 3250, 4732 (1987) Can J Chem *62* 2487 (1984) JACS *107* 4789, 6400 (1985); *108* 3453 (1986)

Equivalent	Reagent(s)	
	E-$PhSO_2CH{=}CHSO_2Ph$ /Na(Hg)	TL *24* 1653 (1983) Can J Chem *62* 2487 (1984) JACS *107* 6400 (1985) JOC *50* 4340 (1985); *52* 4740 (1987) Tetr *42* 1789 (1986)
	 /Na(Hg)	Heterocycles *23* 1119 (1985)
	E-$PhSO_2CH{=}CHSiMe_3$ / n-Bu_4NF	TL *22* 4643 (1981) JOC *48* 4976 (1983)
	Z-$Me_3SiCH{=}CHCO_2H$ / electrolysis	Angew Int *23* 233 (1984)
	$ClCOCH{=}CHCOCl$ /$Pb(OAc)_4$	Syn 117 (1979)
	$MeO_2CC{\equiv}CCO_2Me$ /NaOH/Cu	Tetr *28* 3031 (1972)
	$MeO_2CC{\equiv}CCO_2Me$ /NaOH/CuO	TL 4447 (1976)
	$MeO_2CC{\equiv}CCO_2Me$ /NaOH/ electrolysis	JACS *96* 4671 (1974)
RC≡CH	$RC(NO_2){=}CHSO_2Ph$ / n-Bu_3SnH or Na_2S	TL *27* 1595 (1986)
N≡N	$RO_2CN{=}NCO_2R$ /base/[O]	TL 2433 (1974) JACS *97* 918 (1975)
	 /KOH/$CuCl_2$	JACS *94* 3658 (1972)

9. CYCLIZATION AND RELATED REACTIONS

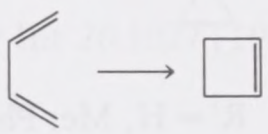
For cyclizations that annulate an alkene-containing moiety onto the carbon-carbon double bond of an enone see also page 653, Section 6.

1. Three-Membered Rings



TL 1239 (1978)

2. Four-Membered Rings



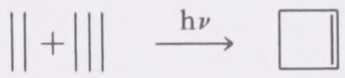
Thermal reactions

JCS 3880 (1955)
JACS *84* 4600 (1962); *86* 1676 (1964); *87* 3996 (1965); *88* 1073, 4800 (1966); *89* 112 (1967); *90* 3582, 5310 (1968); *92* 399 (1970)
JOC *30* 3524 (1965)
TL 3719, 3723 (1969)
Tetr *25* 4375 (1969)
CC 1583 (1970)

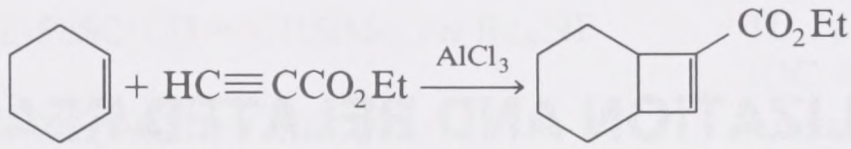
Photochemical reactions

JOC *27* 1910 (1962); *52* 2644 (1987)
JACS *84* 1220 (1962); *88* 2742 (1966); *94* 4794 (1972); *97* 2272 (1975)

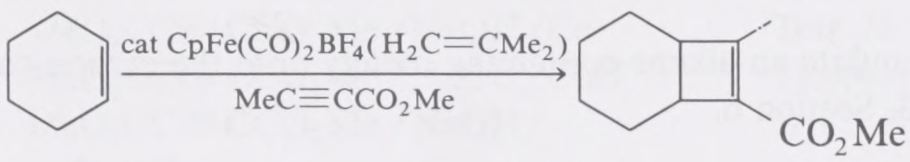
Proc Chem Soc 334 (1962)
Chem Weekb *19* 381 (1964); *21* 1001 (1965)
Rev Pure Appl Chem *16* 117 (1966)
Fortschr Chem Forsch *7* 445 (1967)
Adv Alicyclic Chem *2* 185 (1968)
Intra-Science Chem Reports, Vol 2 (1968)



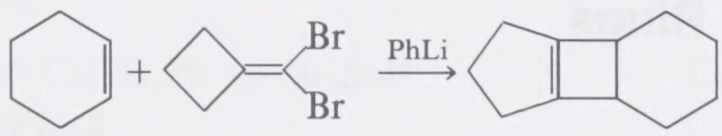
Ber *97* 2942 (1964); *102* 3974 (1969)
TL 3409 (1966); *27* 2703 (1986) (intramolecular); *28* 267 (1987)
JOC *49* 832 (1984) (intramolecular); *51* 5232 (1986) (intramolecular)



JOC *41* 3061 (1976)

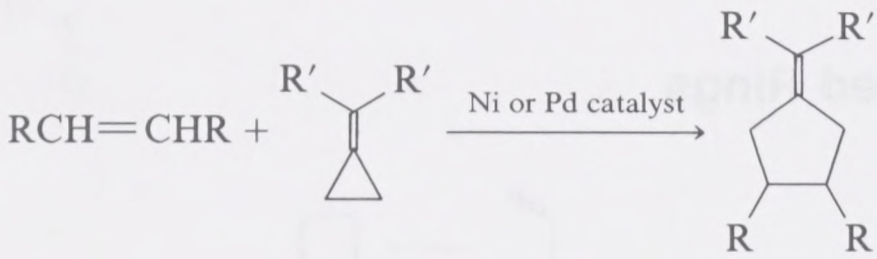


Organomet *1* 397 (1982)



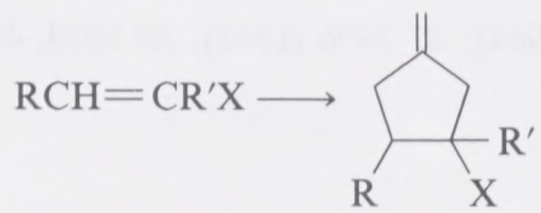
TL *23* 1661 (1982)

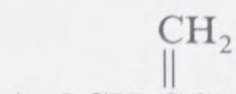
3. Five-Membered Rings



R′ = H, Me, Ph

Angew Int *16* 249 (1977); *21* 622 (1982); *25* 1 (1986) (review)
Ber *113* 3334 (1980); *114* 3313 (1981); *116* 2920 (1983)
JOMC *221* C33 (1981)
TL *26* 1045 (1985)

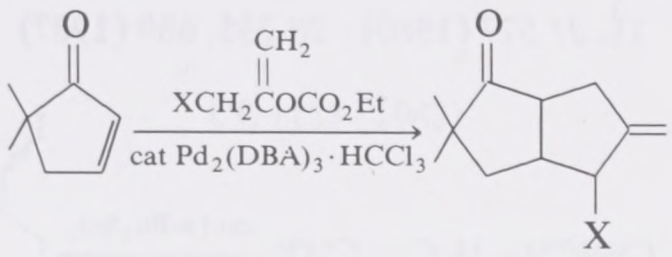




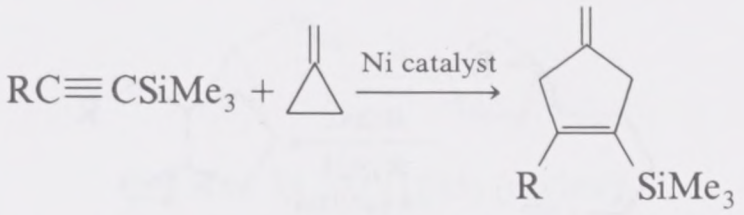
JACS *101* 6429, 6432 (1979); *102* 6359 (1980); *103* 5972, 5974 (1981); *104* 3733, 6668 (1982); *105* 2315, 2326 (1983); *107* 721, 1075, 1293 (1985); *108* 284, 6051 (1986)

Organomet *1* 1543 (1982)
TL *27* 1445, 4137 (1986); *28* 4547 (1987)
Angew Int *25* 1 (1986) (review)

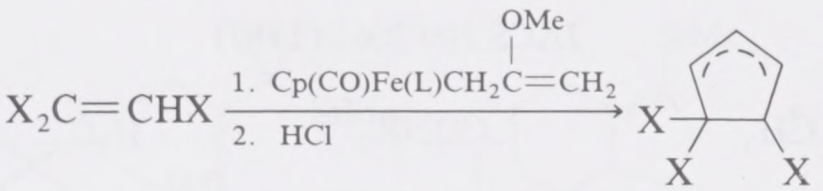
$MsOCH_2C(=CH_2)CH_2SiMe_3$, cat $Ni[P(OEt)_3]_4$ — CC 1201 (1986)



X	
$ArSO_2$	TL *25* 5183 (1984); *28* 6053 (1987)
CN	TL *25* 5183 (1984)

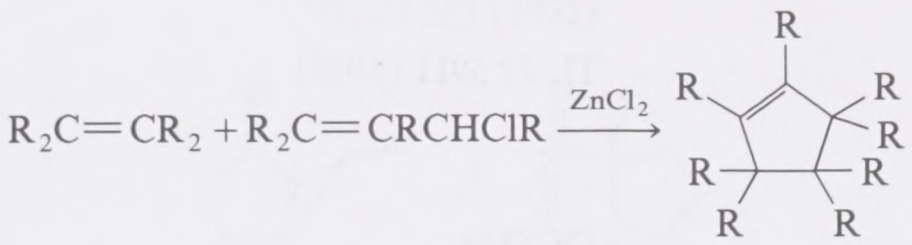


Angew Int *24* 316 (1985)

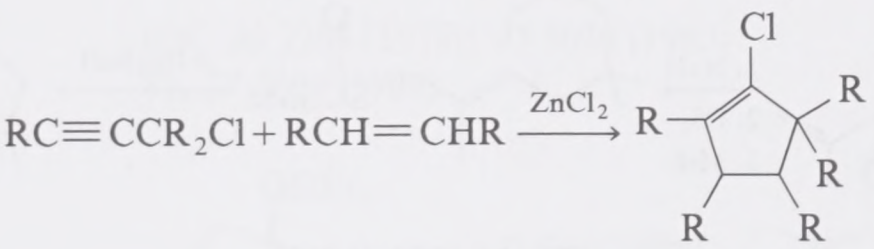


X = Ph, CO_2R, CN

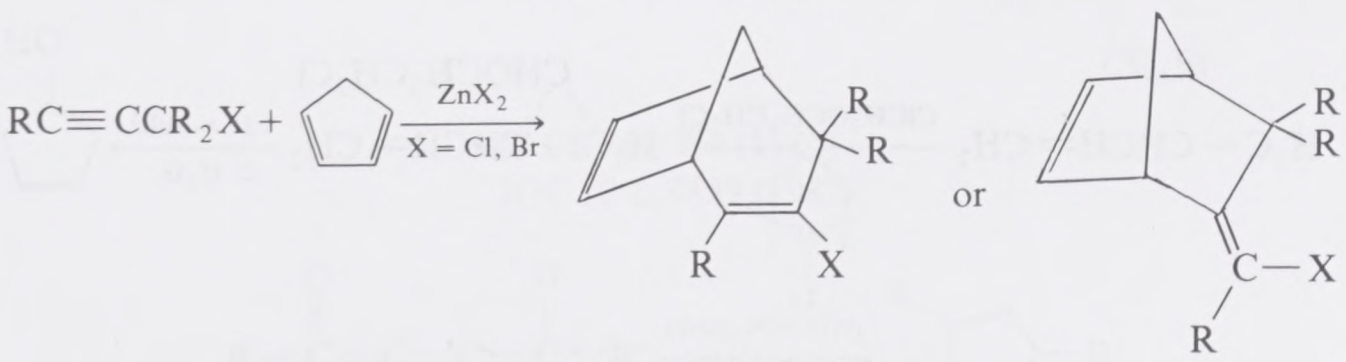
JOMC *243* 451 (1983)



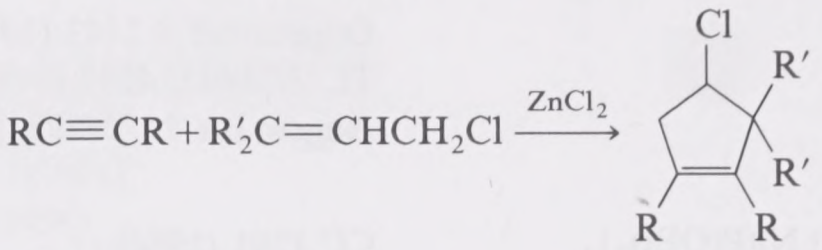
Angew Int *20* 1027 (1981)



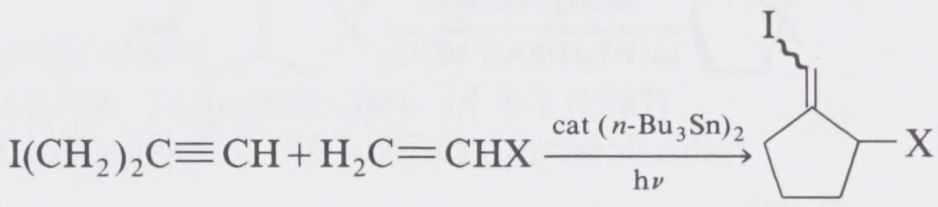
JOC *46* 1041 (1981)



Angew Int *19* 814 (1980)
Ber *115* 3479 (1982)

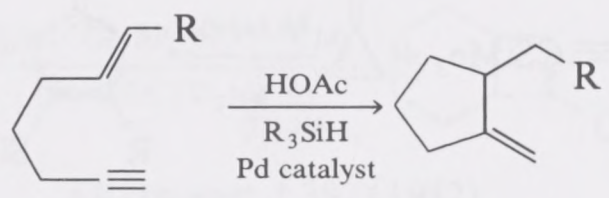


TL *21* 577 (1980); *28* 235, 689 (1987)

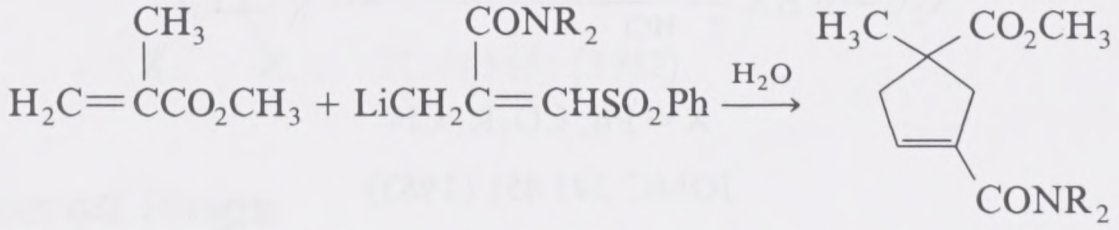


X = CN, CO_2R, SO_2Ph, COR, CHO

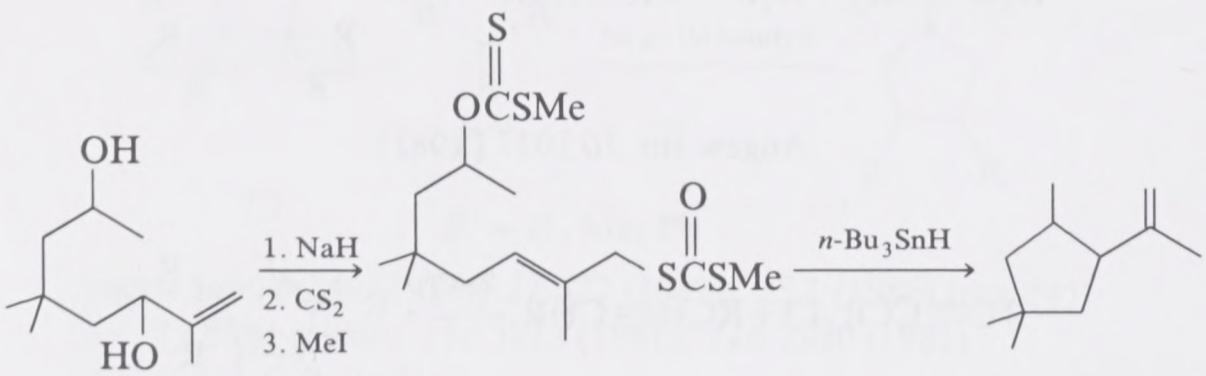
JACS *109* 6558 (1987)



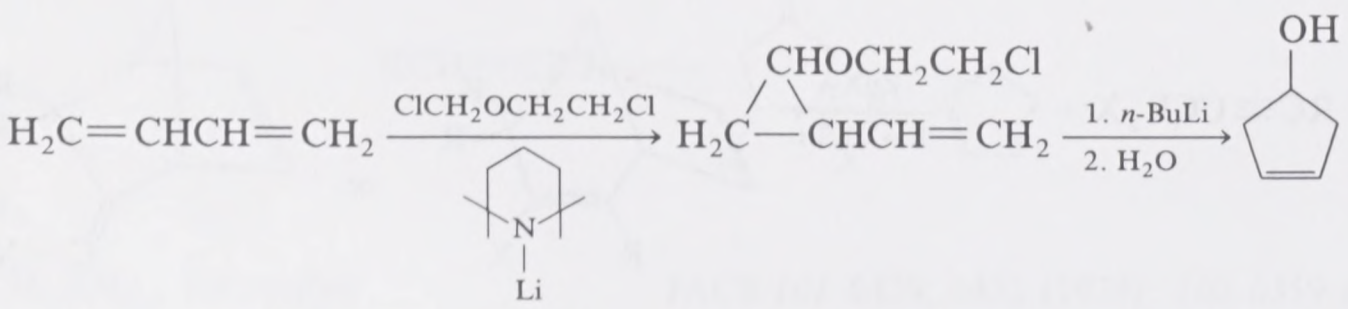
JACS *109* 3061 (1987)



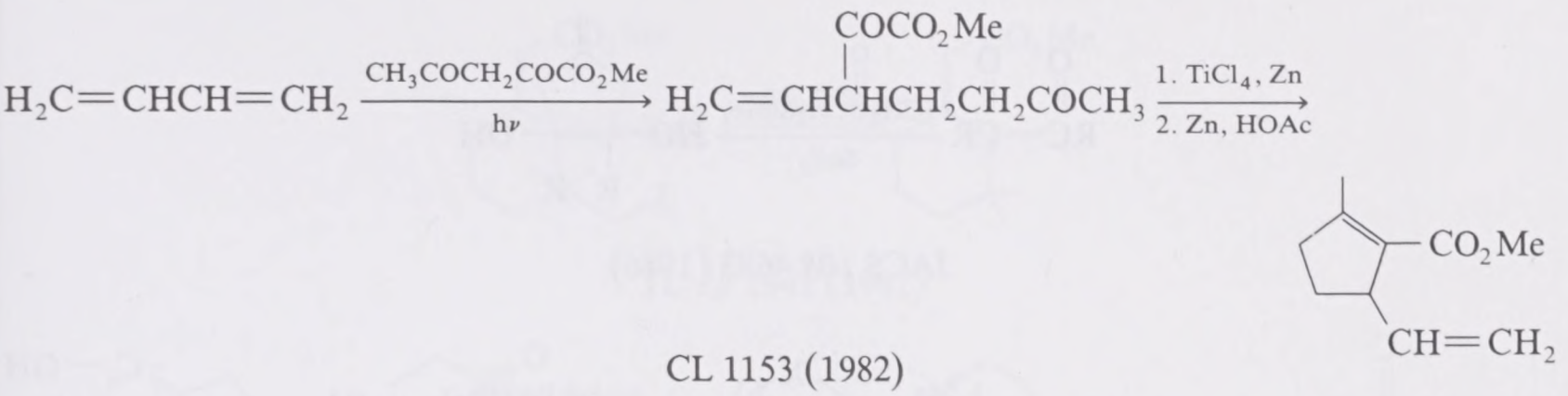
TL *27* 5911 (1986)



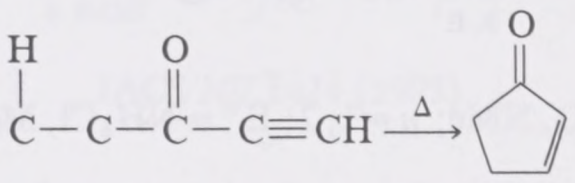
TL *28* 5973 (1987)



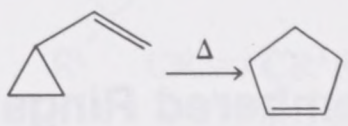
JOC *45* 1340 (1980)
JACS *103* 2443 (1981)



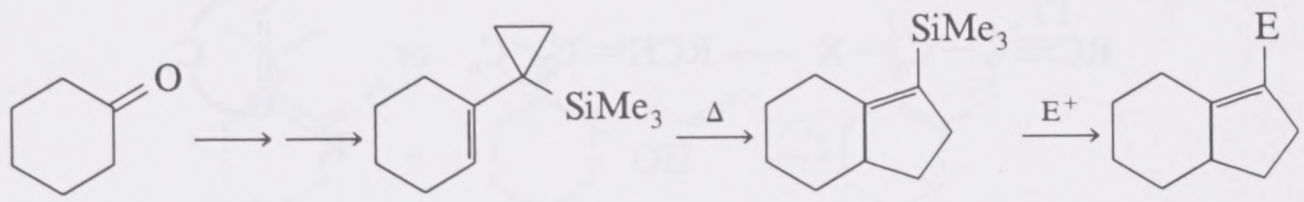
CL 1153 (1982)



Helv *62* 852 (1979); *65* 13, 2413, 2517 (1982)

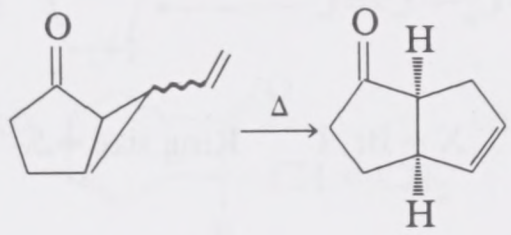


Org Rxs *33* 247 (1985) (review)
JOC *52* 4641 (1987)

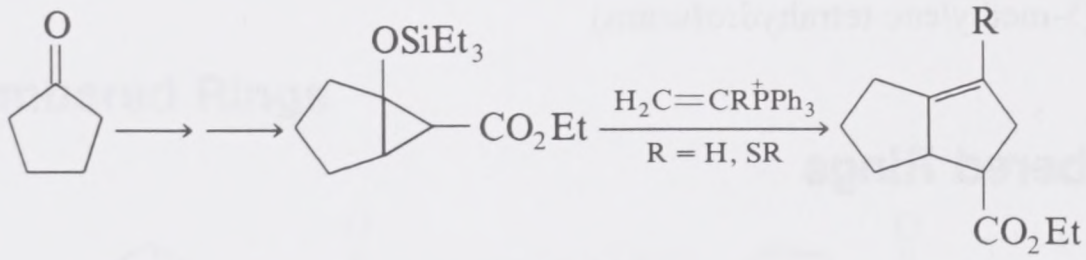


$E^+ = Br_2$ or $RCOCl\text{-}AlCl_3$

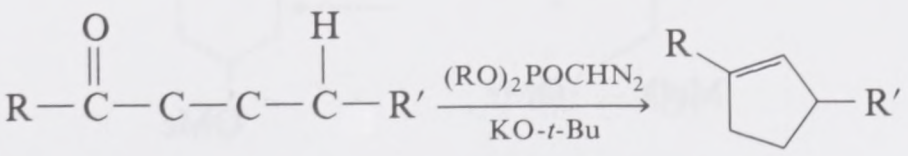
TL *23* 263 (1982)



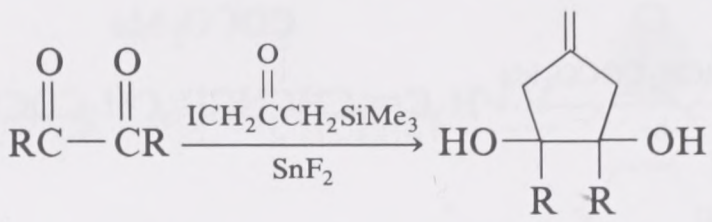
JOC *40* 2265 (1975); *45* 5020 (1980)
TL *27* 2885 (1986)



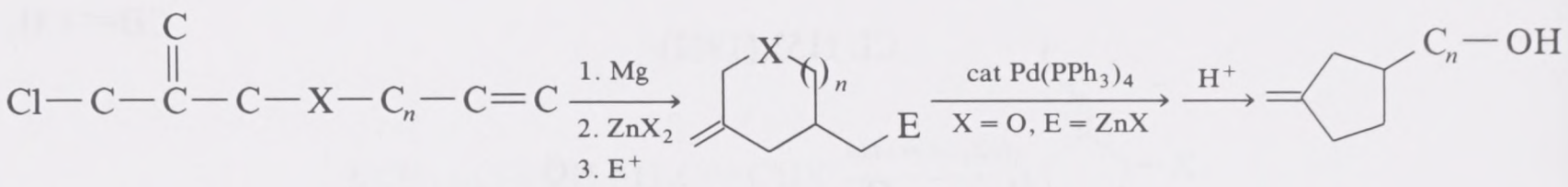
JACS *107* 734 (1985)
JOC *52* 1, 4139 (1987)



JOC *48* 5251 (1983); *50* 2557 (1985)



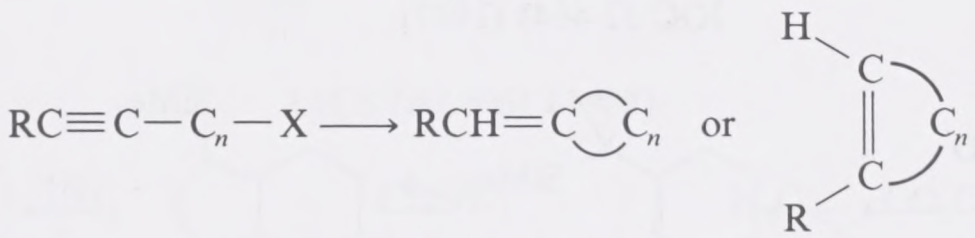
JACS *108* 4683 (1986)



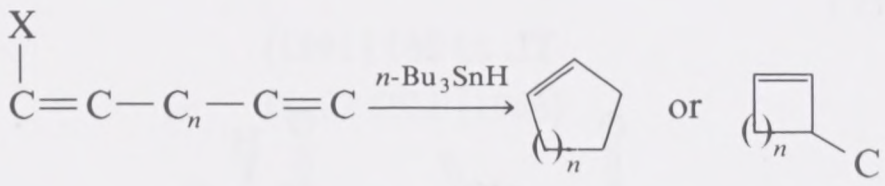
X = O, NMe; $n = 1, 2$; $E^+ = NH_4Cl$, Me_3SnCl

TL *28* 5929 (1987)

4. Five-, Six- and Seven-Membered Rings



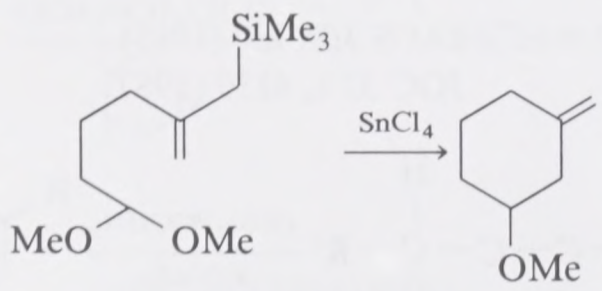
See page 215, Section 2.2.



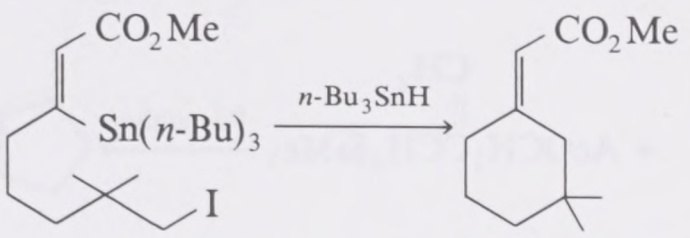
X = Br, I Ring size = 5–7

JACS *104* 2321 (1982)
TL *24* 1871 (1983); *26* 957 (1985) (pyrrolidines); *26* 5927 (1985); *27* 1355 (cyclic alcohols from enol silanes), 4525 (kinetics, mechanism), 4529 (1986)
CC 1445 (1983); 78 (1986) (lactams)
CL 1437 (1984) (3-methylene tetrahydrofurans)

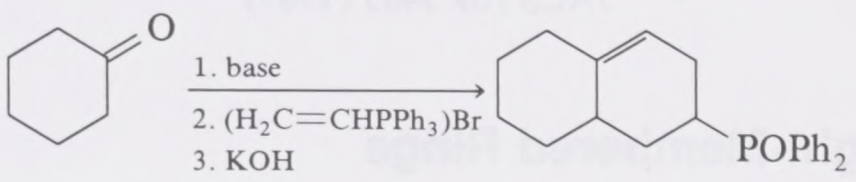
5. Six-Membered Rings



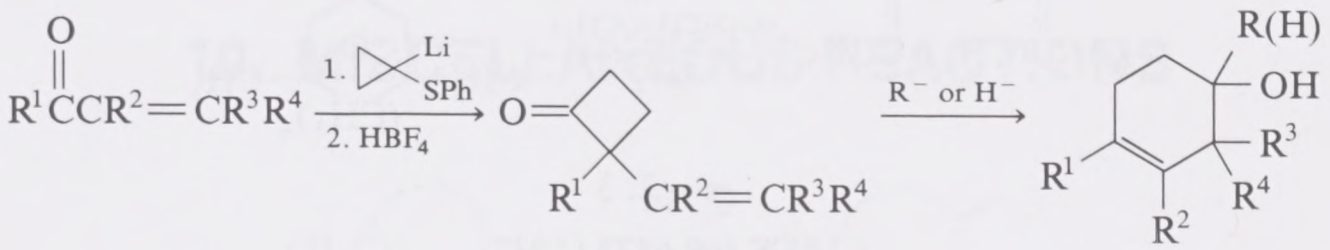
JCS Perkin I 251 (1981)



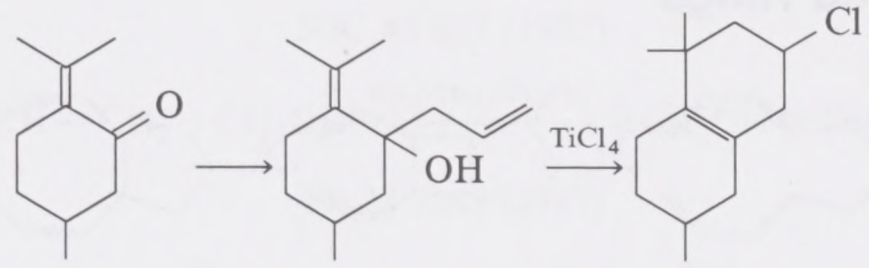
TL *28* 2941 (1987)



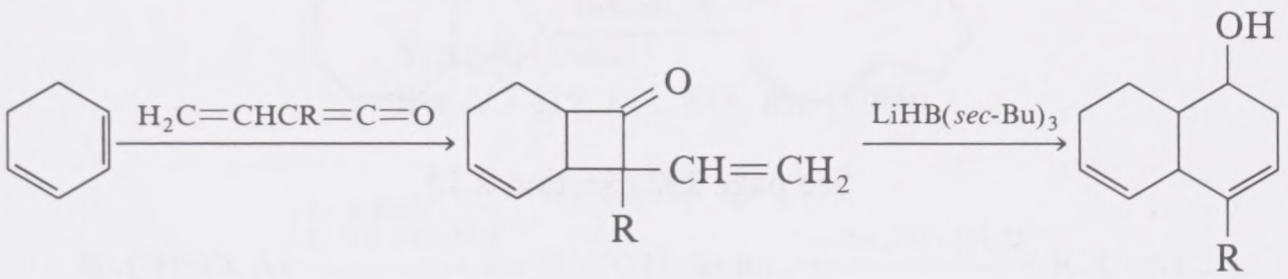
JACS *107* 1424 (1985)



Tetr *37* 3943 (1981)

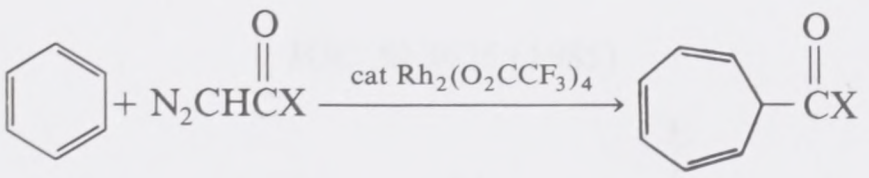


TL *28* 2583 (1987)

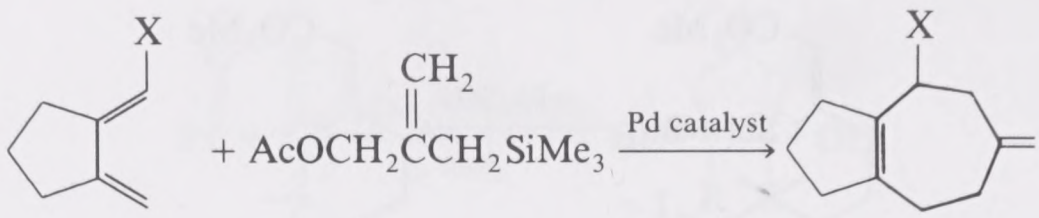


Tetr *37* 3943 (1981)

6. Seven-Membered Rings



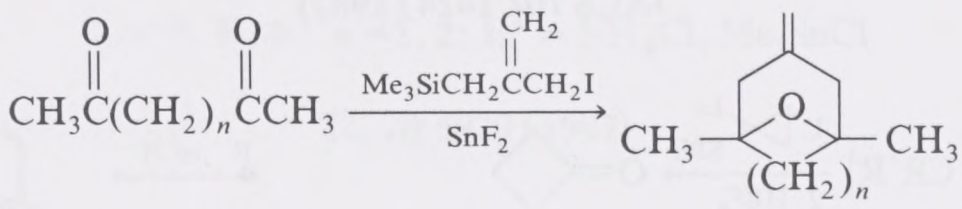
X	
R	CC 491 (1985)
OR	CC 765 (1980) JOC *46* 873 (1981)



X = CO_2R, SO_2Ph

JACS *109* 3483 (1987)

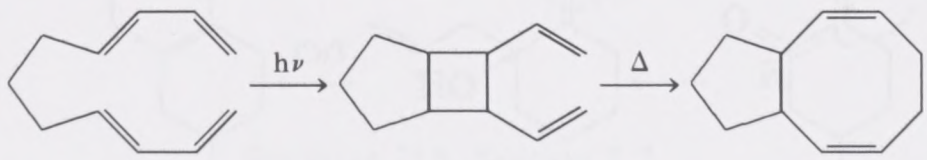
7. Seven- and Eight-Membered Rings



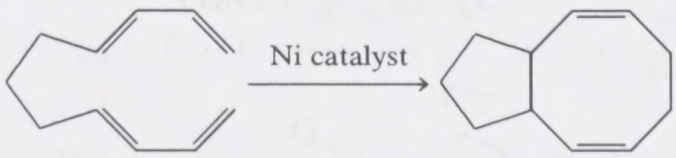
n = 2, 3

JACS *109* 6877 (1987)

8. Eight-Membered Rings

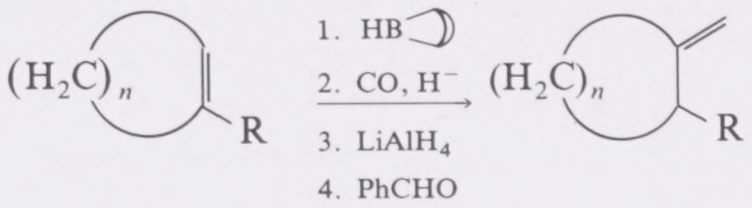


JACS *109* 2523 (1987)



See page 232, Section 2.15.

10. MISCELLANEOUS REACTIONS



JOC *46* 647 (1981)

$$RCH{=}CH_2 + CH_3OR' \xrightarrow{\text{cat } IrH_5(i\text{-}Pr_3P)_2} RCH_2CH{=}CHOR'$$

TL *28* 3249 (1987)

$$RCCHR_2 \xrightarrow[\text{2. KO-}t\text{-Bu}]{\text{1. LiCH}_2\text{SOPh}} RC{-}CR_2$$

Syn 640 (1980)
Ber *113* 819, 831, 845, 856 (1980)

$$R_2CHSO_2Ar \xrightarrow[\text{3. } n\text{-Bu}_3\text{SnCH}_2\text{I}]{\text{1. } n\text{-BuLi; 2. 0.2 } i\text{-Pr}_2\text{NH}} R_2CCH_2SnBu_3 \xrightarrow{n\text{-Bu}_4\text{NF}\cdot 3H_2O} R_2C{=}CH_2$$

JOC *50* 3622 (1985)

$$R_2CHCN \xrightarrow[\text{2. } n\text{-Bu}_3\text{SnCH}_2\text{I}]{\text{1. LiNR}_2} R_2CCH_2SnBu_3 \xrightarrow{\text{MeLi}} R_2C{=}CH_2$$

JOC *50* 3625 (1985)

$$H_2C{=}CHX \xrightarrow[\text{DABCO}]{E^+} H_2C{=}CX$$

X	E^+	
CHO	RCHO	TL *27* 2031, 4307 (1986)
COR	$H_2C{=}CHCOR$ (1,4-addition)	TL *28* 4591 (1987)

$$H_2C{=}CHX \xrightarrow[DABCO]{E^+} H_2C{=}\overset{\displaystyle E}{\overset{|}{C}}X \quad (\textit{Continued})$$

X	E^+	
CO_2R	RCHO	JOC *50* 3849 (1985)
CO_2R, CN	$RCOCO_2R$	TL *28* 4351 (1987)
CN	RCHO	Syn Commun *17* 587 (1987)
	$H_2C{=}CHCN$ (1,4-addition)	TL *28* 4591 (1987)

$$RCH{=}CHC(=O)R \xrightarrow[2.\ R'CHO]{1.\ R_2BSePh} RCH{=}C(C(=O)R)CHOHR'$$

JOC *50* 730 (1985)

ALKYNES

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L. Brandsma and H. D. Verkruijsse, "Synthesis of Acetylenes, Allenes and Cumulenes," Elsevier, New York (1981)

1. ISOMERIZATION

$$RC{\equiv}C(CH_2)_nCH_3 \longrightarrow R(CH_2)_{n+1}C{\equiv}CH$$

Review: Org Rxs *5* 1 (1949)

$NaNH_2$	BSCF [4] *35* 481 (1924) Ann Chim [10] *3* 191, 325 (1925) JOC *34* 222 (1969)
$Na(K)NH_2$, $H_2N(CH_2)_3NH_2$	Rec Trav Chim *96* 160 (1977)
$LiNHCH_2CH_2NH_2$, KO-*t*-Bu	Can J Chem *62* 1333 (1984)
$NaNHCH_2CH_2NH_2$	JOC *45* 734 (1980) Can J Chem *60* 1238 (1982)
$LiNH(CH_2)_3NH_2$, KO-*t*-Bu	Can J Chem *62* 1333 (1984) JOC *52* 1835 (1987)
$NaNH(CH_2)_3NH_2$	Can J Chem *58* 2567 (1980)
$KNH(CH_2)_3NH_2$	JACS *97* 891 (1975); *109* 2138 (1987) TL 2565 (1976); 411 (1977); *22* 4171 (1981); *28* 3857 (1987) CC 959 (1976); 318 (1977)
$KNH(CH_2)_3NH_2$, NH_3	TL *28* 2409 (1987)

$$HOCH_2C{\equiv}CCH_2R \xrightarrow{NaNH(CH_2)_3NH_2} HOCH_2CH_2C{\equiv}CR$$

Can J Chem *58* 2567 (1980)

$$RCH_2C{\equiv}CH \longrightarrow RC{\equiv}CCH_3$$

KOH, EtOH	Org Rxs *5* 1 (1949) (review) JACS *73* 1273 (1951) Quart Rev *24* 585 (1970)
KOEt, EtOH	BSCF 805 (1962)
$NaNH_2$, DMSO	Tetr *26* 2127 (1970)

$$RCH{=}C{=}CH(CH_2)_nCH_3 \xrightarrow{LiNH(CH_2)_3NH_2} R(CH_2)_{n+2}C{\equiv}CH$$

JOC *52* 1835 (1987)

2. ELIMINATION REACTIONS

Review: Angew Int *4* 49 (1965)

$$RCH{=}C(CH_3)_2 \xrightarrow[\text{aq HOAc}]{NaNO_2} RC{\equiv}CCH_3$$

TL *27* 267 (1986)
JOC *51* 2687 (1986)

$$RCH{=}CH_2 + 4\,Li \xrightarrow{THF} RC{\equiv}CLi + 3LiH \xrightarrow{H_2O} RC{\equiv}CH$$

JOC *32* 105 (1967)

$$RCH{=}CHR' \xrightarrow{Br_2} RCH(Br){-}CHR'(Br) \xrightarrow{base} RC{\equiv}CR'$$

Base	
KF-alumina (R = R′ = Ph)	BCSJ *56* 1885 (1983)
NaOH, $(n\text{-}Bu_4N)HSO_4$	TL 4723 (1976)
NaOH or KOH, $HO(CH_2CH_2O)_nH$	JOC *47* 2493 (1982)
KOH, ROH	Org Syn *27* 76 (1947) Org Syn Coll Vol *3* 350 (1955) Ber *89* 1786 (1956) JACS *85* 3492 (1963) J Chem Res (S) 270 (1981)
KOH, phase transfer	Tetr *37* 1653 (1981)
KO-*t*-Bu	Helv *54* 2060 (1971) JOC *51* 1088 (1986) JACS *109* 1868 (1987) TL *28* 6359 (1987)
KO-*t*-Bu, 18-crown-6	Ann 1 (1980)
Na, NH_3	JACS *56* 2064, 2120 (1934) Org Rxs *5* 1 (1949) Rec Trav Chim *85* 123 (1960) Org Syn Coll Vol *4* 763 (1963) TL 41 (1970) J Chem Res (S) 106 (1978)
$NaNH_2$, DMSO	Tetr *26* 2127 (1970)

$$ArCH_2Br \xrightarrow[(PhCH_2NEt_3)Cl]{NaOH,\ HCBr_3} ArC{\equiv}CBr$$

CC 563 (1979)

$$p\text{-}XC_6H_4CHBr_2 \xrightarrow[KO\text{-}t\text{-}Bu]{KOH\ or} p\text{-}XC_6H_4C{\equiv}CC_6H_4X\text{-}p$$

JOC USSR *15* 579 (1979)

$$2°,\ 3°\ RCl + H_2C{=}CHCl \xrightarrow{AlCl_3} RCH_2CHCl_2 \xrightarrow{NaNH_2} RC{\equiv}CH$$

Rec Trav Chim *84* 31 (1965)
J Chem Res (S) 106 (1978)

$$RCH_2X \xrightarrow{LiCHCl_2} RCH_2CHCl_2 \xrightarrow[2.\ H^+\ or\ R'X]{1.\ 3\ n\text{-}BuLi} RC{\equiv}CH(R')$$

Syn 502 (1979)

$$RC(=O)CH_2R' \xrightarrow{PCl_5} RCCl_2CH_2R'\ (or\ RCCl{=}CHR') \xrightarrow{base} RC{\equiv}CR'$$

Review: Angew *72* 391 (1960)

Base

KOH	BSCF *35* 357 (1924) Bull Soc Chim Belg *34* 427 (1925) Ann Chim (10) *16* 421 (1931) JACS *64* 543 (1942) J Chem Res (S) 270 (1981)
KO-*t*-Bu, 18-crown-6	Ann 1 (1980)
$NaNH_2$, mineral oil	JACS *56* 1207 (1934)
$NaNH_2$, NH_3	Org Rxs *5* 1 (1949) Rec Trav Chim *84* 31 (1965) J Chem Res (S) 106 (1978) JACS *106* 5312 (1984)
$NaNH_2$, DMSO	Tetr *25* 4249 (1969)
n-BuLi	Syn 502 (1979)

$$RMgX\ (Li) \xrightarrow[2.\ E^+]{1.\ H_2C{=}CF_2} RC{\equiv}CE$$

R = 1°, 2°, 3° alkyl; allyl; aryl; vinyl

$E^+ = H_2O$, *n*-BuBr, CH_3CHO, Me_3SiCl

TL *23* 4325 (1982)

$$RMgX\ (Li) \xrightarrow{Cl_2C{=}CF_2} RCF{=}CCl_2 \xrightarrow[2.\ E^+]{1.\ 2\ n\text{-BuLi}} RC{\equiv}CE$$

$$E^+ = H_2O,\ CO_2$$

JOC *41* 1487 (1976)

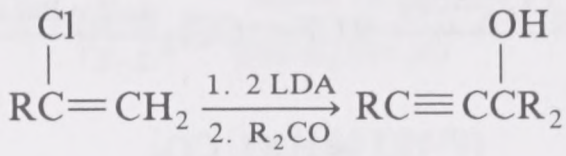
$$RC(X){=}CHR' \xrightarrow{base} RC{\equiv}CR'$$

Review: Angew *72* 391 (1960)

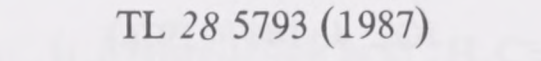
X	Base	
Cl	NaOH, $(n\text{-}Bu_4N)HSO_4$	TL 4723 (1976)
	KOH	JACS *63* 1175 (1941)
	NaOMe, MeOH	JOC *26* 2619 (1961)
	NaOEt	Ann *308* 264 (1899)
	KO-*t*-Bu	JCS Perkin II 795 (1982)
	$NaNH_2$, toluene	JOC *34* 222 (1969)
Cl, Br	KF or Et_4NF	JCS Perkin I 340 (1974)
	$(PhCH_2NMe_3)OH$	BSCF II 125 (1976)
	KO-*t*-Bu, 18-crown-6	Ann 1 (1980)
	$NaNH_2$, mineral oil	JACS *56* 1207 (1934)
	$NaNH_2$, NH_3	Ann Chim [10] *3* 325 (1925); *7* 785 (1962)
		JACS *56* 2064, 2120 (1934)
		Org Syn Coll Vol *1* 185 (1941)
		Org Rxs *5* 1 (1949)
		Org Syn *65* 68 (1987)
Br	K_2CO_3, EtCOMe ($R = CH_2OR$)	JOC *47* 2484 (1982)
	NaOH, EtOH	JACS *76* 4558 (1954)
		J Chem Res (S) 270 (1981)
	KOH	Org Syn Coll Vol *1* 438 (1941)
	KO-*t*-Bu	Angew Int *4* 953 (1965)
	KO-*t*-Bu, *t*-BuOH	Ann *707* 66 (1967)
	DBU	JOC *47* 2484 (1982)
	$NaNH_2$, DMSO	Tetr *26* 2127 (1970)
	NaH or $NaNH_2$, HMPA	BSCF 1293 (1966)
	LDA	JOC *52* 5622 (1987)
I	KOH, EtOH	JOC *34* 3502 (1969)
	KO-*t*-Bu, *t*-BuOH	JOC *34* 3502 (1969)
O_3SCF_3	2,6-$(t\text{-}Bu)_2C_6H_3OK$ or LDA	CC 459 (1981)
O_3SR, $O\overset{+}{P}Ar_3$, $(RO)_2PO_2$	—	Angew Int *8* 429 (1969)

$$RCH{=}C(Cl)CH_3 \xrightarrow{KNH(CH_2)_3NH_2} RCH_2C{\equiv}CH$$

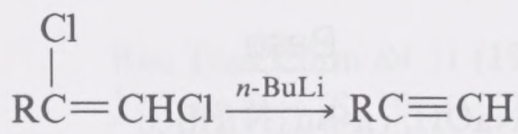
TL *28* 4547 (1987)



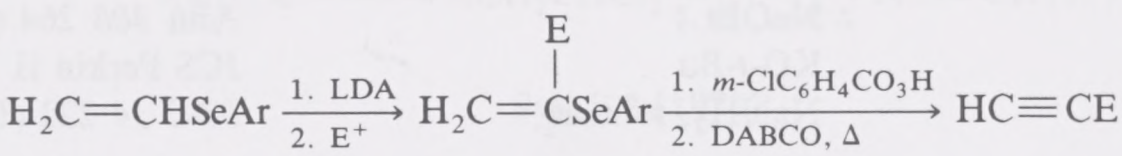
TL *28* 5793 (1987)



Ann *279* 319, 324, 337 (1894)
Angew Int *4* 49 (1965) (review)

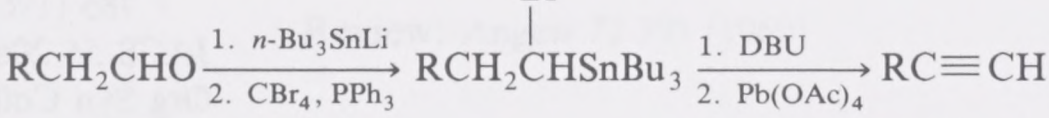


Org Syn *64* 73 (1985)

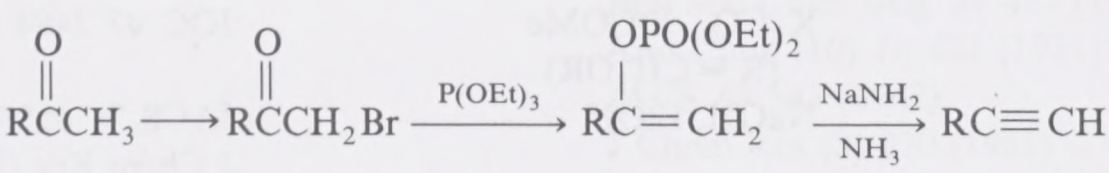


$E^+ = RX, R_2CO$

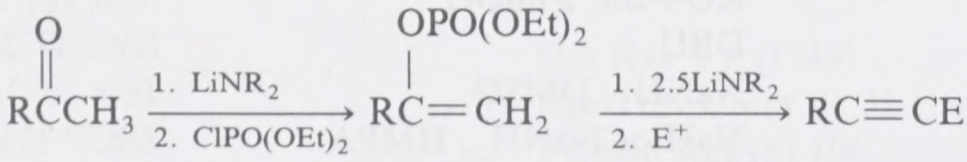
JACS *102* 5967 (1980)



TL *23* 4607 (1982)

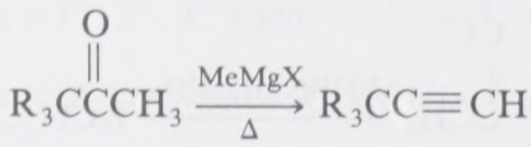


JCS 3712 (1963)

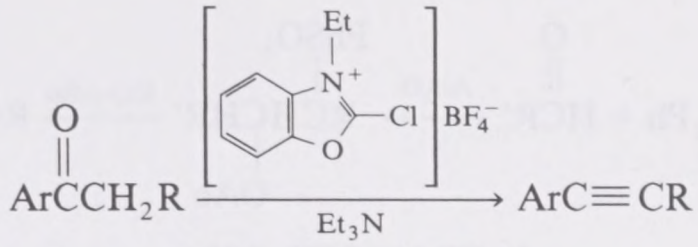


$E^+ = H_2O, CH_2O, ClCO_2Me$

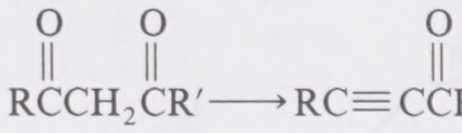
JOC *45* 2526 (1980); *52* 398, 4885 (1987)
Org Syn *64* 44 (1985)
JACS *107* 2568 (1985); *108* 3835 (1986)
TL *28* 5793 (1987)



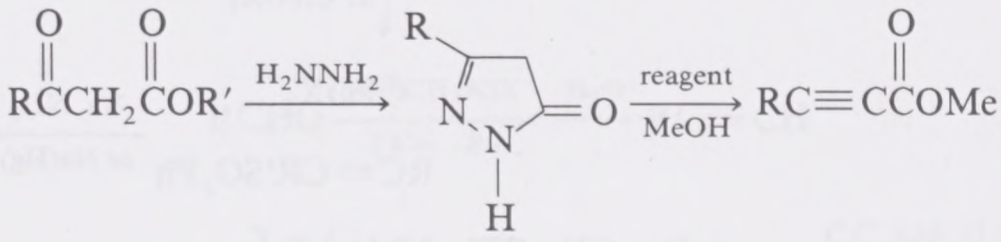
JCS Perkin I 1079 (1982)



CL 481 (1979)

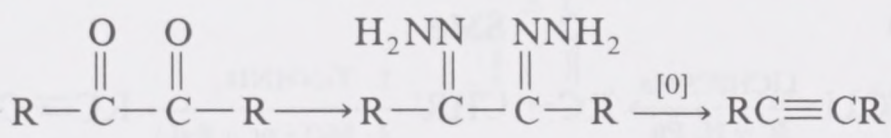


Et_2NCF_2CHFX (X = Cl, CF_3) (R′ = R or OR)	CL 1327 (1980)
$H_2NNH_2/Br_2/NaOH/HCl$ (R′ = OR)	Syn 72 (1981)

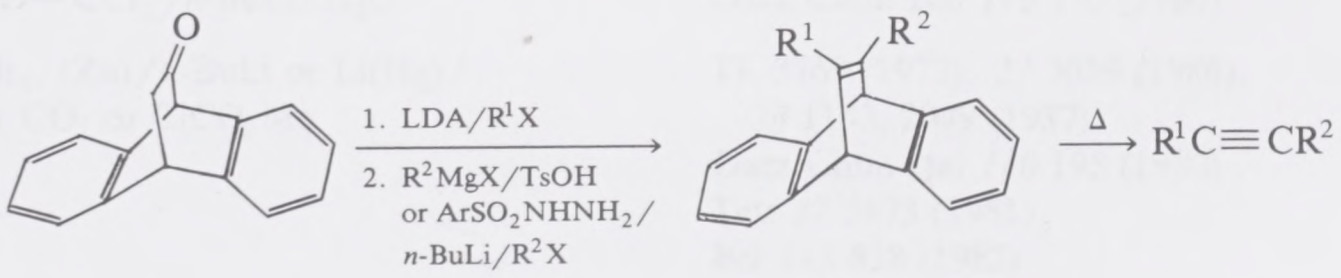


Reagent

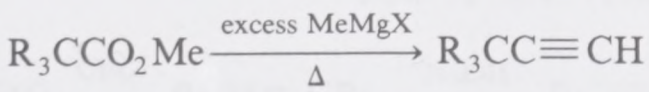
$Tl(NO_3)_3$	Angew Int *11* 48 (1972)
$Pb(OAc)_4$	Syn 1100 (1982)



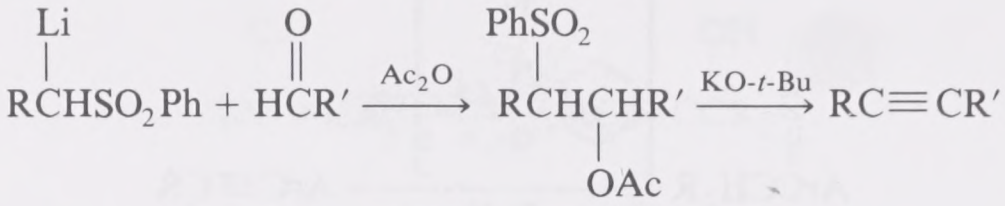
HgO	JACS *74* 3636, 3643 (1952) Helv *35* 1598 (1952) Org Syn Coll Vol *4* 377 (1963)
$Pb(OAc)_4$	TL 4511 (1968)
AgO_2CCF_3, Et_3N	JOC *23* 665 (1958)
$(EtO)_3P$, Δ	JOC *29* 2243 (1964)
O_2, CuCl, py	TL 4573 (1973)



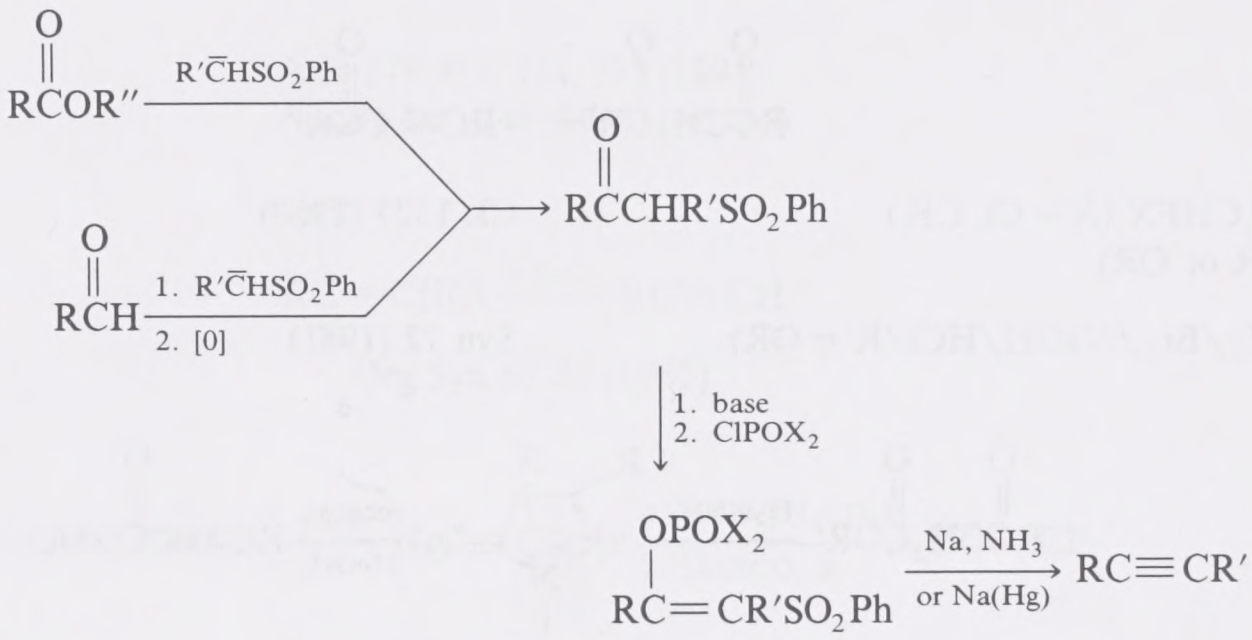
CL 1241 (1981)



JCS Perkin I 1079 (1982)

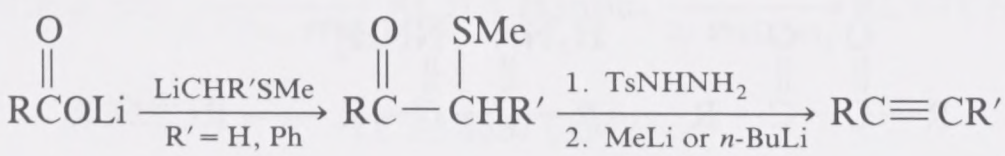


JACS *106* 3670 (1984)
JOC *51* 3830 (1986)

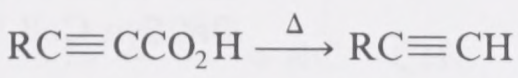


X = OEt, OPh, NMe_2

JACS *100* 4852 (1978)
TL 2625 (1978)
JCS Perkin I 2429 (1979)



JOC *43* 4366 (1978)



Helv *54* 2060 (1971)

3. WITTIG AND RELATED APPROACHES

$$RCHO \xrightarrow[2\ KO\text{-}t\text{-}Bu]{(Ph_3\overset{+}{P}CH_2X)X^-} \xrightarrow{H_2O} RC{\equiv}CH$$

R = aryl > alkyl

X = Cl
X = Br

CC 446 (1978)
TL *21* 4021 (1980);
27 5853 (1986)

$$RCHO \xrightarrow{Ph_3P{=}CHCl} RCH{=}CHCl \xrightarrow[2.\ E^+]{1.\ MeLi\ or\ n\text{-}BuLi} RC{\equiv}CE$$

$\underline{E^+}$

H_2O

JACS *91* 4318 (1969)
TL 1495 (1973)

$ClCO_2Me$

TL *28* 5473 (1987)

$$RCHO \xrightarrow{ylid} RCH{=}CX_2 \xrightarrow[2.\ E^+]{1.\ base} RC{\equiv}CE$$

$E^+ = H_2O, CO_2, ClCO_2Me$

$(Me_2N)_3P{=}CCl_2/n\text{-}BuLi/H_2O$

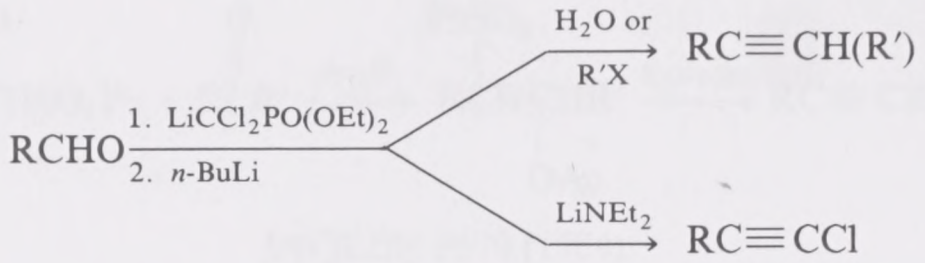
Gazz Chim Ital *110* 195 (1980)

Ph_3P, CBr_4, (Zn)/*n*-BuLi or Li(Hg)/ H_2O or CO_2 or $ClCO_2Me$

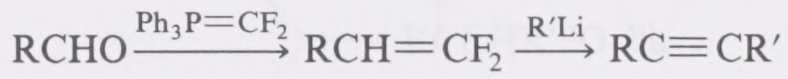
TL 3769 (1972); *27* 3059 (1986);
28 1143, 2099 (1987)
Gazz Chim Ital *110* 195 (1980)
Tetr *37* 3873 (1981)
Ber *115* 828 (1982)
BCSJ *55* 2221 (1982)
JACS *106* 1501 (1984); *108* 2776 (1986)
JOC *52* 5243 (1987)

$$RCHO \xrightarrow[PPh_3]{CBr_4} RCH{=}CBr_2 \xrightarrow[PEG\text{-}400]{NaOH} RC{\equiv}CBr$$

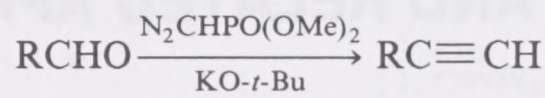
JOC *51* 4354 (1986)

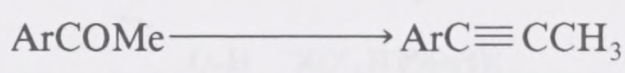


Syn 458 (1975)
JOC *42* 28 (1977)
Gazz Chim Ital *110* 195 (1980)
TL *27* 87 (1986)

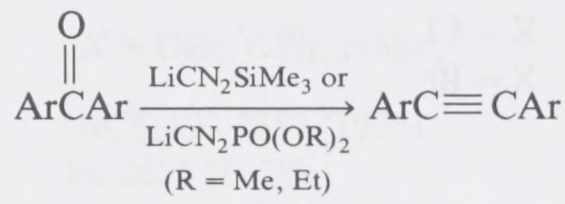


CL 935 (1980)

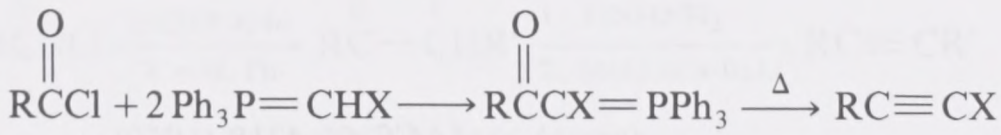




JOC *44* 4997 (1979); *47* 1837 (1982)



JCS Perkin I 869 (1977)



(best if X = Ar, CO_2R, CN)

Proc Chem Soc 302 (1961)
Ber *94* 3005 (1961)
Angew Int *1* 160 (1962)
JCS 2333 (1962); 543 (1964)
TL *23* 343 (1982)

4. ALKYLATION, ALKENYLATION AND ARYLATION OF ALKYNES AND ALLENES

1. Organolithium, -sodium and -magnesium Compounds

See also page 302, Sections 7 and 8.

$$RC{\equiv}CH \longrightarrow RC{\equiv}CM \xrightarrow{R'X} RC{\equiv}CR'$$

M = Li, Na, MgX

JACS *58* 796 (1936); *60* 1882 (1938) (R′X = EtOTs)
JOC *2* 1 (1937); *24* 840 (1959); *51* 4158 (1986)
Org Rxs *5* 1 (1949) (review)
JCS 893 (1951)
Org Syn Coll Vol *4* 117 (1963)
BSCF 2000 (1964); 1525 (1965)
Syn 567 (1972); 441 (1974); 423 (1975)
Syn Commun *3* 245 (1973)
J Chem Res (S) 106 (1978); 190 (1979); 270 (1981) (reviews)
CL 669 (1980)
TL *27* 5445 (1986)

$$HO(CH_2)_nC{\equiv}CH \xrightarrow[NH_3]{2\ LiNH_2} \xrightarrow{RX} HO(CH_2)_nC{\equiv}CR$$

Helv *61* 2275 (1978)

$$HO(CH_2)_nC{\equiv}CH + X(CH_2)_mCO_2H \xrightarrow[\text{or } LiNH_2,\ NH_3]{2n\text{-BuLi}} HO(CH_2)_nC{\equiv}C(CH_2)_mCO_2H$$

$n = 1, 2$; $m = 4, 5, 10, 11$; X = Br, I

TL *27* 573, 2279, 2369 (1986)

$$HC{\equiv}CLi \cdot EDA + I(CH_2)_nCO_2H \xrightarrow{HMPA} HC{\equiv}C(CH_2)_nCO_2H$$

Syn Commun *10* 653 (1980)

$$RC{\equiv}CMgBr + TsOCH_2C{\equiv}CH \longrightarrow RC{\equiv}CCH_2C{\equiv}CH$$

Syn 292 (1979)

$$RC{\equiv}CM + R_2CO \xrightarrow{H_2O} RC{\equiv}CC(OH)R_2$$

M = Li, MgX

A. W. Johnson, "The Chemistry of Acetylenic Compounds," Vol 1, "Acetylenic Alcohols," Edward Arnold and Co., London (1946) (review)
JOC *22* 1611 (1957)
CL 447 (1979); 255 (1980) (asymmetric)
CC 363 (1981) (stereochemistry)

$$HC{\equiv}CC(OH)R_2 \xrightarrow[CuBr_2]{HBr} BrCH{=}C{=}CR_2 \xrightarrow{LiAlH_4} HC{\equiv}CCHR_2$$

JOC *33* 3655 (1968)
J Chem Res (S) 106 (1978)

$$RC{\equiv}CSO_2Ar + R'M \longrightarrow RC{\equiv}CR'$$

R′ = alkyl, aryl; M = Li, MgX

JOC *44* 3444 (1979)

$$RX + LiCH_2C{\equiv}CSiR'_3 \longrightarrow RCH_2C{\equiv}CSiR'_3 \longrightarrow RCH_2C{\equiv}CH$$

R′ = Me, *i*-Pr

TL 5041 (1968); 2247 (1970); *23* 719 (1982); *27* 2187 (1986)
JACS *90* 5618 (1968); *92* 6314 (1970)

$$RX \xrightarrow{LiC{\equiv}CCHLiSPh} \xrightarrow{Li,\ NH_3} \xrightarrow{H^+} RCH_2C{\equiv}CH$$

JOC *46* 5041 (1981)

$$RX \xrightarrow[2.\ BrCH_2CBr{=}CH_2]{1.\ Mg} RCH_2C(Br){=}CH_2 \xrightarrow{NaNH_2} RCH_2C{\equiv}CH$$

BSCF [4] *29* 528 (1921)
Ann Chim [10] *3* 325 (1925)
Org Syn Coll Vol *1* 180, 185 (1941)

$$RCH{=}CHCH_2X \xrightarrow{"BrMgCH_2C{\equiv}CH"} RCH{=}CHCH_2CH_2C{\equiv}CH$$

JCS 4244 (1955)
TL 2249 (1970)

$$RCH_2C{\equiv}CH \xrightarrow{2\ R'Li} \xrightarrow{E_1^+} \xrightarrow{E_2^+} RCHC(E_1){\equiv}CE_2$$

E_1^+ or E_2^+ = RX, $H_2C\overset{O}{\diagup\diagdown}CH_2$, RCHO, R_2CO, CO_2, Me_3SiCl, I_2

JOMC *3* 165 (1965)
JACS *91* 3094 (1969); *98* 8413 (1976); *103* 3112 (1981) (R = SePh)
Tetr *26* 2345 (1970); *28* 5385 (1972)
Israel J Chem *10* 827 (1972)
CC 1030 (1974); 817 (1975); 215 (1979)
Syn 321 (1976)
JCS Perkin I 1218 (1979); 2338 (1980)
Rec Trav Chim *99* 113 (1980)
JOC *46* 5041 (1981) (R = SPh)

$$RCH_2C{\equiv}CCH_3 \xrightarrow[TMEDA]{t\text{-BuLi}} \xrightarrow{BrCH_2CH{=}CH_2} RCH_2C{\equiv}CCH_2CH_2CH{=}CH_2$$

JOC *47* 3364 (1982)

$$RCH_2C{\equiv}CSiMe_3 \xrightarrow[2.\ R'X]{1.\ t\text{-BuLi}} RCHC{\equiv}CSiMe_3 \quad (R' \text{ on the CH})$$

JACS *108* 1359 (1986)

$$BrCH_2C{\equiv}CSiMe_3 \xrightarrow{ArMgX} ArCH_2C{\equiv}CSiMe_3$$

JOC *52* 1889 (1987)

$$R_2CC{\equiv}CR \ (Cl) \xrightarrow{R'MgX} R_2CC{\equiv}CR \ (R')$$

JACS *62* 1798 (1940); *68* 1202 (1946); *86* 5244 (1964); *89* 6177 (1967)
J Chem Res (S) 106 (1978); 190 (1979)

2. Organoboron Compounds

$$RC{\equiv}CH \xrightarrow[2.\ R'_3B]{1.\ base} [\,RC{\equiv}C\bar{B}R'_3\,]Li^+ \xrightarrow{reagent} RC{\equiv}CR'$$

Reagent

I_2

JACS *95* 3080 (1973)
JOC *39* 731 (1974); *46* 2311 (1981); *51* 162, 4507, 4514 (1986); *52* 2919 (1987)
TL 1961 (1975)
Syn 679 (1977)
Ber *115* 828 (1982)

CH_3SOCl

TL 1847 (1973)

$$RCH{=}CH_2 \xrightarrow[3.\ LiC{\equiv}CR']{\substack{1.\ (CH_3)_2CHC(CH_3)_2BHCl \\ 2.\ MeOH}} \xrightarrow[4.\ I_2]{} RCH_2CH_2C{\equiv}CR'$$

JOC *51* 4518, 4521 (1986)

$$RC{\equiv}CH + R'_3B \longrightarrow RC{\equiv}CR'$$

electrolysis CL 999 (1977); 461 (1980)
$Pb(OAc)_4$ CL 413 (1980)

$$RC{\equiv}CH \xrightarrow[2.\ E\text{-}(Sia)_2BCH{=}CHR']{1.\ R''Li} [\,E\text{-}RC{\equiv}CB(Sia)_2CH{=}CHR'\,]Li \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ I_2,\ OH^-} E\text{-}RC{\equiv}CCH{=}CHR'$$

CC 874 (1973)
TL 411 (1977); *27* 539 (1986)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CX \xrightarrow{\text{reagents}} E\text{-}RC{\equiv}CCH{=}CHR'$$

Reagents

E-RCH=CHB$(Sia)_2$, NaOMe, cat $Pd(PPh_3)_4$ TL 3437 (1979)

E-RCH=CHB, NaOMe, CuI JOC *46* 645 (1981)

$$R_3B \xrightarrow{LiC{\equiv}CCH_2Cl} RC{\equiv}CCH_2BR_2 \xrightarrow[LiOMe,\ CuI]{H_2C{=}CR'CH_2Br} RC{\equiv}CCH_2CH_2CR'{=}CH_2$$

CL 1289 (1982)

$$HC{\equiv}C\underset{\displaystyle OAc}{\overset{|}{C}}R_2 \xrightarrow[2.\ R'_3B\ \ 3.\ H_2O]{1.\ n\text{-BuLi}} R'C{\equiv}CCHR_2$$

JOC *42* 2650 (1977)

3. Organoaluminum Compounds

$$RC{\equiv}CH \longrightarrow (RC{\equiv}C)_3Al \xrightarrow{R'X} RC{\equiv}CR'$$

JACS *97* 7385 (1975)

$$RC{\equiv}CAlEt_2 + R'\underset{\displaystyle SO_2Ph}{\overset{|}{C}}HCH{=}C(CH_3)_2 \longrightarrow RC{\equiv}CCHR'CH{=}C(CH_3)_2$$

JACS *108* 1098 (1986)

$$RC{\equiv}CBr + R'_3Al \xrightarrow{\text{cat Ni(mesal)}_2} RC{\equiv}CR'$$

TL 2831 (1978)

4. Organosilicon Compounds

$$Me_3SiC{\equiv}CSiMe_3 \xrightarrow[10\%\ AlCl_3]{3°RX\ (X = Cl,\ Br)} RC{\equiv}CR$$

CC 959 (1982)

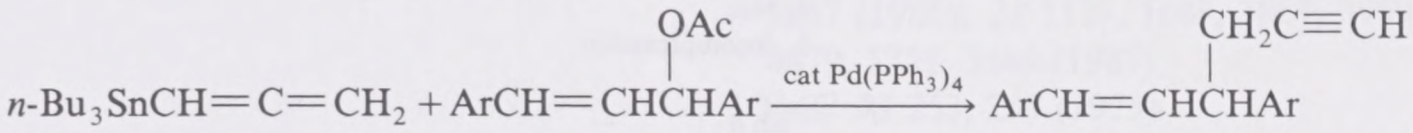
$$RC{\equiv}CSiMe_3 \xrightarrow[AlCl_3]{3°R'Cl} RC{\equiv}CR'$$

CC 959 (1982)
JACS *107* 6546 (1985)

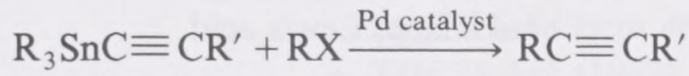
$$RC{\equiv}CSiMe_3 \xrightarrow[\text{cat } PdCl_2(PhCN)_2]{ClCH_2CH{=}CH_2} \begin{matrix} R & & SiMe_3 \\ & C{=}C & \\ Cl & & CH_2CH{=}CH_2 \end{matrix} \xrightarrow{n\text{-}Bu_4NF} RC{\equiv}CCH_2CH{=}CH_2$$

CL 1485 (1982)

5. Organotin Compounds



JOC *48* 5302 (1983)



RX

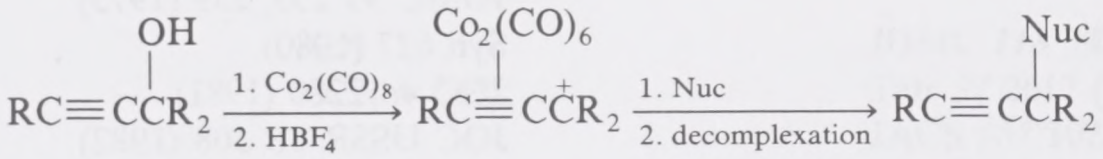
R_fI	TL *28* 5857 (1987)
ArX	Izv Akad Nauk SSSR, Ser Khim 479 (1980) [CA *93* 26019h (1980)] JOC USSR *17* 18 (1981) JOMC *250* 551 (1983) Proc Acad Sci USSR, Chem Sec *272* 333 (1983); *274* 39 (1984)
heterocyclic halides	JACS *109* 2138 (1987) (thiophene)
ArOTf	JACS *109* 5478 (1987)
RCH=CHI	JACS *109* 2138 (1987)
RCH=CHOTf	JACS *106* 4630 (1984); *108* 3033 (1986) TL *27* 1523 (1986)

For RX = RCOCl see also page 686, Section 2.4.



TL *27* 3479 (1986)

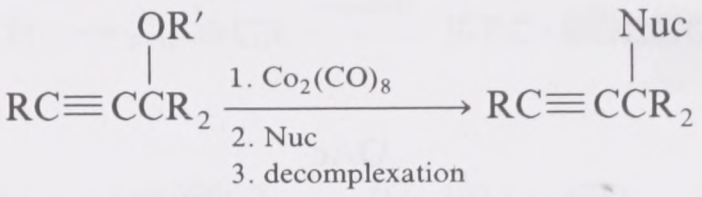
6. Organocobalt Compounds

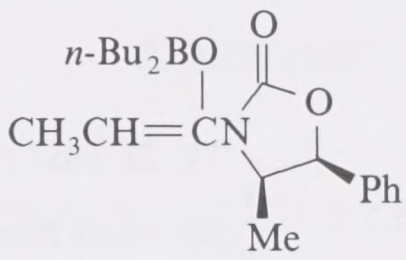


Nuc

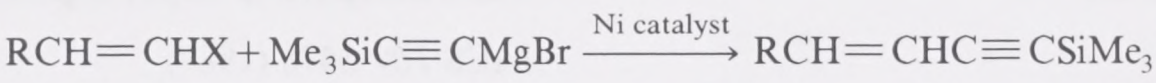
$NaBH_4$	JACS *107* 4999 (1985)
anisole	TL 4163 (1977)
allylic silanes	TL *21* 1595 (1980)
ketones, enol silanes, enol acetates	JACS *102* 2508 (1980)
enol silane	CC 1353 (1987)
isopropenyl acetate	Syn Commun *10* 503 (1980)
β-diketones, β-keto esters	TL 4349 (1978)

See also TL *23* 2555 (1982); *26* 1269 (1985)



R′	Nuc	
Me	allylic silane, $BF_3 \cdot OEt_2$; enol silane, Lewis acid	JACS *108* 3128 (1986)
		JACS *109* 5749 (1987)
Ac	$AlMe_3$ $Al(C{\equiv}CR)_3$	JOMC *212* 115 (1981) TL *24* 2239 (1983)

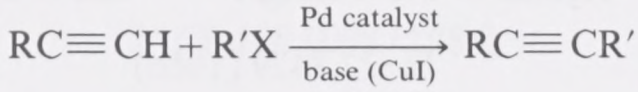
7. Organonickel Compounds



JOC *49* 4733 (1984)

8. Organopalladium Compounds

See also page 301, Section 5.



R′X	
ArX	TL 4467 (1975); *27* 1653 (1986); *28* 2887, 3857, 4879, 5395, 5981 (1987) JOMC *93* 253, 259 (1975) Syn 627 (1980) JOC *46* 2280 (1981) JOC USSR *18* 308 (1982) JACS *107* 5670 (1985); *108* 2481, 3150 (1986)
heterocyclic halides	TL 4467 (1975) (pyridines) JOMC *93* 259 (1975) (thiophene) Chem Pharm Bull *26* 3843 (1978) (pyrimidines); *27* 270 (1979) (quinolines, isoquinolines and acridines); *28* 3488 (1980) (pyridazines); *30* 1865 (1982) (pyrimidines); *34* 1447 (1986) (pyrazines) Syn 627 (1980) (pyridine); 364 (1981) (various heterocycles); 312 (1983) (various heterocycles) Heterocycles *19* 329 (1982) (pyrazines) JOC *50* 2462 (1985) (pyridines); *52* 2469 (pyridines), 3997 (pyrazines and pterin), 5243 (thiophenes) (1987) Tetr *41* 621 (1985) (thiophenes)

ArO_3SR_f	TL *27* 1171 (1986)
$RCH{=}CHX$	TL 4467 (1975); *22* 421 (1981); *27* 2033, 3589, 5857 (1986); *28* 1127, 1649, 3857, 3959, 4875, 4879, 5751, 5849 (1987) JOMC *93* 253, 259 (1975) Syn Commun *11* 917 (1981) J Chem Res (S) 93 (1982) Agric Biol Chem *46* 717 (1982) Tetr *38* 631 (1982) JACS *106* 3548, 5734 (1984); *107* 7515 (1985); *108* 5589 (1986); *109* 1879 (1987) CC 1816 (1986)
$RCH{=}CHO_3SCF_3$	JOC *50* 2302 (1985) TL *27* 1523 (1986)
	Heterocycles *26* 355 (1987)
R″X, CO (R′ = R″CO; R″ = aryl, heterocyclic, vinylic)	CC 333 (1981)
R″COCl (R′ = R″CO; R″ = alkyl, aryl, alkenyl, NMe_2)	Syn 777 (1977)

$$RC{\equiv}CM + R'X \xrightarrow{\text{Pd catalyst}} RC{\equiv}CR'$$

M	R′X	
ZnCl	$RCH{=}CHX$	CC 683 (1977) TL *27* 4351, 5533 (1986)
	ArX	JOC *43* 358 (1978) JACS *108* 3403 (1986)
	ArO_3SR_f	TL *28* 2387 (1987)
MgX	ArX $RCH{=}CHX$	JOMC *118* 349 (1976) Tetr *37* 2617 (1981) JACS *107* 1028 (1985)
SnR_3	—	See page 301, Section 5.
Cu	ArX	JACS *107* 1028 (1985) See also page 304, Section 9 for related reactions

$$RC{\equiv}CH + CO + R'X \xrightarrow[\substack{Et_3N \\ \Delta}]{\text{Pd catalyst}} RC{\equiv}CCR' \quad (\text{O above the C})$$

R′ = aryl, heterocyclic, vinylic

CC 333 (1981)

$$RC{\equiv}CX + R'MgX \xrightarrow{\text{Pd catalyst}} RC{\equiv}CR'$$

JOC *51* 3772 (1986)

9. Organocopper Compounds

Review: Tetr *40* 1433 (1984)

$$RC{\equiv}CH + ArX \xrightarrow[Cu]{K_2CO_3} RC{\equiv}CAr$$

Bull Acad Sci USSR, Div Chem Sci 2539 (1968); 1079 (1970); 1209, 1488 (1971)

$$RC{\equiv}CH + XCH_2C{\equiv}CR' \longrightarrow RC{\equiv}CCH_2C{\equiv}CR'$$

CuI, DBU or DBN Ann 658 (1978)

$CuCl, NH_3$ BSCF 913 (1974)

$$2\ RC{\equiv}CH \longrightarrow RC{\equiv}CC{\equiv}CR$$

Reviews: Russ Chem Rev *32* 229 (1963)
Adv Org Chem *4* 225 (1963)

cat CuCl, NH_4Cl, H_2O	Adv Org Chem *4* 225 (1963) (review) JOC *29* 2051 (1964)
cat CuCl, cat TMEDA, acetone, O_2	JOC *27* 3320 (1962)
cat $Cu(OAc)_2$, py, O_2	JOC *25* 1275 (1960) Adv Org Chem *4* 225 (1963) (review)
CuCl, NH_4Cl, NH_3, H_2O, O_2	JCS 1998 (1952)
$Cu(OAc)_2$, py, MeOH, Et_2O, O_2	JCS 889 (1959)

$$RC{\equiv}CX + HC{\equiv}CR' \xrightarrow[NH_2OH\cdot HCl,\ EtNH_2]{\text{cat CuCl}} RC{\equiv}CC{\equiv}CR'$$

Adv Org Chem *4* 225 (1963) (review)
J Chem Res (S) 199 (1982)
Agric Biol Chem *46* 717 (1982)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CMgX \longrightarrow RC{\equiv}CR'$$

$R_2C{=}CHCH_2OMs$, cat Li_2CuCl_4	JACS *108* 806 (1986)
$RC{\equiv}CCMe_2Cl$, cat CuCl	JACS *107* 6546 (1985)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CCu \xrightarrow{R'X} RC{\equiv}CR'$$

R′X	
ArX	Russ Chem Rev *37* 748 (1968) (review) Bull Acad Sci USSR, Div Chem Sci 2043 (1963) JOC *28* 2163, 3313 (1963); *30* 3857 (1965); *31* 4071 (1966); *42* 2626 (1977); *52* 1339 (1987) JACS *86* 4358 (1964); *88* 3027 (1966); *91* 6464 (1969) Chem Ind 2101 (1964) JCS C 578 (1967); 2173 (1969) CC 718 (1967) J Label Compds *6* 197 (1970)

$RCH{=}CHX$	CC 1259 (1967) JOC USSR *4* 21 (1968) JOC *47* 2109 (1982)
$H_2C{=}CHCH_2X$	JACS *91* 6464 (1969); *109* 3684 (1987) (NaCN added) Compt Rend *270* 354 (1970) BSCF 913 (1974) Ann 658 (1978)
$Me_3SiC{\equiv}CCH_2I$	TL *28* 3547 (1987)

$$MCH_2C{\equiv}CSiR_3 \xrightarrow[2.\ E^+]{1.\ CuI} ECH_2C{\equiv}CSiR_3 \longrightarrow ECH_2C{\equiv}CH$$

M	E^+	
Li	RCHO	JACS *109* 5437 (1987)
MgBr	$R_2C{=}CHCH_2Cl$	JOC *52* 3860, 3883 (1987) TL *28* 527, 723 (1987)
	$R_2C{=}CRCH_2OPO(OEt)_2$	JACS *106* 6006 (1984) TL *28* 527 (1987)

$$R'C{\equiv}CX + RM \longrightarrow R'C{\equiv}CR$$

$X = Br, I$

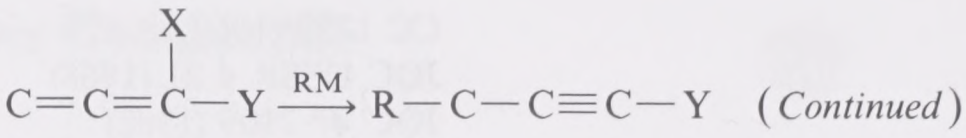
RM	
ArCu	TL 5209 (1972); 1441 (1978)
$RCu{\cdot}MgBr_2$ (R = alkyl, vinyl)	TL 1466 (1975) Tetr *36* 1215 (1980)
R_2CuLi	JOMC *251* 133 (1983)
(RCuCN)Li	JOMC *251* 133 (1983)

$$RC{\equiv}C\overset{\overset{OAc}{|}}{C}R_2 \xrightarrow{R'_2CuLi} RC{\equiv}C\overset{\overset{R'}{|}}{C}R_2 \text{ (or } RR'C{=}C{=}CR_2)$$

CC 876 (1978)
JOC *45* 4740 (1980)

$$C{=}C{=}\overset{\overset{X}{|}}{C}{-}Y \xrightarrow{RM} R{-}C{-}C{\equiv}C{-}Y$$

X	Y	RM	
Br	H	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	JOC *52* 3920 (1987)
Br	H	(PhCuBr)MgBr·LiBr, (RCuBr)MgX·LiBr, (RCuCN)Li (R = 1° alkyl)	TL *28* 6073 (1987)



(*Continued*)

X	Y	RM	
Br	alkyl	Me_3Cu_2Li, $MeCu \cdot n\text{-}Bu_3P$, (RCuCN)Li (R = 1°, 2° alkyl; aryl)	TL *25* 3059 (1984)
Br	alkyl	RCH=CHLi, CuCN	JOC *51* 2230 (1986)
Br	alkyl	(RC≡CCuCN)Li	JACS *103* 4618 (1981)
I	alkyl	RCH=CHCu	TL *23* 1651 (1982)
I	alkyl	(ArCuCN)Li	TL *24* 3291 (1983)
I	OMe	RMgX, CuBr	JOC *45* 1158 (1980)
OMe	H	RMgX, CuX (X = Cl, Br, I)	Rec Trav Chim *93* 183 (1974)

10. Organozinc Compounds

See page 302, Section 8.

11. Organomercury Compounds

$$PhC{\equiv}CX + RHgCl \xrightarrow{h\nu} PhC{\equiv}CR$$

X = I, PhS, $PhSO_2$, $HgC{\equiv}CPh$, $n\text{-}Bu_3Sn$

TL *27* 3479 (1986)

12. Miscellaneous Reactions

$$RC{\equiv}CH + H_2C{=}CHCH{=}CH_2 \xrightarrow{\text{cat } H_2Ru(PR_3)_4} RC{\equiv}CCH{=}CHCH_2CH_3$$

CC 496 (1981)

$$R_fI + HC{\equiv}CCR_2OH \xrightarrow{\text{electrolysis}} R_fCH{=}CICR_2OH \xrightarrow[\Delta]{OH^-} R_fC{\equiv}CH$$

CC 433 (1982)

HALIDES

GENERAL REFERENCES

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/4, G. Thieme Verlag, Stuttgart (1960) (bromine and iodine compounds)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/3, G. Thieme Verlag, Stuttgart (1962) (fluorine and chlorine compounds)

Quart Rev *16* 44 (1962) (The Fluorination of Organic Compounds)

W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York (1969)

R. D. Chambers, "Fluorine in Organic Chemistry," Wiley-Interscience, New York (1973)

"The Chemistry of the Carbon-Halogen Bond," Ed. S. Patai, J. Wiley, New York (1973)

Org Rxs *21* 125 (1974) (Modern Methods to Prepare Monofluoroaliphatic Compounds)

Tetr *34* 3 (1978) (Introduction of Fluorine into Organic Molecules: Why and How)

Angew Int *20* 647 (1981) (Methods of Fluorination in Organic Chemistry)

"The Chemistry of Halides, Pseudo-Halides and Azides," Eds. S. Patai and Z. Rappoport, J. Wiley, New York (1983)

1. HALOGENATION OF HYDROCARBONS

Reviews:

C. Walling, "Free Radicals in Solution," J. Wiley, New York (1957), pp 347–396
Quart Rev *14* 336 (1960)
JACS *87* 2161, 2172 (1965)
W. A. Pryor, "Free Radicals," McGraw-Hill, New York (1966), pp 179–213
M. L. Poutsma, "Methods in Free Radical Chemistry," Ed. E. S. Huyser, Vol 1, Marcel Dekker, New York (1969), pp 79–193
W. A. Thaler, "Methods in Free Radical Chemistry," Ed. E. S. Huyser, Marcel Dekker, New York (1969), Vol 2, pp 121–227
Syn 7 (1970)

1. Aliphatic Halogenation

Fluorination

F_2	JACS *98* 3034, 3036 (1976) TL *21* 5067 (1980) Nouv J Chim *4* 239 (1980) J Fluorine Chem *20* 689 (1982) JOC *51* 3522 (1986); *52* 2769, 4928 (1987)
ClF_3	JOC *52* 798 (1987)
CF_3OF	JACS *92* 7494 (1970); *98* 3034, 3036 (1976) Nouv J Chim *4* 239 (1980)

Chlorination

Cl_2	JCS 144 (1960)
SO_2Cl_2	JACS *61* 2142 (1939); *62* 927 (1940) JCS 1851 (1951)
Cl_3CSO_2Cl	JACS *82* 5246 (1960)
NCS	JOC *18* 649 (1953)

$C_6H_5ICl_2$	JOC *29* 3692 (1964); *32* 1517 (1967) CL 961 (1979)
t-C_4H_9OCl	JACS *89* 4891, 4895 (1967)
PCl_5	Angew *77* 506 (1955)
R_2NCl, CF_3CO_2H, $FeSO_4 \cdot 7\ H_2O$	JOC *44* 3728 (1979)

Bromination

Br_2	JCS 144 (1960) Rec Trav Chim *83* 67 (1964)
Cl_3CSO_2Br	JOC *30* 38 (1965)
NBS	JCS 2240 (1952) JOC *18* 649 (1953)
$(C_6H_5)_2C{=}NBr$	JOC *32* 223 (1967)
Cl_3CBr, DBU (activated CH)	CL 73 (1978)
$(NC)_2CBr_2$ (activated CH)	BCSJ *37* 547 (1964)

Iodination

t-C_4H_9OI	JACS *90* 808 (1968)

2. Allylic Halogenation

Reviews:

Chem Rev *43* 271 (1948) (NBS); *63* 21 (1963) (NBS)
Angew *71* 349 (1959) (NBS)

Chlorination

$C_6H_5SO_2NClC_6H_{13}$	Ann *703* 34 (1967)
t-C_4H_9OCl	JACS *83* 3877 (1961) TL *21* 781 (1980)
NCS, TsNSO	JOC *44* 4204 (1979)
NCS, cat $(ArSe)_2$	JOC *44* 4204, 4208 (1979)
$PhSeCl_3/H_2O$, $NaHCO_3$	JOC *52* 4086 (1987)
HOCl	TL *21* 441 (1980)
NaCl, H_2O, H_2SO_4, CH_2Cl_2, electrolysis	TL *22* 3193 (1981)

Bromination

NBS	JOC *14* 375 (1945); *50* 2007 (1985) Chem Rev *43* 271 (1948) (review) JACS *73* 5153 (1951); *106* 3297 (1984); *108* 1251 (1986) Org Syn Coll Vol *4* 108 (1963)
$(C_6H_5)_2C{=}NBr$	JOC *32* 223 (1967)

3. Benzylic Halogenation

Reviews:

Chem Rev *43* 271 (1948) (NBS); *63* 21 (1963) (NBS)
Angew *71* 349 (1959) (NBS)

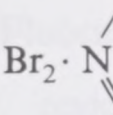
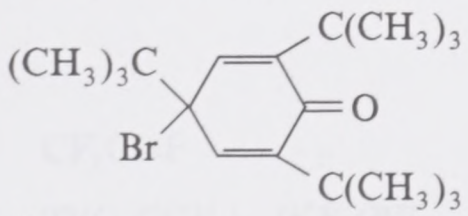
Fluorination

CF_3OF	JACS *92* 7494 (1970)

Chlorination

SO_2Cl_2	JACS *61* 2142 (1939) JCS 1851 (1951) Tetr *25* 4363 (1969); *26* 2041 (1970)
SO_2Cl_2, cat $Pd(PPh_3)_4$	CL 223 (1978)
Cl_2, PCl_5	Org Syn Coll Vol *2* 133 (1943)
PCl_5	JOC *34* 3655 (1969)
$C_6H_5ICl_2$	JOC *29* 3692 (1964)
t-C_4H_9OCl	JACS *82* 6108, 6113 (1960); *89* 4885, 4891, 4895 (1967)
Cl_2O ($ArCH_3 \longrightarrow ArCCl_3$)	JACS *104* 4680 (1982)

Bromination

Br_2	Org Syn Coll Vol *2* 443 (1943); *3* 788 (1955); *4* 984 (1963)
$Br_2 \cdot$  polymer	JOC *51* 929 (1986)
$CuBr_2$, *t*-BuO_2H, Ac_2O	Syn Commun *11* 669 (1981)
NBS	Chem Rev *43* 271 (1948) (review) Org Syn Coll Vol *4* 921 (1963) JOC *50* 2128, 2557, 2939 (1985); *51* 3407 (1986)
$BrCCl_3$	JACS *82* 391 (1960)
CBr_4	JACS *54* 2025 (1932)
$(C_6H_5)_2C{=}NBr$	JOC *32* 223 (1967)
	Tetr *25* 4357 (1969)

Iodination

t-C_4H_9OI	JACS *90* 808 (1968)

2. AROMATIC HALOGENATION

See page 365, Section 9, for substitution of OH by halogen.

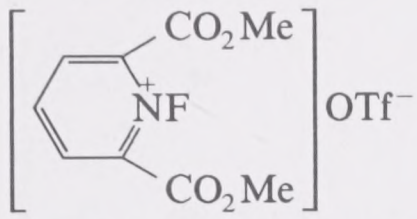
$$Ar-H \longrightarrow Ar-X$$

Reviews:

E. T. McBee and H. B. Hass, Ind Eng Chem *33* 137 (1941)
P. H. Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill, New York (1958), p 204
P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworths Scientific Publications, London (1959)
H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Ed. G. Olah, Interscience Publishers, New York (1964), Vol III, Pt. 2, p 1517
R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York (1965), pp 119–155

Fluorination

review	Chem Eng News, July 9, 72 (1962)
F_2	JOC *35* 723, 4020 (1970) TL *28* 255 (1987) (pyridines)
XeF_2	Israel J Chem *17* 71 (1978)
XeF_2, HF	JACS *91* 1563 (1969)
CF_3OF	CC 806 (1968) JACS *92* 7494 (1970) JCS Perkin I 2889 (1972) Anal de Quim *70* 871 (1974) JOC *39* 2120 (1974); *41* 3413 (1976) Israel J Chem *17* 60 (1978)
CF_3COF	JOC *46* 4629 (1981); *49* 806 (1984)
$Tl(O_2CCF_3)_3/KF/BF_3$	JOC *42* 362 (1977)
$CsSO_4F$	JACS *103* 1964 (1981)
$CsSO_4F$, cat BF_3	CC 148 (1981) Tetr *40* 189 (1984) JOC *50* 3609 (1985); *51* 3242 (1986)

$(CF_3SO_2)_2NF$	JACS *109* 7194 (1987)
	TL *27* 4465 (1986)
(and other substituted pyridinium salts)	

Chlorination

Cl_2	JOC *50* 2145 (1985) (phenols)
Cl_2, H_2O	TL *28* 4805 (1987) (aryl ethers)
Cl_2, silica	TL 3395 (1974) CL 1423 (1980)
Cl_2, $FeCl_3$	CL 1423 (1980)
SO_2Cl_2	Org Syn Coll Vol *3* 267 (1955) (phenol) Austral J Chem *28* 1113 (1975) (phenol) JOC *46* 4486 (1981); *50* 2145 (1985); *52* 4485 (1987) (all phenols only) TL *23* 4569 (1982) (phenol)
SO_2Cl_2, cat $(PhS)_2$, cat $AlCl_3$ or $FeCl_3$	JOC *50* 2145 (1985) (phenols)
S_2Cl_2, SO_2Cl_2, $AlCl_3$	JCS *127* 2677 (1925) JACS *82* 4254 (1960)
$CuCl_2$	Org Syn Coll Vol *5* 206 (1973)
$TiCl_4$, CF_3CO_3H	TL 2611 (1970)
Cl_2O, H_2SO_4 or CF_3SO_3H	JACS *104* 4680 (1982)
Cl_2O, $POCl_3$, $(CF_3SO_2)_2O$	Ber *112* 1677 (1979)
NaOCl, HOAc	JCS 1056 (1909) JACS *108* 1000 (1986)

Bromination

Br_2 vapor	Org Syn Coll Vol *4* 256 (1963)
Br_2, CCl_4	Org Syn Coll Vol *1* 121 (1941); *2* 95 (1943); *3* 134 (1955); *5* 147 (1973)
Br_2, CS_2	Org Syn Coll Vol *4* 128 (1941)
Br_2, H_2O	JOC *52* 4485 (1987)
Br_2, H_2O, H^+	Org Syn Coll Vol *2* 97, 592 (1943); *4* 947 (1963)
Br_2, HOAc	Org Syn Coll Vol *2* 100, 173 (1943) JOC *52* 4485 (1987)
Br_2, HOAc, NaOAc	JOC *52* 4485 (1987)
Br_2, KBr, H_2O	JOC *52* 4485 (1987)
Br_2, H_2O_2, *n*-Bu_4NBr	CC 1421 (1987)

Br_2, *t*-$BuNH_2$	JOC *32* 2358 (1967) (phenols) JACS *108* 806 (1986)
Br_2, silica	TL 3395 (1974)
Br_2, Fe	Org Syn Coll Vol *1* 123 (1941); *3* 138 (1955); *4* 114 (1963)
Br_2, $AlCl_3$	Org Syn Coll Vol *5* 117 (1973)
Br_2, $Tl(OAc)_3$	TL 1623 (1969) JOC *37* 88 (1972)
Br_2, AgO_3SR	Syn 693 (1978)
Br_2, $AgNO_3$, HOAc, HNO_3	JCS 573 (1950)
Br_2, $AgSO_4$, H_2SO_4	JCS 573 (1950)
Br_2, $Hg(NO_3)_2$, HOAc	JCS 573 (1950)
Br_2, $KBrO_3$, HOAc, H_2SO_4	JCS 573 (1950)
$KBrO_3$, H_2SO_4	JOC *46* 2169 (1981)
HOBr, $HClO_4$ or H_2SO_4	JCS 997 (1962)
HOBr, HOAc	JCS 2317 (1954)
HBr, H_2O_2, *n*-Bu_4NBr	CC 1421 (1987)
$Hg(OAc)_2/Br_2$	JCS 637 (1926)
NBS	JACS *80* 4327 (1958) JOC *30* 304 (1965); *44* 4733 (1979)
CBr_4	JACS *54* 2025 (1932)
$CuBr_2$	JACS *86* 427 (1964)

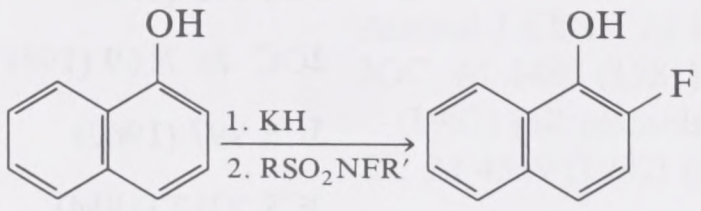
Iodination

I_2	Org Syn Coll Vol *2* 347 (1943) TL *27* 5963 (1986)
I_2, alumina	TL *27* 2207 (1986)
I_2, HNO_3	Org Syn Coll Vol *1* 323 (1932)
I_2, AgO_2CCF_3	Org Syn Coll Vol *4* 547 (1963)
I_2, SO_3, H_2SO_4	Org Syn Coll Vol *3* 796 (1955) JCS C 1480 (1970)
I_2, $NaNO_2$, H_2SO_4	JACS *65* 1273 (1943)
I_2, KIO_3, H_2SO_4	JACS *65* 1273 (1943)
I_2, Ag_2SO_4	JCS 150 (1952)
I_2, $AlCl_3$, $CuCl_2$	CL 1481 (1982)
I_2, $CuCl_2$	JOC *35* 3436 (1970)
I_2, HgO	Org Syn Coll Vol *2* 357 (1943)

I_2, $HIO_4 \cdot 2\ H_2O$	BCSJ *39* 128 (1966) CC 1476 (1987)
I_2, $PhI(O_2CCF_3)_2$	Syn 486 (1980)
I_2, CF_3CO_2H, electrolysis	Acta Chem Scand B *34* 47 (1980)
ICl	Org Syn Coll Vol *2* 196, 343, 349 (1943)
MI (M = *n*-Bu_4N, Li, Na, K, I), $(NH_4)_2[Ce(NO_3)_6]$, CH_3CN	BCSJ *54* 2847 (1981)
$FeI_2 \cdot 4\ H_2O$, $CuCl_2$	JOC *35* 3436 (1970)
$Tl(O_2CCF_3)_3/KI$	TL 2427 (1969) JACS *93* 4841 (1971)

$$ArH \xrightarrow{RLi} ArLi \xrightarrow{RSO_2NFR'} ArF$$

JACS *106* 452 (1984)



JACS *106* 452 (1984)

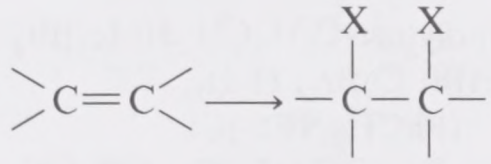
$$ArH + RCHO + HCl \longrightarrow ArCHR \quad (Cl)$$

Org Syn Coll Vol *3* 195 (1955); *4* 980 (1963)

3. HALOGENATION OF ALKENES

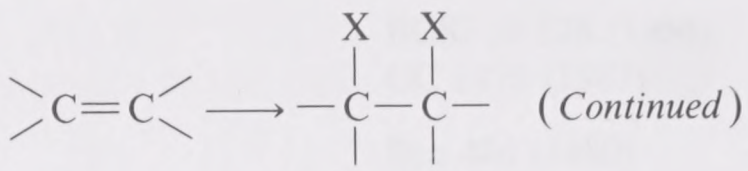
See also page 340, Section 4; and page 215, Section 2 (halogenation of vinyl metallics).

1. Halogen Addition

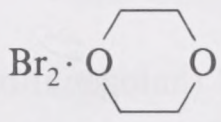
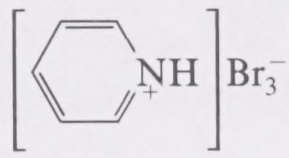


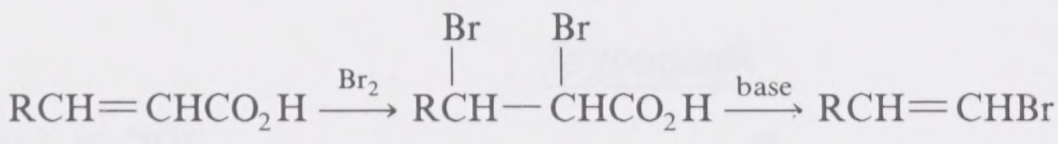
Review: H. O. House, "Modern Synthetic Reactions," 2nd ed, W.A. Benjamin, Inc. (1972), pp 422–429

X	Reagent(s)	
F	F_2	JOC *31* 1859, 3871 (1966); *51* 3607 (1986)
		JACS *88* 1822 (1966); *89* 609 (1967)
		JCS Perkin I 1105 (1982)
	XeF_2	JACS *86* 5021 (1964)
		JOC *42* 1559 (1977)
		JCS Perkin I 2169 (1977)
		Israel J Chem *17* 71 (1979)
		J Fluorine Chem *20* 13 (1982)
	XeF_2, H^+	TL 1015 (1974)
		JOC *41* 4002 (1976); *43* 696 (1978); *44* 1255 (1979)
		Tetr *33* 1017 (1977)
	XeF_2, $BF_3 \cdot OEt_2$	TL 363 (1977)
	XeF_4	JACS *86* 5021 (1964)
	$CsSO_4F$	JOC *52* 919 (1987)
	CF_3OF	JCS Perkin I 1105 (1982)

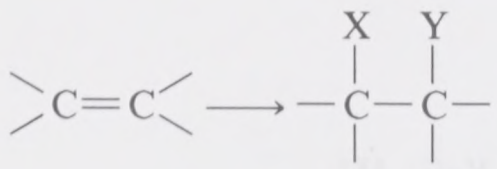


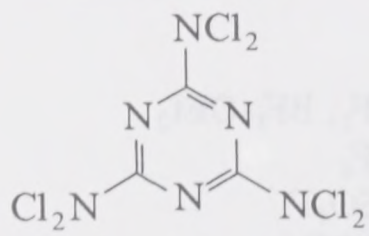
(*Continued*)

X	Reagent(s)	
Cl	Cl_2	JACS *61* 940 (1939); *63* 2541 (1941); *73* 3329 (1951)
	SO_2Cl_2	JACS *61* 940, 3432 (1939)
	PCl_5	JACS *61* 940 (1939)
	NCS, HCl	JACS *81* 2191 (1959)
	HCl, $CaCl_2$, H_2O_2, $(PhCH_2NEt_3)Cl$	Syn 676 (1977)
	[polymer-$C_6H_4CH_2\overset{+}{N}Me_3$]$ICl_2^-$	CC 1278 (1980)
Br	Br_2	Org Syn Coll Vol *1* 521 (1941); *2* 171, 177, 270 (1943); *4* 195 (1963)
		Zh Obshch Khim *24* 610 (1954)
		Ber *56* 1262 (1923) J Chem Ed *31* 291 (1954) Syn 966 (1979) (selective diene addition) TL *22* 623 (1981)
	[polymer-$C_6H_4CH_2NMe_3$]Br_3^-	Syn 143 (1980)
	HBr, $CaBr_2$, H_2O_2, $(PhCH_2NEt_3)Cl$	Syn 676 (1977)
	NaBr, H_2O, H_2SO_4, CH_3CN, electrolysis	JOC *46* 3312 (1981)
I	I_2, CuO–HBF_4, NaI	CC 1491 (1987)

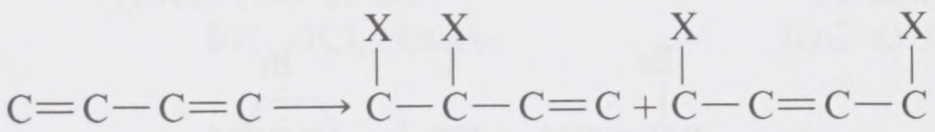


JCS 2012 (1950)
JACS *75* 2645 (1953)
JOC *27* 2339 (1962)
BSCF 1736 (1971)
J Chem Res (S) 270 (1981)



X	Y	Reagent(s)	
F	Cl	 , HF	Bull Acad Sci USSR, Div Chem Sci 1016 (1966) JOC USSR *5* 1879 (1969); *7* 1382, 1876 (1971); *8* 1139 (1972)

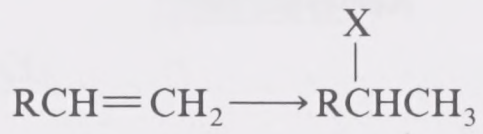
F	Cl, Br, I	review	Russ Chem Rev *41* 740 (1972)
F	Br	XeF_2, Br_2	Israel J Chem *10* 271 (1977)
		AcNHBr, HF	JACS *81* 2191, 4107 (1959); *82* 4001 (1960)
			Chem Ind 452 (1963)
			JOC *29* 1202 (1964)
			Can J Chem *43* 1689 (1965)
			Syn 217 (1978)
		NBS, HF	TL *28* 4003 (1987)
		1,3-dibromo-5,5-dimethylhydantoin, HF	Can J Chem *43* 1689 (1965)
			J Fluorine Chem *31* 99 (1986)
			JOC *52* 658 (1987)
			TL *28* 4003 (1987)
		1-bromo-3,5,5-trimethylhydantoin, HF	Can J Chem *43* 1689 (1965)
		NBS, R_3N, HF	TL *27* 4449 (1986)
F	I	$I(py)_2BF_4$, BF_4^-	Angew *24* 319 (1985)
		$I(collidine)_2BF_4$	Syn 551 (1987)
		NIS, HF	JACS *82* 4001, 4007 (1960)
Cl	Br	AcNHBr, LiCl, HCl	JACS *81* 2191 (1959)
Cl	I	ICl	JCS Perkin I 226 (1977)
			CC 1577 (1987)
		$I(py)_2BF_4$, Cl^-	Angew Int *24* 319 (1985)
Br	I	$I(py)_2BF_4$, Br^-	Angew Int *24* 319 (1985)



X		
Cl		JACS *52* 4043 (1930); *73* 244 (1951)
		JCS 829 (1934); 3204 (1962)
		J Gen Chem USSR *27* 253 (1957)
		JOC *31* 4167 (1966); *33* 2946 (1968); *37* 2228 (1972); *39* 736 (1974); *41* 334 (1976)
Br		Helv *5* 756 (1922)
		JCS 729 (1928)
		JACS *75* 2512 (1953); *81* 5943 (1959)
		J Gen Chem USSR *24* 453 (1954)
		JOC *33* 2342 (1968); *34* 2779 (1969); *35* 2967 (1970); *37* 2228 (1972); *38* 4109 (1973)

2. Hydrohalogenation

2.1. Markovnikov Addition



Reviews:

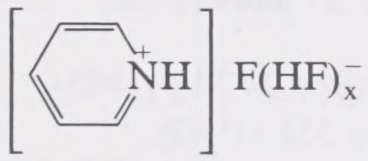
Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/3, pp 99–108 (X = F) and pp 812–822 (X = Cl); Vol V/4, pp 102–124 (X = Br) and pp 535–539 (X = I); G. Thieme, Stuttgart (1962 and 1960 respectively)

P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York (1966), Chpt 5

C. A. Buehler and D. E. Pearson, "Survey of Organic Chemistry," Wiley Interscience, New York (1970), Vol 1, p 356

H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York (1972), pp 446–452

Examples:



Syn 779 (1973)
JOC *44* 3872 (1979)

aq HX (X = Cl, Br, I)
(phase transfer)

JOC *45* 3527 (1980)

HCl

Org Syn Coll Vol *2* 336 (1943)
JOC *51* 5191 (1986)

HBr

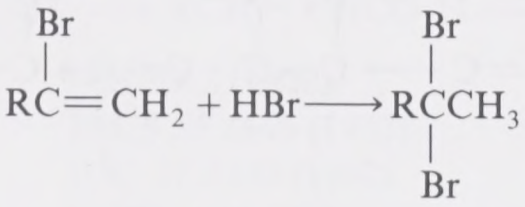
JACS *68* 1805 (1946)
Org Syn Coll Vol *3* 576 (1955)
JOC *21* 1362 (1956)

KI, H_3PO_4

Org Syn Coll Vol *4* 543 (1963)

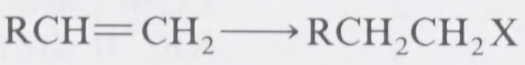
I_2, Al_2O_3

TL *28* 4497 (1987)



JACS *58* 1806 (1936)

2.2. Anti-Markovnikov Addition



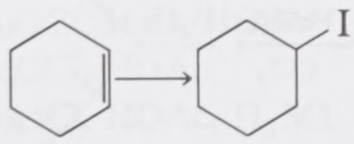
X	Reagents	
Cl	BH_3 or 9-BBN/Cl_2NTs	J Chem Res (S) 376 (1981)
Br	HBr, peroxides	JOC *11* 281 (1946); *47* 5372 (1982) JACS *68* 1101 (1946); *109* 6937 (1987)

		Chem Rev *62* 599 (1962) (review)
		Org Rxs *13* 150 (1963) (review)
	HBr, hν	JOC *21* 1362 (1956); *42* 1709 (1977)
		Org Rxs *13* 150 (1963) (review)
		Tetr *25* 5149 (1969)
	$BH_3/Hg(OAc)_2/Br_2$	JACS *92* 3221 (1970)
	BH_3/Br_2, $NaOCH_3$	JACS *92* 6660 (1970)
		JOC *51* 5291 (1986)
	BH_3/Br_2	JACS *92* 7212 (1970)
		JOC *46* 3113 (1981)
	BH_3/BrCl	JOC *46* 3113 (1981)
	BH_3/NaBr, chloramine T	JOC *46* 3113 (1981)
	9-BBN/Br_2	JOMC *26* C51 (1971)
	i-Bu_3Al, cat Cp_2ZrCl_2/NBS	TL *28* 5793 (1987)
	$LiAlH_4$, Cp_2TiCl_2/Br_2	CL 1117 (1977)
Cl, Br	$LiAlH_4$, $TiCl_4/CuX_2$	CL 833 (1978)
	$LiAlH_4$, $TiCl_4$ or $ZrCl_4/X_2$	JOMC *142* 71 (1977)
	$HSiCl_3$, cat H_2PtCl_6/KF/CuX_2	TL 1809 (1978)
		Organomet *1* 369 (1982)
Br, I	Cl_2AlH, cat Et_3B/X_2, py	JACS *108* 6036 (1986)
Cl, Br, I	$HSiCl_3$, cat H_2PtCl_6/KF/X_2 or NBS	JACS *100* 290 (1978)
		Organomet *1* 355 (1982)
I	$(Sia)_2BH/I_2$, NaOH	JACS *90* 5038 (1968)
	BH_3/I_2, $NaOCH_3$	JACS *98* 1290 (1976)
		Syn 114 (1976)
	$\left(\bigcirc\right)_2$BH/I_2, $NaOCH_3$	JACS *107* 3915 (1985)
	BH_3/NaI, chloramine T	JOC *46* 2582 (1981); *52* 28 (1987)
	BH_3/ICl, NaOAc	JOC *45* 3578 (1980)
	$\left(\bigcirc\right)_2$BH/ICl, NaOAc	Syn Commun *11* 521 (1981)
	i-Bu_3Al, cat Cp_2ZrCl_2/I_2	TL *21* 1501 (1980)

$$RCH{=}CHBr \text{ or } RC(Br){=}CH_2 \xrightarrow[\text{peroxides}]{HBr} RCH(Br)CH_2Br$$

JACS *58* 1806 (1936)

2.3. Unknown Regiochemistry



I_2, CuO-HBF_4, Et_3SiH	CC 1491 (1987)
$I(py)_2BF_4$, Et_3SiH	Angew *24* 319 (1985)

2.4. Isomerization—Addition

$$RCH{=}CH(CH_2)_nCH_3 \xrightarrow[2.\ E^+]{1.\ HZrClCp_2} R(CH_2)_{n+2}CH_2X$$

$E^+ = NCS, PhICl_2, NBS, Br_2, I_2 \qquad X = Cl, Br, I$

JACS *96* 8115 (1974); *98* 262 (1976)
Angew Int *15* 333 (1976)
JOC *46* 1821 (1981)

3. Hydrogen Substitution

$$R_2C{=}CHR \xrightarrow[HF]{AcNHBr} \xrightarrow{KOH} R_2C{=}CRF$$

Syn 217 (1978)

$$RCH{=}CHR \xrightarrow{PhSeCl_3} RCH(Cl){-}CHR(PhSeCl_2) \xrightarrow[NaHCO_3]{\overset{\Delta}{H_2O}} RC(Cl){=}CHR$$

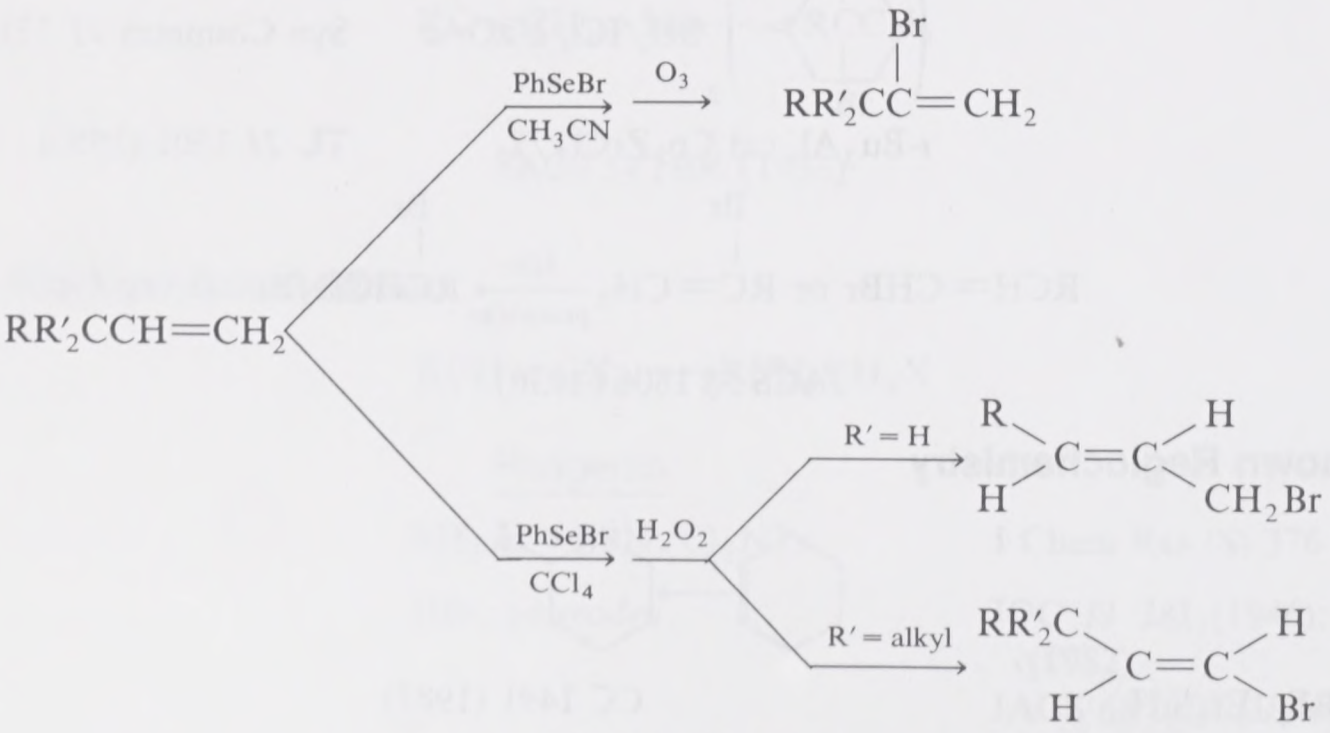
JOC *52* 4086 (1987)

$$RCH{=}CH_2 \xrightarrow[2.\ SO_2Cl_2]{1.\ PhSeCl} RCHCH_2SeCl_2Ph \xrightarrow[NaHCO_3]{\overset{\Delta}{H_2O}} RC(Cl){=}CH_2$$

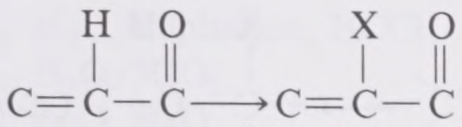
TL *28* 1463 (1987)

$$RCH{=}CH_2 \xrightarrow[\substack{2.\ O_3\\3.\ py,\ \Delta}]{1.\ PhSeCl} RC(Cl){=}CH_2$$

JACS *109* 7543 (1987)



TL 3909 (1977)



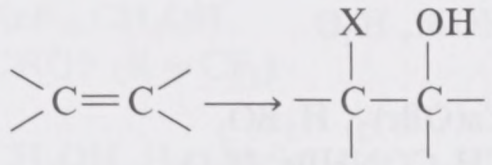
X	Reagent(s)	
Cl, Br	PhSeX, py	TL *22* 3301 (1981)
Br	$Br_2/NaHCO_3$	Syn 389 (1982)
	Br_2/Et_3N	TL *28* 6485 (1987)

$$H_2C{=}CRCO_2R \xrightarrow[2.\ NaO\text{-}i\text{-}Pr]{1.\ Br_2} BrCH{=}CRCO_2\text{-}i\text{-}Pr$$

JOC *50* 2195 (1985)

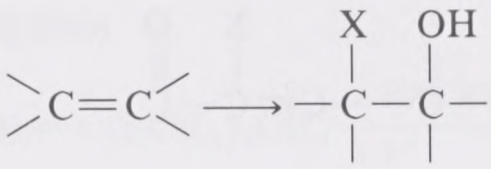
4. Halofunctionalization

For the synthesis of vinylic halides via halofunctionalization of alkynes see page 240, Section 2.21.



Review: Russ Chem Rev *41* 740 (1972)

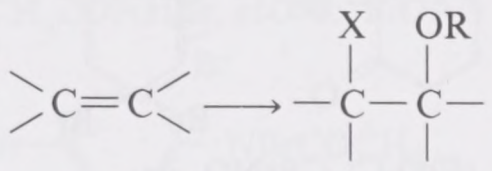
X	Reagents	
Cl	Cl_2, H_2O	JCS *119* 1774 (1921); *121* 2595 (1922); 1817 (1949)
		Ber *61* 510, 518 (1928)
		JACS *72* 4608 (1950)
		Org Syn *33* 15 (1953)
		Ann *596* 140 (1955)
	Cl_2, H_2O, $HgCl_2$	Ann *596* 138 (1955)
	Cl_2, H_2O, $HgCl_2$, $NaOH/HNO_3$	Org Syn Coll Vol *1* 158 (1941)
	Cl_2, H_2O, $NaHCO_3$, CO_2	JCS 1817 (1949)
	HOCl, H_2O	Helv *35* 1263 (1952); *39* 423 (1956)
		Ber *89* 2424 (1956)
		JACS *79* 2341 (1957)
	HOCl, H_2O, $CuCl_2$	Rec Trav Chim *50* 261 (1931)
	$EtOCl/H_2O$	Ber *58* 572 (1925)
	t-BuOCl, H_2O, HOAc	JCS 114 (1946); 239 (1949)
	t-BuOCl, HOAc	Helv *35* 1263 (1952)
	t-BuOCl, HOAc, H_2SO_4	JACS *63* 2541 (1941)
	NaOCl, H_2O, CO_2	JCS 1817 (1949)
	KOCl, H_2O, CO_2	JACS *44* 148 (1922)
	$Ca(OCl)_2$, HOAc, H_2O	JACS *58* 2396 (1936)



(*Continued*)

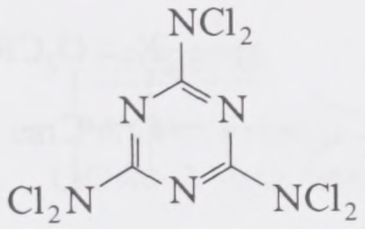
X	Reagents	
	$Ca(OCl)_2$, CO_2, H_2O	JACS *67* 516 (1945); *71* 2666 (1949) BSCF 1240 (1964)
	Me_3SiCl, H_2O_2	Syn Commun *9* 37 (1979)
	$TiCl_4$, *t*-BuO_2H or $(t\text{-BuO})_2$	JOC *50* 915 (1985)
	$ClNHCONH_2$, HOAc, H_2O	Org Syn Coll Vol *4* 157 (1963)
	TsNClNa, H_2O	Syn 362 (1981)
Br	Br_2, H_2O	Ann *348* 285 (1906) JCS *111* 240 (1917); *117* 359 (1920); *119* 1774 (1921)
	Br_2, H_2O, KBr	JCS *101* 758 (1912); 1487 (1928) JOC *18* 1586 (1953)
	Br_2, H_2O, Na_2CO_3	Ber *54* 1945 (1921)
	Br_2, H_2O, $NaHCO_3$, CO_2	JCS 1817 (1949)
	Br_2, H_2O, HgO	Helv *7* 108 (1924) JCS 285 (1936); 1817 (1949)
	HOBr, H_2O	Helv *35* 1263 (1952) JACS *79* 2341 (1957)
	$Ca(OBr)_2$, H_3BO_3	Ber *32* 3490 (1899)
	$CH_3CONHBr$, H_2O	Ber *59* 1279 (1926) JACS *64* 2780 (1942); *74* 1160 (1952); *78* 1740 (1956) Helv *26* 562, 586, 705, 721, 1799 (1943) Gazz Chim Ital *108* 643 (1978) JOC *52* 4384 (1987)
	$CH_3CONHBr$, H_2O, H^+	JACS *61* 1576 (1939); *79* 1130 (1957) JOC *18* 1586 (1953); *51* 3407 (1986)
	$CH_3CONHBr$, H_2O, HOAc, NaOAc	Helv *27* 821 (1944); *28* 1420 (1945); *30* 1616 (1947)
	NBS, H_2O	JACS *74* 1160 (1952); *76* 4373 (1954); *77* 2549 (1955) Can J Chem *43* 2398 (1965) JOC *35* 2670 (1970)
	NBS, H_2O, DMSO	JACS *90* 5498 (1968)
	NBS, H_2O, H^+	JCS 401 (1952) JACS *76* 5017 (1954)
I	I_2, H_2O	Ber *58* 794, 1064, 1071 (1925); *59* 113, 375 (1926); *60* 991 (1927) JCS C 928 (1970)

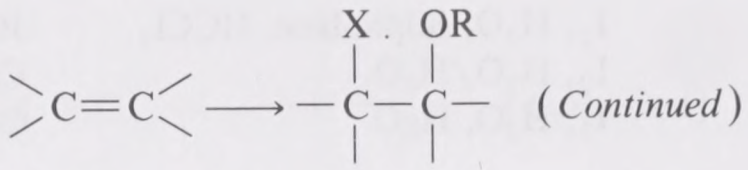
	I_2, H_2O, sulpholane, $HCCl_3$	JCS Perkin I 226 (1977)
	I_2, H_2O/H_2O_2	Can J Chem *42* 2710 (1964)
	I_2, H_2O, HgO	Compt Rend *130* 1766 (1900); *131* 528 (1900); *135* 1055 (1902)
		JCS 1817 (1949)
	I_2, H_2O, CuO-HBF_4	CC 1491 (1987)
	I_2, H_2O, $NaNO_2$, H^+	JCS C 846 (1970)
	I_2, H_2O, KIO_3, H^+	JCS C 846 (1970)
	I_2, PDC, molecular sieves	Tetr *39* 1765 (1983)
	I_2, AgO_2CCF_3/MeOH	TL *27* 4245 (1986)
	$I(py)_2BF_4$, H_2O	Angew Int *24* 319 (1985)



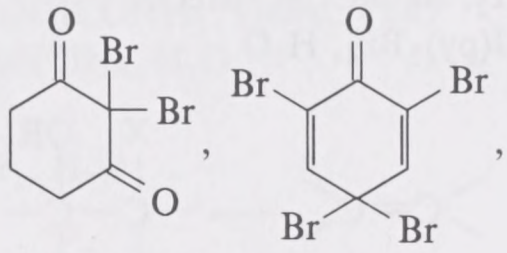
For intramolecular reactions see page 445, Section 2.

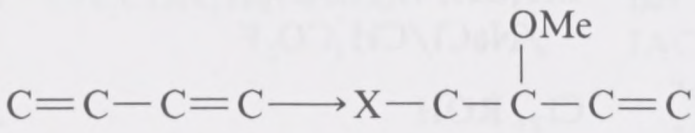
Review: Russ Chem Rev *41* 740 (1972)

X	Reagents	
F	$CsSO_4F$, ROH	JOC *52* 919 (1987)
	XeF_2, CH_3OH	JOC *50* 2751 (1985)
	CF_3OF (R = CF_3)	CC 227 (1969)
		JCS Perkin I 739 (1974)
	CH_3OH, $Hg(OAc)_2$ /NaCl/CH_3CO_2F	JOC *52* 2588 (1987)
Cl	Cl_2, ROH	JACS *48* 2166 (1926)
	t-BuOCl, ROH	JACS *63* 858, 1624 (1941); *72* 4608 (1950); *73* 2302 (1951)
		Chem Rev *54* 925 (1954) (review)
	$PhSO_2NCl_2$, ROH	J Gen Chem USSR *8* 370 (1938) [CA *32* 519 (1938)]
		JACS *76* 693 (1954)
	 , CH_3OH	JOC USSR *5* 1879 (1969); *7* 1876 (1971)
Br	Br_2, ROH	JACS *46* 1727 (1924); *48* 2166 (1926); *71* 1096 (1949); *74* 5518 (1952)
		Helv *35* 762 (1952)
	Br_2, ROH, $AgNO_3$	Ann *516* 231 (1935)
	$CH_3CONHBr$, ROH	Ber *59* 1279 (1926)
		JACS *65* 2196 (1943); *74* 1160 (1952)
		JOC *17* 233 (1952)
	NBS, ROH	JACS *76* 4368, 4373 (1954)
		TL *28* 2009 (1987)

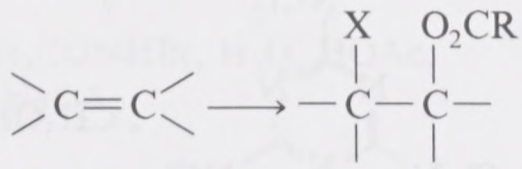


(*Continued*)

X	Reagent(s)	
	$PhSO_2NBr_2$, ROH	JACS *69* 2001 (1947); *76* 693 (1954)
	$BrC(NO_2)_3$, ROH	Ber *55* 2099 (1922); *56* 1239 (1923); *57* 2039 (1924); *59* 1279, 1876 (1926)
		Ber *59* 1876 (1926)
	$(EtO_2C)_2CBrNO_2$ or $(NO_2)_2CBr_2$; ROH	
I	ICl, ROH	JACS *50* 2249 (1928)
	I_2, MeOH	JCS Perkin I 226 (1977)
	I_2, MeOH, HgO	Compt Rend *135* 1055 (1902)
	I_2, ROH, $Cu(OAc)_2 \cdot H_2O$	Syn 402 (1978)
	I_2, ROH/Cl_2	JACS *50* 2249 (1928)
	NIS, ROH	JACS *109* 8119 (1987)
	$I(py)_2BF_4$, ROH	Angew Int *24* 319 (1985)

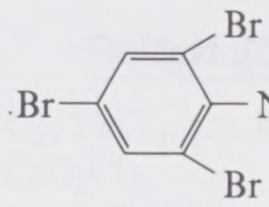


X	Reagents	
Br	Br_2, MeOH	JOC *35* 539 (1970)
I	I_2, $CuO \cdot HBF_4$, MeOH	CC 1491 (1987)
	$I(py)_2BF_4$, MeOH	TL *27* 1715 (1986)



For iodolactonization see page 941, Section 8.

X	Reagent(s)	
F	CH_3CO_2F	CC 443 (1981)
	CF_3CO_2F	JOC *45* 672 (1980)
Cl	Cl_2, RCO_2H	JACS *61* 1457 (1939); J Gen Chem USSR *25* 709 (1955)
	Cl_2, Ac_2O, NaOAc	JACS *61* 1457 (1939)
	Cl_2, AgO_2CR	Ber *68* 824 (1935)

	t-BuOCl, RCO_2H	JACS *63* 858 (1941)
	CrO_2Cl_2, AcCl	TL 3523 (1977)
	AcOCl	Ann *519* 165 (1935)
	$TsNClNa \cdot 3\ H_2O$, RCO_2H	TL *21* 1709 (1980)
Br	Br_2/NaOAc	JACS *76* 693 (1954)
	Br_2, AgO_2CR	Ber *68* 824 (1935)
		JCS 1515, 2934 (1952); 762 (1954)
	Br_2, $Hg(OAc)_2$, HOAc	J Gen Chem USSR *25* 709 (1955)
	RCO_2Br	Ann *519* 165 (1935)
	$CH_3CONHBr$, HCO_2H	Ber *59* 1279 (1926)
	$CH_3CONHBr$, HOAc, LiOAc	TL *27* 4253 (1986)
	 $NBrCOCH_3$,	JCS 762 (1954)
	RCO_2H, py	
	$BrC(NO_2)_3$, HCO_2H	Ber *56* 1239 (1923)
I	ICl, TlO_2CR	JCS Perkin I 226 (1977)
	I_2, NaO_2CR	JCS Perkin I 226 (1977)
	I_2, KOAc, Al_2O_3	CC 1301 (1987)
	I_2, AgO_2CR	Ber *65* 1339 (1932); *67* 1729 (1934)
	$I(py)_2BF_4$, RCO_2H	Angew Int *24* 319 (1985)

$$C{=}C{-}C{=}C \xrightarrow[X = Cl,\ Br]{XO_2CR} \overset{X}{\underset{|}{C}}{-}\overset{O_2CR}{\underset{|}{C}}{-}C{=}C$$

JOC *37* 2228 (1972)

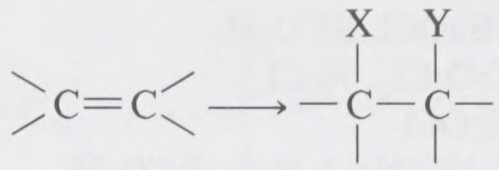
$$C{=}C{-}C{=}C \longrightarrow \overset{X}{\underset{|}{C}}{-}C{=}C{-}\overset{O_2CR}{\underset{|}{C}}$$

X	Reagents	
Cl	cat $Pd(OAc)_2$, LiCl, $LiOAc \cdot 2\ H_2O$, benzoquinone	TL *23* 1617 (1982); *28* 4199 (1987) Tetr *41* 5761 (1985) JACS *107* 3676 (1985)
I	I_2, HOAc, CuO-HBF_4	CC 1491 (1987)

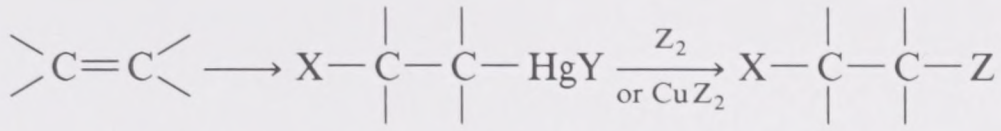
$$C{=}C{-}C{=}C \xrightarrow[Nuc\ or\ Nuc^-]{I(py)_2BF_4} I{-}C{-}\overset{Nuc}{\underset{|}{C}}{-}C{=}C \text{ or } I{-}C{-}C{=}C{-}C{-}Nuc$$

Nuc = H, Cl, OMe, O_2CH, NO_2, $NHCOCH_3$

TL *27* 1715 (1986)



X	Y	Reagent(s)	
Cl	N_3	Cl_2, NaN_3	TL 3309 (1969) Acct Chem Res *4* 9 (1971) (review)
Br	N_3	Br_2, NaN_3	JACS *90* 216 (1968) TL 3309 (1969) Acct Chem Res *4* 9 (1971) (review)
I	N_3	ICl, NaN_3	JACS *87* 4203 (1965); *89* 2077 (1967) TL 3309 (1969) Acct Chem Res *4* 9 (1971) (review)
		I_2, NaN_3, Al_2O_3	CC 1301 (1987)
		I_2, NaN_3, Adogen 464, H_2O, $HCCl_3$	Syn 462 (1977)
		I_2, NaN_3, sulpholane, $HCCl_3$	JCS Perkin I 226 (1977)
I	NO_2	I_2, CuO, HBF_4, $NaNO_2$	CC 1491 (1987)
		$I(py)_2BF_4$, NO_2^-	Angew Int *24* 319 (1985)
I	NCO	$I(py)_2BF_4$, NCO^-	Angew Int *24* 319 (1985)
I	$NHCOCH_3$	$I(py)_2BF_4$, CH_3CN	Angew Int *24* 319 (1985)
I	O_2SAr	I_2, CuO-HBF_4, NaO_2SAr	CC 1491 (1987)
I	SCN	ICl, KSCN, $HCCl_3$, sulpholane	TL 1531 (1976)
		I_2, $(SCN)_2$	TL 3567 (1972)
		I_2, KSCN, $HCCl_3$, sulpholane	TL 1531 (1976)
		I_2, KSCN, 18-crown-6, $HCCl_3$	Syn 462 (1977)
		I_2, KSCN, Adogen 464, H_2O, $HCCl_3$	Syn 462 (1977)
		I_2, KSCN, Al_2O_3	CC 1301 (1987)
		I_2, TlSCN, $HCCl_3$, sulpholane	TL 1531 (1976)
I	C_6H_4OMe	I_2, CuO-HBF_4, C_6H_5OMe	CC 1491 (1987)
I	Ar	$I(py)_2BF_4$, Ar-H	Angew Int *24* 319 (1985)

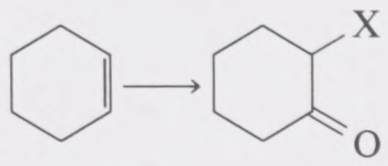


X = HO, RO, RO_2, RCO_2, R_2N, RCONH, N_3, F

Y = OAc, O_2CCF_3, NO_3, F, Cl

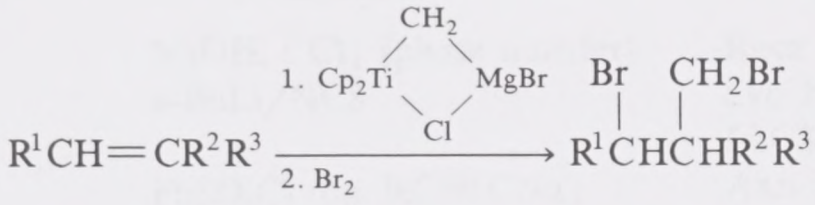
Z = Cl, Br, I

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986) (review)



X	Reagent(s)	
Cl	O_2, $FeCl_3$, py, hν	JOC *46* 509 (1981)
	CrO_2Cl_2	Syn Commun *11* 7 (1981)
I	I_2, PCC	TL *21* 4521 (1980)

5. Miscellaneous Reactions

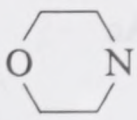


TL *24* 3935 (1983)

4. HALOGENATION OF ALKYNES

See also page 215, Section 2; and page 337, Section 5, for additional preparations of vinylic halides.

$$RC{\equiv}CH \longrightarrow RC{\equiv}CX$$

X	Reagent(s)	
Cl	NaOH, CCl_4 (phase transfer)	Rocz *49* 1779 (1975)
	n-BuLi/NCS	Syn 296 (1979)
		JACS *101* 5101 (1979)
	$PhSO_2Cl$ (on $RC{\equiv}CNa$)	Ann Chim [10] *16* 309 (1931)
		JACS *56* 1106 (1934)
		BSCF 1447 (1957)
	n-BuLi/Cl_2	Tetr *22* 965 (1966)
	HOCl	Ber *63* 1868, 1886 (1930)
		Can J Chem *32* 500 (1954)
		JACS *85* 1648 (1963)
Br	DBU, Cl_3CBr	CL 73 (1978)
	NaOH, Br_2	JCS 2295 (1963)
	HOBr	Ber *63* 1868 (1930)
		BSCF 1447 (1957)
		Arch Pharm *290* 118 (1959)
		JACS *85* 1648 (1963)
	n-BuLi/NBS	JACS *94* 4013 (1972)
	n-BuLi/Br_2	Tetr *22* 965 (1966)
		JACS *89* 5086 (1967)
	BrCN (on $RC{\equiv}CMgBr$)	Ann Chim [10] *5* 5 (1926)
I	I_2, NH_3	JACS *54* 787 (1932); *55* 2150 (1933); *56* 1207 (1934)
		JCS 741 (1933)
	I_2, 	JOC *27* 3305 (1962)
	HOI	Ber *37* 4412 (1904); *63* 1886 (1930)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CX \quad (\textit{Continued})$$

X	Reagent(s)	
I	I_2, $Hg(OAc)_2$	Bull Acad Sci USSR, Div Chem Sci 869 (1968)
	$NaOCH_3/I(py)_2BF_4$	Syn 661 (1987)
	Na, NH_3/I_2	JACS *55* 2150 (1933); *56* 1106 (1934)
	RLi/I_2	Tetr *22* 965 (1966)
		JACS *89* 5086 (1967); *107* 1028 (1985)
		JOC *51* 5320 (1986)
	Na/I_2	Ann *308* 264 (1899)
	ICN (on $RC{\equiv}CMgBr$)	Ann Chim [10] *5* 5 (1926)

$$RC{\equiv}CR' \longrightarrow RC(X){=}CR'X$$

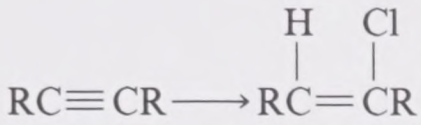
X	Reagent(s)	
Cl	SO_2Cl_2	BCSJ *54* 2843 (1981)
Br	Br_2	TL 1629 (1970)
	[polymer-$C_6H_5CH_2\overset{+}{N}Me_3$]$Br_3^-$	Syn 143 (1980)
I	I_2, alumina	TL *29* 35 (1988)

$$RC{\equiv}CH + HBr \xrightarrow[\text{peroxides}]{} RCH{=}CHBr + RCH(Br)CH_2Br$$

JACS *58* 1806 (1936)

$$RC{\equiv}CH \longrightarrow RC(X){=}CH_2$$

X	Reagent(s)	
Cl	HCl	JOC *62* 1367 (1940); *39* 1124 (1974)
		Chem Ber *106* 2001 (1973)
	$(Et_4N)HCl_2$	JCS Perkin I 1797 (1977)
Br	HBr	JACS *58* 1806 (1936)
		Helv *54* 2060 (1971)
	$(Et_4N)HBr_2$	Syn 805 (1980)
	$RLi/Me_3SiCl/HBr$	JOC *39* 3307 (1974)
	B-Br-9-BBN/HOAc	TL *24* 731 (1983)
I	I_2, Al_2O_3	TL *28* 4497 (1987)
	B-I-9-BBN/HOAc	TL *24* 731 (1983)

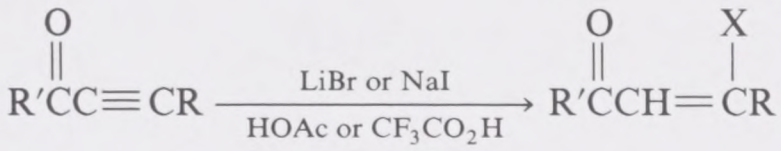


HCl, Lewis acid

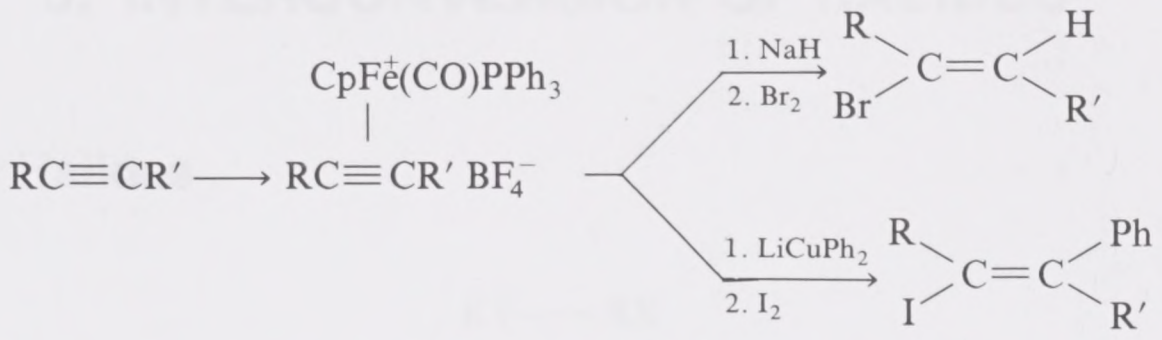
CC 857 (1972)
JCS Perkin I 2491 (1973)
JACS *98* 3295 (1976)

$(Et_4N)HCl_2$

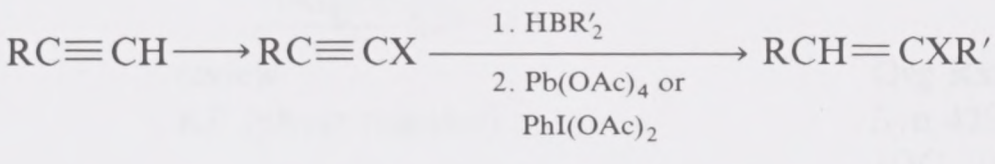
JCS Perkin I 1797 (1977)



TL *27* 4763 (1986)

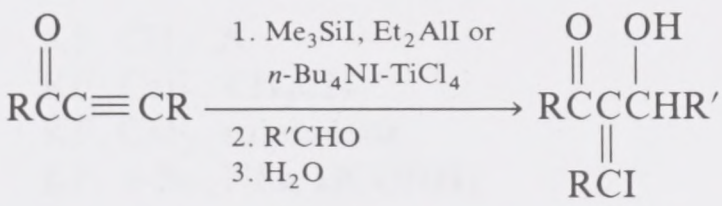


JACS *102* 5923 (1980)

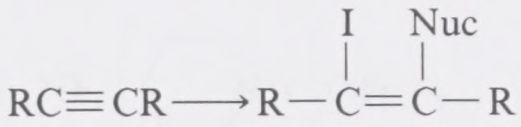


X = Cl, Br

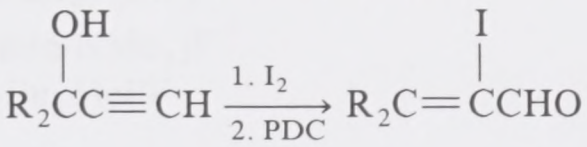
BCSJ *53* 1652 (1980)



TL *27* 4767 (1986)



See page 215, Section 2.

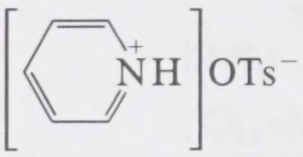


TL *22* 1041 (1981)

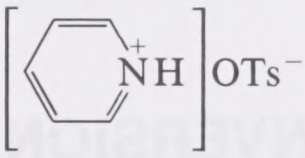
5. INTERCONVERSION OF HALIDES

1. Aliphatic Halides

$$RY \longrightarrow RX$$

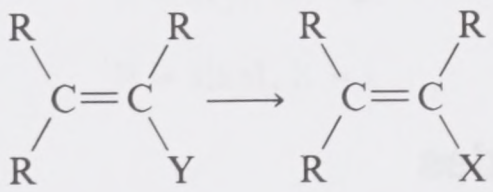
X	Y	Reagent(s)	
F	—	review	Org Rxs *2* 49 (1944)
Cl		KF (phase transfer)	Syn 428 (1974) JOC *50* 879 (1985)
		KF, $HOCH_2CH_2OH$	JACS *79* 2311 (1957)
		KF, $(HOCH_2CH_2)_2O$	Coll Czech Chem Commun *39* 2616 (1974)
		KF, CH_3CN	CL 761 (1981)
		KF, CaF_2, CH_3CN	CC 791, 793 (1986)
		KF, CaF_2, sulpholane	CC 791 (1986)
		KF, *n*-Bu_4NBr, $HCONH_2$	TL *27* 1499 (1986)
		CsF, CaF_2, sulpholane	CC 791 (1986)
		n-Bu_4NF (no solvent)	JOC *49* 3216 (1984)
		n-Bu_4NF,  OTs^-	TL *28* 4419 (1987)
		$(n\text{-}Bu_4N)HF_2$	TL *28* 4733 (1987)
		[resin-$\overset{+}{N}Me_3$]F^-	Syn 472 (1976)
		n-Bu_3MePF	TL 353 (1979) Tetr *36* 1931 (1980)
		$AgBF_4$	TL *28* 5347 (1987) (gem dihalides and trihalides)
		Mg/TsNFR	JACS *106* 452 (1984)
Br		KF (phase transfer)	Syn 428 (1974)
		KF, cat 18-crown-6	JACS *96* 2250 (1974) JOC *40* 782 (1975)
		KF, $HOCH_2CH_2OH$	Org Syn Coll Vol *4* 525 (1963)

$RY \longrightarrow RX$ (*Continued*)

X	Y	Reagent(s)	
		KF, $(HOCH_2CH_2)_2O$	Coll Czech Chem Commun *39* 2616 (1974)
		KF, $H(OCH_2CH_2)_nOH$	CL 283 (1978)
		KF, HMPA	BSCF 334 (1969)
		KF, CH_3CN	CL 761 (1981)
		KF, CaF_2, CH_3CN	CC 793 (1986)
		KF, *n*-Bu_4NBr, $HCONH_2$	TL *27* 1499 (1986)
		n-Bu_4NF (no solvent)	JOC *49* 3216 (1984)
		n-Bu_4NF, 	TL *28* 4419 (1987)
		$(n\text{-}Bu_4N)HF_2$	TL *28* 4733 (1987)
		[resin-$\overset{+}{N}Me_3$]F^-	Syn 472 (1976) JCS Perkin I 2248 (1979)
		n-Bu_3MePF	TL 353 (1979) Tetr *36* 1931 (1980)
		$(Ph_4P)HF_2$	CC 672 (1985)
		KF, $(Ph_4P)Br$	TL *28* 111 (1987)
		Mg/TsNFR	JACS *106* 452 (1984)
		$Li/FClO_3$	Ber *102* 1944 (1969)
		AgF	JOC *40* 782 (1975)
			TL *28* 4003 (1987)
		HgF_2	JACS *70* 2310 (1948) JOC *40* 782 (1975)
	I	[resin-$\overset{+}{N}Me_3$]F^-	JCS Perkin I 2248 (1979)
		$(n\text{-}Bu_4N)HF_2$	TL *28* 4733 (1987)
		AgF	JOC *40* 782 (1975)
		$AgBF_4$	TL *28* 5347 (1987) (gem dihalides)
		HgF_2	JOC *40* 782 (1975)
Cl	Br	LiCl, CH_3COCH_3	JCS 3173 (1955)
		NaCl, H_2O, phase transfer	CC 1250 (1986)
		cat NaCl, *i*-PrCl	BCSJ *49* 1989 (1976)
		[resin-$\overset{+}{N}Me_3$]Cl^-	Syn 472 (1976)
		graphite-$SbCl_5$	TL 763 (1974)
		ClF_2CCO_2Ag	TL 3447 (1970)
	I	cat NaCl, *n*-PrCl	BCSJ *49* 1989 (1976)
		Cl_2	TL *27* 6055 (1986)
		$PhICl_2$	TL *27* 6055 (1986)
		graphite-$SbCl_5$	TL 763 (1974)
Br	—	review	Houben-Weyl, Vol V/4, p 354
	Cl	HBr, cat $FeBr_3$	CC 1013 (1987)
		LiBr, CH_3COCH_3	JACS *77* 4903 (1955)
		LiBr, phase transfer	CC 1250 (1986)

		NaBr, CH_3OH	JACS *39* 1730 (1917); *77* 165 (1955)
		cat NaBr, EtBr	BCSJ *49* 1989 (1976)
		$CaBr_2$	BSCF *1* 860 (1934)
		$CaBr_2$, R_4NBr	Syn 34 (1984)
		$AlBr_3$	JACS *78* 491 (1956)
		[resin-$\overset{+}{N}Me_3$]Br^-	Syn 472 (1976)
	I	cat NaBr, EtBr	BCSJ *49* 1989 (1976)
		Mg/Br_2	JACS *41* 287 (1919)
		Br_2	TL *27* 6055 (1986)
I	—	review	Houben-Weyl, Vol V/4, p 595
	F	Me_3SiI	JOC *46* 3727 (1981)
	Cl	HI, cat FeI_3	CC 1013 (1987)
		NaI, CH_3COCH_3	JACS *109* 5491 (1987)
		KI, *n*-Bu_4PI, silica	Syn 952 (1979)
		NaI, $ZnCl_2$	JCS Perkin I 416 (1976)
		NaI, $FeCl_3$	JCS Perkin I 416 (1976)
		NaI, $FeCl_3$ or $HgCl_2$	TL 2691 (1974)
		cat NaI, MeI	BCSJ *49* 1989 (1976)
		Me_3SiI	JOC *46* 3727 (1981)
	Br	NaI, phase transfer catalyst	JOC *50* 5828 (1985)
		NaI, CH_3COCH_3	JCS 1605 (1936)
		NaI, HMPA	JACS *90* 6225 (1968)
		NaI, benzo-15-crown-5	CC 879 (1974)
		cat NaI, MeI	BCSJ *49* 1989 (1976)
		KI, DMF	JOC *34* 3519 (1969)
		KI, crown ether	CC 879 (1974)
		KI, *n*-Bu_4PI, silica	Syn 952 (1979)
		[resin-$\overset{+}{N}Me_3$]I^-	Syn 472 (1976)
		Mg/I_2	JACS *41* 287 (1919)
		$Mg/HgBr_2/I_2$	JACS *61* 1585 (1939); *91* 5774 (1969)

2. Vinylic Halides



X	Y	Reagent(s)	
F	I	*t*-BuLi/$PhSO_2NF$-*t*-Bu	JACS *108* 2445 (1986)
Cl, Br	I	CuX	JOMC *93*, 415 (1975)
I	Br	KI, Zn, $NiBr_2$	CL 1435 (1978)
		KI, $NiBr_2$, electrolysis	TL *27* 3497 (1986)

3. Aromatic Halides

$$ArX \xrightarrow[\text{pyridine}]{CuY} ArY$$

X = Br, I Y = Cl, Br, I

Proc Chem Soc 113 (1962)
JCS 1097, 1108 (1964)
Tetr *40* 1433 (1984) (review)

$$ArY \longrightarrow ArX$$

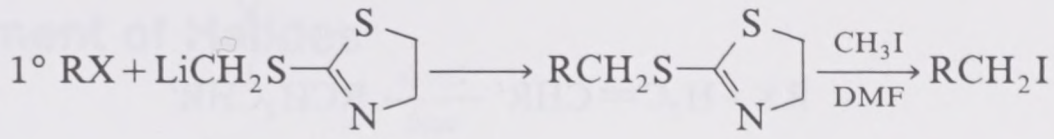
X	Y	Reagent(s)	
F	Cl	KF, DMF or DMSO	JOC *28* 1666 (1963)
		KF, sulfolane	JCS 6264 (1965)
		KF, $(Ph_4P)Br$	TL *28* 111 (1987)
	Br	$Li/FClO_3$	Ber *102* 1944 (1969)
		Mg/TsNF-*t*-Bu	JACS *106* 452 (1984)
		KF, sulfolane	JCS 6264 (1965)
Cl	Br	Mg/Ph_3PCl_2	JOC *32* 3710 (1967)
		CuCl	BSCF 720 (1973)
	I	CCl_4, hν	JOC *35* 528 (1970)
Br	I	Mg/Br_2	JACS *41* 287 (1919)
I	Cl	NaI, DMF	JOC *23* 305 (1958)
		CuI·alumina or charcoal	CC 1409 (1987)
	Br	Mg/I_2	JACS *41* 287 (1919)
			JOC *3* 55 (1938)
		Mg/ICN	Ann Chim *4* 28 (1915)
		NaI, CH_3COCH_3	JOC *28* 218 (1963)
		KI, I_2, Ni, DMF	JOC *52* 691 (1987)
		KI, $NiBr_2$, Zn	CL 191 (1978)
		KI, $NiBr_2$, electrolysis	TL *27* 3497 (1986)
		KI, CuI, HMPA	JACS *108* 3150 (1986)
		KI, cat $Pd(OAc)_2$, NaOEt, HMPA	BCSJ *48* 3298 (1975)
		CuI·alumina or charcoal	CC 1409 (1987)

4. Homologation of Halides

$$1^\circ \quad RX + LiCH_2SPh \longrightarrow RCH_2SPh \xrightarrow[\text{DMF}]{CH_3I,\ NaI} RCH_2I$$

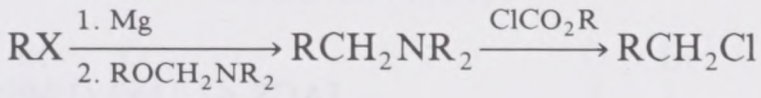
X = Br, I

TL 5787 (1968)

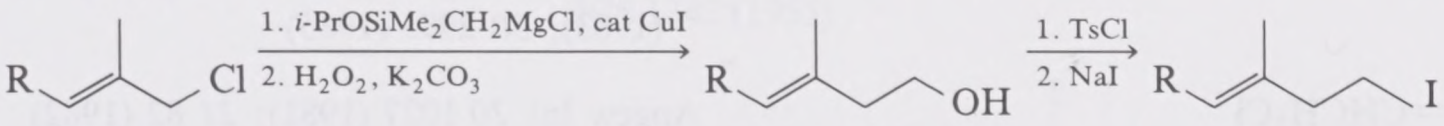


X = Cl, Br

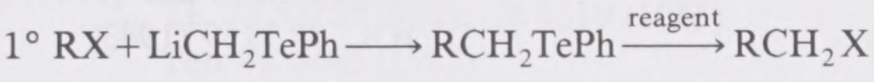
TL 2743 (1972)



TL *28* 427 (1987)

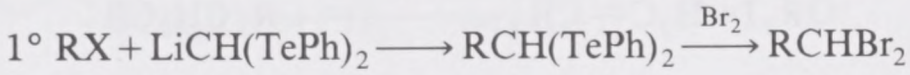


JOC *52* 4885 (1987)

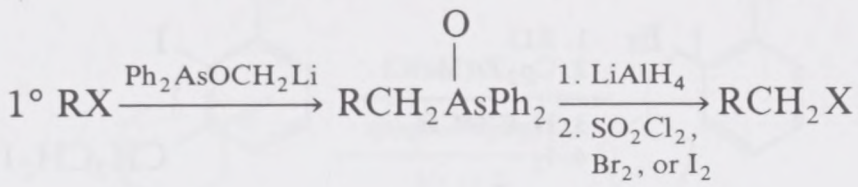


X = Cl, Br, I

Reagent: $SOCl_2$, Br_2, I_2, MeI-NaI

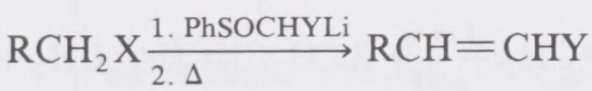


CL 1081 (1982)



X = Cl, Br, I

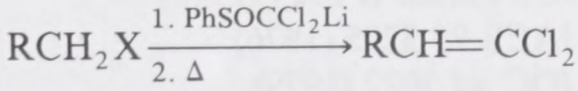
Ber *115* 645 (1982)



R = aryl, X = Br

R = alkyl, X = I

Y	
F	TL *24* 725 (1983)
Cl	TL 617 (1979)



TL *24* 527 (1983)

$$RX + H_2C{=}CHR' \xrightarrow[\text{acid}]{\text{Lewis}} RCH_2\underset{\displaystyle X}{\underset{|}{C}}HR'$$

X = Cl, Br

Review: Angew Int *20* 184 (1981)

RX

RX

JACS *67* 1152 (1945); *75* 6217 (1953)
JOC *48* 1159 (1983)

ArCHRX

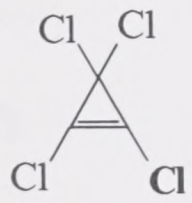
JOC *29* 2685 (1964); *44* 3022 (1979); *48* 1159 (1983); *50* 2995 (1985)

$Me_2C{=}CHCH_2Cl$

Angew Int *20* 1027 (1981); *21* 82 (1982)

RCHClOR

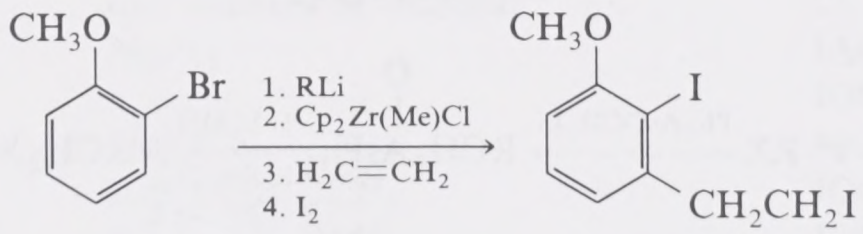
Ann *525* 151 (1936)
Angew Int *6* 335 (1967) (review)
JOC *48* 1159 (1983)



TL *28* 4517 (1987)

$$R_fI + H_2C{=}CR_2 \xrightarrow{\text{cat Raney Ni}} R_fCH_2\underset{\displaystyle I}{\underset{|}{C}}R_2$$

CC 498 (1986)



JACS *109* 7137 (1987)

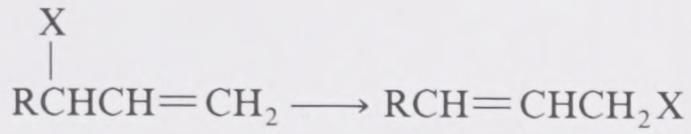
$$RX + H_2C{=}CHCH{=}CH_2 \xrightarrow[\text{acid}]{\text{Lewis}} RCH_2\underset{\displaystyle X}{\underset{|}{C}}HCH{=}CH_2 + RCH_2CH{=}CHCH_2X$$

Angew Int *20* 184 (1981)
Ber *115* 3528 (1982) (R = propargylic)
JOC *48* 1159 (1983)

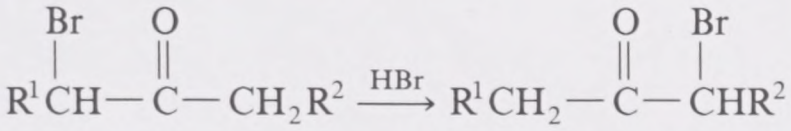
$$RX + R'C{\equiv}CR' \xrightarrow[\text{acid}]{\text{Lewis}} RR'C{=}CXR'$$

CC 857 (1972)
JCS Perkin I 2491 (1973); 353 (1974)
JCS Perkin II 1517 (1976)
JACS *98* 3295 (1976)
JOC *44* 3022 (1979)
Angew Int *20* 184 (1981)

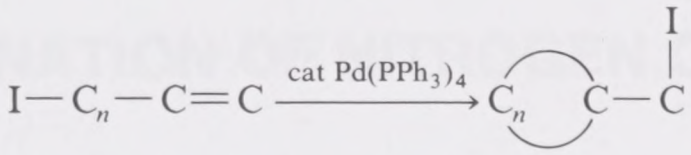
5. Rearrangement of Halides



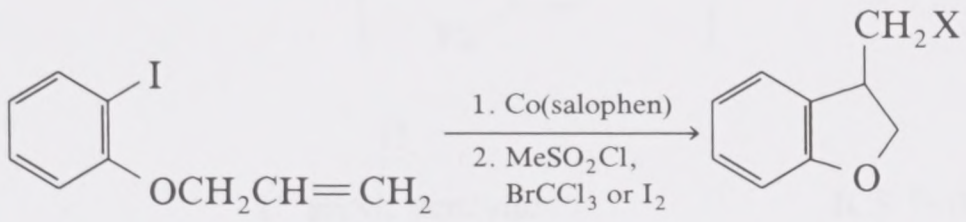
JCS 2720 (1959)



JOC *19* 538 (1954)
JCS 1342 (1955)

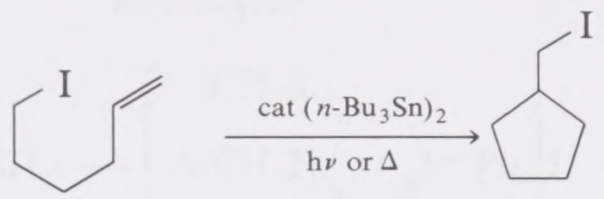


TL *23* 5315 (1982); *26* 1519 (1985)
Tetr *41* 5465 (1985)
CC 1375 (1986)

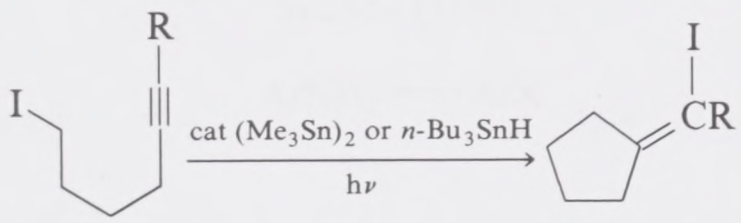


X = Cl, Br, I

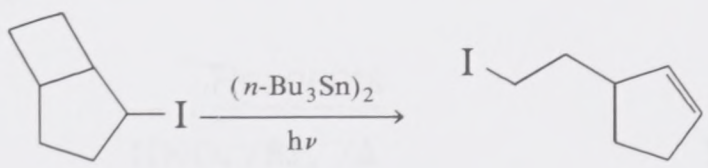
TL *28* 1451 (1987)



TL *27* 5821 (1986); *28* 2477 (1987)

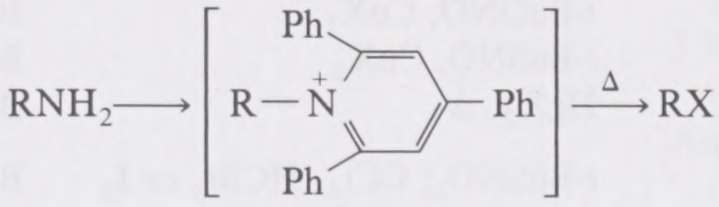


JACS *108* 2489 (1986)
TL *28* 2477 (1987)

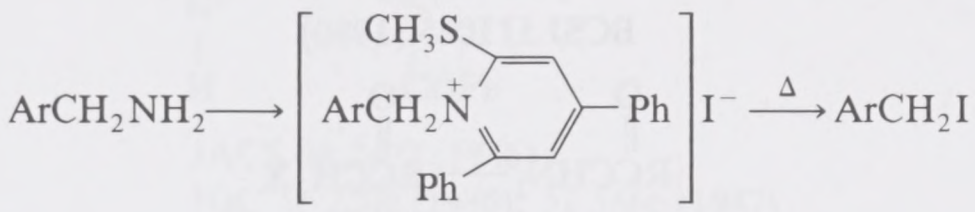


TL *28* 5063 (1987)

6. HALOGENATION OF NITROGEN COMPOUNDS



X	R	
F	1° alkyl, benzylic	JCS Perkin I 2901 (1980)
Br	1° alkyl, benzylic	JCS Perkin I 1890 (1980)
I	1°, 2° alkyl; benzylic; aryl; heterocyclic	Syn 634 (1977) JCS Perkin I 433 (1979)



Syn 853 (1980)

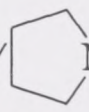
$ArNH_2 \longrightarrow ArX$

Reviews:

Chem Rev *40* 251 (1947)
Quart Rev *6* 358 (1952)
"The Chemistry of Diazonium and Diazo Groups," Ed. S. Patai, J. Wiley, New York (1978), Part 1, pp 288–290

X	Reagents	
F	$HNO_2/BF_4^-/\Delta$	Ber *60* 1186 (1927) Org Rxs *5* 193 (1949)
	$[C_5H_5\overset{+}{N}H]F(HF)_x^-/NaNO_2$	JOC *44* 3872 (1979)
	$HCl, NaNO_2/HPF_6, \Delta$	Org Syn Coll Vol *5* 133 (1973)
Cl	$HCl, NaNO_2/Cu$	Ber *23* 1220 (1890)
	$HCl, NaNO_2/CuCl$	Org Syn Coll Vol *1* 170 (1941); *2* 130 (1943)

$ArNH_2 \longrightarrow ArX$ (*Continued*)

X	Reagents	
	H_2SO_4, $NaNO_2$/CuCl	Org Syn Coll Vol *4* 160 (1963) JACS *108* 1000 (1986)
Br	HBr, $NaNO_2$/Cu	Org Syn Coll Vol *1* 135 (1941)
	HBr, $NaNO_2$/CuBr	Org Syn Coll Vol *3* 185 (1955) JACS *109* 3378 (1987)
	H_2SO_4, $NaNO_2$/CuBr	JOC *51* 1339 (1987)
	AmONO, $HCBr_3$	JCS C 1249 (1966)
I	HNO_2/  /KI, H^+	Syn 572 (1980)
	HCl, $NaNO_2$/KI	JOC *51* 1339 (1987)
	H_2SO_4, $NaNO_2$/KI, Cu	Org Syn Coll Vol *2* 355 (1943)
	AmONO, I_2	JOC *33* 1636 (1968)
	I_2, DMSO on $(ArN_2)BF_4$	Syn Commun *11* 639 (1981)
Cl, Br	*t*-BuONO, CuX_2	JOC *42* 2426 (1977)
	t-BuSNO, CuX_2	BCSJ *53* 1065 (1980)
	HgX_2, Δ	Ber *65* 1605 (1932)
Cl, Br, I	*t*-$BuSNO_2$; CCl_4, $HCBr_3$ or I_2	BCSJ *53* 2023 (1980)
Br, I	KX, H_2SO_4/$NaNO_2$/Cu	Ber *23* 1220 (1890)
	HNO_2/Et_2NH/Me_3SiCl, LiBr or NaI	JOC *46* 5239 (1981)

$$ArNH_2 + H_2C{=}CHR \xrightarrow[CuX_2]{t\text{-BuSNO}} ArCH_2\underset{\displaystyle X}{\underset{|}{C}}HR$$

X = Cl, Br

BCSJ *53* 1065 (1980)

$$RC(=O)CHN_2 \longrightarrow RC(=O)CH_2X$$

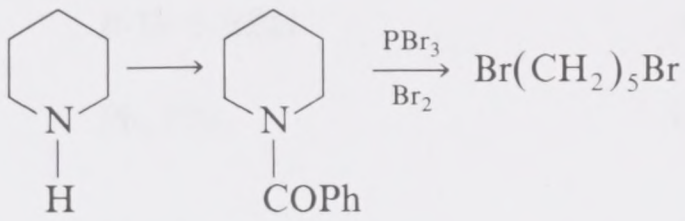
X	Reagent(s)	
F	$[C_5H_5\overset{+}{N}H]F(HF)_x^-$	JOC *44* 3872 (1979)
	HF	Bull Acad Sci USSR, Div Chem Sci 363 (1956) Ber *89* 864 (1956) JACS *79* 1959 (1957) Chem Ind 394 (1957)
Cl	HCl	Helv *27* 1108 (1904) JCS 1310 (1928) JACS *68* 2220 (1946); *72* 3477 (1950); *74* 2082 (1952); *76* 1185 (1954) Org Syn Coll Vol *3* 119 (1955)
Br	HBr	JOC *12* 767, 776 (1947); *18* 868 (1953) JCS 278 (1948) JACS *74* 2082, 2550 (1952)

$$R_2CN_2 \xrightarrow{X_2} R_2CX_2$$

X	
F	JOC *46* 3917 (1981)
Cl	J Prakt Chem [2] *38* 433 (1888) Ber *86* 1467 (1953); *87* 971 (1954)
Br	J Prakt Chem [2] *38* 433 (1888) Ber *66* 1541 (1933); *86* 1467 (1953); *87* 971 (1954) JACS *72* 3655 (1950)
I	Ber *18* 1283 (1885); *19* 2460 (1886); *27* 1888 (1894); *28* 2374 (1895); *35* 897 (1902); *60* 1364 (1927); *66* 1541 (1933) J Prakt Chem [2] *38* 422, 433 (1888) Ann *325* 143 (1902); *394* 36 (1912) JACS *65* 1458, 1516 (1943)

$$R_2C{=}NNH_2 \xrightarrow{IF} R_2CF_2$$

JACS *109* 896 (1987)



JACS *68* 2402 (1946)
JOC *51* 2206 (1986); *52* 5466 (1987)

7. HALOGENATION OF ETHERS

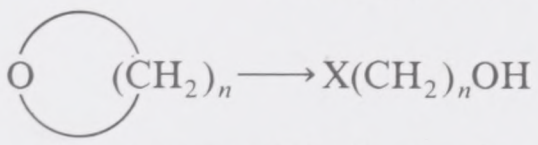
$$R-O-R' \longrightarrow RX$$

X	Reagent(s)	
Cl	BCl_3	Chem Ind 609 (1963) (R′ = Me)
	PhCOCl, cat n-Bu_3SnCl, cat $PhCH_2PdCl(PPh_3)_2$	JOC *47* 1215 (1982) (R = $PhCH_2$)
Br	HBr, H_2SO_4	JOC *52* 5480 (1987)
	HBr, HOAc	Syn 771 (1978)
	HBr, cat $[n\text{-}C_{16}H_{33}P(n\text{-}Bu)_3]Br$	Syn 771 (1978)
	BBr_3	Chem Ind 609 (1963) (R′ = Me)
	B-Br-9-BBN	JOMC *156* 221 (1978) (R = 3° > 2° > 1° alkyl)
	Ph_3PBr_2	Chem Ind 200 (1969) (R′ = *t*-Bu)
I	Me_3SiI	JOC *42* 3761 (1977)
	H_2SiI_2	JOC *52* 4846 (1987)

See also page 501, Section 6, for cleavage of ethers to alcohols plus organic halides.

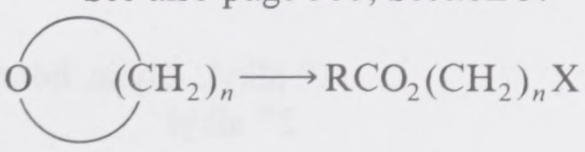
$$R_2\overset{\overset{\displaystyle OMe}{|}}{C}C\equiv CR \longrightarrow R_2\overset{\overset{\displaystyle Cl}{|}}{C}C\equiv CR$$

HCl, $ZnCl_2$	JACS *107* 6546 (1985)
CH_3COCl, cat $SnCl_4$	JACS *107* 6546 (1985)



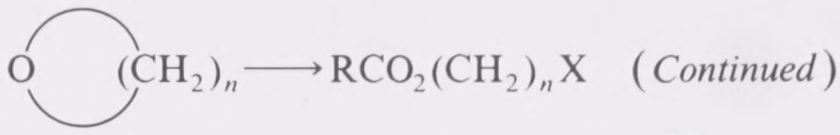
$$\text{O}\!\!\bigcirc\!\!(CH_2)_n \longrightarrow X(CH_2)_nOH$$

See also page 508, Section 3.



$$\text{O}\!\!\bigcirc\!\!(CH_2)_n \longrightarrow RCO_2(CH_2)_nX$$

X	n	Reagent(s)	
Cl	2	PhCOCl, cat n-Bu_3SnCl, cat $PhCH_2PdCl(PPh_3)_2$	JOC *47* 1215 (1982)



(*Continued*)

X	n	Reagent(s)	
	2	PhCOCl, cat *n*-Bu_2SnCl_2, cat Ph_3P	TL *27* 3021 (1986)
	3–5	RCOCl, cat $K[Pt(C_2H_4)Cl_3]$	JOC *48* 751 (1983)
	4	CH_3COCl, cat $Rh_2(C_2H_4)_4Cl_2$	JOC *48* 751 (1983)
	4	RCOCl, cat $ZnCl_2$	JACS *61* 2667 (1939)
	4	RCOCl, cat $Mo(CO)_6$	JOC *38* 64 (1973)
Br	2, 4, 5	$(CH_3CO)_2O$, $MgBr_2$	JOC *40* 3571 (1975)
	4	CH_3COBr	TL 3813 (1965)
	4	CH_3COBr, cat $ZnCl_2$	JCS 1536 (1954) JOC *51* 3372 (1986)
	4	CH_3COBr, cat $K[Pt(C_2H_4)Cl_3]$	JOC *48* 751 (1983)
I	4,5	RCOCl, NaI	TL *23* 681 (1982)

$ROSiR'_3 \longrightarrow RX$

X	Reagent(s)	R	
F	$PhPF_4$	1°, 2°, 3° alkyl	TL 847 (1972) Tetr *29* 1877 (1973) BSCF 2861 (1974) JOC *44* 3406 (1979)
	n-Bu_4NF or $(PhCH_2NMe_3)F$, RSO_2F (R = Me, *p*-Tol), molecular sieves	1° alkyl, 1° benzylic	TL *26* 4207 (1985)
Br	$Ph_3P \cdot Br_2$	1°, 2° alkyl	JOC *51* 4941 (1986)
	CBr_4, PPh_3, CH_3COCH_3	1° alkyl, allylic, benzylic; 2° alkyl	TL *28* 1697 (1987)
I	Me_3SiCl, NaI	1°, 2°, 3° alkyl; 1° benzylic	Syn 379 (1979)

ROTHP ⟶ RX

X	Reagents	R	
Br	Br_2, Ph_3P	1° alkyl	JOC *40* 2410 (1975); *44* 4603 (1979) Syn Commun *6* 21 (1976) JACS *101* 4773 (1979); *107* 686 (1985)
	Br_2, $Ph_2PCH_2CH_2PPh_2$	2° alkyl, 1° allylic, 1° propargylic	TL *28* 767 (1987)
I	I_2, $Ph_2PCH_2CH_2PPh_2$	1°, 2° alkyl; 1° allylic	TL *28* 767 (1987)

8. HALOGENATION OF ALCOHOLS

Review: Tetr *36* 1901 (1980) (allylic alcohols)

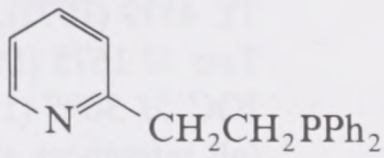
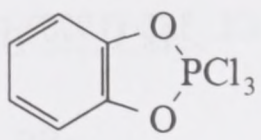
1. Direct Methods

$$ROH \longrightarrow RX$$

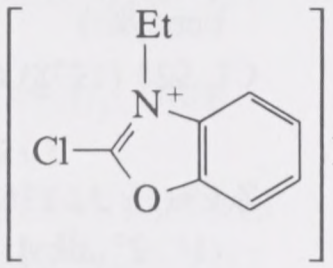
X	Reagent(s)	
F	HF, KF	JACS *85* 1609 (1963) (3° benzylic)
	$[C_5H_5\overset{+}{N}H]F(HF)_x^-$	JOC *44* 3872 (1979) (2°, 3° alkyl)
	Et_2NCF_2CHClF	J Gen Chem USSR *29* 2125 (1959) (1° alkyl)
		TL 1065 (2° alkyl), 1249 (1°, 2° alkyl) (1962)
		JOC *29* 2187 (1964) (1°, 2° alkyl); *44* 3406 (1979) (2° alkyl)
		Coll Czech Chem Commun *39* 2616 (1974) (1° alkyl)
	Et_2NSF_3	JOC *40* 574 (1975) (1°, 2°, 3° alkyl; allylic; benzylic); *43* 1090 (1978) (2° alkyl); *44* 3406 (1979) (2° alkyl); *52* 4804 (1987) (2° alkyl)
		TL 573 (1977) (1° alkyl); 1823 (1979) (2° alkyl); *28* 3891 (1987) (2° alkyl)
		JACS *109* 3046 (1987) (2° allylic)
	$(Me_2N)_2SF_2$	JOC *40* 574 (1975) (2° alkyl, allylic)
	n-Bu_4NF, RSO_2F (R = Me, *p*-Tol), molecular sieves	TL *26* 4207 (1985) (1° alkyl)
	$PhPF_4$	Chem Pharm Bull *21* 867 (1973) (1°, 2° alkyl); *23* 196 (1975) (2° alkyl)
		BSCF 2861 (1974) (2° alkyl)

ROH ⟶ RX (*Continued*)

X	Reagent(s)	
F	Ph_2PF_3	Chem Pharm Bull *16* 1784 (1968) (1°, 2° alkyl; benzylic)
	Ph_3PF_2	Chem Pharm Bull *16* 1009, 1784 (1968) (both 1°, 2° alkyl)
Cl	HCl	Org Syn Coll Vol *1* 286, 288, 519 (1932) (all 1° alkyl) Org Syn Coll Vol *1* 144 (1941) (3° alkyl) JACS *78* 653 (1956) (benzylic); *82* 6163 (1960) (allylic); *92* 4461 (1970) (allylic) BSCF 632 (1974) (allylic) JOC *47* 2590 (1982) (2° benzylic)
	aq HCl (phase transfer)	Syn 37 (1974) (1° alkyl)
	HCl, $ZnCl_2$	Helv *20* 1462 (1937) (1° alkyl) Org Syn Coll Vol *1* 142 (1941) (1° alkyl) JCS 636 (1943) (1°, 2°, 3° alkyl)
	HCl, $CaCl_2$, CuCl, Cu	JOC *26* 725 (1961) (3° propargylic)
	$TiCl_4$, PhNHMe	BCSJ *54* 1456 (1981) (1° allylic)
	$[C_5H_5\overset{+}{N}H]F(HF)_x^-$, NaCl	JOC *44* 3872 (1979) (1°, 2°, 3° alkyl; benzylic)
	$(COCl)_2$, DMF	JACS *107* 3285 (1985) (1° alkyl)
	AcCl	JACS *108* 3762 (1986) (3° benzylic)
	$H_2C{=}CHOCOCl$	TL *28* 2933 (1987) (1° benzylic)
	$(CF_3CO)_2O/LiCl$	Syn 511 (1987) (1° alkyl)
	$Ph_3P \cdot Cl_2$	JACS *86* 964 (1964) (1°, 2°, 3° alkyl)
	Ph_3P, NCS	TL 3937 (1973) (2° alkyl) JACS *106* 3286 (1984) (1° benzylic)
	Ph_3P, $Cl_3CCOCCl_3$	JOC *44* 359 (1979) (allylic); *46* 824 (1981) (1°, 2° alkyl; allylic)
	Ph_3P, CCl_4	Angew Int *14* 801 (1975) (review) Can J Chem *44* 1331 (1966) (1°, 2° alkyl) Tetr *23* 359 (1967) (1°, 2° alkyl) CC 1358 (1968) (1°, 2° alkyl) JOC *37* 1466 (1972) (allylic); *43* 1150 (2° alkyl), 2821 (mechanism) (1978); *51* 5291 (1986) (1° alkyl) JACS *96* 3684 (1974) (propargylic); *98* 5016 (1976) (allylic); *108* 1019 (1986) (1° allylic) BSCF 607 (1975) (allylic)

Ph_3P, CCl_4, py	Carbohydr Res *61* 511 (1978) (1° alkyl)
Ph_3P, Cl_3CCCl_3	Syn 139 (1983) (2° alkyl)
polymer-Ar_3P, CCl_4	CC 622 (1975) (1° alkyl) JOC *40* 1669 (1975) (1°, 2° alkyl; benzylic)
 , CCl_4, $HCCl_3$	JOC *52* 4999 (1987) (1°, 2° alkyl)
$(PhO)_3P$, HCl	JCS 2224 (1953) (1°, 2°, alkyl; allylic)
$(PhO)_3P$, Cl_2	JCS 2281 (1954) (1°, 2°, 3° alkyl)
$(PhO)_3P$, NCS	TL 3937 (1973) (2° alkyl, 1° benzylic)
$(PhO)_3P$, CCl_4	JCS 2224 (1953) (1° alkyl) Chem Ind 900 (1966) (1°, 2° alkyl; benzylic)
$(n\text{-}C_8H_{17})_3P$, CCl_4	Can J Chem *46* 86 (1968) (1°, 2° alkyl; benzylic)
$(PhO)_3P$, $C_6H_5CH_2Cl$	JCS 2224 (1953) (1°, 2° alkyl; allylic) JOC *30* 2635 (1965) (2° alkyl)
$(Me_2N)_3P$, CCl_4	CC 1350 (1968) (1° alkyl) BSCF 607 (1975) (allylic)
PCl_3, DMF	Syn 398 (1976) (1°, 2° alkyl; allylic)
$POCl_3$	JOC *27* 1449 (1962) (1° alkyl)
$POCl_3$, DMF and other amides	Syn 746 (1980) (1°, 2°, 3° alkyl; benzylic)
Me_2NPOCl_2	CL 923 (1978) (1°, 2° alkyl)
	Z Chem *22* 126 (1982) (1°, 2° alkyl; 1° benzylic)
PCl_5	JCS 1138 (1946); 1709 (1953) (both 2° alkyl) JCS C 1124 (1970) (2° alkyl)
$SOCl_2$	JACS *51* 3475 (1929) (1° benzylic); *62* 2295 (1940) (1° benzylic); *73* 2239 (1951) (1° alkyl); *75* 2053 (1953) (1° alkyl, benzylic); *107* 3950 (1985) (1° alkyl) Ann *479* 211 (1930) (1°, 2° allylic) JCS 684 (1942) (1° benzylic); 636 (1943) (1°, 2° alkyl); 1138 (1946) (2° alkyl); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 2720 (1959) (2° allylic) Org Syn Coll Vol *4* 333 (1963) (1° alkyl) JCS C 1124 (1970) (2° alkyl) TL 2931 (1970) (2° alkyl); 87 (1971) (1° alkyl)

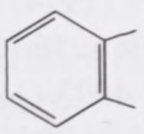
ROH ⟶ RX (*Continued*)

X	Reagent(s)	
Cl		BSCF 632 (1974) (allylic) JOC *52* 547 (1987) (1° alkyl)
	NCS, Me_2S	TL 4339 (1972); 3857 (1976) Tetr *32* 1675 (1976) JOC *51* 3098 (1986) (all references allylic or benzylic)
	MsCl, LiCl, 2,6-lutidine or *s*-collidine	JOC *36* 3044 (1971) (1°, 2° allylic); *51* 858 (1986) (2° allylic); *52* 3860, 3883 (1987) (both 1° allylic) TL *28* 723 (1987) (1° allylic)
	TsCl, py, Δ	Compt Rend C *276* 683 (1973) (allylic)
	TsCl, DMAP	TL 393 (1984) (1° allylic) CC 590 (1986) (1° allylic)
	Me_3SiCl	TL *27* 1907 (1986) (cyclopropylcarbinyl)
	$ZnCl_2$, PPh_3, $EtO_2CN{=}NCO_2Et$	JOC *49* 3027 (1984) (1°, 2° alkyl; 1° allylic) Syn Commun *16* 611 (1986) (2° alkyl)
	$PdCl_2(PhCN)_2$	TL 4575 (1978) (2° alkyl)
	 BF_4^-, Et_4NCl	CL 383 (1977) (1°, 2° alkyl)
Br	HBr	Helv *20* 1462 (1937) (1° alkyl) JCS 636 (1943) (1°, 2° alkyl) Org Syn Coll Vol *2* 246 (1943); *3* 227 (1955) (both 1° alkyl) JOC *50* 2759 (1985) (3° alkyl); *52* 5560 (1987) (1°, 2° benzylic; 2° allylic) JACS *109* 3098 (1987) (1° benzylic)
	HBr (phase transfer)	TL *28* 1223 (1987) (1°, 2° alkyl)
	HBr, H_2SO_4	Org Syn Coll Vol *1* 25–35 (1941) (1° alkyl; allylic) JCS 636 (1943) (1° alkyl); 132 (1953) (1°, 2° alkyl)
	HBr, LiBr or $CaBr_2$	BCSJ *53* 1181 (1980) (3° alkyl)
	$[C_5H_5\overset{+}{N}H]F(HF)_x^-$, NH_4Br	JOC *44* 3872 (1979) (1°, 2°, 3° alkyl; benzylic)
	$TiBr_4$, PhNHMe	BCSJ *54* 1456 (1981) (1° allylic)

$ZnBr_2$, Ph_3P, $EtO_2CN{=}NCO_2Et$	JOC *49* 3027 (1984) (1° alkyl, 1° allylic); *52* 2960 (1° alkyl), 4191 (1° alkyl) (1987)
P, Br_2	Org Syn Coll Vol *1* 36 (1941) (1°, 2°, 3° alkyl)
PBr_3	JACS *48* 1080 (1926) (1°, 2° alkyl); *51* 280 (1929) (1°, 2°, 3° alkyl); *62* 2295 (1940) (2° alkyl); *68* 2513 (1946) (2°, 3° alkyl); *82* 410 (1960) (2° alkyl); *93* 7016 (1971) (allylic); *98* 4925 (1976) (allylic); *107* 2712 (1985) (1° allylic)
	JCS 636 (1943) (1°, 2° alkyl); 2005 (1952) (1° propargylic)
	Org Syn Coll Vol *2* 358 (1943) (1° alkyl); *3* 370 (1955) (1° alkyl)
	Helv *29* 1133 (1946) (3° allylic, rearrangement)
	JOC *26* 3645 (1961) (2° alkyl); *39* 2135 (1974) (allylic); *52* 4047 (1° allylic), 5594 (1° alkyl) (1987)
PBr_3, py	Ann *479* 211 (1930) (1°, 2° allylic)
	JACS *70* 3314 (1948) (1° alkyl); *71* 1292 (1949) (1° propargylic); *76* 803 (1954) (1° alkyl)
	JCS 3650 (1950) (1° alkyl)
	Org Syn Coll Vol *3* 793 (1955) (1° alkyl)
	JOC *41* 1262 (1976) (allylic)
PBr_3, CaH_2	TL 3857 (1976) (allylic)
	JACS *99* 3513 (1977) (allylic)
PBr_5	JCS 1709 (1953) (2° alkyl)
	JOC *26* 3645 (1971) (2° alkyl)
Ph_3P, Br_2	Ann 626 26 (1959) (1°, 2° alkyl)
	JACS *86* 964 (1964) (1°, 2° alkyl); *99* 1612 (1977) (1° alkyl); *107* 5238 (1985) (1°, 2° alkyl)
	JOC *30* 2635, 2639, 3469 (1965) (all 2° alkyl)
	TL 341 (1965) (2° alkyl)
	Syn 901 (1981) (1° allylic)
$Ph_2PCH_2CH_2PPh_2$, Br_2	TL *28* 767 (1987) (1° allylic, 1° propargylic)
n-Bu_3P, Br_2	JACS *86* 964 (1964) (1°, 2° alkyl)
$(PhO)_3P$, Br_2	JCS 2281 (1954) (1°, 2°, 3° alkyl)
	TL 483 (1963) (1°, 2° alkyl)
	JCS C 2260 (1967) (1°, 2° propargylic and allenic)
$(PhO)_3P$, NBS	TL 3937 (1973) (2° alkyl)
$(PhO)_3P$, $C_6H_5CH_2Br$	JCS 2224 (1953) (1° alkyl, allylic)

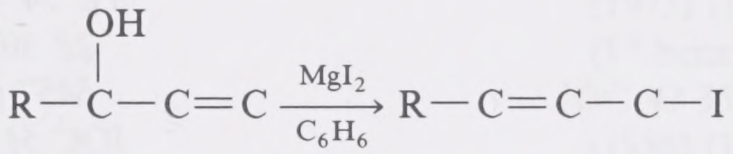
ROH ⟶ RX (*Continued*)

X	Reagent(s)	
Br	Ph_3P, NBS	JCS 2337 (1962) (1° alkyl) JOC *34* 212 (1969) (1° alkyl); *51* 2637 (1986) (1° alkyl) TL 3937 (1973) (2° alkyl) JACS *99* 3167 (1977) (1° alkyl); *107* 7515 (1985) (1° allylic); *108* 1035 (1986) (1° alkyl)
	Ph_3P, NBA	TL 3937 (1973) (2° alkyl)
	Ph_3P, CBr_4	JACS *92* 2139 (1970) (allylic); *95* 8749 (1973) (1° alkyl); *109* 2738 (1987) (1° benzylic) JOC *42* 353 (1977) (1° alkyl); *51* 5291 (1986) (1° alkyl) TL *28* 675 (1° allylic), 3225 (2° allylic), 6425 (1° alkyl) (1987)
	Ph_3P, CBr_4, py	Carbohydr Res *61* 511 (1978) (1° alkyl)
	$Ph_2PCH_2CH_2PPh_2$, CBr_4	JOC *51* 789 (1986) (1° allylic)
	$(n\text{-}C_8H_{17})_3P$, CBr_4	Can J Chem *46* 86 (1968) (1° alkyl, benzylic) CL 85 (1986) (1° allylic) TL *27* 1607 (1986) (1° allylic)
	Ph_3P, $BrCl_2CCCl_2Br$	Syn 139 (1983) (1°, 2° alkyl) TL *28* 5751 (1987) (1° allylic)
	Ph_3P, Br_3CCBr_3	Syn 139 (1983) (2° alkyl)
	Ph_3P; 2,4,5-tribromoimidazole	JCS Perkin I 681 (1982) (1°, 2° alkyl)
	$SOBr_2$	JOC *26* 3645 (1961) (2° alkyl) TL 87 (1971) (1° alkyl)
	Me_2S, NBS	TL 4339 (1972) (allylic, benzylic) JACS *108* 1019 (1986) (1° allylic)
	BH_3, Br_2	Chem Ind 223 (1965) (?)
	$NaBH_4$, Br_2	Chem Ind 223 (1965) (?)
	Me_3SiBr	TL 4483 (1978) (1°, 2°, 3° alkyl; benzylic)
	Me_3SiCl, LiBr	JOC *45* 1638 (1980) (1°, 2°, 3° alkyl; allylic; benzylic)
	$(Me_3Si)_2$, $(C_5H_5NH)Br_3$	JOC *45* 1638 (1980) (1°, 2° alkyl; allylic; benzylic)
	$(CF_3CO)_2O$/LiBr	Syn 511 (1987) (1° alkyl; 1° allylic) TL *28* 4745 (1987) (1° allylic)
	PhSeCN, $n\text{-}Bu_3P/Br_2$, Et_3N	CC 656 (1980) (2° alkyl)
I	HI	Helv *20* 1462 (1937) (1° alkyl) JCS 636 (1943) (1°, 2° alkyl)
	KI, H_3PO_4	JOC *15* 491 (1950) (1°, 2°, 3° alkyl) Org Syn Coll Vol *4* 323 (1963) (1° alkyl)
	HI, LiI or CaI_2	BCSJ *53* 1181 (1980) (3° alkyl)

$[C_5H_5\overset{+}{N}H]F(HF)_x^-$, KI	JOC *44* 3872 (1979) (1°, 2°, 3° alkyl; benzylic)
NaI, $BF_3 \cdot OEt_2$	TL *28* 4969 (1987) (1° benzylic)
P, I_2	Org Syn Coll Vol *2* 322, 399 (1943) (both 1° alkyl)
P_2I_4	TL 1801 (1979) (1°, 2°, 3° alkyl and benzylic)
Ph_3P, I_2	JACS *86* 964 (?), 2093 (1° alkyl) (1964)
$R_3P \cdot I_2$ (R = *n*-Bu, Ph), HMPA	Austral J Chem *35* 517 (1982) (1°, 2° alkyl; 1° propargylic and allylic)
Ph_3P, I_2, imidazole	CC 978 (1979) (1°, 2° alkyl)
	JCS Perkin I 2866 (1980) (1°, 2° alkyl); 681 (1982) (1°, 2° alkyl)
	TL *24* 4883 (1983) (1° propargylic); *28* 3091 (1° alkyl), 5391 (1° alkyl), 5457 (1° alkyl) (1987)
	JOC *51* 858 (1° alkyl), 4726 (1° alkyl) (1986)
	JACS *109* 1186 (1° alkyl), 4717 (1° alkyl), 6187 (1° alkyl) (1987)
	CC 877 (1987) (1° alkyl)
Ph_3P; 2,4,5-triiodoimidazole	CC 978 (1979) (1°, 2° alkyl)
	JCS Perkin I 2866 (1980) (1°, 2° alkyl); 681 (1982) (1° alkyl)
Ph_3P, NIS	TL 3937 (1973) (2° alkyl)
Ph_3P, ICH_2CH_2I	Syn 139 (1983) (1°, 2° alkyl)
Ph_3P, CI_4, py	Carbohydr Res *61* 511 (1978) (1° alkyl)
Ph_3P, ZnI_2, $EtO_2CN{=}NCO_2Et$	JOC *49* 3027 (1984) (1° alkyl)
	Syn Commun *16* 611 (1986) (2° alkyl)
	TL *28* 2977 (1987) (1° alkyl)
$(PhO)_3P$, I_2	JCS 2281 (1954) (1°, 2° alkyl)
$(PhO)_3P$, CH_3I	JCS 2224 (1°, 2°, 3° alkyl; allylic; benzylic), 3002 (1° alkyl) (1953)
	JACS *86* 2093 (1964); *88* 5684 (1966) (both 1° alkyl)
	Austral J Chem *21* 513 (1968) (2° alkyl)
	JOC *35* 2319 (1° alkyl), 2868 (2° alkyl) (1970)
	Org Syn *51* 44 (1971) (1° alkyl)
	TL *28* 3123 (1987) (1° alkyl)
	JOC *32* 4160 (1967) (1°, 2° alkyl)
$(Me_2N)_3P \cdot I_2$, HMPA	Austral J Chem *35* 517 (1982) (1° allylic)
BH_3, I_2	Chem Ind 1582 (1964) (1°, 2° alkyl; benzyl)
$NaBH_4$, I_2	Chem Ind 223 (1965) (?)
$MeSiCl_3$, NaI	JOC *48* 3667 (1983) (2°, 3° alkyl; benzylic)

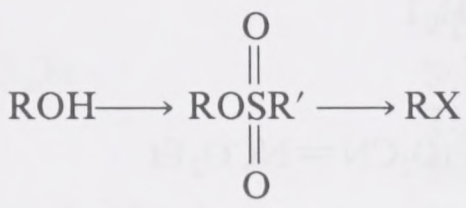
ROH⟶RX (*Continued*)

X	Reagent(s)	
	Me_3SiI	TL 2659 (1977) (1°, 2°, 3° alkyl; benzylic)
	$Me_3SiSiMe_3$, I_2	Angew Int *18* 612 (1979) (1°, 2° alkyl; benzylic)
	Me_3SiCl, NaI	JOC *44* 1247 (1979) (1°, 2°, 3° alkyl; allylic; benzylic)
		TL *28* 5063 (1987) (2° alkyl)
	MgI_2	TL *28* 6441 (1987) (3° alkyl)
	$(CF_3CO)_2O/LiCl$	Syn 511 (1987) (1° alkyl)



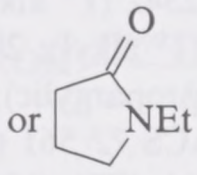
Syn 608 (1984)

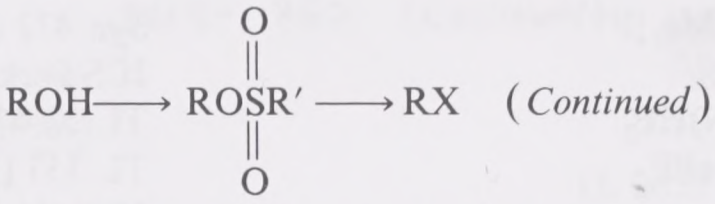
2. Via Sulfonates



$R' = CH_3$, C_6H_5, p-$C_6H_4CH_3$, CF_3

X	Reagent(s)	
F	KF (phase transfer)	Syn 428 (1974) (1°, 2° alkyl); 430 (1975) (2° alkyl)
	KF, CH_3OH	JACS *80* 5559 (1958) (1° alkyl)
	KF, $HOCH_2CH_2OH$	JCS 872 (1958) (1° alkyl)
		Chem Ind 157 (1958) (1°, 2° alkyl)
	KF, $O(CH_2CH_2OH)_2$	JACS *77* 4899 (1955) (1°, 2° alkyl)
		Can J Chem *34* 757 (1956) (1° alkyl)
	KF, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	n-Bu_4NF (no solvent)	JOC *49* 3216 (1984) (1°, 2° alkyl)
	n-Bu_4NF, solvent?	TL *28* 4003 (1987) (2° alkyl)
	n-Bu_4NF, Et_2O	JACS *109* 3046 (1987) (1° alkyl)
	n-Bu_4NF, THF	JOC *44* 2194 (1979) (2° alkyl)
	n-Bu_4NF, CH_3COCH_3 or $CH_3COCH_2CH_3$	JCS 954 (1962) (2° alkyl)
	n-Bu_4NF, CH_3CN	Carbohydr Res *5* 292 (1967) (1°, 2° alkyl)
	n-$Bu_4NF \cdot 3\ H_2O$; o-$Cl_2C_6H_4$, CH_3CN or THF	JOC *52* 658 (1987) (1° alkyl)

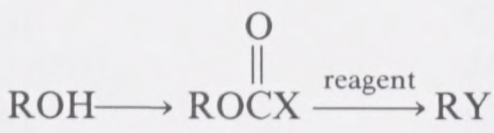
	$[\text{resin-}\overset{+}{\text{N}}\text{Me}_3]\text{F}^-$	Syn 472 (1976) (1°, 2° alkyl) JCS Perkin I 2248 (1979) (1°, 2° alkyl)
	$(n\text{-Bu}_4\text{N})\text{HF}_2$	TL *28* 4733 (1987) (1°, 2° alkyl)
	$n\text{-Bu}_3\text{MePF}$	TL 353 (1979) (2° alkyl) JOC *44* 3406 (1979) (2° alkyl) Tetr *36* 1931 (1980) (1° alkyl)
Cl	LiCl, ROH ($CH_3COCH_2CH_3$)	JCS 315 (2° alkyl), 326 (1° alkyl) (1949); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 954 (1962) (2° alkyl)
	LiCl, HMPA	TL 1393 (1969) (allylic) JOC *44* 2369 (1970) (1° alkyl) JACS *99* 1612 (1977) (allylic)
	LiCl, CH_3CONEt_2	
		JOC *44* 2369 (1970) (1° alkyl)
	LiCl, DMF	JOC *51* 5291 (1986) (1° alkyl)
	LiCl, DMF, collidine	Tetr *27* 5979 (1971) JOC *36* 3044 (1971) BSCF 607 (1975) TL 3681 (1976) (all allylic)
	NaCl or KCl, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KCl (phase transfer)	Syn 430 (1975) (2° alkyl)
	$n\text{-Bu}_4\overset{+}{\text{N}}\text{Cl}$, $CH_3COCH_2CH_3$	JCS 954 (1962) (2° alkyl)
	$[\text{resin-}\overset{+}{\text{N}}\text{Me}_3]\text{Cl}^-$	JCS Perkin I 2248 (1979) (2° alkyl)
	$(C_5H_5NH)Cl$	Monatsh *83* 1398 (1952) (1° alkyl) JACS *80* 2726 (1958) (1° alkyl) JOC *26* 2883 (1961) (2° alkyl)
	TsCl, py, Δ (direct)	Compt Rend C *276* 683 (1973) (1° allylic)
Br	HBr	JOC *27* 4349 (1962) (1° alkyl)
	LiBr, THF	JACS *107* 2712 (1985) (1° allylic)
	LiBr, CH_3COCH_3	JCS 954 (1962) (2° alkyl) JOC *35* 2803 (1970) (1° alkyl); *52* 2337 (1987) (1° alkyl) JACS *107* 2730 (1985) (1° allylic); *109* 6937 (1987) (1° alkyl)
	LiBr, CH_3CONEt_2	JOC *44* 2369 (1979) (1° alkyl)
	NaBr	JOC *26* 3645 (1961) (2° alkyl) Org Syn Coll Vol *4* 753 (1963) (1° alkyl)
	NaBr, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KBr (phase transfer)	Syn 430 (1975) (2° alkyl)
	KBr, dicyclohexyl-18-crown-6	CC 879 (1974) (1°, 2° alkyl)
	$CaBr_2$	JCS 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic) JOC *27* 624 (1962) (2° alkyl)



$$R' = CH_3,\ C_6H_5,\ p\text{-}C_6H_4CH_3,\ CF_3$$

X	Reagent(s)	
Br	$MgBr_2$	J Lipid Res *7* 568 (1966) (1° alkyl)
	n-Bu_4NBr, C_6H_6	JOC *45* 4387 (1980) (1°, 2° alkyl)
	n-Bu_4NBr, $CH_3COCH_2CH_3$	JCS 954 (1962) (2° alkyl)
	n-Bu_4NBr, HMPA	JACS *107* 3271 (1985) (1° alkyl)
	$(C_5H_5NH)Br$	Monatsh *83* 1398 (1952) (1° alkyl)
I	NaI	JCS 315 (2° alkyl), 326 (1°, 2° alkyl), 2542 (1° alkyl) (1949); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 955 (1962) (2° alkyl)
		JACS *72* 561 (1950); *83* 1460 (1961); *91* 4771 (1969) (all 1° alkyl); *107* 2124 (1° propargylic), 7967 (1° alkyl) (1985); *108* 468 (1986) (1° alkyl)
		JOC *21* 1487 (1956) (1° alkyl); *52* 4517 (1° alkyl); 4810 (1° propargylic) (1987)
		Can J Chem *34* 757 (1956) (1° alkyl)
	NaI, copper bronze	JACS *107* 196 (1985) (1° alkyl)
	NaI or KI, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KI	Monatsh *82* 970 (1951) (1°, 2° alkyl)
	KI (phase transfer)	Syn 430 (1975) (2° alkyl)
	$(C_5H_5NH)I$	Monatsh *83* 1398 (1952) (1° alkyl)
	n-Bu_4NI, C_6H_6	JOC *45* 4387 (1980) (1°, 2° alkyl)
		TL *28* 2941 (1987) (1° alkyl)
	ZnI_2	JACS *109* 4717 (1987) (1° allylic)

3. Via Haloformates

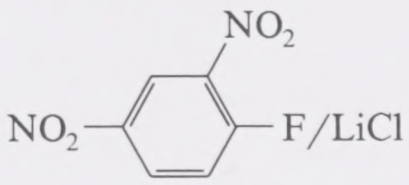


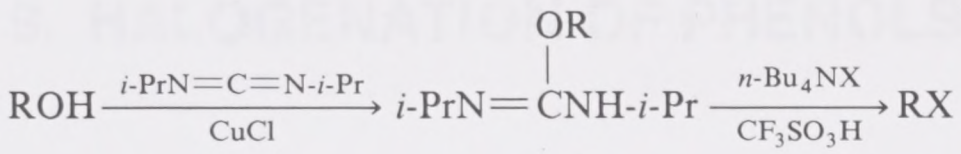
X	Y	Reagent	
F	F	$BF_3 \cdot OEt_2$	JACS *77* 5033 (1955)
Cl	F	TlF	JACS *77* 3099 (1955)
Cl	Cl	$BF_3 \cdot OEt_2$	JACS *77* 5033 (1955)
Cl	Cl	NaCl	JOC *32* 2633 (1967)
Cl	Cl	PPh_3	Ann *698* 106 (1966)
Cl	Br	NaBr	JOC *32* 2633 (1967)
Cl	I	NaI	JOC *32* 2633 (1967)

4. Other Approaches

For approaches via silyl ethers see page 349, Section 7.

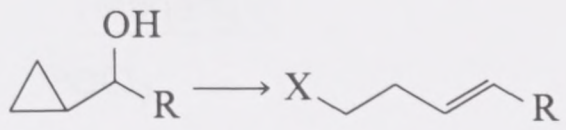
$$ROH \longrightarrow RX$$

X	Reagent(s)	
F	Ph_2NCN, KO-*t*-Bu/HF or HBF_4/Δ	Can J Chem *43* 3173 (1965)
Cl		BSCF 405 (1975)



X = Br, I

TL *28* 4445 (1987)



See page 151, Section 34.

9. HALOGENATION OF PHENOLS

For ring halogenation see page 315, Section 2.

$$ArOH \longrightarrow ArX$$

X	Reagent(s)	
Cl	$POCl_3$	JCS 678 (1944) JACS *76* 6073 (1954) Org Syn Coll Vol *3* 272 (1955) JOC *27* 1462 (1962)
	$POCl_3$, PCl_5	JACS *76* 1109 (1954) JCS 1666 (1964)
	PCl_5	JCS 1666 (1964)
	PCl_5, C_6H_5COCl	JCS 1666 (1964)
	$COCl_2$, Ph_3P	Ann *698* 106 (1966)
Br	Ph_3P, Br_2	JACS *86* 964 (1964)

10. HALOGENATION OF SULFUR AND SELENIUM COMPOUNDS

$$RSO_3H \text{ or } RSH \xrightarrow[PPh_3]{I_2} RI$$

Syn 371 (1981)

$$RCH(SPh)_2 \xrightarrow{HgF_2} \underset{|}{\overset{F}{}}RCHSPh$$

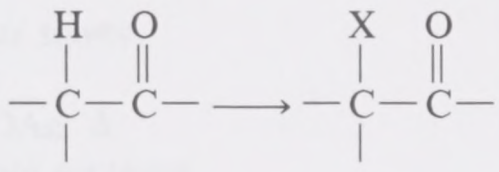
TL *28* 3901 (1987)

$$RSeR' \xrightarrow{Br_2} RBr$$

TL 2647 (1976)

11. HALOGENATION OF CARBONYL AND RELATED COMPOUNDS

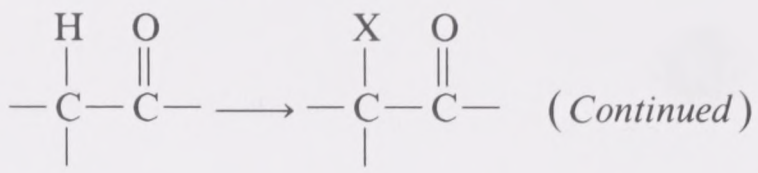
1. Aldehydes and Ketones



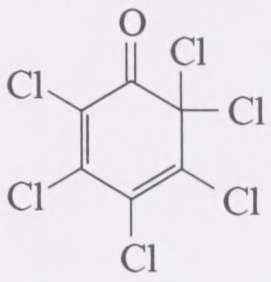
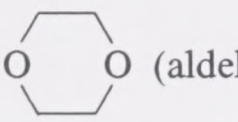
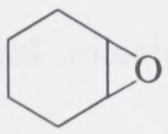
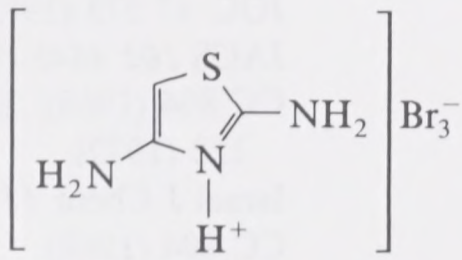
Review:

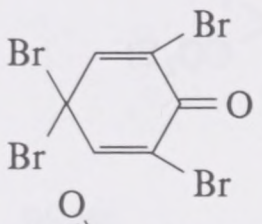
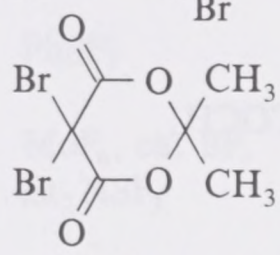
H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., Menlo Park, California (1972), pp 459–478

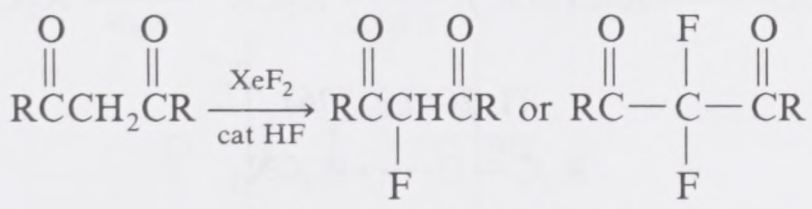
X	Reagent(s)	
F	F_2 (on enol silane)	TL *27* 2715 (1986) JOC *52* 4307 (1987) (2-fluoro-1,3-diketones)
	F_2/NaO_2CCF_3 (on enol acetate)	CC 479 (1979) JACS *101* 2782 (1979)
	$FClO_3$, py (on enol ether)	JACS *81* 5259 (1959)
	$FClO_3$ (on enamine)	JOC *23* 1406 (1958)
	XeF_2, cat HF (on enol ester)	JOC *47* 573 (1982)
	CF_3OF (on enol silane)	JACS *102* 4845 (1980)
	CF_3OF (on enol ester)	CC 804 (1968); 1497 (1969); 122 (1972) Israel J Chem *17* 60 (1978)
	CF_3OF (on enol ether and enamine)	CC 804 (1968) Israel J Chem *17* 60 (1978)
	R_fOF (on enol ester)	CC 122 (1972)
	$CF_2(OF)_2$ (on enol ester)	CC 122 (1972)
	SF_5OF (on enol ester)	CC 122 (1972)
	$(C_5H_5NF)OTf$ (on enol silane)	TL *27* 4465 (1986)
	$MeLi/RSO_2NFR'$ (on enol acetate)	JACS *106* 452 (1984)
	KH/RSO_2NFR'	JACS *106* 452 (1984)



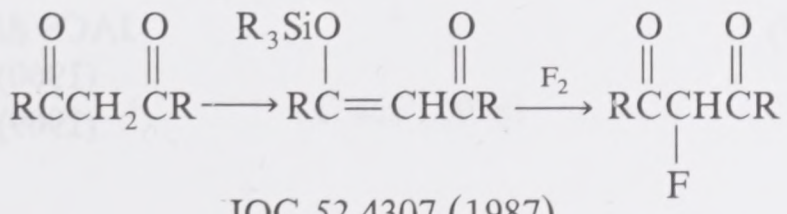
(*Continued*)

X	Reagent(s)	
Cl		Syn 1018 (1982)
	(aryl ketones only)	
	SO_2Cl_2 (ketones only)	JOC *37* 4090 (1972); *46* 4486 (1981)
		Syn Commun *11* 7 (1981)
	$CuCl_2 \cdot 2\ H_2O$, LiCl, H_2O	JACS *77* 5274 (1955)
	$CuCl_2$ or $FeCl_3$ (on enol silane)	JOC *45* 2022 (1980)
	$TlCl_3$	CC 1336 (1986)
	[polymer-$C_6H_4CH_2\overset{+}{N}Me_3$]$ICl_2^-$	CC 1278 (1980)
	NCS (on enol silane)	TL *27* 2563 (1986)
	t-BuOCl, HOAc	JOC *51* 3380 (1986)
	LDA/CF_3SO_2Cl	JACS *107* 7771 (1985)
Br	Br_2 (ketones)	BSCF 4169 (1969)
		JACS *108* 1251 (1986)
	Br_2,  (aldehydes)	BSCF 1465 (1973)
	Br_2, hν, 	JCS Perkin I 501 (1977)
	Br_2, HOAc	JACS *72* 362 (1950)
		JOC *35* 186 (1970); *51* 3380 (1986)
	Br_2 (on enol ether)	BSCF 4169 (1969)
	Br_2 (on enol silane)	JACS *109* 2435 (1987)
	Br_2 (on enolate)	JOC *38* 2576 (1973)
	Br_2, $AlCl_3$	JOC *48* 2520 (1983)
	$(C_5H_5\overset{+}{N}H)Br_3^-$	JACS *70* 417 (1948)
		TL *23* 3405 (1982)
	(pyrrolidone)$_3 \cdot HBr_3$	Can J Chem *47* 706 (1969)
		JOC *52* 5624 (1987)
		Syn 488 (1980)
	$(Ph\overset{+}{N}Me_3)Br_3^-$	TL (9) 24 (1959)
		BSCF 1822 (1961); 90 (1962)
		JACS *106* 3539 (1984)
		JOC *52* 4792 (1987)
	[polymer-$C_6H_4CH_2\overset{+}{N}Me_3$]$Br_3^-$	Syn 64 (1979); 143 (1980)
	$[Ph_3\overset{+}{P}(CH_2)_2CO_2H]Br_3^-$	TL 373 (1975)
	NBS	JACS *109* 7230 (1987)
	NBS (on enol acetate)	JACS *75* 3513 (1953)

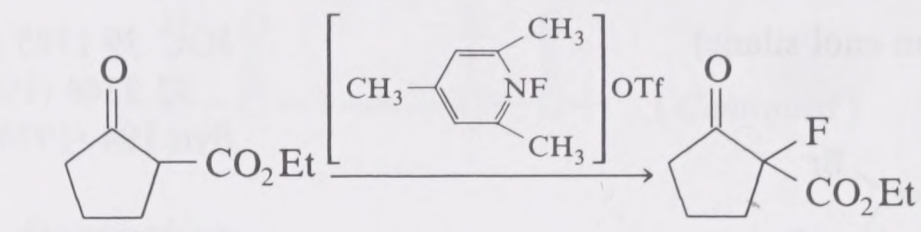
	NBS (on enol silane)	JOC *39* 1785 (1974); *52* 3346 (1987) Syn 194 (1976)
	 (enones)	Tetr *29* 1625 (1973)
		Syn 140 (1978) JACS *107* 7524 (1985)
	(aldehydes, ketones, enones)	
	$NCCHBrCON(CH_3)_2$ or $BrCH(CN)_2$	Tetr *31* 231 (1975)
	$NCCBr_2CON(CH_3)_2$	Ind J Chem B *17* 305 (1980)
	PhSeBr	JOC *51* 3380 (1986)
	$CuBr_2$	JOC *27* 4397 (1962); *29* 3459 (1964); *40* 1990 (1975)
I	I_2, CaO or KOH	JACS *80* 250 (1958); *81* 439 (1959) JOC *25* 1966 (1960)
	I_2 (on enolate)	TL 2817 (1979)
	I_2, PCC, molecular sieves (on enol silane)	Syn Commun *12* 1127 (1982)
	I_2, $Cu(OAc)_2$, HOAc, Δ (ketones and enol acetates)	Syn 312 (1981)
	I_2, $AgOAc/(Et_3NH)F$ (on enol silane)	JOC *44* 1731 (1979)
	I_2, TlOAc (on enol acetate)	JCS Perkin I 126 (1978)
	NIS (on enol acetate)	JACS *75* 3493 (1953); *76* 1722 (1954); *77* 3826 (1955)
	Me_3SiI, $(Me_3Si)_2NH/NaI$, m-$ClC_6H_4CO_3H$	JOC *52* 3919 (1987)
	NaI, m-$ClC_6H_4CO_3H/H_3O^+$ (on enol silane or enamine)	JOC *52* 3919 (1987)
Cl, Br	X_2 (on enol silane)	JOC *39* 1785 (1974) Syn 194 (1976)
	X_2 (on enamine)	Acta Chem Scand B *32* 646 (1978)
	NBS or NCS (on enol borinate)	Can J Chem *50* 2387 (1972)
Cl, Br, I	NH_4X, electrolysis (on enol acetate or silane)	JOC *45* 2731 (1980)
	$Pb(OAc)_4$, X^- (on enol ether, acetate or silane)	Syn 1021 (1982)



JOC *47* 573 (1982)

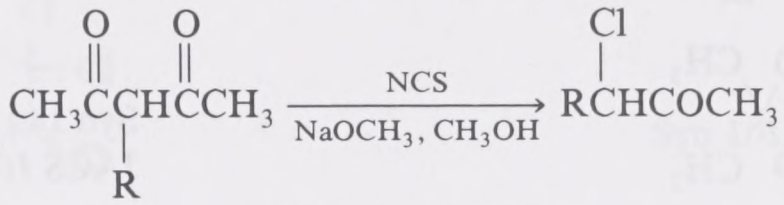


JOC *52* 4307 (1987)

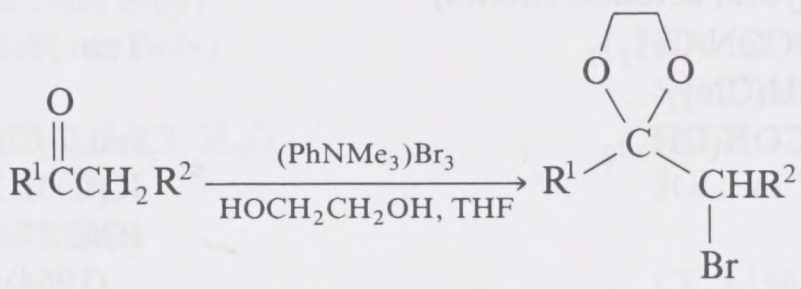


(or enolate)

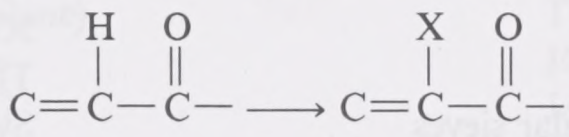
TL *27* 4465 (1986)



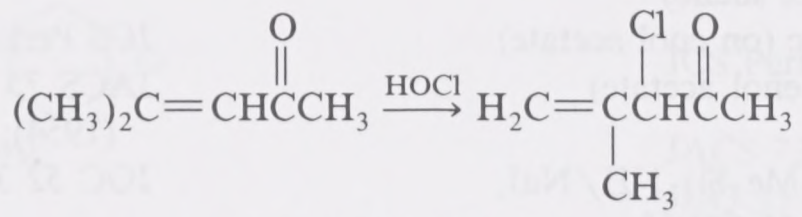
TL *28* 5505 (1987)



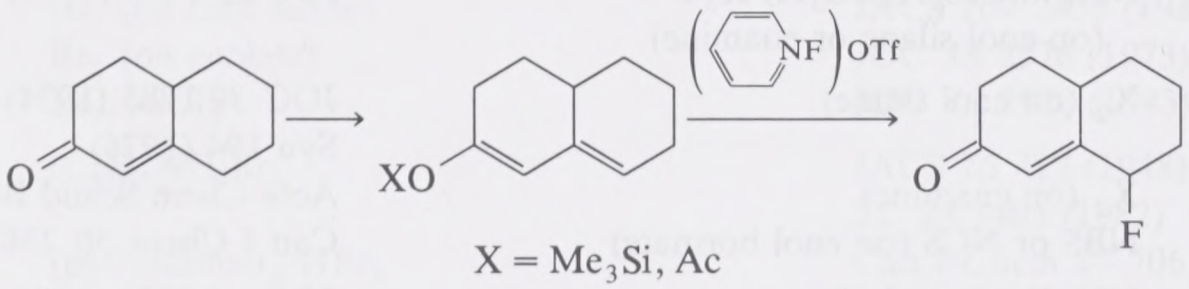
Syn 309 (1982)



X	Reagents	
Cl, Br	PhSeX, py	TL *22* 3301 (1981)
Br	Br_2/Et_3N	JOC *33* 1454 (1968); *47* 5088 (1982)

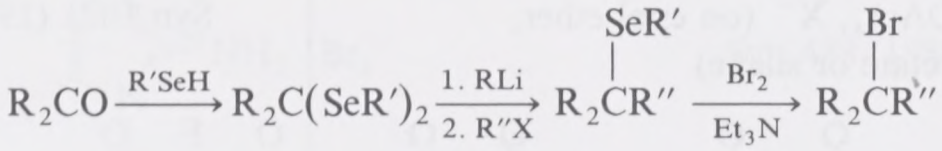


TL *22* 5019 (1981)

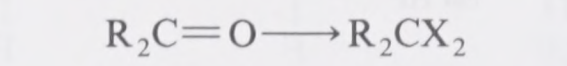


X = Me_3Si, Ac

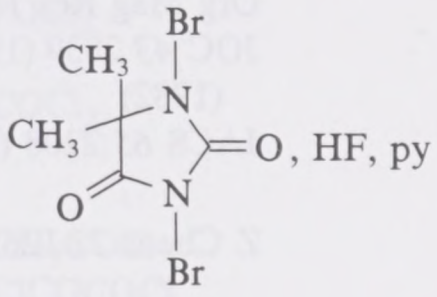
TL *27* 4465 (1986)

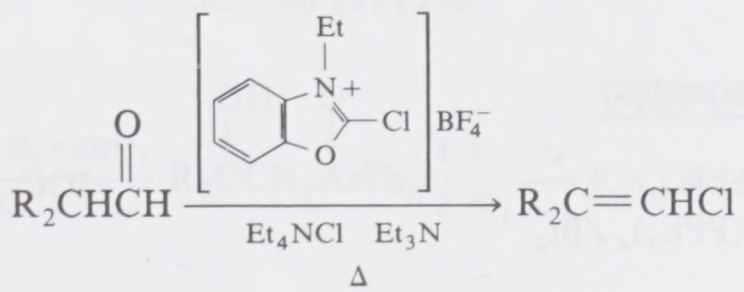


TL 2647 (1976)

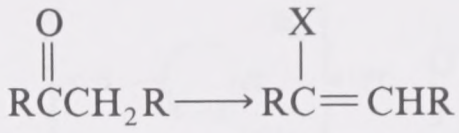


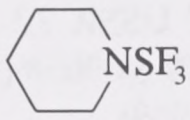
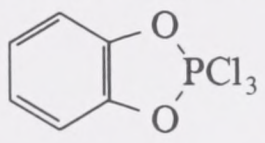
X	Reagent(s)	
F	SF_4, (HF)	JACS *81* 3165 (1959); *82* 543 (1960); *89* 88 (1967); *91* 1386 (1969); *94* 2020 (1972)

		JOC *26* 2436 (1961); *27* 3164, 4086 (1962); *31* 991 (1966); *36* 818 (1971) J Med Chem *6* 174 (1963) Tetr *20* 1625 (1964) Org Rxs *21* 1 (1974) (review) JOC USSR *17* 1260 (1981)
	$PhSF_3$	JACS *84* 3058 (1962); *91* 1386 (1969)
	MoF_6, cat BF_3	Tetr *27* 3965 (1971)
	Et_2NSF_3	Syn 787 (1973) JOC *40* 574 (1975) JCS Perkin I 1354 (1979) JACS *109* 3046 (1987)
	$HSCH_2CH_2SH$, $BF_3 \cdot 2$ HOAc/	JOC *51* 3508 (1986)
		
Cl	PCl_5	Ann *115* 29 (1860); *196* 259 (1879); *314* 369 (1901); *401* 121 (1913); *612* 1 (1958); 1 (1980) Compt Rend *136* 94 (1903) Ber *40* 2160 (1907); *43* 2940 (1910) JACS *50* 172 (1928); *59* 2434 (1937); *71* 3439 (1949); *72* 3952 (1950); *73* 1007, 5382 (1951); *108* 3762 (1986) Org Syn Coll Vol *2* 573 (1943) JCS 1425 (1952); 3116 (1954)
	PCl_5, PCl_3	Ann *435* 190 (1924); *501* 219 (1933)
Br	PCl_3Br_2	Ber *7* 759 (1874); *8* 406 (1875) JCS *45* 522 (1884) Ann *235* 299 (1886) Rec Trav Chim *50* 316, 837 (1931)
	HBr (on PhCHO) BBr_3 (on ArCHO)	Ann *341* 15 (1905) Syn Commun *9* 341 (1979)
I	H_2NNH_2/I_2, Et_3N	JCS 470 (1962) Austral J Chem *23* 989 (1970)
	$Me_2NNH_2/H_2NNH_2/I_2$, Et_3N	JOC *33* 4317 (1968)

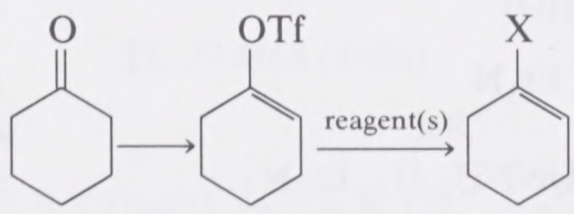


CL 465 (1978)

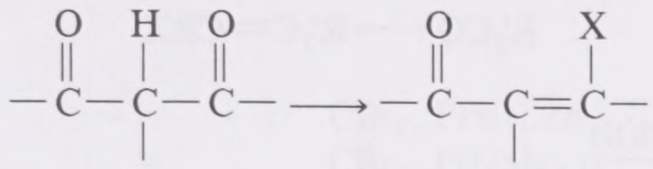


X	Reagent(s)	
F		JOC *50* 2007 (1985)
Cl	PCl_5	Ann *308* 264 (1899); 1 (1980) JACS *56* 1207 (1934); *59* 2434 (1937); *63* 1175 (1941); *65* 2208 (1943); *77* 1691 (1955); *90* 395 (1968); *109* 7838 (1987) Org Mag Res *10* 192 (1977) JOC *43* 2839 (1978); *47* 1084 (1982)
	PCl_5, PCl_3, $POCl_3$	JACS *65* 2208 (1943)
		Z Chem *22* 126 (1982)
I	N_2H_4/I_2, Et_3N	JCS 470 (1962) JACS *91* 2115 (1969); *103* 6526 (1981); *104* 6646 (1982) CC 174 (1969) JOC *34* 3502 (1969) Austral J Chem *23* 989 (1970); *24* 1425 (1971) BCSJ *53* 3252 (1980) JCS Perkin I 3017 (1982)
	N_2H_4/I_2, 	JACS *103* 7122 (1981)
	N_2H_4/I_2, quanidine base	TL *24* 1605 (1983); *27* 1811 (1986) JOC *50* 2438 (1985)
	N_2H_4, I_2, DABCO	JOC *48* 4058 (1983)

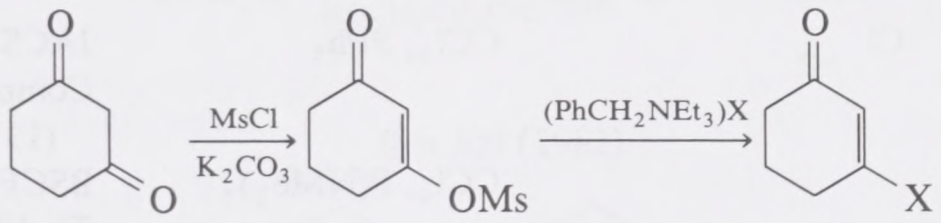
See also page 158, Section 45.3.



X	Reagent(s)	
Br	$Me_3SnSnMe_3$, cat $Pd(PPh_3)_4/Br_2$	JOC *51* 277 (1986)
I	MgI_2, Et_3N	Syn 222 (1986)

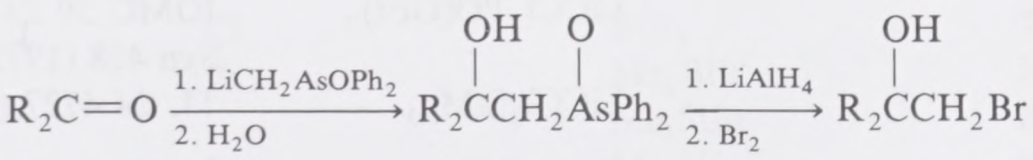


X	Reagent(s)	
Cl	PCl_3	JCS *83* 110, 494 (1903); 1996 (1955); 2431 (1956) JACS *72* 1645 (1950) Can J Chem *37* 1870 (1959) J Gen Chem USSR *31* 3719 (1961) JOC *30* 1129 (1965) JCS Perkin II 142 (1972)
	PCl_5	JACS *77* 1136 (1955) (β-keto ester)
	$POCl_3$	JCS *83* 110 (1903) Ann *612* 158 (1958)
	$COCl_2$	Coll Czech Chem Commun *24* 2378 (1959) J Gen Chem USSR *30* 563 (1960)
	CH_3COCl ClCOCOCl	Ber *94* 96 (1961) Syn 47 (1974) JOC *41* 636 (1975)
	PPh_3, CCl_4	Syn 708 (1975)
	$Ph_3P \cdot Cl_2$, Et_3N	Syn Commun *5* 193 (1975) Can J Chem *60* 210 (1982)
Br	PBr_3	JCS *83* 110, 494 (1903) JOC *30* 1129 (1965) JCS Perkin II 142 (1972)
	Ph_3P, CBr_4	Syn 708 (1975)
	$Ph_3P \cdot Br_2$, Et_3N	Syn Commun *5* 193 (1975) Can J Chem *60* 210 (1982)
I	$Ph_3P \cdot I_2$, Et_3N	Syn Commun *5* 193 (1975) Can J Chem *60* 210 (1982)



X = Cl, Br, I

JOC *46* 197 (1981)



Ber *115* 645 (1982)

$$R'_2CO \longrightarrow R'_2C{=}CRX$$

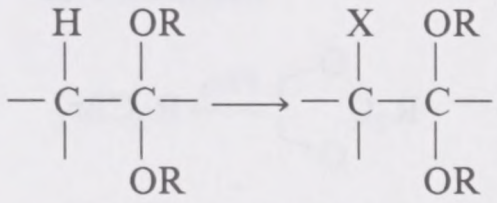
X	Reagent(s)	
F	$Ph_3P{=}CHF$	Syn 75 (1969) Ber *104* 2885 (1971) JOC *40* 2796 (1975)
	$Ph_3P{=}CHR$ /PhLi/$FClO_3$	Syn 38 (1969)
	$[(n\text{-}Bu_3P)_2CF]Cl$/NaOH (R = H)	JACS *107* 2811 (1985); *109* 3046 (1987)
Cl	$Ph_3P{=}CHCl$	JACS *82* 1510 (1960); *83* 1617 (1961) Ber *94* 1373 (1961); *99* 689 (1966) CC 446 (1978)
	$Ph_3P{=}CHR$ /*n*-BuLi or PhLi/$Cl_2IC_6H_5$	Syn 38 (1969) TL 447 (1970)
	$Ph_3P{=}CHR$ /*n*-BuLi/NCS	TL 447 (1970)
Br	$Ph_3P{=}CHBr$	Angew Int *1* 51 (1962) Ber *99* 689 (1966) TL *21* 4021 (1980)
	$Ph_3P{=}CBrR$	JOC *43* 2833 (1978) TL *27* 1995 (1986)
	$Ph_3P{=}CHR$ /PhLi/Br_2	Syn 38 (1969)
	$LiCHBr_2$/Zn, HOAc	TL *22* 3745 (1981)
I	$Ph_3P{=}CHR$ /*n*-BuLi/$Hg(OAc)_2$/I_2	TL 447 (1970)

$$R_2CO \longrightarrow R_2C{=}CXY$$

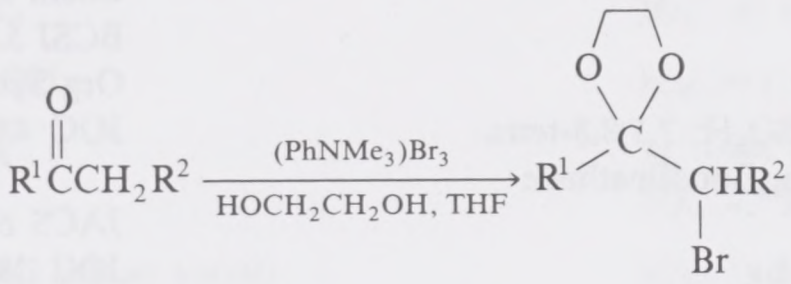
X	Y	Reagent(s)	
F	F	NaO_2CCF_2Cl, PPh_3	TL 1461 (1964)
F	Cl	NaO_2CCFCl_2, PPh_3	TL 71 (1968)
		$HCFCl_2$, KO-*t*-Bu, PPh_3	JACS *84* 854 (1962) TL 71 (1968)
Cl	Cl	CCl_4, PPh_3	JACS *84* 1312 (1962) Compt Rend C *276* 903 (1973)
		CCl_4, $P(NMe_2)_3$	BSCF 2047 (1971) TL 1035 (1971)
		$BrCCl_3$, $P(NMe_2)_3$	TL 1239 (1977); *28* 5473 (1987)
		$HCCl_3$, KO-*t*-Bu, PPh_3	JACS *84* 854 (1962)
		$LiCCl_2PO(OEt)_2$	JOMC *59* 237 (1973) Syn 458 (1975)
		$LiCCl_2SiMe_3$	TL *24* 4727 (1983)
Br	Br	CBr_4, PPh_3	JACS *84* 1745 (1962) BSCF 3145 (1972) Compt Rend C *274* 1357 (1972)

	TL 3769 (1972); 1373 (1975); *28* 5145 (1987)
CBr_4, PPh_3, Zn	TL 3769 (1972)
CBr_4, $P(NMe_2)_3$	TL 1035 (1971)
$HCBr_3$, KO-*t*-Bu, PPh_3	JACS *84* 854 (1962)

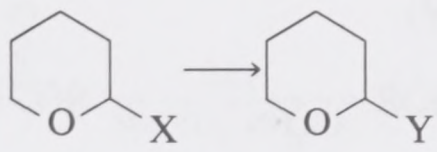
2. Acetals



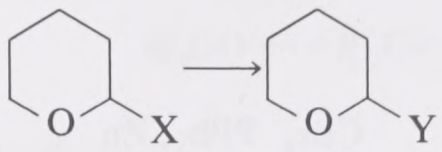
Cl_2 or Br_2	BSCF 2735 (1973)
Br_2	BSCF 4169 (1969)
Br_2, hν	Ber *95* 803 (1962)
Br_2, 2-methoxynaphthalene	JOC *52* 3018 (1987) (chiral)
Br_2, py	JACS *64* 1963 (1942)
Br_2, $CaCO_3$	JACS *49* 2517 (1927); *64* 1966 (1942)
Br_2, cat HBr	Angew *25* 259 (1986)
Br_2, (HBr), electrolysis	Syn Commun *10* 821 (1980)
$(Ph\overset{+}{N}Me_3)Br_3^-$	BSCF 1822 (1961)
	Tetr *19* 861 (1963)
$(C_5H_5\overset{+}{N}H)Br_3^-$	JACS *84* 2344 (1962)
NBS, hν	JACS *73* 973 (1951)
NBS, $(PhCO_2)_2$	Ber *95* 803 (1962)



Syn 309 (1982)

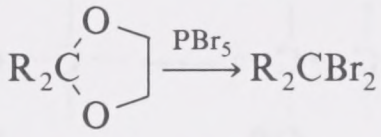


X	Y	Reagent(s)	
OR	Cl	BCl_3	TL *28* 5595 (1987)
	Br	Me_2BBr	JOC *49* 3912 (1984)
		Me_3SiBr	Ber *113* 3058 (1980)
	I	Me_3SiI	Ber *113* 3075 (1980)
			Carbohydr Res *115* 95 (1983)
		Me_3SiCl, NaI	Ann 1052 (1984)



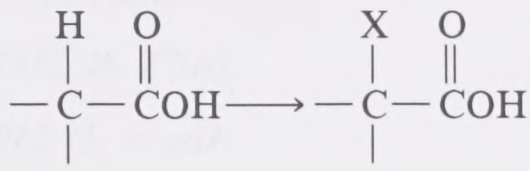
(*Continued*)

X	Y	Reagent(s)	
O_2CR	Br	Me_3SiBr	Ber *113* 3075 (1980)
	I	Me_3SiI	Ber *113* 3075 (1980)
		Me_3SiCl, NaI	Ann 1052 (1984)



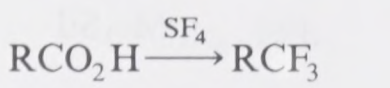
JACS *108* 1265 (1986)

3. Carboxylic Acids



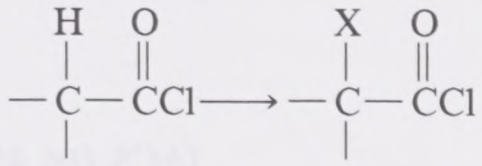
Review: Chem Rev *52* 237 (1953)

X	Reagent(s)	
F	*n*-BuLi/$ArSO_2NFR'$	JACS *106* 452 (1984)
	CF_3OF (on silyl ketene acetal)	JACS *102* 4845 (1980)
Cl	Cl_2, O_2, $ClSO_3H$, (chloranil)	JOC *40* 2960 (1975) Chem Ind 538 (1977) BCSJ *52* 255 (1979) Org Syn *59* 20 (1980)
	Cl_2; $ClSO_3H$; 7,7,8,8-tetra-cyanoquinodimethane	JOC *48* 1364 (1983)
	SO_2Cl_2	JACS *69* 86 (1947)
	$SOCl_2$, hν	JOC *38* 3919 (1973)
	LDA/CCl_4	JOC *52* 307 (1987)
Br	Br_2, P, $(H_2O)/H_2O$	Ber *14* 891 (1881); *20* 2026 (1887); *22* 1745 (1889); *24* 938, 2388 (1891) Ann *242* 141 (1887) Org Syn Coll Vol *2* 74 (1943) JACS *71* 2581 (1949)
I	I_2, $Cu(OAc)_2$, HOAc	CL 1509 (1984)
	I_2, CuCl, $CuCl_2$	CL 1509 (1984)



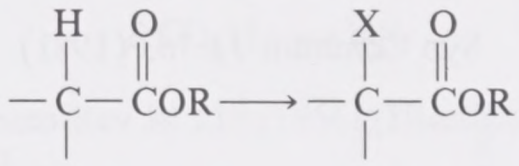
JACS *82* 543 (1960)

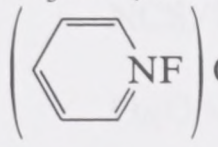
4. Acid Halides

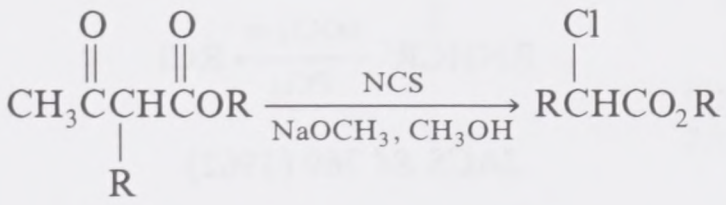


X	Reagent(s)	
Cl	NCS, $SOCl_2$	JOC *40* 3420 (1975)
Br	NBS, $SOCl_2$	JOC *40* 3420 (1975)
I	I_2, $SOCl_2$	JOC *40* 3420 (1975)

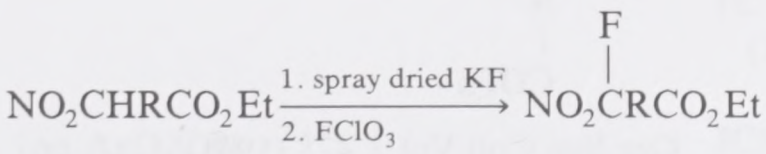
5. Esters



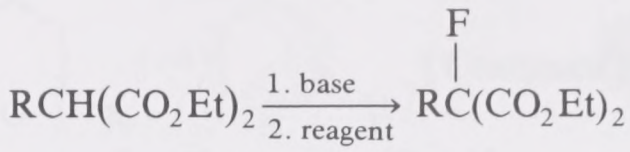
X	Reagent(s)	
F	CF_3OF (on silyl ketene acetal)	JACS *102* 4845 (1980)
	 (on silyl ketene acetal)	TL *27* 4465 (1986)
Cl	Cl_2, PCl_5	JACS *66* 2074 (1944)
Cl, Br	LDA/CX_4	JOC *43* 3687 (1978)
Br	P, Br_2/ROH	Syn 39 (1969)
Br, I	$LiNR_2/X_2$	TL 3995 (1971); *28* 2477 (1987) JOC *43* 3687 (1978)
I	ICl (on silyl ketene acetal) LDA/$ZnCl_2/I_2$	JOC *52* 4414 (1987) JOC *52* 4414 (1987)



TL *28* 5505 (1987)

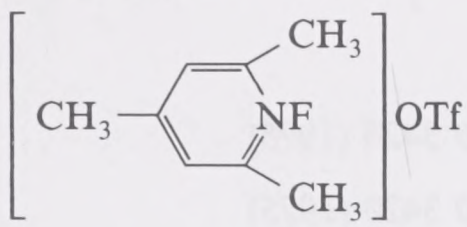


JOC *52* 5061 (1987)

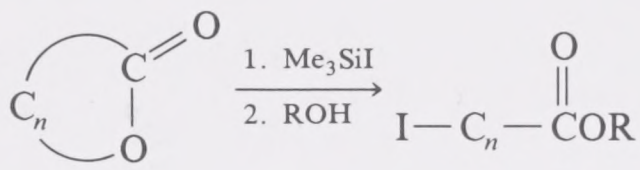


Reagent

$ArSO_2NFR$ JACS *106* 452 (1984)

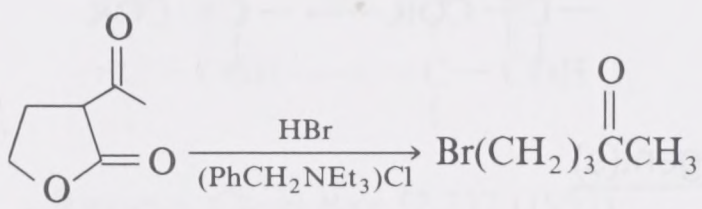


TL *27* 4465 (1986)



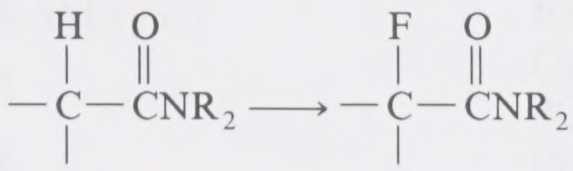
$n = 2–5$

Syn Commun *11* 763 (1981)



Syn Commun *10* 897 (1980)

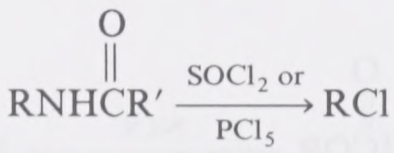
6. Amides



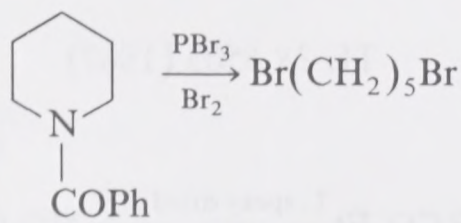
CF_3OF (on enol silane) JACS *102* 4845 (1980)

R_fOF (on enol silane) JOC *51* 1482 (1986)

base/$ArSO_2NFR$ JACS *106* 452 (1984)



JACS *84* 769 (1962)



Org Syn Coll Vol *1* 428 (1941)
JACS *68* 2402 (1946); *71* 2808 (1949)
JOC *51* 2206 (1986); *52* 5466 (1987)

12. HALODECARBOXYLATION OF ACIDS AND DECARBONYLATION OF ACID HALIDES

$$RCO_2H \longrightarrow RX$$

Review: Chem Rev *56* 219 (1956) (Hunsdieker reaction)

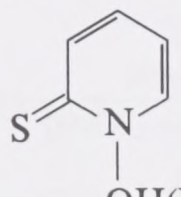
X	Reagent(s)	
F	XeF_2, HF	JOC *48* 4158 (1983)
Cl	$NCS/Pb(OAc)_4$	Syn 493 (1973)
		JACS *107* 516 (1985)
	$Pb(OAc)_4$, LiCl	JACS *87* 2500 (1965); *107* 199, 7978 (1985)
		JOC *30* 3265 (1965)
		Org Rxs *19* 279 (1972) (review)
	$Pb(O_2CR)_4$, CCl_4, hν	Ann *735* 47 (1970)
Br	AgO or KOH- $AgNO_3/Br_2$	Org Syn Coll Vol *3* 578 (1955)
		Org Rxs *9* 332 (1957)
	Tl_2CO_3/Br_2	JCS Perkin I 2608 (1981)
	$TlOEt/Br_2$	JOC *34* 1172 (1969)
		JCS Perkin I 2608 (1981)
	HgO, Br_2, (hν)	JOC *26* 280 (1961); *30* 415 (1965); *34* 3216 (1969); *37* 664 (1972); *44* 3405 (1979); *52* 460 (1987)
		Org Syn *43* 9 (1963)
		JACS *106* 2194 (1984); *109* 7230 (1987)
		Syn Commun *14* 983 (1984) (*gem*-dibromocycloalkanes)
		TL *27* 5371 (1986); *28* 5263 (1987)
I	I_2 (on AgO_2CR)	JCS 368 (1941)
	t-C_4H_9OI, (hν)	JCS 2438 (1965)
		JOC *45* 4226 (1980)

$RCO_2H \longrightarrow RX$ (*Continued*)

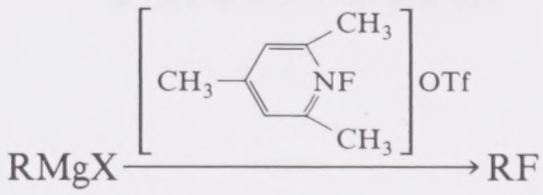
X	Reagent(s)	
	$Pb(OAc)_4$, I_2	JCS 2438 (1965) JOC *31* 1857 (1966) Org Rxs *19* 279 (1972) (review)
	$PhI(OAc)_2$, I_2, (hν)	JOC *51* 402 (1986) CC 675 (1987) TL *28* 6381 (1987)
	HgO, I_2	JOC *37* 664 (1972)

$RCX \longrightarrow RX$

Review: Syn 157 (1969)

X	R	Reagent(s)	
Cl	alkyl, aryl	cat $ClRh(PPh_3)_3$	JACS *88* 3452 (1966); *90* 99 (1968)
	aryl	cat Pd/C, $PdCl_2$ or $Pd(PPh_3)_4$	TL *23* 371 (1982)
Br	aryl, vinylic	 /$BrCCl_3$, AIBN	TL *26* 5939 (1985)
	aryl	cat $ClRh(CO)(PPh_3)_2$	JACS *90* 99 (1968)
I	aryl	cat $ClRh(PPh_3)_3$	JOC *33* 1928 (1968)
Cl, Br	aryl	cat $ClRh(PPh_3)_3$	JACS *89* 2338 (1967)

13. HALOGENATION OF ORGANOMETALLICS



TL *27* 4465 (1986)

$$ArB(OH)_2 \xrightarrow[\text{chloramine-T}]{NaX} ArX$$

X = Br, I

Org Prep Proc Int *14* 359 (1982)

$$ArSnR_3 \xrightarrow{CsSO_4F} ArF$$

CC 1623 (1986)

$$RCH{=}CHSn(n\text{-}Bu)_3 \xrightarrow[X = Br, I]{X_2} RCH{=}CHX$$

TL *28* 2033 (1987)
JOC *52* 3687 (1987)

See also page 215, Section 2, for additional preparations of vinylic halides via hydrometallation-halogenation.

$$R_3CSeR' \xrightarrow[Et_3N]{Br_2} R_3CBr$$

TL 2647 (1976)

AMINES

GENERAL REFERENCES

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol XI/1, G. Thieme, Stuttgart (1957)

P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," W. A. Benjamin, New York (1965), Vol 1, pp 60–78 and 115–122

L. Spialter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," Macmillan, New York (1965)

"Chemistry of the Amino Group," Ed. S. Patai, Interscience, New York (1968)

"The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives," Ed. S. Patai, J. Wiley, New York (1982)

1. FROM ALKANES

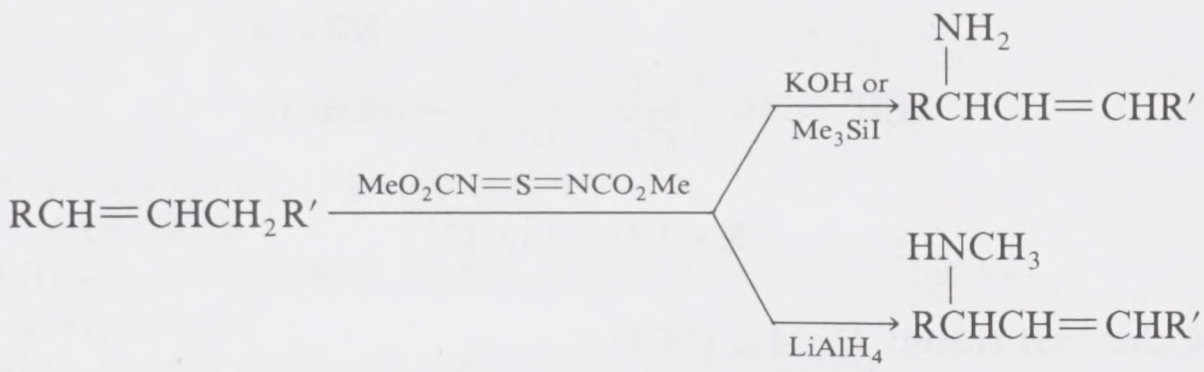
$$R_3CH + AlCl_3 + NCl_3 \longrightarrow R_3CNH_2$$

Tetr *23* 3563 (1967)

2. FROM ALKENES

Review: Tetr *39* 703 (1983)

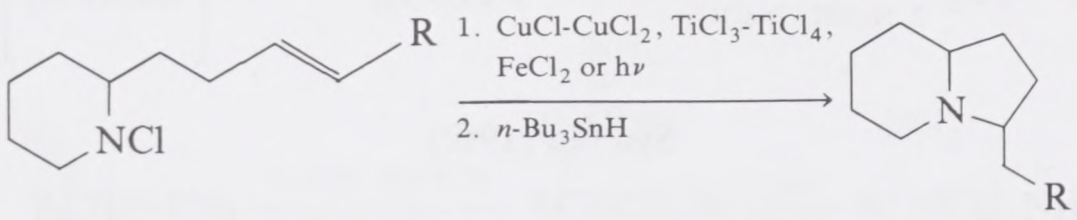
For analogous syntheses of amides and sulfonamides see also page 824, Section 3.



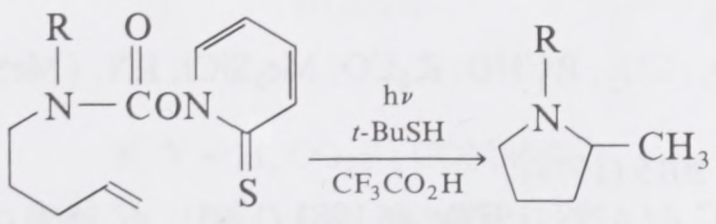
JOC *48* 3561 (1983)

$$RNH_2\ (R_2NH) + H_2C{=}CH_2 \xrightarrow[\Delta]{\text{cat NaNHR}} RNHCH_2CH_3$$

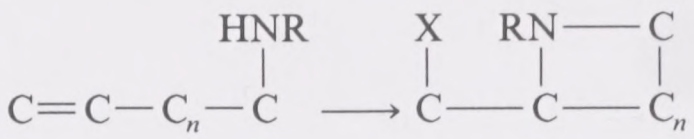
JOC *22* 646 (1957)
Org Syn Coll Vol *5* 575 (1973)



BSCF 111, 115 (1970)
TL 3107 (1970); 903 (1971); 2191 (1974); *22* 61 (1981)
Acct Chem Res *8* 165 (1975)
JOC *51* 5043 (1986)

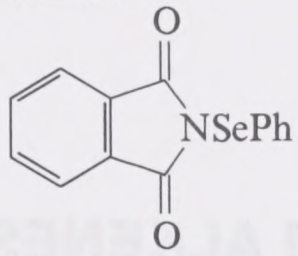


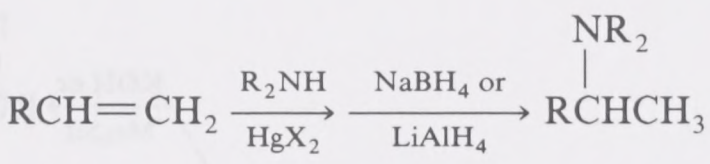
JACS *109* 3163 (1987)



Review:

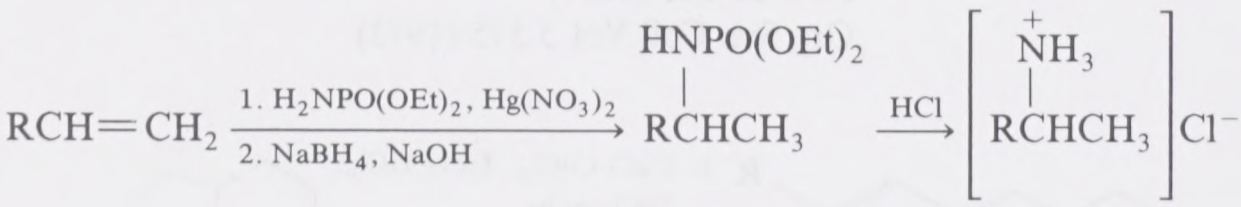
P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 6

X	Reagent	
PhSe	PhSeBr	JOC *44* 287 (1979)
		JACS *107* 3891 (1985)
HgX	HgX_2	R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 6 (review)

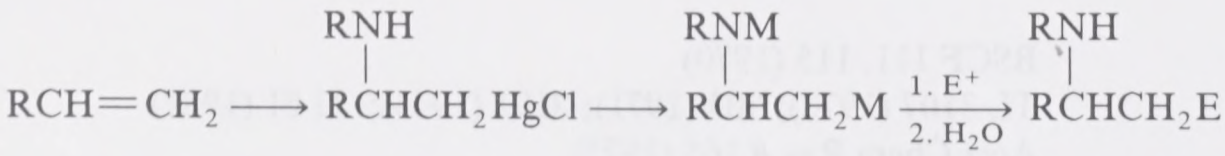


$X = NO_3$, OAc, Cl

Compt Rend C *262* 1591 (1966); *272* 1141 (1971)
TL 5165 (1967); 2289 (1969); 4399 (1971)
BSCF 583 (1970)
Syn 806 (1974); 116, 467 (1975)
R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 6 (review)



Syn 918 (1982)



M = alkali metal

$E^+ = D_2O, O_2, CO_2$, RCHO, R_2CO, Me_3SiCl, RX, $(MeS)_2$, $R_2C{=}NR$

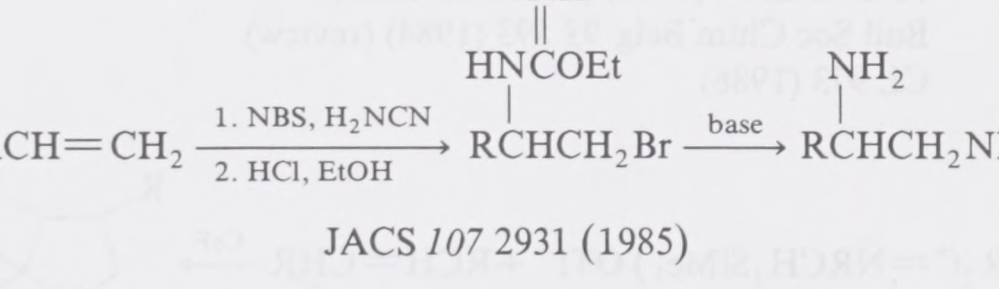
TL 2015 (1978)
JOC *44* 4798 (1979); *46* 1281 (1981); *47* 1560 (1982)

$$RCH{=}CH_2 \xrightarrow{BH_3} \xrightarrow{\text{reagent(s)}} RCH_2CH_2NH_2$$

Reagent(s)

NH_2OSO_3H — JACS *88* 2870 (1966); JOC *32* 3199 (1967); Syn 196 (1974)

NH_4OH, NaOCl — CC 62 (1982)



JACS *108* 6761 (1986)

$$RCH{=}CH_2 \xrightarrow{HBX_2} RCH_2CH_2BX_2 \xrightarrow{R'N_3} \xrightarrow{H_2O} RCH_2CH_2NHR'$$

X = Cl or alkyl

JACS *93* 4329 (1971); *94* 2114 (1972); *95* 2394 (1973)

$$XCH{=}CH_2 + HNR_2 \longrightarrow XCH_2CH_2NR_2$$

$X = COR, CO_2H, CO_2R, CONR_2, CN$

Org Syn Coll Vol *1* 196 (1941); *3* 93, 258 (1955)
JCS 399 (1945); 4166 (1957)
JACS *68* 1259 (1946); *69* 971 (1947); *71* 1901, 2532 (1949); *108* 8112 (1986)
Org Rxs *5* 79 (1949) (review)
JOC *23* 94 (1958); *24* 1096 (1959); *42* 1650 (1977); *52* 5742 (1987)
Org Syn Coll Vol *4* 146 (1963) [$Cu(OAc)_2 \cdot H_2O$ catalyzed]
BSCF 1717 (1971)
Chem Pharm Bull *25* 1319 (1977)
TL *28* 1757 (intramolecular), 1761 (intramolecular), 3103 (1987)

$$R_2C{=}CH_2 + HNR'_2 \xrightarrow[\text{Rh catalyst}]{CO,\ H_2O} R_2CHCH_2CH_2NR'_2$$

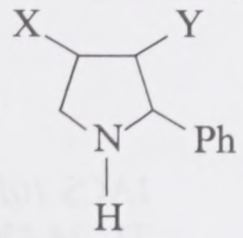
JOC *47* 445 (1982)

$$RCH{=}CH_2 \xrightarrow[2.\ HCl,\ EtOH]{1.\ NBS,\ H_2NCN} RCHCH_2Br \xrightarrow{\text{base}} RCHCH_2NH_2$$

(NH, HNCOEt; NH_2)

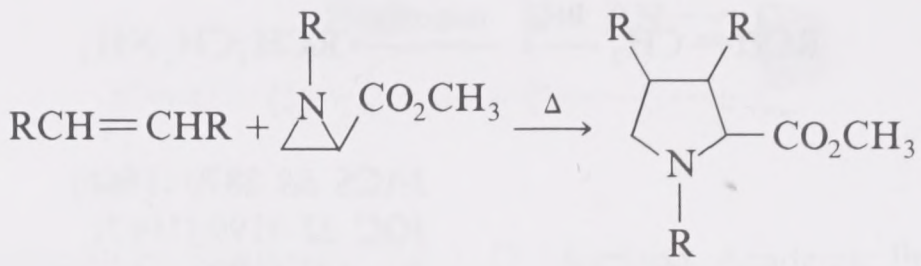
JACS *107* 2931 (1985)

$$XCH{=}CHY \xrightarrow[Me_3SiOTf]{Me_3SiCH_2N{=}CHPh}$$

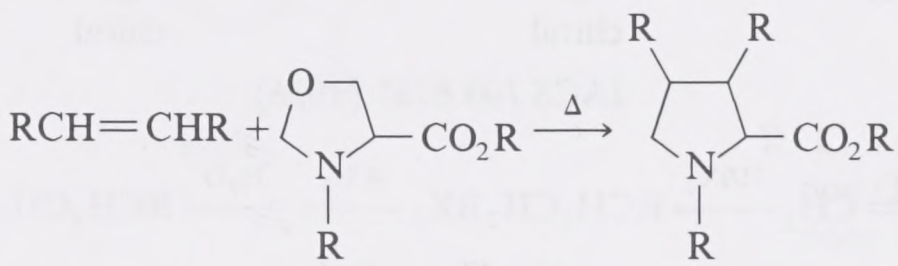


X, Y = H, CO_2R, CONMeCO

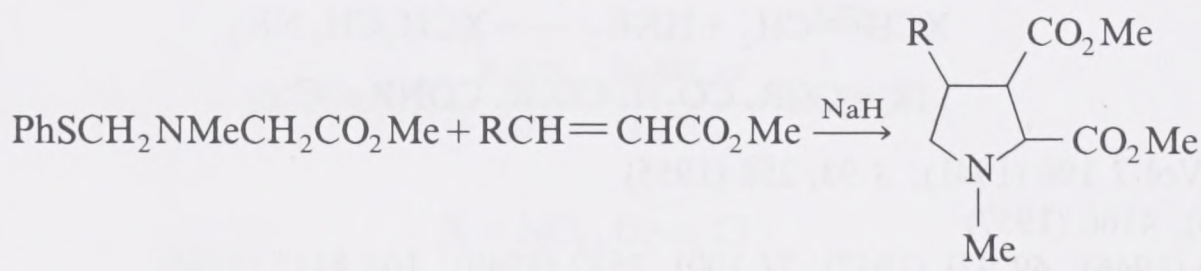
TL *23* 2589 (1982)



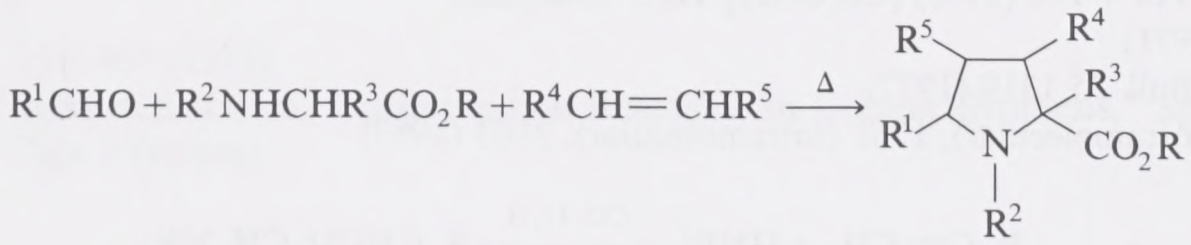
JACS *89* 1753 (1967)
Angew Int *8* 602 (1969)
CC 1187, 1188 (1971)
BSCF 709 (1974)
JOC *50* 2309 (1985)



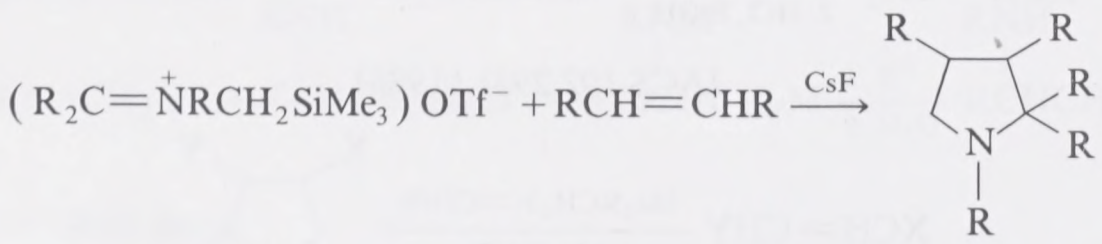
TL *28* 2973 (intramolecular), 2975 (1987)



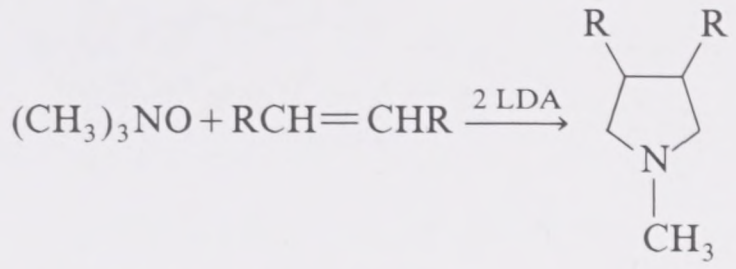
TL *25* 1579 (1984)



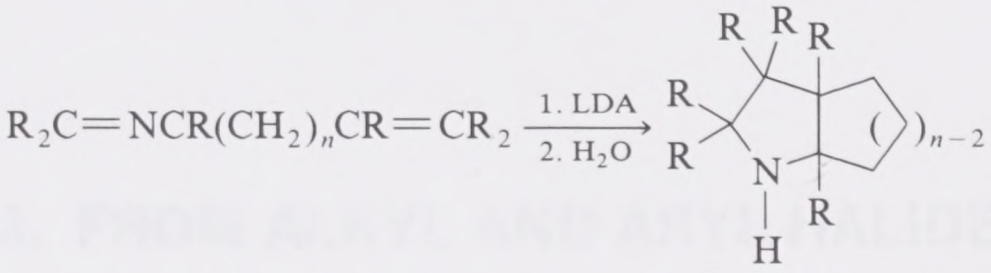
CC 109 (1978); 180, 182 (1984); 1566 (1985)
TL 2823, 2885 (1978); *25* 4613 (1984); *26* 2775 (1985)
JOC *48* 2994 (1983) (intramolecular)
Bull Soc Chim Belg *93* 593 (1984) (review)
CL 973 (1986)



JACS *101* 6452 (1979); *102* 7993 (1980)
TL *24* 4303 (1983)
JOC *48* 1554 (1983)
Chem Rev *86* 941 (1986) (review)

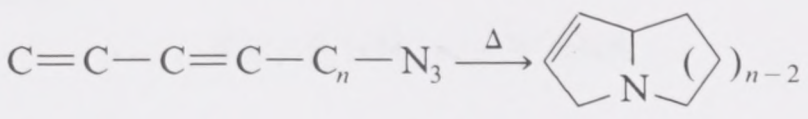


CC 31 (1983)
Heterocycles *23* 653 (1985)
Can J Chem *63* 725 (1985)



$n = 1, 2$

JACS *108* 2769 (1986)



$n = 1, 2$

3. FROM ALKYL AND ARYL HALIDES

See also page 401, Section 4.

$$RX + R'NH_2 \longrightarrow R'NHR$$

X	
halide	JCS 992 (1930) JACS *54* 1499, 3441, 4457 (1932); *82* 6163 (1960) Org Syn Coll Vol *1* 102 (1941); *2* 290 (1943); *3* 256 (1955); *4* 466 (1963); *5* 88 (1973)
tosylate	JACS *55* 345 (1933) JCS 694 (1955)
sulfate	Org Syn Coll Vol *5* 1018 (1973)
phosphate	Org Syn Coll Vol *5* 1085 (1973)

$$RX + LiNR'_2 \longrightarrow RNR'_2$$

Ind Eng Chem *29* 1361 (1937); *33* 218 (1941)

$$RC{\equiv}CX + LiNR_2 \longrightarrow RC{\equiv}CNR_2$$

Angew *3* 506 (1964); *6* 767 (1967)

$$ArX + HNMe_2 \xrightarrow{\Delta} ArNMe_2$$

JACS *71* 740 (1949)

$$ArX + HNR_2 \xrightarrow{\text{Cu catalyst}} ArNR_2$$

Org Syn Coll Vol *2* 15 (1943); *3* 307 (1955)
JACS *72* 888 (1950) (intramolecular); *109* 1496 (1987)
Tetr *40* 1433 (1984) (review)

$$ArX + (K)NaNR_2 \longrightarrow ArNR_2$$

JOC *48* 4397 (1983); *50* 1334 (1985); *51* 5157 (1986); *52* 2619 (1987)

$$ArX + n\text{-}Bu_3SnNR_2 \xrightarrow{\text{cat } PdCl_2(PAr_3)_2} ArNR_2$$

CL 927 (1983)

$$R_3N + R'X \longrightarrow \left[R_3\overset{+}{N}R'\right]X^-$$

Org Syn Coll Vol *4* 85, 98, 582, 585 (1963); *5* 315, 608, 825, 883, 989 (1973)

$$RNH_2 \xrightarrow{PhCHO} PhCH{=}NR \xrightarrow[2.\ NaOH]{1.\ R'X} RNHR'$$

$R'X = RI, R_2SO_4$

Org Syn Coll Vol *5* 736, 758 (1973)

$$RX + H_2NN(CH_3)_2 \longrightarrow \left[\begin{array}{c} CH_3 \\ | \\ R\overset{+}{N}NH_2 \\ | \\ CH_3 \end{array}\right] X^- \xrightarrow{HNO_2} RN(CH_3)_2$$

R = 1°, 2° alkyl; benzylic; propargylic

Syn Commun *12* 801 (1982)

$$RX \longrightarrow RN_3 \longrightarrow RNH_2$$

See page 409, Section 5.

$$ArNH_2 \xrightarrow[Et_3N]{Ph_3PBr_2} ArN{=}PPh_3 \xrightarrow[2.\ OH^-]{1.\ 1°\ RX} ArNHR$$

Syn 295 (1980)

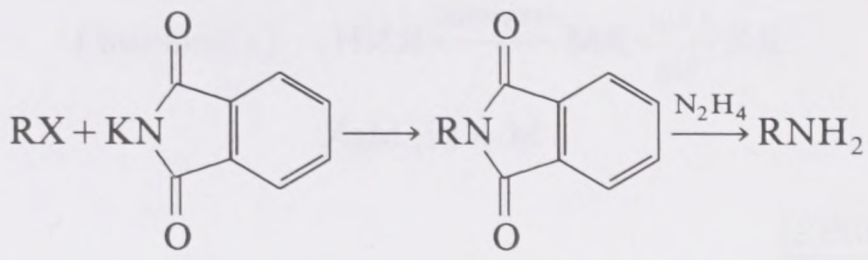
$$R'NH_2 \longrightarrow R'NHY \xrightarrow[2.\ RX]{1.\ base} \begin{array}{c} R \\ | \\ R'NY \end{array} \longrightarrow RNHR'$$

Y	
$COCF_3$	JOC *39* 1315 (1974) TL 4987 (1978)
SO_2CF_3	Tetr *31* 2517 (1975)
SO_2CH_2COPh	Tetr *31* 2517 (1975)
$PO(OEt)_2$	Angew Int *16* 107 (1977)

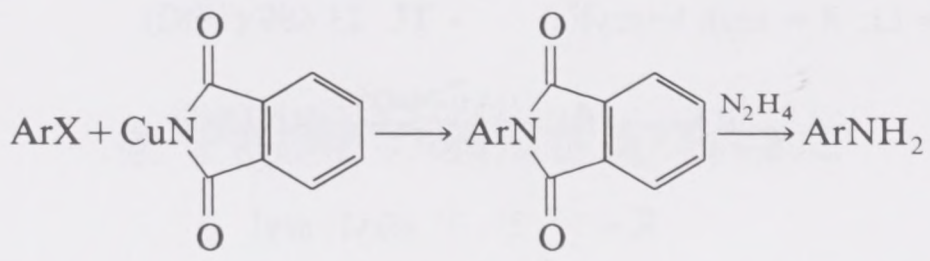
$$RX + ArNHC(=O)R' \xrightarrow[\text{crown ether}]{\text{KO-}t\text{-Bu}} \xrightarrow{2\ H_2O} RNHAr$$

$RX = MeI, H_2C{=}CHCH_2Br$

Syn Commun *9* 757 (1979)

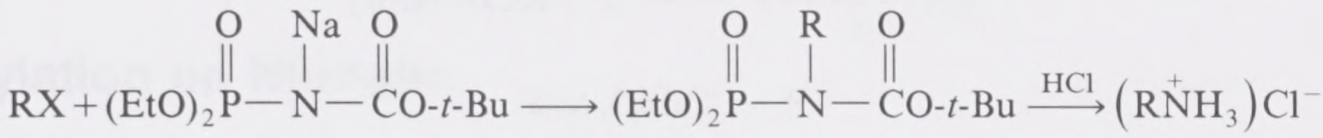


Org Syn Coll Vol *2* 83 (1943)
JACS *72* 2786 (1950)
Angew Int *7* 919 (1968)
Syn 389 (1976) (phase transfer)
BCSJ *55* 1671 (1982) (phase transfer)



X = Br, I

CC 578 (1969)



Syn 922 (1982)

$$RX + NaN(SiMe_3)_2 \xrightarrow{HCl} RNH_2$$

Ber *94* 2311 (1961)

$$ArI + CuN(SiMe_3)_2 \xrightarrow{CH_3OH} ArNH_2$$

CC 256 (1974)

$$RX \xrightarrow{LiN(SAr)_2} RN(SAr)_2 \xrightarrow{HCl} RNH_2$$

TL 3411 (1970)
BCSJ *44* 2797 (1971)

$$RX \xrightarrow{(CH_2)_6N_4} \xrightarrow{H^+} RNH_2$$

Org Rxs *8* 204 (1954)
Syn 161 (1979)

$$RX \xrightarrow[Mg]{Li\ or} RM \xrightarrow{reagent(s)} RNH_2$$

M = Li, MgX

Reagent(s)

NH_2Cl	JACS *58* 27 (1936); *63* 1692 (1941)
NH_2OCH_3	JCS 781 (1946)
NH_2OCH_3, CH_3Li (M = Li; R = 1°, 2°, 3° alkyl; aryl; benzylic)	JOC *47* 2822 (1982) JACS *108* 6016 (1986)

$$RX \xrightarrow[Mg]{Li\ or} RM \xrightarrow{reagent(s)} RNH_2 \quad (\textit{Continued})$$

M = Li, MgX

Reagent(s)	
$NH_2O_2PPh_2$	TL *23* 5399 (1982)
$N_3CH_2SiMe_3$ (R = aryl only)	CC 1322 (1983) TL *27* 6193 (1986)
N_3CH_2SPh/KOH or HCO_2H (R = aryl only)	JACS *103* 2484 (1981)
$R^1C(N_3)=CHR^2$ (M = Li; R = aryl, benzylic)	TL *23* 699 (1982)

$$RX \longrightarrow RLi \xrightarrow[2.\ H_2O]{1.\ LiNMeOMe} RNHMe$$

R = 1°, 2°, 3° alkyl; aryl

JACS *108* 6016 (1986)

$$RX \xrightarrow[Mg]{Li\ or} \xrightarrow{(Me_2\overset{+}{N}=CH_2)X^-} RCH_2NMe_2$$

R = 1° alkyl, aryl

X	
O_2CCF_3	Syn Commun *6* 539 (1976)
I	TL 1299 (1977); *28* 3241 (1987)

For related reactions see page 401, Section 4.

$$2\ RX \xrightarrow[2.\ (MeO)_2CHNR'_2]{1.\ 2\ Mg} \xrightarrow{H_2O} R_2CHNR'_2$$

Syn 757 (1978)

$$RX \xrightarrow[2.\ Ph_2PON=CHOEt]{1.\ Mg} Ph_2\overset{O}{\overset{\|}{P}}NHCHR_2 \xrightarrow[2.\ NaOH]{1.\ HCl} R_2CHNH_2$$

R = 1° alkyl, aryl

Syn 691 (1979)

$$H_2C=CR^1CH_2Br \xrightarrow[2.\ Zn(Cu)\ 3.\ Al(Hg)]{1.\ R^2C\equiv NO} R^2\overset{NH_2}{\overset{|}{C}}HCH_2CR^1=CH_2$$

Angew Int *18* 78 (1979)

4. FROM OTHER AMINES

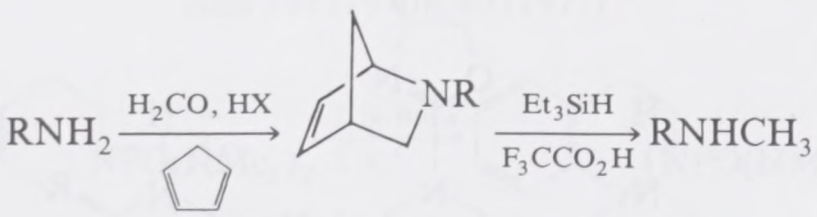
For imines → amines see also page 421, Section 9.

1. Alkylation on Nitrogen

See also page 397, Section 3; page 419, Section 8; and page 421, Section 9.

$$R_2NH \longrightarrow R_2NR'$$

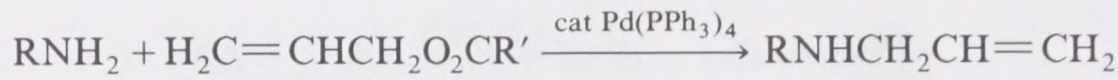
$[(R'O)_3\overset{+}{P}CH_3]BF_4^-$	JOC *49* 4877 (1984)
R'_2CuLi, O_2	JOC *45* 2739 (1980)
$(Ar_2I)X$, cat $Cu(OAc)_2$ ($R' = Ar$)	JOC *45* 2127 (1980)
Ph_3Bi, cat $Cu(OAc)_2$ ($R' = Ph$)	TL *28* 887 (1987)
$Ph_3Bi(OAc)_2$, cat Cu ($R' = Ph$)	TL *27* 3615 (1986)
$Ph_3Bi(OAc)_2$, cat $Cu(OAc)_2$ ($R' = Ph$)	J Gen Chem USSR *55* 413, 2232 (1985)
$PhPb(OAc)_3$, cat $Cu(OAc)_2$ or $Cu(O_2CCF_3)_2$ ($R' = Ph$)	TL *28* 3111 (1987)



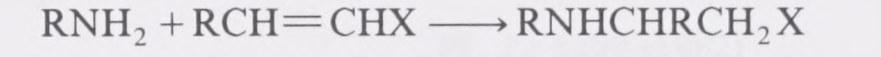
JOC *52* 5746 (1987)

$$RNH_2 \cdot HX + H_2CO + n\text{-}Bu_3SnCH_2CH{=}CH_2 \longrightarrow RNH(CH_2)_2CH{=}CH_2$$

JOC *52* 1378 (1987)

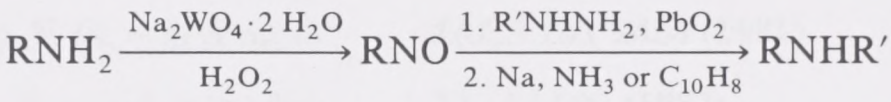


Tetr *33* 2615 (1977) (review)
J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer Verlag, Berlin (1980) (review)
R. F. Heck, "Palladium Reagents in Organic Synthesis," Academic Press, London (1985) (review)

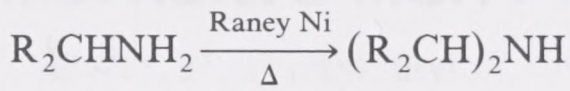


$X = COR, CO_2H, CO_2R, CONR_2, CN$

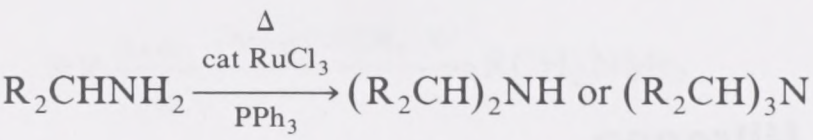
See page 391, Section 2.



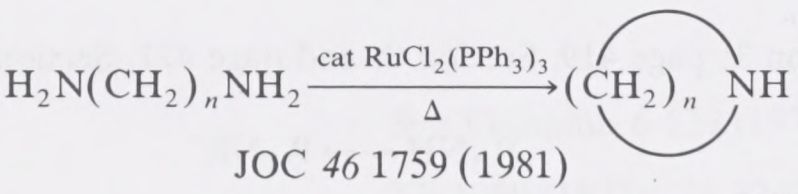
JOC *50* 5391 (1985)
Org Syn *65* 166 (1987)



Syn 70 (1979)



JOC *46* 1759 (1981)

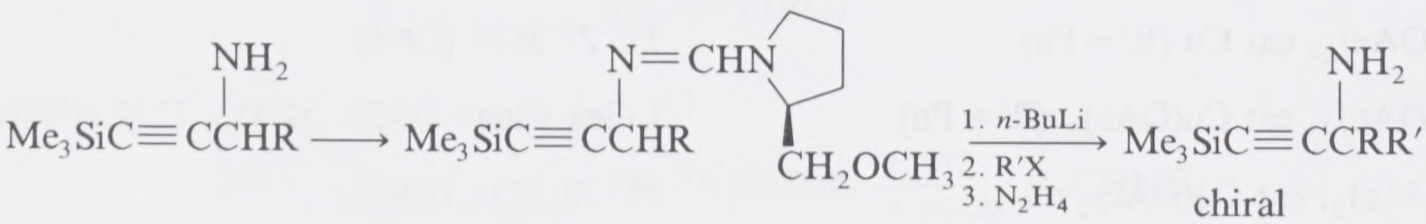


JOC *46* 1759 (1981)

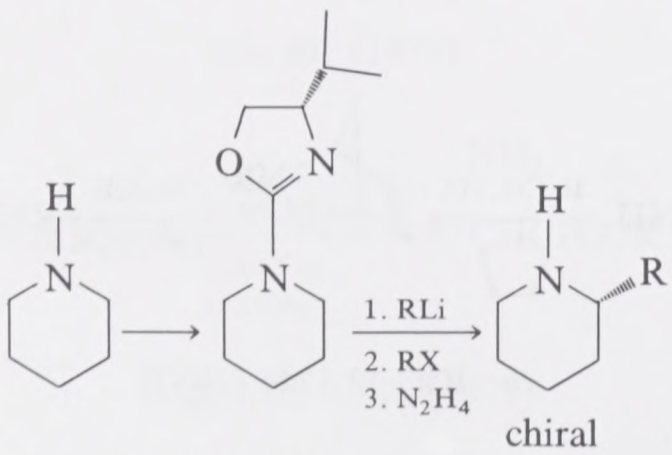
2. Alkylation on Carbon

For a review of metalation and electrophilic substitution of amine derivatives adjacent to nitrogen see Chem Rev *84* 471 (1984).

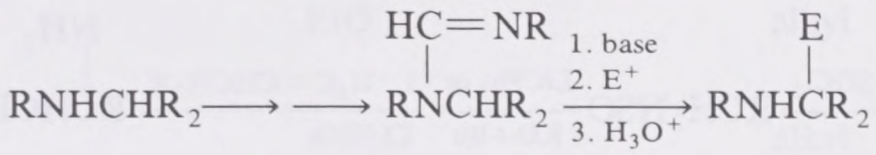
See page 900, Section 4, for alkylation on carbon next to an amide nitrogen.



Ann 1668 (1983)

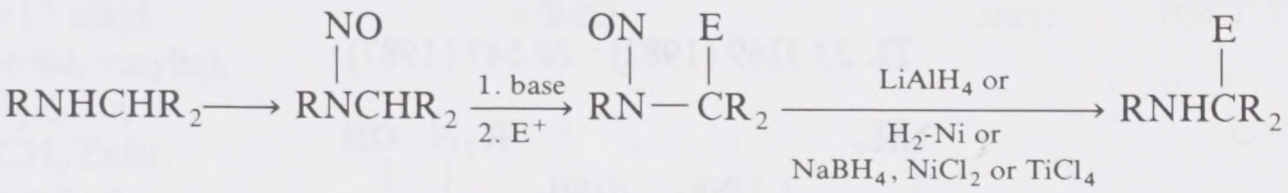


JOC *51* 3076 (1986)
JACS *109* 1265 (1987) (mechanism)



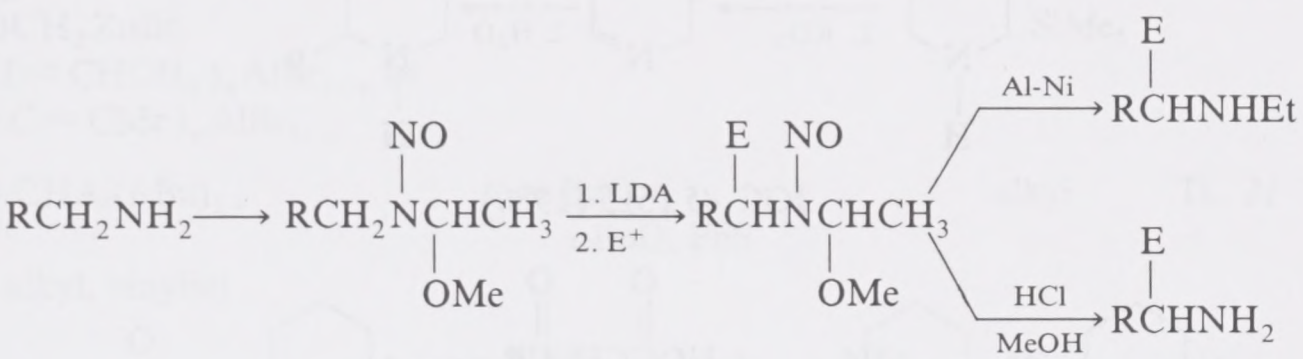
$E^+ = RX, RCHO, R_2CO$

JACS *102* 7125 (1980); *105* 117 (1983); *106* 3270 (1984); *107* 7974 (1985) (chiral); *109* 1262 (1987) (chiral, mechanism)
TL *22* 5115, 5119 (1981); *27* 1465 (1986) (chiral)
JOC *51* 3108 (1986) (chiral)



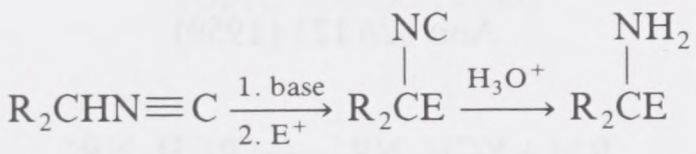
$E^+ = RX, R_2CO$

Angew Int *14* 15 (1975)
Ber *108* 1293 (1975); *110* 1852 (1977); *111* 2630 (1978)
Can J Chem *53* 2473 (1975)
Syn 548 (1976); 423 (1979); 741 (1980) (reduction)
Org Syn *58* 113 (1978)
Chem Rev *78* 275 (1978) (review)
JCS Perkin I 579 (1979)



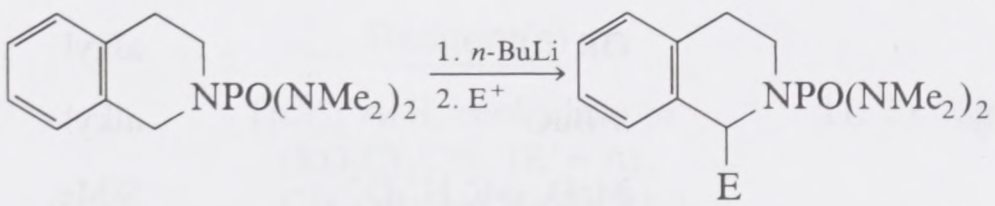
$E^+ = RX, RCHO, R_2CO$

JOC *48* 2388 (1983)



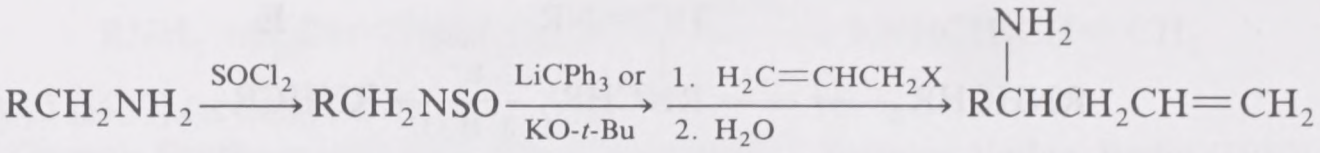
$E^+ = RX, R_2CO$

Angew Int *10* 491 (1971)
Ann 183 (1976); 40 (1977)

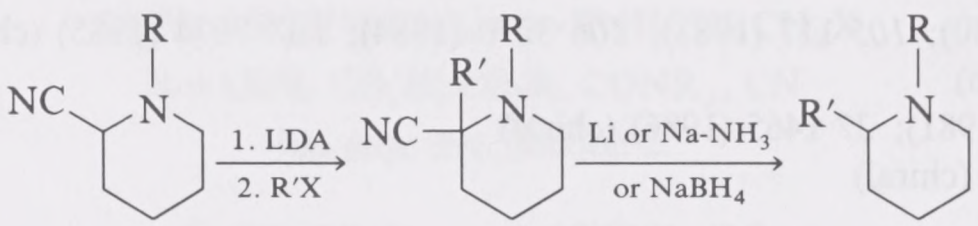


$E^+ = RX, RCHO, R_2CO, epoxide, ArH \cdot CrO_3, I_2, Me_3SiCl, n\text{-}Bu_3SnCl$

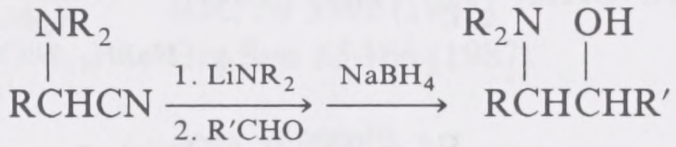
Helv *64* 643 (1981)
Tetr *39* 1963 (1983)



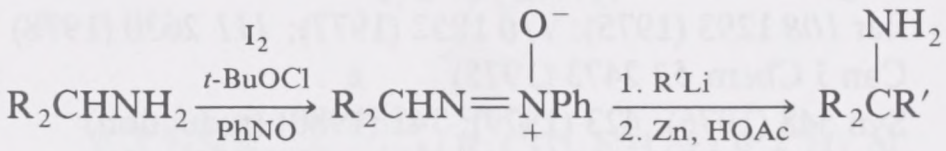
JACS *100* 2894 (1978)



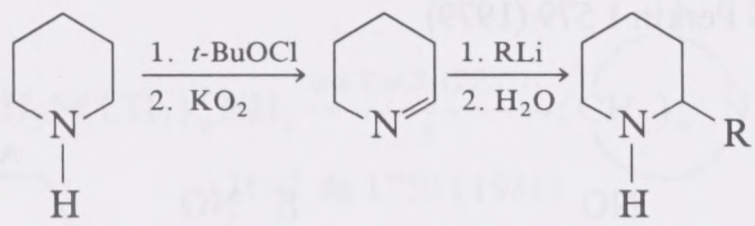
TL *23* 3369 (1982); *28* 547 (1987)



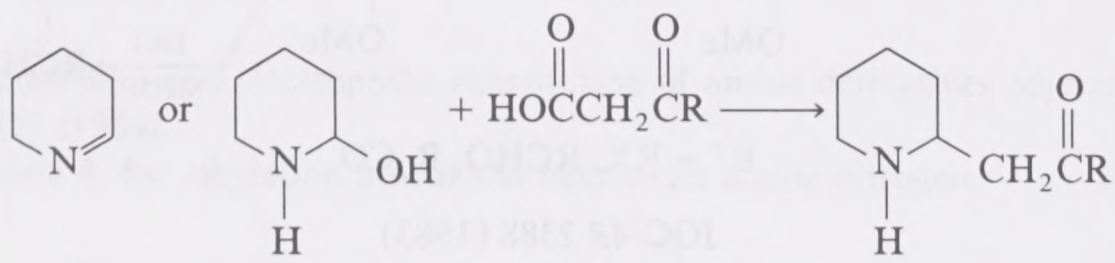
TL 771 (1979)



JCS Perkin I 2030 (1979)



JOC *45* 1515 (1980)

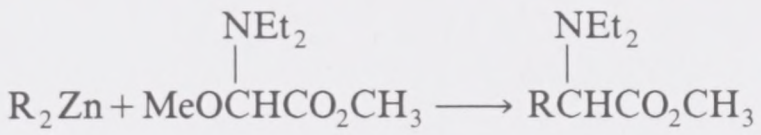


Ann *626* 123 (1959)

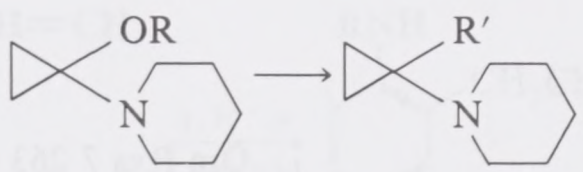
$$RM + YCH_2NR'_2 \longrightarrow RCH_2NR'_2$$

RM	Y	R′	
$CH_3CH_2CH{=}CHCH_2M$ (M = Li, MgX, ZnX)	*n*-BuO, *n*-BuS	alkyl	BSCF 2544 (1968)
n-BuMgBr	OR	alkyl	TL *28* 547 (1987)
RMgX (R = 1° alkyl)	*n*-BuO	alkyl	BSCF II 148 (1983)
RMgBr (R = Me, $PhCH_2$, allyl, propargyl, alkynyl, aryl)	MeO, *c*-$C_6H_{13}O$	$SiMe_3$	Angew Int *23* 53 (1984)
RMgX (1° alkyl, allyl, benzyl, aryl)	*n*-BuO	alkyl	JCS *123* 532 (1923)

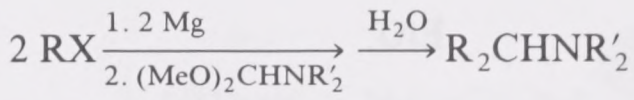
RMgX (1°, 2°, 3° alkyl; allyl; benzyl)	EtO	alkyl	JACS *62* 1450 (1940)
RMgX (1°, 2° alkyl; benzylic; aryl)	*n*-BuO	alkyl	JACS *77* 1098 (1955)
RMgX (R = 1°, 2° alkyl; allylic; aryl)	PhS	alkyl	JOC *32* 272 (1967)
PhMgBr	CN	alkyl	BSCF 3803 (1968) TL *28* 741 (1987)
RMgX (R = 1° alkyl, CH_2CO_2-*t*-Bu, vinylic), EtO_2CCH_2ZnBr, Et_2NCOCH_2ZnBr, $(EtO_2C)_2CRZnBr$ (R = H, Me)	*n*-BuO	alkyl	BSCF II 395 (1982)
$RC{\equiv}CCH_2M$ (M = MgX, AlX_2, ZnX); $CH_3CH{=}CHCH_2M$ (M = Li, MgX, AlX_2, ZnX, Cu)	*n*-BuO	alkyl	JOMC *198* 1 (1980)
$RC{\equiv}CMgBr$	*n*-BuO	alkyl	BSCF II 21 (1983)
$RC{\equiv}CMgX$, Et_2NCOCH_2ZnBr, $(CH_3CH{=}CHCH_2)_nAlBr_{3-n}$ or $(H_2C{=}C{=}CMe)_nAlBr_{3-n}$	OR	*i*-Pr, $SiMe_3$	TL *28* 1659 (1987)
E-$RCH{=}CHAl(i\text{-}Bu)_2$, R_2CuLi (R = 1° alkyl, vinylic)	*n*-BuO, *i*-BuO, PhS	alkyl	TL *21* 3763 (1980)



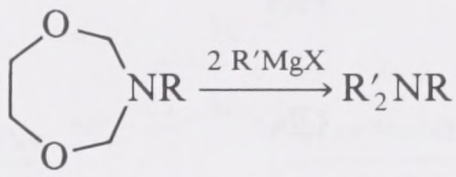
JOMC *256* 193 (1983)



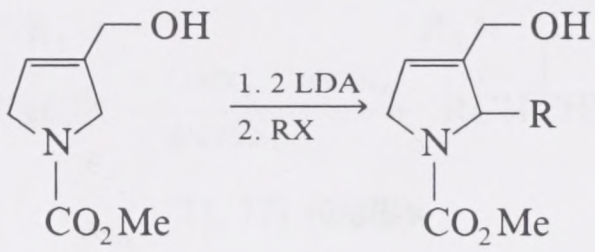
R	Reagent(s)	
H	$TiCl_4$; ArH, enol silane or $(RO_2C)_2CH_2$ [R′ = Ar, CH_2OR or $CH(CO_2R)_2$]	TL *23* 785 (1982)
$SiMe_3$	R′MgX (R = 1° alkyl, aryl, vinylic)	TL *23* 785 (1982)
H or $SiMe_3$	KCN, HOAc (R′ = CN)	TL *23* 1413 (1982)



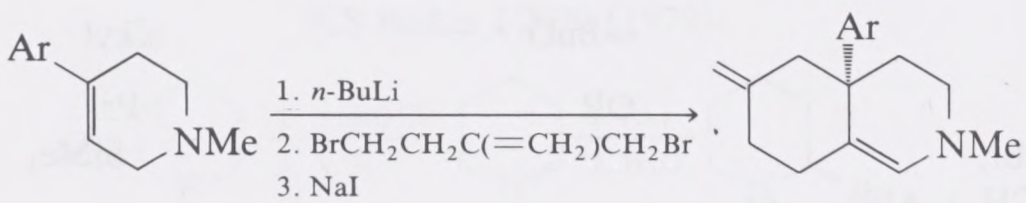
Syn 757 (1978)



TL *24* 1597 (1983)



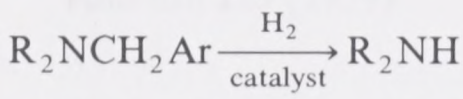
JOC *48* 1129 (1983)



TL *23* 285 (1982)

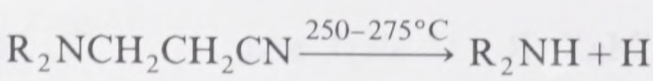
3. Dealkylation

Review: Houben-Weyl, Vol XI/1, p 961

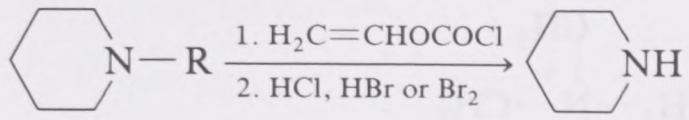


Catalyst

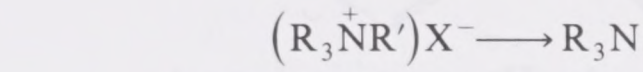
review	Org Rxs *7* 263 (1953)
Pd-C	Helv *35* 1162 (1952) J Chem Res (S) 164 (1981)
$PdCl_2$-C	JACS *65* 1984 (1943); *72* 3410 (1950); *75* 5598 (1953)



JOC *17* 1043 (1952)

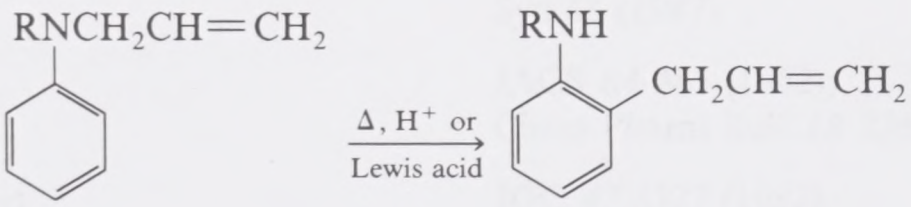


TL 1567 (1977)

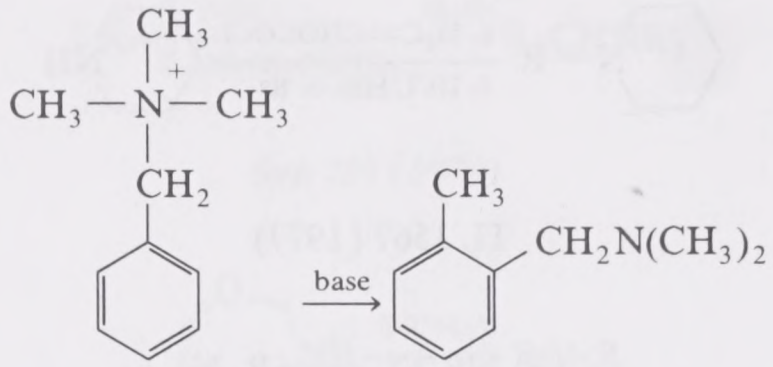


Reagent(s)	R′	X	
Δ	Me, benzylic, allylic	halide	Org Rxs *7* 142 (1953) (review)
	Me	OAc	Tetr *24* 5493 (1968)
	alkyl	OH	Org Rxs *11* 317 (1960) (review)
$LiAlH_4$	Me	I	JACS *82* 4651 (1960)
	Me, Et	I	JCS 1729 (1965)
LiI	Me	OTs	JOC *28* 2407 (1963)
KO_2CH, HCO_2H	Me	Br	Coll Czech Chem Commun *26* 471 (1961)
KOAc	Me	Br	Coll Czech Chem Commun *26* 471 (1961)
NaSPh	Me	Cl	TL 1375 (1966)
	Me, Et	I	JCS 1729 (1965)
$H_2NCH_2CH_2OH$	various alkyl	halide, ClO_4	Ber *90* 395, 403 (1957)

4. Rearrangement

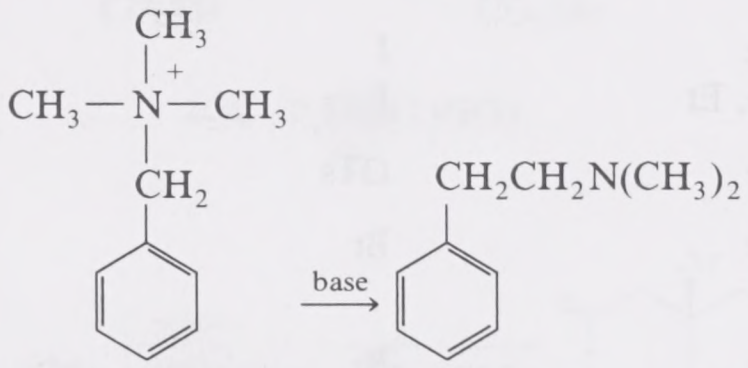


JOC *22* 1418 (1957)
TL 4661 (1971); *25* 3159 (1984)
Helv *56* 105 (1973); *60* 978 (1977)
Yakugaku Zasshi *97* 553 (1977)
JOC USSR *15* 2350 (1979); *19* 920 (1983)
Bull Acad Sci USSR, Div Chem Sci 1910 (1982)
Chem Pharm Bull *31* 2220 (1983)



Sommelet–Hauser rearrangement

JACS *73* 4122 (1951)
Org Syn *34* 61 (1954)
Org Rxs *18* 403 (1970) (review)
A. R. Lepley, A. G. Giumanini in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1971), Vol 3, p 297 (review)
JOC *36* 984 (1971); *44* 2348 (1979)
I. Zugravescu, M. Petrovanu, "N-Ylid Chemistry," McGraw-Hill, New York (1976), Chpt 2 (review)



Stevens rearrangement

Org Rxs *18* 403 (1970) (review)
A. R. Lepley, A. G. Giumanini in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1971), Vol 3, p 297 (review)
JOC *36* 984 (1971); *44* 2348 (1979)
I. Zugravescu, M. Petrovanu, "N-Ylid Chemistry," McGraw-Hill, New York (1976), Chpt 2 (review)

5. FROM AZIDES

See also page 391, Section 2.

$RN_3 \longrightarrow RNH_2$

H_2, cat Pd or Pt	Chem Rev *54* 1 (1954)
H_2, cat Pd-C	J Med Chem *12* 658 (1969) CC 915 (1970); 1738 (1987) JOC *36* 250 (1971); *37* 335 (1972); *50* 3095 (1985); *51* 1069, 5373 (1986) Ber *105* 1524 (1972) TL *28* 4601 (1987)
H_2, cat Pd-$CaCO_3$	Syn 590 (1975)
H_2, cat PdO	JACS *76* 2887 (1954)
H_2, cat PtO_2	JOC *27* 3045 (1962); *40* 1659 (1975) TL *28* 4499 (1987)
$(NH_4)O_2CH$, cat Pd-C	TL *24* 1609 (1983); *28* 6133 (1987)
BH_3	JACS *87* 4203 (1965)
$NaBH_4$	JOC *23* 127 (1958)
$NaBH_4$, MeOH, THF	Syn 48 (1987)
$NaBH_4$, *i*-PrOH, Δ	JACS *84* 485 (1962); *86* 1427 (1964) Chem Pharm Bull *18* 2368 (1970)
$NaBH_4$ (phase transfer)	JOC *47* 4327 (1982)
$LiAlH_4$	JACS *73* 5865 (1951); *91* 2961 (1969); *92* 6302 (1970); *108* 2034 (1986) Chem Rev *54* 1 (1954) JOC *27* 2925 (1962); *31* 684 (1966); *51* 5373 (1986) Carbohydr Res *3* 318 (1967) CL 635 (1977)
n-Bu_3SnH	JACS *107* 519 (1985) TL *28* 6381 (1987)

n-Bu_2SnH_2	TL *28* 5941 (1987)
Zn, HCl	CC 64 (1970) JCS C 414 (1971)
Zn, HOAc	JCS C 414 (1971)
$SnCl_2$, MeOH	TL *27* 1423 (1986); *28* 4597 (1987)
$TiCl_3$, H_2O	Syn 65 (1978)
VCl_2, H_2O (R = aryl only)	Syn 815 (1976)
$CrCl_2$, H_2O	CC 64 (1970) JCS C 414 (1971) Tetr *29* 1801 (1973)
$MoCl_5$, Zn, H_2O, THF	Syn 830 (1980)
$P(OEt)_3$/TsOH, EtOH	TL *28* 6513 (1987)
$P(OEt)_3$/HCl	Syn 202 (1985)
PPh_3, H_2O	TL *24* 763 (1983); *28* 379, 1757, 1761 (1987) BSCF 815 (1985) JOC *52* 5044 (1987)
PPh_3/HBr	Ann *591* 117 (1955)
PPh_3/NH_4OH or NaOH	JOC *40* 1659 (1975) TL *27* 227 (1986)
H_2S, solvent?	Chimia *22* 141 (1968)
H_2S, H_2O	JACS *73* 2327 (1951)
H_2S, H_2O, py	Syn 45 (1977)
H_2S, EtOH	JOC *33* 2910 (1968) Tetr *23* 387 (1967); *25* 3313 (1969) Monatsh *101* 724 (1970)
$HS(CH_2)_3SH$, Et_3N	TL 3633 (1978)
PhSH, $Sn(SPh)_2$, Et_3N	TL *28* 5941 (1987)
$Na_2S \cdot 9\ H_2O$, Et_3N, MeOH	JOC *44* 4712 (1979)
NaTeH	CL 1733 (1984)
$CH_3COCH_2COCH_3$, Et_3N	J Heterocyclic Chem *10* 565 (1973) JOC *40* 1066 (1975) Syn 491 (1977) TL *28* 5941 (1987)

$$RCH{=}\overset{\displaystyle N_3}{\overset{|}{C}}R' \xrightarrow{LiAlH_4} RCH_2\overset{\displaystyle NH_2}{\overset{|}{C}}HR'$$

JOC *42* 2935 (1977)

6. FROM NITRO COMPOUNDS

Reviews:

R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York (1965), Chpt 5
M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 10
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley and Sons, New York (1978), Chpt 5
P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 8

$RNO_2 \longrightarrow RNH_2$

R = alkyl

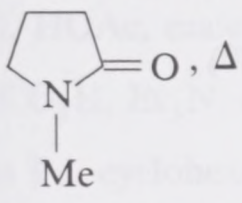
H_2, Raney Ni	Ber *86* 939 (1953)
H_2, Raney Ni, HOAc	Org Syn Coll Vol *4* 221 (1963)
H_2, cat Pd-C	Ber *86* 939 (1953) JACS *81* 505 (1959) CL 797 (1981)
$(NH_4)O_2CH$, cat Pd-C	TL *25* 3415 (1984) JOC *51* 4856 (1986)
cat Pd, 	JCS 3586 (1954)
H_2, cat PtO_2	JOC *37* 335 (1972)
H_2, cat $RhCl_3(py)_3$-$NaBH_4$	JCS Perkin I 2509 (1973)
H_2, KOH, cat $RuCl_2(PPh_3)_3$	JOC *40* 519 (1975)
CO, $Ru_3(CO)_{12}$, NaOH (phase transfer)	TL *21* 2603 (1980)
$N_2H_4 \cdot 2\ H_2O$, Ni_2B	JOC *51* 4294 (1986)
$LiBH_4$, MeOH, diglyme	JOC *51* 4000 (1986)
$NaBH_4$, cat Pd-C	Syn 713 (1987)

$NaBH_4$, cat $NiCl_2 \cdot 6\ H_2O$	TL *26* 6413 (1985) JOC *51* 4856 (1986)
$NaBH_4$, $CoCl_2 \cdot 6\ H_2O$	TL 4555 (1969) CC 344 (1986)
$LiAlH_4$	JACS *70* 3738 (1948); *73* 1293 (1951) TL *28* 6281 (1987)
Mg(Hg)-$TiCl_4$, *t*-BuOH, THF	Syn Commun *13* 495 (1983)
Al(Hg), H_2O	JACS *90* 3245 (1968) TL *28* 6281 (1987)
Sn, HCl	Org Syn Coll Vol *2* 617 (1943)
Zn, HCl	TL *28* 577 (1987)
Fe, HCl	JACS *73* 1293 (1951)

$$ArNO_2 \longrightarrow ArNH_2$$

Review: Org Rxs *20* 455 (1973) (sulfides and polysulfides)

H_2, cat Ni	JACS *61* 3564 (1939)
H_2, cat Raney Ni	JOC *18* 1506 (1953); *51* 3903 (1986) JACS *76* 5149 (1954) Acta Chem Scand *9* 1079 (1955) Org Syn Coll Vol *3* 59, 63 (1955); *4* 357 (1963); *5* 1130 (1973)
H_2, cat KBH_4-$NiCl_2 \cdot 6\ H_2O$-C	Carbohydr Res *88* 323 (1981)
H_2, cat Pd-C	JOC *37* 335 (1972); *51* 3308 (1986); *52* 1844, 5717 (1987) Org Syn Coll Vol *5* 829 (1973) Syn 940 (1982) JACS *107* 3328 (1985)
H_2, cat $Pd(acac)_2$, py	Chem Ind 1057 (1975)
H_2, cat PtO_2	Org Syn Coll Vol *1* 240 (1941)
H_2, cat PtO_2, K_2CO_3, CH_3OH	JOC *44* 409 (1979)
H_2, cat Pt salt-$NaBH_4$	JACS *84* 2828 (1962)
H_2, cat CoS_x, *i*-PrOH	JOC *44* 3671 (1979)
H_2, cat $RhCl_3(py)_3$-$NaBH_4$	JCS Perkin I 2509 (1973)
H_2, cat Ru	JOC *44* 1233 (1979)
H_2, cat $RuCl_2(PPh_3)_3$	TL 2163 (1975)
cat Pd-C, 	JCS Perkin I 1300 (1975)
cat Pd, 	JCS 3586 (1954)
$PhNHNH_2$	JCS 330 (1929)

N_2H_4, (catalysts)	Chem Rev *65* 51 (1965)
N_2H_4, graphite	TL *26* 6233 (1985)
N_2H_4, Raney Ni	JACS *75* 4334 (1953); *76* 5149 (1954) J Gen Chem USSR *27* 261 (1957) Can J Chem *38* 2363 (1960) TL *23* 147 (1982) BCSJ *56* 3159 (1983)
N_2H_4, cat Pd-C	Org Syn Coll Vol *5* 30 (1973) JCS Perkin I 444 (1977)
N_2H_4, $FeCl_3 \cdot 6\ H_2O$, C, CH_3OH	CL 259 (1975) JOC *50* 5092 (1985); *52* 1339 (1987)
N_2H_4, Fe(III) oxide	Syn 834 (1978)
$(NH_4)O_2CH$, cat Pd-C	TL *25* 3415 (1984)
$(Et_3NH)O_2CH$, cat $RuCl_2(PPh_3)_3$, cat Pd-C	JOMC *309* C63 (1986)
$(Et_3NH)O_2CH$, cat $Pd(OAc)_2(PAr_3)_2$	JOC *42* 3491 (1977)
$(Et_3NH)O_2CH$, cat Pd-C	JOC *42* 3491 (1977); *45* 4992 (1980) JACS *108* 1000 (1986)
HCO_2H, cat Pd-C	JCS Perkin I 443 (1977)
phosphinic acid or sodium phosphinate or phosphorous acid or sodium phosphite, cat Pd-C	JCS Perkin I 443 (1977)
NaO_2CH, KH_2PO_4, 	Syn Commun *11* 925 (1981)
CO, H_2O, Se, Et_3N	Angew Int *19* 1008 (1980)
$Fe(CO)_5$	Can J Chem *48* 1543 (1970)
$Fe(CO)_5$, CO, H_2O, Et_3N	JACS *100* 3969 (1978)
$Fe_2(CO)_9$, aq NaOH, C_6H_6	JACS *99* 98 (1977)
$Fe_3(CO)_{12}$, CH_3OH, Δ	JOC *37* 930 (1972)
$Fe_3(CO)_{12}$, Al_2O_3	CC 821 (1980)
$Fe_3(CO)_{12}$, aq NaOH, C_6H_6, cat $(PhCH_2NEt_3)Cl$	JACS *99* 98 (1977)
$Fe_3(CO)_{12}$, KOH, 18-crown-6	Angew Int *16* 41 (1977)
$(Et_4N)HFe_3(CO)_{11}$	JOMC *171* 85 (1979)
CO, cat $Pd(OAc)_2$, PR_3, HOAc, H_2O	Bull Acad Sci USSR, Div Chem Sci 1223 (1986)
CO, H_2O, Rh catalyst, Δ	TL 3385 (1971)

CO, $Ru_3(CO)_{12}$, NaOH (phase transfer)	TL *21* 2603 (1980)
$LiBH_4$, MeOH, diglyme	JOC *51* 4000 (1986)
$NaBH_2S_3$	Can J Chem *49* 2990 (1971)
$NaBH_4$, cat Pd-C	Syn 713 (1987)
$NaBH_4$, cat Pd-C, H_2O	JCS 371 (1962)
$NaBH_4$, $SnCl_2 \cdot 2\ H_2O$, EtOH	Chem Pharm Bull *29* 1443 (1981)
$NaBH_4$, $TiCl_4$	Syn 695 (1980)
$NaBH_4$, $FeCl_2$	Chem Ind 480 (1983)
$NaBH_4$, $CoCl_2 \cdot 6\ H_2O$	TL 4555 (1969)
$NaBH_4$, $NiCl_2 \cdot 6\ H_2O$	Chem Pharm Bull *29* 1159 (1981)
$NaBH_4$, $NiX_2(PPh_3)_2$ (X = Cl, Br, I)	JCS Japan *92* 1225 (1971)
$NaBH_4$, CuCl	Chem Ind 75 (1984)
$NaBH_4$, $Cu(OAc)_2$	TL *27* 1205 (1986)
$NaBH_4$, cat $Cu(acac)_2$	JCS Perkin I 2409 (1979)
KBH_4, cat $PdCl_2$	BSCF 1996 (1959)
$LaNi_5H_6$	JOC *52* 5695 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)
Al_2Te_3, H_2O	Angew Int *19* 1009 (1980)
Mg(Hg)-$TiCl_4$, *t*-BuOH, THF	Syn Commun *13* 495 (1983)
$TiCl_3$, H_2O	Chem Pharm Bull *28* 2515 (1980)
$CrCl_2$, CH_3OH	Syn 792 (1977)
Li, NH_3, CH_3OH	Syn Commun *12* 293 (1982)
Na, NH_3, CH_3OH	JACS *69* 1657 (1947) Syn Commun *12* 293 (1982) JOC *51* 3904 (1986)
Zn, H_2O	Org Syn Coll Vol *2* 447 (1943)
Zn, HCl	Proc Ind Acad Sci A *44* 331 (1956)
Zn, NaOH	Org Syn Coll Vol *2* 501 (1943)
Zn, NH_3	Tetr *5* 340 (1959)
Fe	JACS *66* 1781 (1944) JOMC *65* 289 (1974)
Fe, HOAc	Org Syn Coll Vol *2* 471 (1943)
Fe, HCl	Org Syn Coll Vol *2* 160 (1943); *5* 346 (1973)
$FeSO_4$, HCl	Org Syn Coll Vol *3* 56 (1955)

Sn, HCl	JACS *61* 1001 (1939); *91* 3544 (1969); *109* 3098 (1987) Org Syn Coll Vol *1* 455 (1941); *2* 175 (1943) JCS 1133 (1949)
$SnCl_2 \cdot 2\ H_2O$, EtOH	TL *25* 839 (1984)
$SnCl_2$, HCl	Ber *62* 3035 (1929) Org Syn Coll Vol *2* 130, 254 (1943); *3* 239, 453 (1955) Chem Ind 888 (1972)
$SnBr_2$, HBr	Org Syn Coll Vol *2* 132 (1943)
Na_2S	Org Syn Coll Vol *3* 86 (1955)
Na_2S, S, NaOH	Org Syn Coll Vol *4* 31 (1963)
Na_2S, S, NH_4Cl	JOC *51* 3903 (1986)
Na_2S_2	Org Syn Coll Vol *5* 1067 (1973)
$Na_2S_2O_4$	Org Syn Coll Vol *3* 69 (1955)
$(NH_4)_2S$	Org Syn Coll Vol *1* 52 (1941); *3* 82, 242 (1955)
NaTeH (sterically hindered Ar only)	CL 1373 (1983)
paraffin, 360–390°C	Syn 23 (1978)

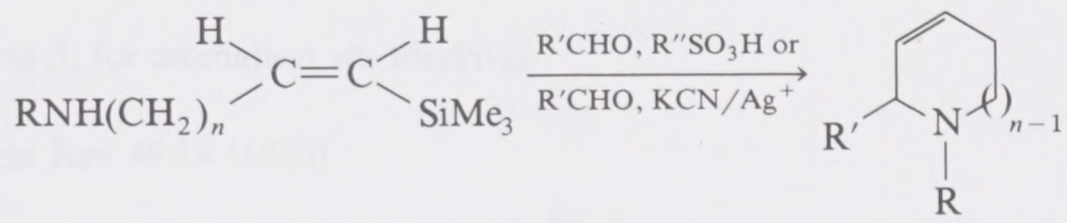
$$NO_2—Ar—NO_2 \longrightarrow NO_2—Ar—NH_2$$

H_2, cat Pd	JOC *8* 331 (1943)
Raney Ni, *i*-PrOH, HOAc	Chem Ind 477 (1983)
Ni, HOAc, maleic acid	Chem Ind 826 (1983)
HCO_2H, Et_3N, cat Pd-C	JOC *45* 4992 (1980)
cat Pd, cyclohexene	JCS 3586 (1954)
cat Pd-C, cyclohexene	JCS Perkin I 1300 (1975)
Fe, HOAc	Syn 924 (1978)
$SnCl_2$, HCl	Ber *19* 2161 (1886) Rec Trav Chim *65* 207, 331 (1946)
sulfides and polysulfides	Org Rxs *20* 455 (1973) (review)

$$ArNO_2 \longrightarrow ArNMe_2$$

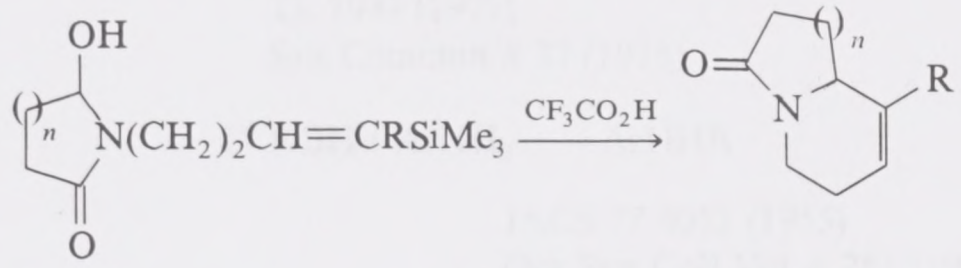
H_2, CH_2O, CH_3OH, Raney Ni	Ind J Chem B *14* 904 (1976)
H_2, CH_2O, EtOH, cat Pd-C	Org Syn Coll Vol *5* 552 (1973)

7. HETEROATOM AND METAL DISPLACEMENT



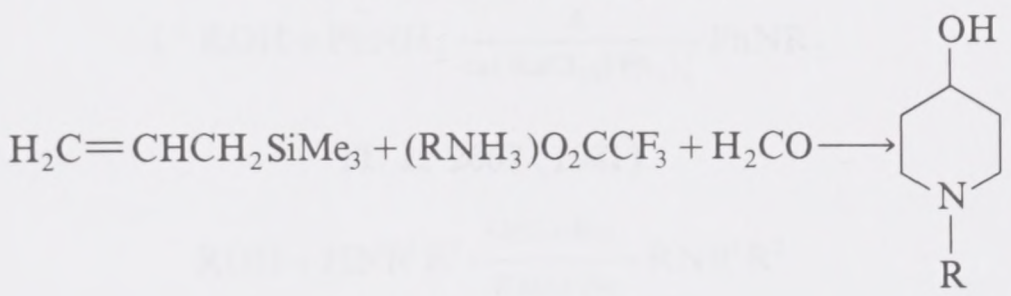
$n = 2, 3$

JACS *109* 6097, 6107 (1987)

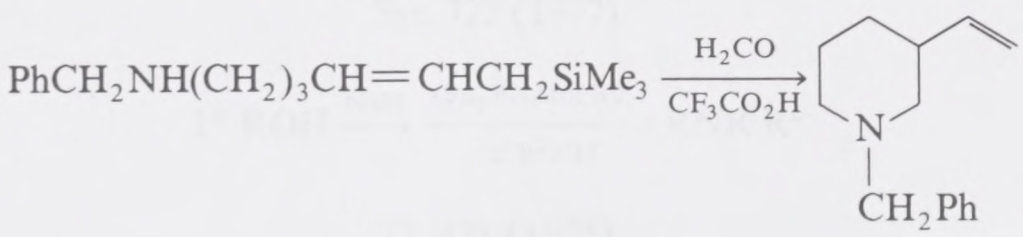


$n = 1, 2$

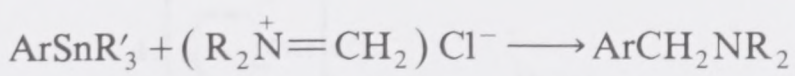
JACS *109* 6097, 6115 (1987)



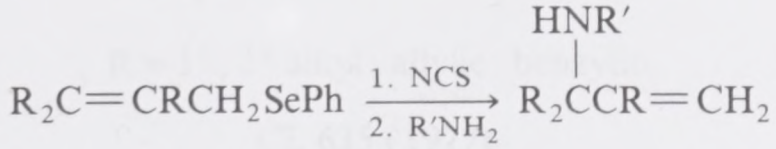
JACS *108* 3513 (1986)



TL *27* 5067 (1986)



TL *27* 5011 (1986)



JOC *51* 5243 (1986)

8. FROM ALCOHOLS

See page 397, Section 3, for amination via tosylates.

Review: Russ Chem Rev *49* 14 (1980)

$$ROH + HNMe_2 \xrightarrow[\text{cat } CuO,\ Cr_2O_3,\ Na_2O,\ SiO_2]{H_2,\ \Delta} RNMe_2$$

TL 1937 (1977)
Syn Commun *8* 27 (1978)

$$1^\circ\ ROH + ArNH_2 \longrightarrow ArNHR$$

Raney Ni — JACS *77* 4052 (1955)
Org Syn Coll Vol *4* 283 (1963)

KOH, Δ — Org Syn Coll Vol *4* 91 (1963)

$$1^\circ\ ROH + PhNH_2 \xrightarrow[\text{cat } RuCl_2(PPh_3)_3]{\Delta} PhNR_2$$

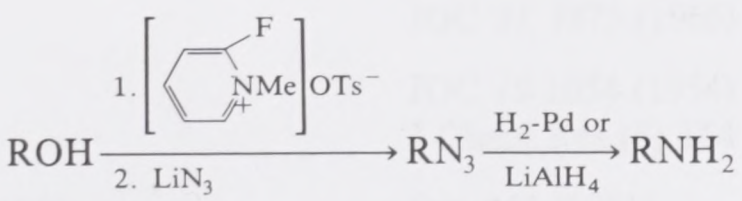
TL *22* 2667 (1981)

$$ROH + HNR^1R^2 \xrightarrow[\text{Raney Ni}]{Al(O\text{-}t\text{-}Bu)_3} RNR^1R^2$$

Syn 722 (1977)

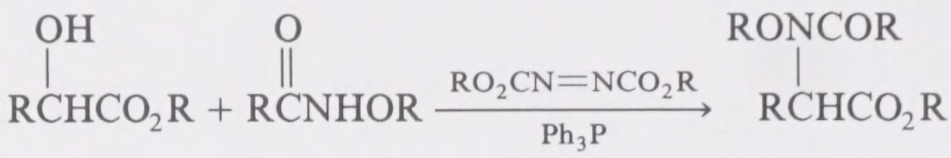
$$1^\circ\ ROH \xrightarrow{NaH} \xrightarrow[R^1R^2NH]{(Ph_3\overset{+}{P}NMePh)I^-} RNR^1R^2$$

TL 471 (1975)

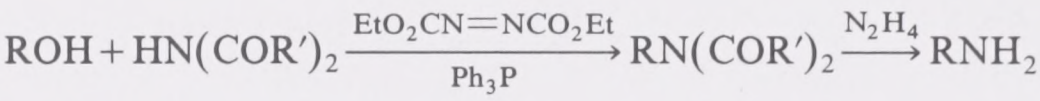


R = 1°, 2° alkyl; allylic; benzylic

CL 635 (1977)

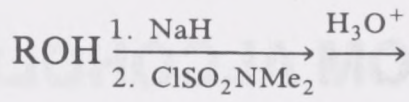


JOC *52* 4978 (1987)



JACS *94* 679 (1972)
JOC *52* 5127 (1987)

For further alkylations of imides see page 397, Section 3.



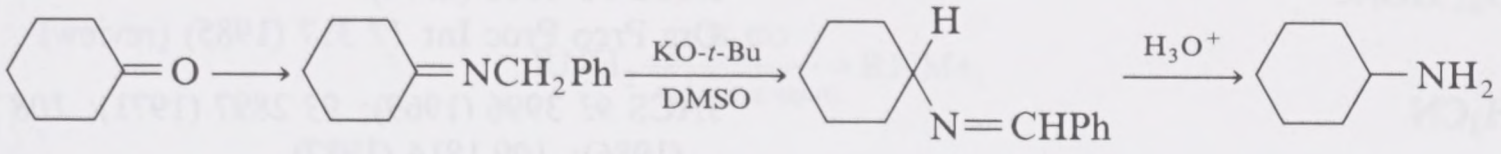
R = allylic, benzylic

JACS *87* 5261 (1965)

JOC *25* 214 (1960)

9. FROM ALDEHYDES AND KETONES

1. Transamination



Can J Chem *48* 570 (1970)

2. Reductive Amination

$$R_2C{=}O + R'NH_2 \rightleftharpoons R_2C{=}NR' \xrightarrow[\text{agent}]{\text{reducing}} R_2CHNHR'$$

Reviews:

Org Rxs *4* 174 (1948)
M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 16
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley and Sons, New York (1978), Chpt 10
Russ Chem Rev *49* 14 (1980)
JOC *48* 3412 (1983) (stereoselectivity of various metal hydride reagents)

Reducing agent	
H_2, cat Pd-C	JOC *51* 3635 (1986)
H_2, cat Pt-C	JOC *31* 3875 (1966)
Raney nickel	JOC *19* 1054 (1954) J Chem Res (S) 164 (1981)
i-PrOH, Na_2CO_3, cat $ClRh(PPh_3)_3$	Syn 442 (1981)
HCO_2H	Org Rxs *5* 301 (1949)
Zn, acid	JACS *62* 2159 (1940); *63* 972, 2843 (1941)

Reducing agent (*continued*)	
BH_3	JOC *30* 2877 (1965) BSCF 4439 (1970)
$BH_3 \cdot py$, HOAc	JCS Perkin I 717 (1984)
$BH_3 \cdot Me_2NH$	JOC *26* 1437 (1961)
$BH_3 \cdot Me_2NH$, HOAc	JOC *48* 3412 (1983)
$BH_3 \cdot t\text{-}BuNH_2$	TL *22* 3447 (1981)
$BH_3 \cdot t\text{-}BuNH_2$, HOAc	JOC *48* 3412 (1983) TL *25* 695 (1984)
$(CF_3CO_2)_2BH$	JOC *46* 355 (1981)
$NaBH_4$	JOC *22* 1068 (1957); *28* 3259 (1963); *48* 3412 (1983); *51* 486 (1986) Chem Pharm Bull *17* 98 (1969) JACS *107* 7524 (1985) TL *28* 749 (1987)
$NaBH_4$, HOAc	JACS *96* 7812 (1974) Org Prep Proc Int *17* 317 (1985) (review)
$NaBH_3CN$	JACS *91* 3996 (1969); *93* 2897 (1971); *108* 1039 (1986); *109* 1814 (1987) Syn 135 (1975) (review) CC 1088 (1979) Org Prep Proc Int *11* 201 (1979) (review) TL *21* 789 (1980); *22* 3447 (1981) JOC *48* 3412 (1983); *52* 5044 (1987)
$NaBH_3CN$, HOAc	Org Prep Proc Int *17* 317 (1985) (review)
$NaBH_3CN$, HCl	TL *23* 1929 (1982)
$NaBH_3CN$, $ZnCl_2$	JOC *50* 1927 (1985)
$(n\text{-}Bu_4N)BH_3CN$	JOC *46* 3571 (1981)
$NaHBR_2CN$	TL *22* 3447 (1981)
$LiHBEt_3$	TL *22* 3447 (1981); *25* 695 (1984)
$LiHB(sec\text{-}Bu)_3$	TL *22* 3447 (1981); *25* 695 (1984) JOC *48* 3412 (1983)
$NaHB(O_2CCHR^1NR^2COR^3)_3$ (chiral)	TL *22* 3869 (1981)
$i\text{-}Bu_2AlH$	TL *23* 1929 (1982)
$i\text{-}Bu_2AlH$, *n*-BuLi	TL *23* 1929 (1982)
$LiAlH_4$	Org Rxs *6* 469 (1951) JOC *23* 535 (1958) BSCF 4439 (1970) TL *23* 1929 (1982)
$LiAlH_4$; $NaOCH_3$, $Ti(O\text{-}i\text{-}Pr)_4$, LiCl, $NiCl_2$, $TiCl_3$, $TiCl_4$, $BF_3 \cdot OEt_2$, or R_3Al (R = Me, *i*-Bu)	TL *23* 1929 (1982)

$Mg(AlH_4)_2$	TL *23* 1929 (1982)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	JOC *48* 3412 (1983)
Et_3SiH, CF_3CO_2H	Bull Acad Sci USSR, Div Chem Sci 1345 (1968)
$MFe(CO)_4H$ (M = Na, K)	Syn 733 (1974) BCSJ *49* 1378 (1976) Tetr *42* 259 (1986)
$LaNi_5H_6$	JOC *52* 5695 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)
$Na_2S_2O_4$, H_2O, Δ	Austral J Chem *32* 201 (1979)
PhSeH	TL *21* 3385 (1980)
C_8K	Syn 30 (1979)

$$R_2NH \xrightarrow[NaBH_4\text{-}CF_3CO_2H \text{ or } NaBH_3CN\text{-}HOAc]{\text{paraformaldehyde}} R_2NCH_3$$

Syn 709 (1987)

$$RNH_2 \xrightarrow[\text{reducing agent}]{H_2CO} RNMe_2$$

Reducing agent

$MFe(CO)_4H$ (M = Na, K)	Syn 733 (1974)
$NaBH_4$, MeOH	TL 261 (1973)
$NaBH_3CN$, $ZnCl_2$, MeOH	JOC *50* 1927 (1985)
$NaBH_3CN$, CH_3CN	JOC *37* 1673 (1972)
$NaBH_4$, H_2SO_4	Anal Chem *48* 484 (1976) Syn 743 (1980)

$$R_2C{=}O \xrightarrow[NaBH_3CN \text{ or } LiBH_3CN]{NH_4OAc} R_2CHNH_2$$

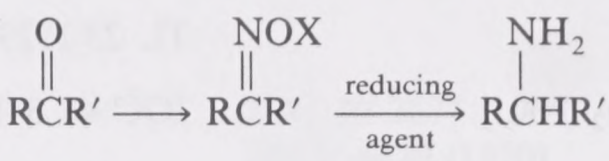
JACS *93* 2897 (1971); *107* 8066 (1985)
Syn 135 (1975) (review)
JOC *52* 2615, 4274 (1987)
TL *28* 773 (1987)

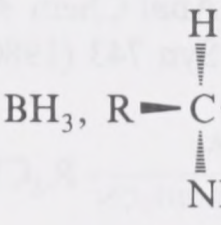
$$R_2C{=}O \xrightarrow[HCO_2H]{(NH_4)O_2CH} \xrightarrow{H_2O} R_2CHNH_2$$

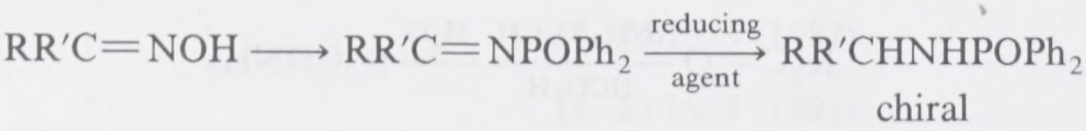
$$RNH_2 \xrightarrow[HCO_2H]{H_2CO} RN(CH_3)_2$$

Reviews:

Org Rxs *5* 301 (1949)
"The Acyclic Aliphatic Tertiary Amines," p 44

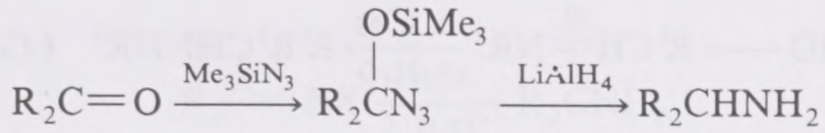


X	Reducing Agent	
H	H_2, cat PtO_2	JOC *31* 1342, 1346 (1966); *37* 335 (1972)
	H_2, cat Pd-C	Org Syn Coll Vol *5* 376 (1973)
	H_2, cat Pd-C, HCl	JACS *50* 3370 (1928)
	Raney nickel	JCS C 531 (1966)
	Na, EtOH	Org Syn Coll Vol *2* 318 (1943)
	Na, *n*-PrOH	JOC *31* 1342, 1346 (1966)
	Na(Hg), HOAc	JACS *71* 2257 (1949)
	Al(Hg), H_2O	Angew Int *18* 78 (1979)
	BH_3	JOC *34* 1817 (1969); *51* 105 (1986)
		JCS Perkin I 643 (1979)
	$NaBH_2S_3$	Can J Chem *48* 735 (1970)
	$NaBH_4$, $TiCl_4$	Syn 695 (1980)
	$NaBH_4$, $NiCl_2 \cdot 6\ H_2O$	Ber *117* 856 (1984)
	$NaBH_4$, MoO_3	Chem Ber *117* 856 (1984)
		TL *28* 5497 (1987)
	$LiAlH_4$	JOC *17* 294 (1952); *50* 3948 (1985); *52* 4717 (1987)
		J Biol Chem *211* 725 (1954)
CH_3	BH_3	JOC *34* 1817 (1969)
		JCS Perkin I 643 (1979)
	$NaBH_3(O_2CCF_3)$	Chem Pharm Bull *26* 2897 (1978)
$PhCH_2$	$LiAlH_4$	JOC *52* 3211 (1987)
R, $SiMe_3$	BH_3, 	JCS Perkin I 2039, 2615 (polymer-supported reagent) (1985)
$POPh_2$	$NaBH_4/H^+$	TL *28* 5619 (1987)
	$LiHB(sec\text{-}Bu)_3/H^+$	TL *28* 5619 (1987)
Ac, Ts	BH_3	CC 590 (1967)

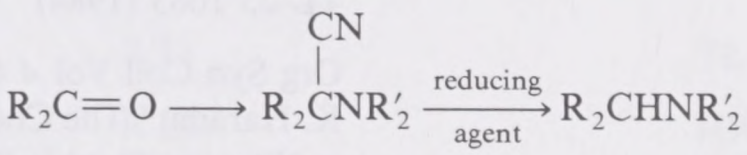


Reducing agent: $LiAlH_4$-(R) or (S)-bi-2-naphthol; $LiAlH_4$-1,2(S)-diphenyl-3(R)-methyl-4-(dimethylamino)-2-butanol; or potassium 9-0-(1,2 : 5,6-di-0-isopropylidene-α-D-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane

JOC *52* 702 (1987)

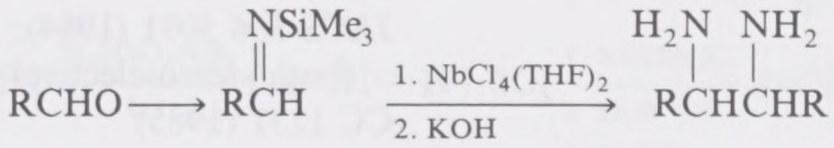


TL 2737 (1977)



Reducing agent

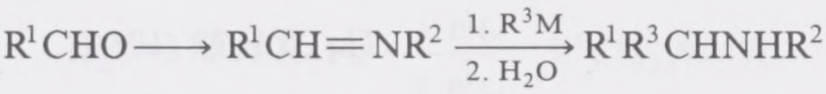
Na, NH_3	TL 61 (1976) Chem Pharm Bull *25* 2689 (1977)
$NaBH_4$	TL 3105 (1969)



JACS *109* 3152 (1987)

3. Alkylative Amination

See also page 401, Section 4.



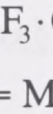
Reviews:

Chem Rev *63* 489 (1963)
K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970)

R^3M

RLi	K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 271–272 (review)
$CpFe(CO)(PPh_3)COCH_2M$ (M = Li, $AlEt_2$)	JACS *106* 441 (1984)
$RCHLiCO_2R$	See page 873, Section 2.
$LiCH(NCS)CO_2R$, $BF_3 \cdot OEt_2$	TL *24* 4503 (1983) JACS *105* 5946 (1983)
RLi [R = Me, $RC{\equiv}C$, $RCOCH_2$, CH_2CO_2R, $RCHNO_2$, $CH(NCO)CO_2Et$]; $BF_3 \cdot OEt_2$	TL *24* 4503 (1983)
$CH_3CH{=}CHCH_2M$ [M = Li, MgCl, B ), $Sn(n\text{-}Bu)_3$ ($BF_3 \cdot OEt_2$)]	JOC *50* 3115 (1985) (diastereoselectivity)

$$R^1CHO \longrightarrow R^1CH{=}NR^2 \xrightarrow[2.\ H_2O]{1.\ R^3M} R^1R^3CHNHR^2 \quad (\textit{Continued})$$

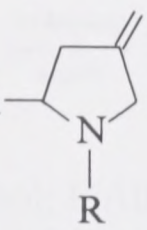
R^3M	
$RC{\equiv}CLi$, $BF_3{\cdot}OEt_2$	TL *25* 1083 (1984)
RMgX	Org Syn Coll Vol *4* 605 (1963) K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 266–271 Syn 223 (1987)
RMgBr (R = Et, Ph); $BF_3{\cdot}OEt_2$	TL *24* 4503 (1983)
$H_2C{=}CHCH_2M$ [M = MgCl, $B(OMe)_2$, B  , $(AlEt_3)MgCl$, $Ti(O\text{-}i\text{-}Pr)_3$, ZnBr]	CC 814 (1985)
$RCH{=}CHCH_2B$ 	JACS *106* 5031 (1984); *108* 7778 (1986) (both stereoselective) CC 1131 (1985)
$H_2C{=}CHCH_2B(OR)_2$	Ann 2000 (1983)
$Me_3SiC{\equiv}CCHRB$  or $Me_3SiC(B$  $){=}C{=}CHR$	JOC *50* 2193 (1985)
n-$Bu_3SnCH_2CH{=}CHR$ (R = H, Me); $BF_3{\cdot}OEt_2$ or $TiCl_4$	JOC *50* 146 (1985)
$Cp_2TiCHRCH{=}CH_2$	JOMC *224* 327 (1982)
RCu, $BF_3{\cdot}OEt_2$	TL *25* 1079 (1984)
R_2CuLi, $BF_3{\cdot}OEt_2$	TL *25* 1079 (1984)
$RCH(ZnBr)CO_2ZnBr$	JOMC *231* 185 (1982)

$$R^1CH{=}NR^2 \xrightarrow[2.\ R_2CO]{1.\ NbCl_3(DME)} R^1CH(NHR^2)CR_2(OH)$$

JACS *109* 6551 (1987)

$$ArCH{=}NAr + H_2C{=}C(OSiMe_3)R \xrightarrow{\text{cat } Me_3SiOTf} ArCH(NHAr)CH_2C(=O)R$$

CC 1053 (1987)

$$RCH{=}NR \longrightarrow$$


$Me_3SiCH_2C(=CH_2)CH_2OMs$, cat $Ni[P(OEt)_3]_4$ or $Pd_2(DBA)_3{\cdot}HCCl_3$-8 $P(OEt)_3$	CC 1201 (1986)
n-$Bu_3SnCH_2C(=CH_2)CH_2OAc$, $BF_3{\cdot}OEt_2$ / Pd catalyst	JACS *107* 1778 (1985)

$$R_2C{=}NX \xrightarrow[2.\ H_3O^+]{1.\ R'M} R_2\underset{\displaystyle R'}{\underset{|}{C}}NH_2$$

X	R′M	
OCH_2Ph	R′Li	TL *28* 4973 (1987)
SAr	R′Li	JOC *42* 398 (1977)
	$H_2C{=}CHCH_2B(OR)_2$	TL *27* 2079 (1986)
$SiMe_3$	R′Li	Syn 461 (1982) JOC *48* 289 (1983)
	R′MgX	JOC *48* 289 (1983)
COR	R′Li	Angew *21* 203 (1982)

$$ArCHO \xrightarrow[H^+]{H_2NSO_2NH_2} (ArCH{=}N)_2SO_2 \xrightarrow[2.\ H_2O,\ py\\ 3.\ NaOH]{1.\ RLi(MgX)} \underset{\displaystyle R}{\underset{|}{Ar}}CHNH_2$$

TL *27* 3957 (1986)

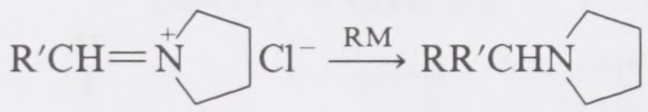
$$RCHO \longrightarrow RCH{=}NOR'' \xrightarrow[2\ R'MgX]{2\ R'Li\ or} \xrightarrow{BH_3} RR'CHNH_2$$

R = aryl > alkyl

TL *27* 3033 (1986)

$$H_2C{=}NOCH_2Ph \xrightarrow[2.\ R^2Li\\ 3.\ R^3X]{1.\ R^1Li} R^1CH_2NR^2R^3$$

CC 305 (1987)



RM	
RMgX (R = 1° alkyl)	BSCF II 148 (1983)
$RC{\equiv}CMgX$	BSCF II 21 (1983)
RMgX (R = 1° alkyl, vinylic, CH_2CO_2R'), RZnX [R = CH_2COX (X = CO_2Et, $CONEt_2$), $CR(CO_2Et)_2$]	BSCF II 395 (1982)

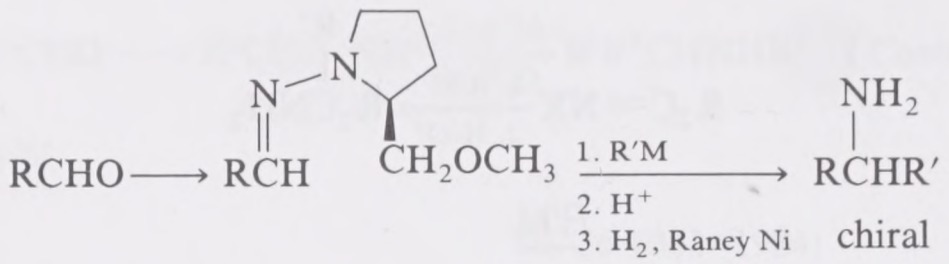
$$RCHO \longrightarrow RCH{=}NNMe_2 \xrightarrow[2.\ H_2,\ cat\ PtO_2]{1.\ R'Li} RCHR'NH_2$$

JACS *108* 8265 (1986)

$$\underset{\displaystyle O}{\underset{\|}{Ar}}CH \longrightarrow \underset{\displaystyle NNR'_2}{\underset{\|}{Ar}}CH \xrightarrow[2.\ H_2,\ cat\ Pd\text{-}C]{1.\ RMgX} \underset{\displaystyle NH_2}{\underset{|}{Ar}}CHR$$

chiral chiral

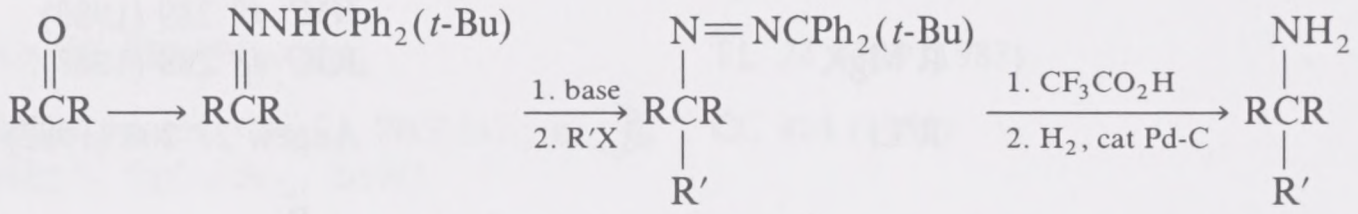
CC 668 (1979)



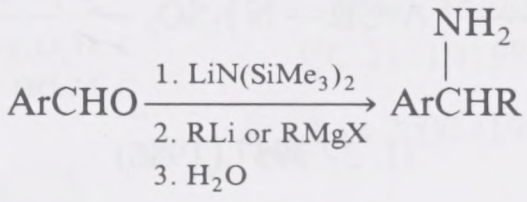
R′M

RLi — Angew Int *25* 1109 (1986)

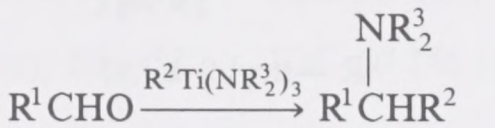
$RCeCl_2$ — JACS *109* 2224 (1987)



CC 176 (1986)

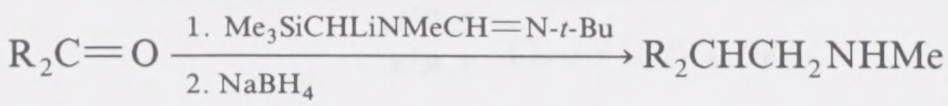


JOC *48* 289 (1983); *52* 4665 (1987)

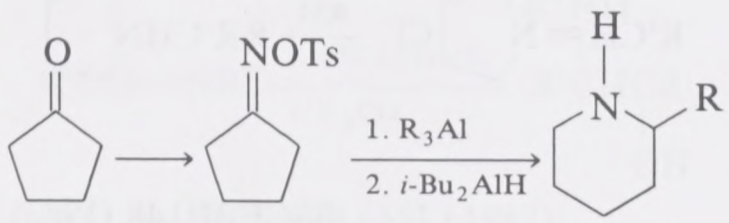


R^1 = *t*-Bu, aryl, vinylic

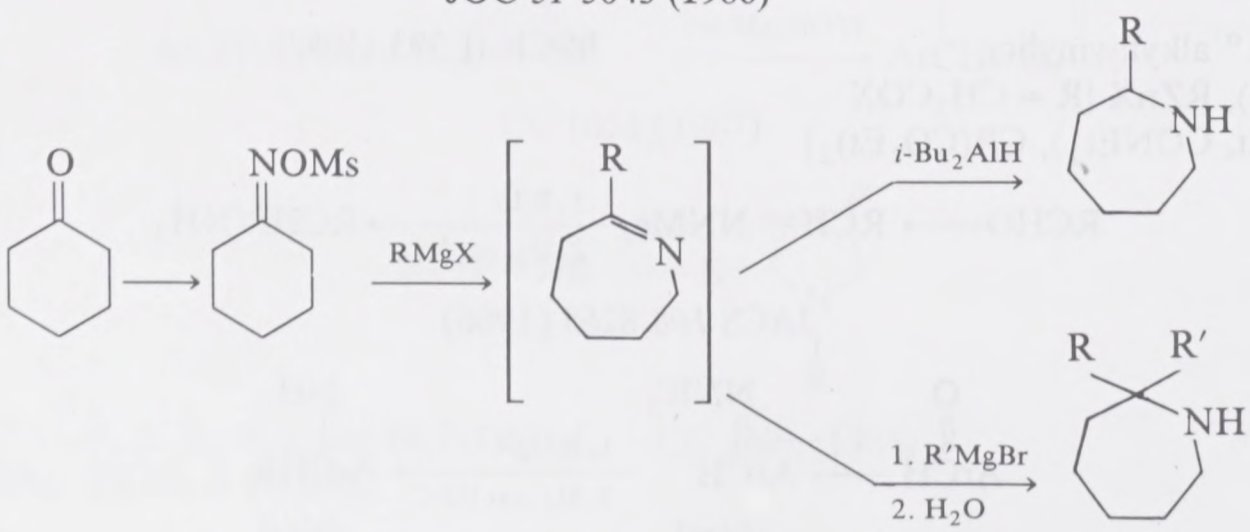
Helv *65* 2598 (1982)



JACS *104* 877 (1982)



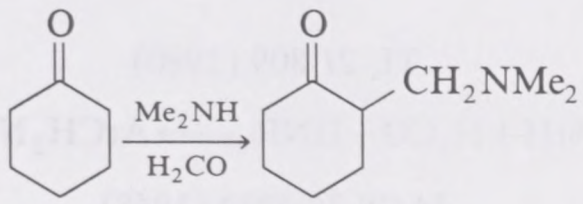
JACS *103* 7368 (1981)
JOC *51* 5043 (1986)



R′ = allyl, propargyl

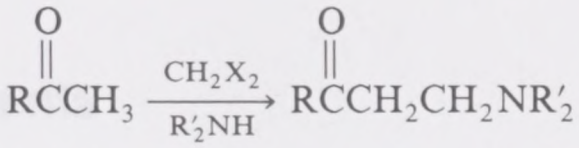
TL *23* 3395 (1982)

4. Mannich and Related Reactions

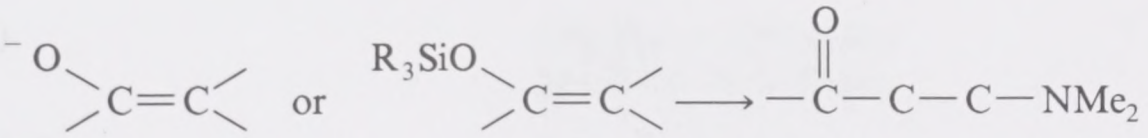


Reviews:

Org Rxs *1* 303 (1942); *7* 99 (1953)
Org Syn Coll Vol *3* 305 (1955)
Angew *68* 265 (1956)
B. Riechert, "Die Mannich Reaktion," Springer, Berlin (1959)
H. Hellman and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, Weinheim, Germany (1960)
Syn 703 (1973)



Angew Int *21* 922 (1982)
BCSJ *55* 1331 (1982)



$(Me_2\overset{+}{N}{=}CH_2)O_2CCF_3^-$

JACS *99* 944 (1977)
Tetr *35* 613 (1979)
Org Rxs *59* 153 (1980)

$(Me_2\overset{+}{N}{=}CH_2)Cl^-$

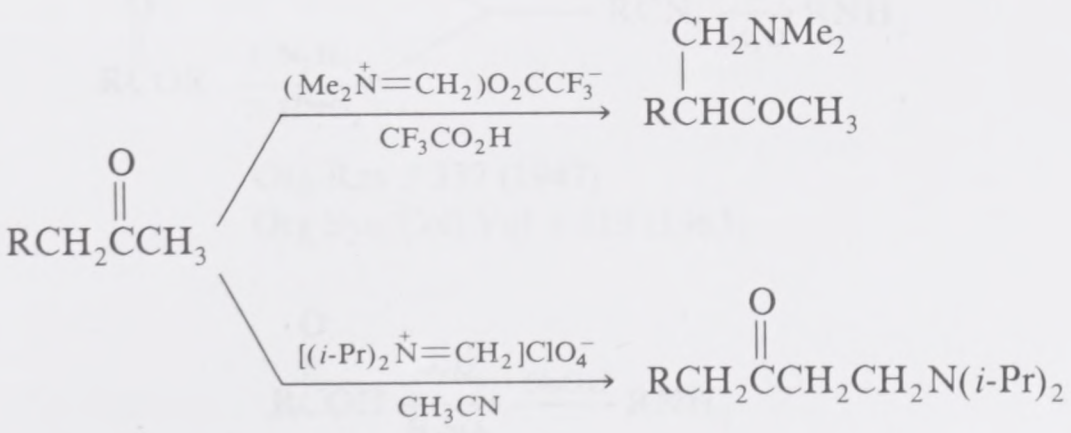
TL *23* 703, 1419 (1982)
JACS *107* 2474 (1985) (on enol carbonate)

$(Me_2\overset{+}{N}{=}CH_2)I^-$

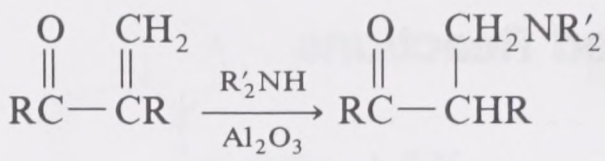
JACS *95* 602 (1973) (on enol borinates); *98* 6715 (1976); *99* 6066 (1977)
TL 1621 (1977); *21* 805 (1980)

$Me_2NCH_2NMe_2$, $ClCH_2I$

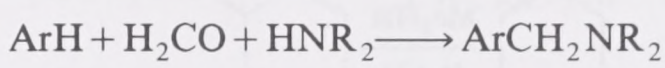
CL 1213 (1980)
BCSJ *55* 534 (1982)



Tetr *33* 295 (1977)



TL *21* 809 (1980)

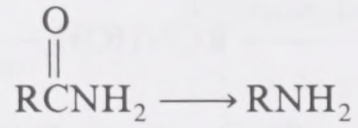


JACS *70* 4232 (1948)

10. FROM CARBOXYLIC ACIDS AND ACID DERIVATIVES

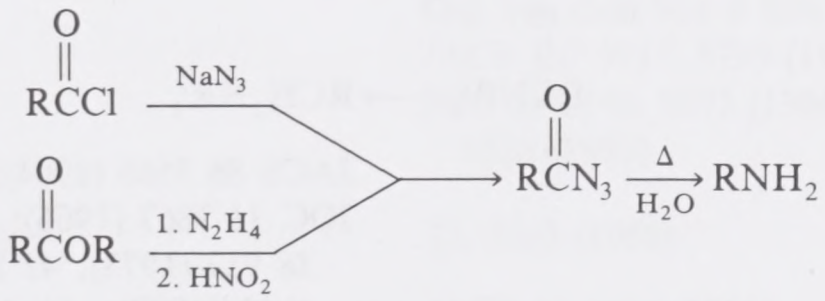
1. Molecular Rearrangements

Hoffman

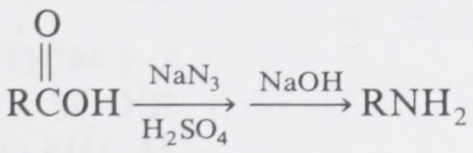


NaOX (X = Br, I)	Org Rxs *3* 267 (1946) JACS *71* 3929 (1949)
PhIO, HCO_2H, H_2O	Syn 538 (1983)
$PhI(O_2CCF_3)_2$	Biochem Biophys Res Commun *80* 1 (1978) JOC *44* 1746 (1979); *49* 4272, 4277 (1984)
$PhI(OH)OTs/OH^-$	JOC *51* 2669 (1986)
$Pb(OAc)_4/R'XH$ (X = O, NH)/H^+ or OH^-	CC 161 (1965) TL 4039 (1965) JACS *87* 1141 (1965) JOC *40* 3554 (1975)

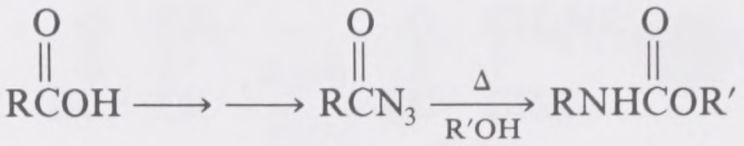
Curtius



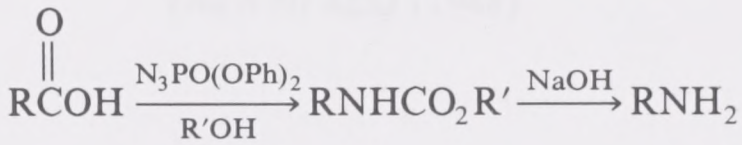
Org Rxs *3* 337 (1947)
Org Syn Coll Vol *4* 819 (1963)



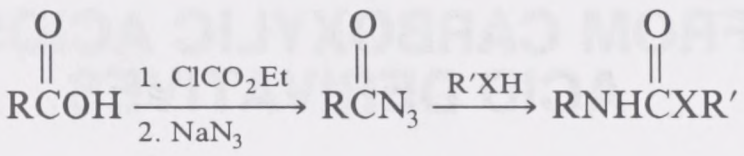
Org Syn Coll Vol *5* 273 (173)



Org Rxs *3* 337 (1947) (review)
TL *25* 3515 (1984)
JOC *51* 3007, 5123 (1986); *52* 4875 (1987)



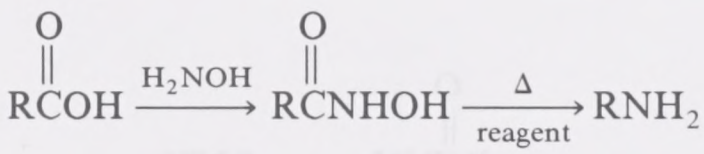
JACS *94* 6203 (1972)
Tetr *30* 2151 (1974)



X = O, NH

JOC *26* 3511 (1961); *43* 2164 (1978)

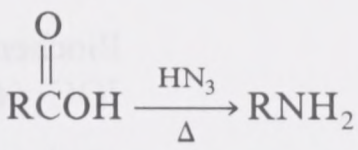
Lossen



Reagent: $SOCl_2$, Ac_2O, P_2O_5, or PPA

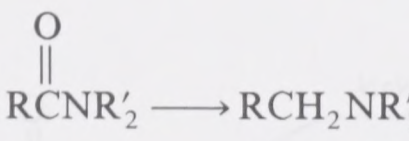
Chem Rev *33* 242 (1943)

Schmidt



Org Rxs *3* 307 (1946)

2. Reduction of Amides and Imides

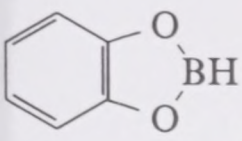


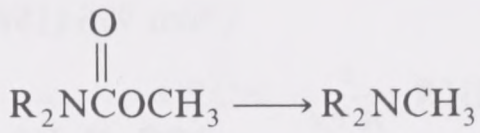
BH_3

JACS *86* 3566 (1964); *107* 1421 (1985)
JOC *31* 3867 (1966); *33* 3637 (1968); *38* 912 (1973); *41* 149 (1976); *42* 4148 (1977); *51* 4856, 5373 (1986); *52* 5742 (1987)
J Heterocyclic Chem *5* 875 (1968)
Syn 752 (1978)

$BH_3 \cdot SMe_2$

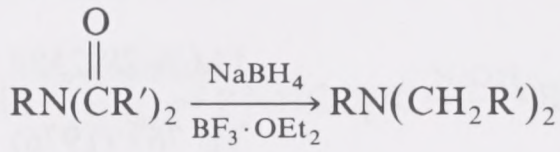
Syn 441 (1981)
JOC *47* 3153 (1982)
TL 3315 (1982); *28* 4601 (1987)

$BH_3 \cdot SMe_2$, $BF_3 \cdot OEt_2$	Syn 996 (1981)
	JOC *42* 512 (1977)
$NaBH_4$, $TiCl_4$	Syn 695 (1980)
$NaBH_4$, $CoCl_2 \cdot 6\ H_2O$	TL 4555 (1969)
$NaBH_4$, $AlCl_3$	JACS *78* 2582 (1956)
$NaBH_4$, HOAc	TL 763 (1976)
$NaBH_4$, $MeSO_3H$	JOC *46* 2579 (1981)
$NaBH_4$, py	Chem Pharm Bull *17* 98 (1969)
$NaBH_4$, CF_3CH_2OH	JOC *50* 3948 (1985)
$(Et_3O)BF_4/NaBH_4$	TL 61 (1968)
$(Et_3O)BF_4/NaBH_4$, $SnCl_4$	Syn 652 (1977)
$POCl_3/NaBH_4$	TL 219 (1976); *27* 2103 (1986) JOC *42* 2082 (1977)
$POCl_3$/Zn, EtOH	Experientia *33* 101 (1977)
$HSCH_2CH_2SH/NaBH_4$	Chem Ind 322 (1976)
$LiBH_4$, MeOH, diglyme	JOC *51* 4000 (1986)
$LiBH_3CN$	JACS *91* 3996 (1969)
AlH_3	JACS *88* 1464 (1966); *90* 2927 (1968); *109* 6124 (1987)
i-Bu_2AlH	Bull Acad Sci USSR, Div Chem Sci 2046 (1959) Ann *623* 9 (1959) Syn 617 (1975) JOC *50* 2443 (1985); *52* 5745 (1987)
$LiAlH_4$	Org Rxs *6* 469 (1941) Helv *31* 1397 (1948); *38* 2036 (1955) Org Syn Coll Vol *4* 339, 354, 564 (1963) JACS *107* 5717, 5739 (1985); *108* 2034 (1986) JOC *51* 3140, 5373 (1986); *52* 1844, 2018, 5320 (1987)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	TL 3303 (1968)
$LiHAl(OCH_3)_3$	JACS *87* 5614 (1965)
P_4S_{10}/Raney nickel	JOC *16* 131 (1951)
$P_2S_5/MeI/NaBH_4$ or $NaBH_3CN$	JOC *46* 3730 (1981)
(*p*-$MeOC_6H_4)_2P_2S_4/(Et_3O)BF_4/$ $NaBH_4$	TL *21* 4061 (1980)



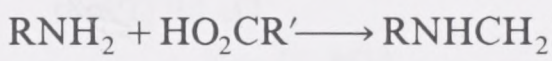
BH_3 JOC *46* 2431 (1981)

$LiAlH_4$ J Label Compds *6* 261 (1970)
JOC *46* 2431 (1981); *51* 3295 (1986)



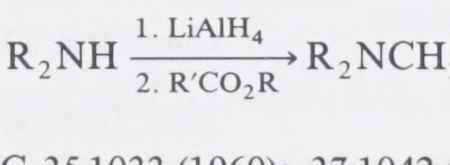
Ann 461 (1979)

3. Reductive Alkylation

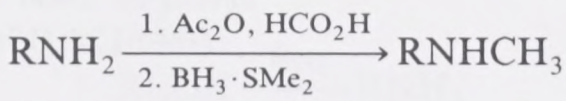


$NaBH_4$ JACS *96* 7812 (1974)
JOC *40* 3453 (1975)
Syn 766 (1978)

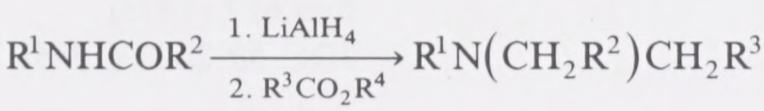
$BH_3 \cdot NMe_3$ Syn 1013 (1983)

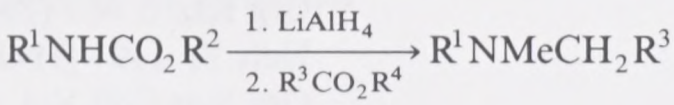


JOC *25* 1033 (1960); *27* 1042 (1962)
Syn 608 (1975)

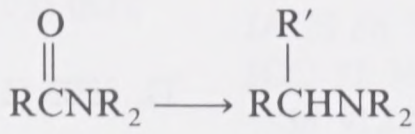


TL *23* 3315 (1982)





TL 3395 (1979)



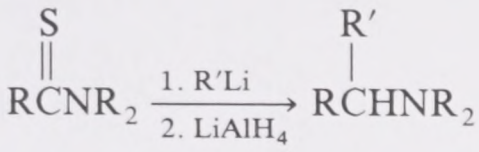
n-PrMgBr/$NaBH_3CN$ (R′ = *n*-Pr; lactam) JACS *107* 5534 (1985)

$ArLi/BH_3 \cdot SMe_2$ JOC *50* 2719 (1985)

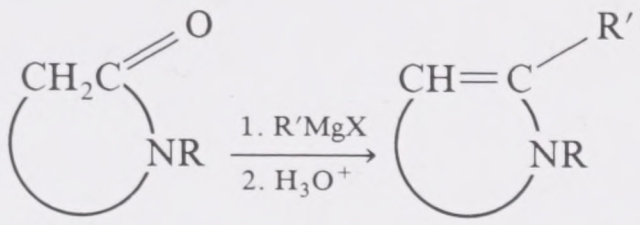
$ArLi/LiAlH_4$ or $BH_3 \cdot SMe_2$ or $NaBH_4$-CF_3CO_2H (R′ = Ar) JOC *50* 3885 (1985)

$ArLi/NaBH_3CN$ (R′ = Ar; lactams) JOC *45* 3664 (1980)

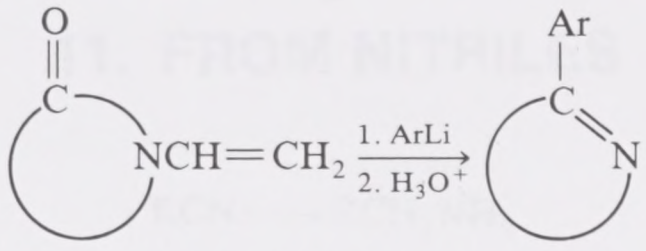
$RC{\equiv}CBF_2/LiAlH_4$ (R′ = $RC{\equiv}C$; lactams) TL *24* 1719 (1983)



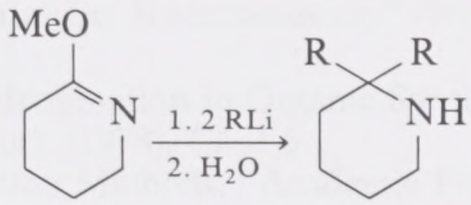
TL *28* 1529 (1987)



Coll Czech Chem Commun *7* 482 (1935); *8* 533 (1936)
JACS *55* 295, 2543 (1933); *64* 2588 (1942); *79* 5279 (1957)

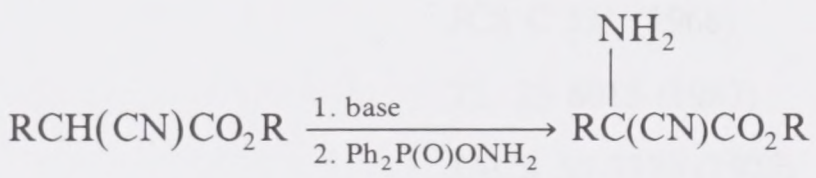


Syn 242 (1977)
JOC *47* 3652 (1982)



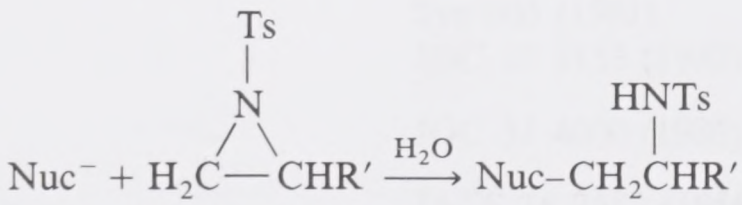
JACS *109* 4940 (1987)

4. α-Amination



TL *23* 5399 (1982); *28* 4385 (1987)

5. Ring Opening of *N*-Tosyl Aziridines



$Nuc^- = R_2CuLi$; $R_2CuLi, BF_3 \cdot OEt_2$; $(R_2CuCN)Li_2$; $H_2C{=}CHCH_2MgCl$; $RC{\equiv}CLi$;
$NaN_3, BF_3 \cdot OEt_2$; $LiBr, BF_3 \cdot OEt_2$; Li_2NiBr_4; Li_2CuCl_4; NaSPh; NaSH

TL *27* 4157 (1986); *28* 3341 (1987)

11. FROM NITRILES

$$RCN \longrightarrow RCH_2NH_2$$

Reviews:

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 12
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley and Sons, New York (1978), Chpt 6
P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 7

H_2, cat $HRh(PPr^i_3)_3$	CC 870 (1979)
H_2, cat Ni	Org Syn Coll Vol *3* 229, 358, 720 (1955) JOC *25* 1658 (1960) JCS C 531 (1966)
H_2, cat Raney Ni	TL *28* 6015 (1987)
H_2, cat Pd	JACS *50* 3370 (1928) JCS 426 (1942)
H_2, cat PtO_2	JOC *37* 335 (1972)
BH_3	JACS *82* 681 (1960) JOC *51* 4856 (1986)
$BH_3 \cdot SMe_2$	Syn 605 (1981) JOC *47* 3153 (1982)
$LiBH_4$, MeOH, diglyme	JOC *51* 4000 (1986)
$NaBH_4$, $AlCl_3$	JACS *78* 2582 (1956)
$NaBH_4$, $CoCl_2 \cdot 6\ H_2O$	TL 4555 (1969) JACS *104* 6801 (1982); *108* 67 (1986)
KBH_4, cat $PdCl_2$	BSCF 1996 (1959)
$NaBH_3O_2CCF_3$	TL 2875 (1976)

$RCN \longrightarrow RCH_2NH_2$ (*Continued*)

$NaBH_3OH$	JOC *42* 3963 (1977)
AlH_3	JACS *90* 2927 (1968)
i-Bu_3Al	Ann *623* 9 (1959)
$LiAlH_4$	JACS *70* 3738 (1948); *77* 2544 (1955) Org Rxs *6* 469 (1951) JOC *52* 2301 (1987)
$LiAlH_4$, $AlCl_3$	JACS *77* 2544 (1955) Chem Pharm Bull *32* 873 (1984) Syn 40 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)

$$RCN \xrightarrow[2.\ NaBH_4]{1.\ (Et_3O)BF_4} RCH_2NHEt$$

JOC *34* 627 (1969)

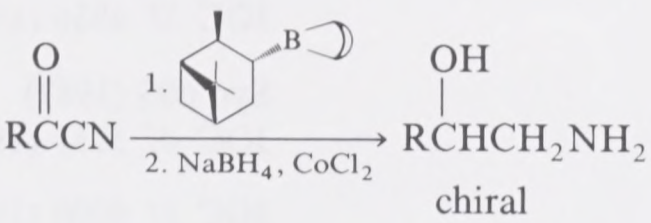
$$RCN \xrightarrow{R'MgX} \left[RC(=NH)R' \right] \xrightarrow[\text{agent}]{\text{reducing}} RCH(NH_2)R'$$

Reducing agent

Li, NH_3	JOC *51* 5338 (1986); *52* 3901 (1987) (CuBr catalyzed Grignard addition)
H_2, Pt catalyst	JACS *72* 876 (1950); *74* 4607 (1952)
$NaBH_4$	JACS *109* 3378 (1987)
$LiAlH_4$	JACS *75* 5898 (1953)

$$RCN \xrightarrow[3.\ KOH]{\substack{1.\ n\text{-}Bu_3SnH \\ 2.\ NbCl_4(THF)_2}} RCH(NH_2)CH(NH_2)R$$

JACS *109* 3152 (1987)



JOC *50* 3237 (1985)

ETHERS

GENERAL REFERENCES

A. Resowsky, "The Chemistry of Heterocyclic Compounds," Interscience, New York (1964), Vol 19, pt 1 (epoxides)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/3, G. Thieme, Stuttgart (1965): ethers, p 1; epoxides, p 367; oxetanes, p 489; tetrahydrofurans, p 517

"The Chemistry of the Ether Linkage," Ed. S. Patai, Interscience, New York (1967)

"The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues," Ed. S. Patai, J. Wiley, New York (1980)

Tetr *39* 2323 (1983) (Recent Advances in the Preparation and Synthetic Applications of Oxiranes)

Syn 629 (1984) (Synthetically Useful Reactions of Epoxides)

1. FROM OTHER ETHERS

See also page 455, Sections 1 and 2; and page 467, Section 3.

$$ArOSiMe_2(t\text{-}Bu) + RX \xrightarrow[DMF]{KF} ArOR$$

$$RX = PhCH_2Br, MeI$$

TL *28* 4139 (1987)

$$ArCH_2OMe \xrightarrow[2.\ E^+]{1.\ base} \underset{\displaystyle E}{\underset{|}{ArCH}}OMe$$

$$E^+ = RX, R_2CO, RCO_2Et$$

TL 4155 (1979)
JCS Perkin I 1652 (1981)

$$RM + XCH_2OR \longrightarrow RCH_2OR$$

X = halogen

RM	
RMgX	Ber *97* 636 (1964) Angew Int *6* 335 (1967) (review) TL *28* 2225 (1987)
R_2CuLi	TL *28* 2225 (1987)

$$\underset{\displaystyle Cl}{\underset{|}{RCHOR}} + H_2C{=}CHCH_2SiMe_3 \xrightarrow[(X = I,\ OTf)]{cat\ Me_3SiX} \underset{\displaystyle CH_2CH{=}CH_2}{\underset{|}{RCHOR}}$$

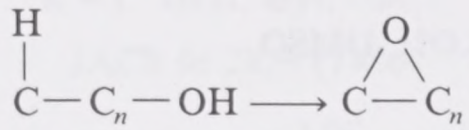
CL 409 (1983)

$$Br{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OR + H_2C{=}CHCH_2SiMe_3 \xrightarrow{AgBF_4} H_2C{=}CHCH_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OR$$

JOC *48* 1557 (1983)

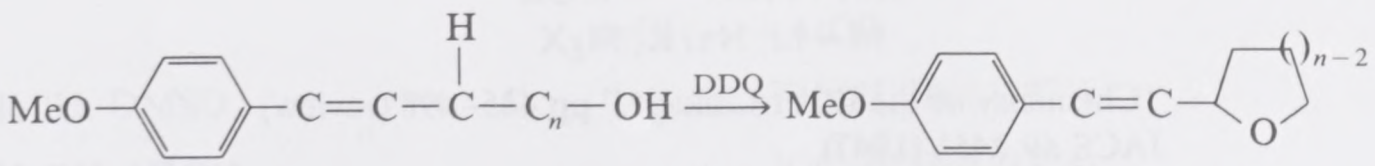
2. ALKYLATION OF ALCOHOLS AND PHENOLS

See also page 462, Section 5.



Review: Syn 501 (1971) (hypoiodite reaction)

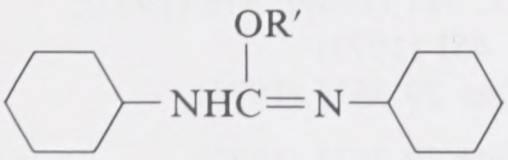
Reagent(s)	n	
Cl_2, Ag_2CO_3	3	Tetr *29* 3675 (1973)
Cl_2, HgO	3	Tetr *29* 3675 (1973)
Br_2, AgOAc	3	TL 1049 (1973) Tetr *29* 3675 (1973) JOC *47* 3559 (1982)
Br_2, Ag_2CO_3	3	Tetr *29* 3675 (1973)
Br_2, Ag_2O	3	JACS *86* 3905, 5503 (1964) JOC *30* 3216 (1965) CC 981 (1969); 976 (1970); 451 (1973) Tetr *29* 3675 (1973)
Br_2, HgO	3	Tetr *29* 3675 (1973)
I_2, HgO	3, 4	JACS *87* 1807 (1965); *109* 8117 (1987) CC 981 (1969) TL *24* 5915 (1983); *25* 2035 (1984); *28* 4951 (1987)
NIS, hν	3	JOC *50* 3015 (1985)
DDQ	3, 4	TL *28* 5175 (1987)



$n = 3, 4$

Heterocycles *23* 553 (1985)

$$ROH + R'X \xrightarrow{\text{reagent(s)}} ROR'$$

R′X	Reagent(s)	
MeI, EtX (X = Br, I), $PhCH_2X$ (X = Cl, Br)	Ag_2O	JCS *83* 1021, 1037 (1903) JACS *73* 4043 (1951); *108* 4603 (1986); *109* 6124 (1987) JOC *26* 4553 (1961); *27* 290 (1962); *52* 3889, 4647 (1987) JCS C 2372 (1969) TL *28* 4019, 5353 (1987)
MeCl, Me_2SO_4	NaOH, C_6H_6	Syn 123 (1979)
Me_2SO_4	NaOH, *n*-Bu_4NI	Angew Int *12* 846 (1973)
1° alkyl, benzylic chloride, $BrCH_2CO_2R$	NaOH, cat (*n*-Bu_4N)HSO_4	TL 3251 (1975); *28* 4143 (1987)
1° alkyl bromide and iodide	KOH, DMSO	Tetr *35* 2169 (1979)
R_2SO_4 (R = Me, Et)	KOH, DMSO	Syn 428 (1979)
MeI	NaH	TL 21 (1973) Syn 434 (1974) JACS *109* 3353 (1987)
$PhCH_2Br$	NaH, DMF	JOC *52* 4665 (1987)
1° alkyl bromide and iodide, $PhCH_2Cl$	NaH, HMPA	BSCF 1866 (1965)
1° alkyl bromide, benzylic chloride	cat $Ni(acac)_2$, Δ	Syn 803 (1977)
2,4-$Me_2C_6H_3CH_2Cl$	K_2CO_3, KI, CH_3CN	Syn 987 (1982)
1° alkyl iodide, $PhCH_2Br$	KF, alumina	BCSJ *55* 2504 (1982)
	—	Ber *99* 1479 (1966)
$[(R'O)_3\overset{+}{P}CH_3]BF_4^-$	—	JOC *49* 4877 (1984)

$$HO(CH_2)_nX \xrightarrow{\text{base}} (H_2C)_n\!\!\bigcirc\!\!O$$

"Heterocyclic Compounds," Ed. R. C. Elderfield, Wiley, New York (1950), Vol 1, p 8
JACS *72* 1593 (1950); *75* 4778 (1953)
JOC *52* 3860, 3883 (1987)
TL *28* 723, 1781, 2709 (1987)

$$R'X + MOR \longrightarrow R'OR$$
$$M = Li, Na, K, MgX$$

"Chemistry of the Ether Linkage," pp 445–498 (review)
JACS *69* 2451 (1947)
JCS 616 (1948)
JOC *43* 4682 (1978); *52* 4495 (1987)

$$ArX + KOR \xrightarrow{\Delta} ArOR$$

Org Syn Coll Vol *5* 926 (1973)

$$ArI + ArOH \xrightarrow[DMSO]{2\ KO\text{-}t\text{-}Bu} ArOAr$$

JOC *47* 4374 (1982)

$$ArX + HOR \xrightarrow{Cu\ catalyst} ArOR$$

Tetr *40* 1433 (1984) (review)

$$ArX + NaOAr \xrightarrow[\Delta]{Cu} ArOAr$$

Org Syn Coll Vol *2* 445 (1943)
Chem Rev *38* 405 (1946) (review)
JOC *29* 3624 (1964); *32* 2501 (1967)
Tetr *40* 1433 (1984) (review)

$$R'X + CuOR \longrightarrow R'OR$$

R = 1° alkyl, aryl, vinylic

JACS *96* 2829 (1974)

$$RX + (ArO)_3PO \xrightarrow[DMF]{KOH} ArOR$$

$RX = n\text{-}C_8H_{17}Br$, $PhCH_2Br$, ArCl

Syn 828 (1982)

$$ROH \longrightarrow ROR'$$

CH_2N_2, cat $BF_3 \cdot OEt_2$	JACS *80* 2584 (1958) Angew *70* 105 (1958)
CH_2N_2 or CH_3CHN_2, cat $BF_3 \cdot OEt_2$	Z Naturforsch B *14* 209 (1959)
$RCHN_2$, cat $AlCl_3$ or $BF_3 \cdot OEt_2$	Ann *677* 55 (1964)
CH_2N_2, cat HBF_4	JACS *80* 2584 (1958) Tetr *6* 36 (1959)
CH_2N_2, silica gel	TL 4405 (1979)
$RCOCHN_2$, cat $BF_3 \cdot OEt_2$	JACS *72* 5161 (1950)

$$ROH + (R'_3O)BF_4 \longrightarrow ROR'$$

R' = Me, Et

JOC *42* 1801 (1977)

$$ROH + Ph_3Bi(OAc)_2 \xrightarrow[X = Cl,\ OAc]{cat\ CuX_2} ROPh$$

J Gen Chem USSR *55* 2232 (1985)

$$ArOH \longrightarrow ArOR$$

MeI, KOH, DMSO	Tetr *35* 2169 (1979)
MeI, NaOH, HMPA	JOC *39* 1968 (1974)
Me_2SO_4, NaOH	Org Syn Coll Vol *1* 58 (1941)

1° RBr, K_2CO_3	Org Syn Coll Vol *3* 140 (1955)
RX (1° RCl, RBr, RI; 2° RBr), $KF\text{-}Al_2O_3$	CL 755 (1959) BCSJ *55* 2504 (1982)
RX (1° RI, allyl or benzyl Br), KF-Celite	CL 45 (1979)
RX (R = 1°, 2° alkyl; benzylic), Et_4NF, DMF	Can J Chem *57* 1887 (1979)
RX (R = 1°, 2° alkyl; allylic; benzylic), NaOH, $(PhCH_2NEt_3)Br$, H_2O, CH_2Cl_2	Tetr *30* 1379 (1974)
RX (R = 1°, 2° alkyl; allylic; benzylic), anion exchange resin	Syn 113 (1977)
RX (3° RCl), cat $Ni(acac)_2$, $NaHCO_3$	Syn 186 (1982)
$(Me_3O)BF_4$	J Prakt Chem 867 (1964)
$Me_2\overset{+}{S}O\overline{C}H_2$	TL 867 (1964)
$(Me_3S)I$, Ag_2O	Ann *611* 117 (1958)
Me_3SOH	JOC *44* 638 (1979)
Me_3SeOH	TL 1787 (1979)
ROH (R = 1°, 2° alkyl), $EtO_2CN{=}NCO_2Et$, PPh_3	JCS Perkin I 461 (1975) Chem Ind 281 (1975) TL 2243 (1978) Heterocycles *20* 1975 (1983) JOC *50* 3095 (1985)
ROH (R = 2° allylic), $EtO_2CN{=}NCO_2Et$, $n\text{-}Bu_3P$	JACS *107* 3891 (1985)
CH_2N_2, cat HBF_4	JACS *80* 2584 (1958) Tetr *6* 36 (1959) Org Syn Coll Vol *5* 245 (1973)
$Ph_4BiO_2CCF_3$ (R = Ph)	CC 503 (1981)
$Ph_3Bi(OAc)_2$, cat Cu or $Cu(OAc)_2$ (R = Ph)	J Gen Chem USSR *55* 2232 (1985) TL *27* 3619 (1986)

$$2\ ROH \longrightarrow ROR$$

Reagent	R	
H_3PO_4	benzhydryl	JACS *73* 2630 (1951)
$ZnCl_2$	2° allylic; 1° or 2° benzylic	JOC *52* 3917 (1987)

$CuSO_4$, 180°C	1° alkyl	Acta Chem Scand B *31* 721 (1977)
DMSO, 175°C	1°, 2° benzylic	JOC *42* 2012 (1977)

$$ROH + R'OH \longrightarrow ROR'$$

H^+	JACS *54* 2088 (1932); *70* 2400 (1948) Org Syn Coll Vol *4* 72 (1963)
DMSO, 175°C (R = benzylic)	JOC *42* 2012 (1977)
$ZnCl_2$ (R = allylic or benzylic)	JOC *52* 3917 (1987)

$$HO(CH_2)_nOH \longrightarrow (H_2C)_n \quad O$$

DMSO, Δ ($n = 4, 5$)	JOC *28* 1388 (1963); *29* 123 (1964)
various Brönsted and Lewis acids ($n = 4$)	Tetr *37* 2149 (1981)
$ZnCl_2$ ($n = 4, 5, 11$)	JOC *52* 3917 (1987)
Nafion-H ($n = 4$–7)	Syn 474 (1981)
Amberlyst 15, Δ ($n = 5$)	Syn 208 (1973)
$(CH_3)_2C(OAc)COBr$/Amberlite IRA-400, CH_3OH ($n = 2$)	TL *24* 367 (1984); *28* 4959 (1987)
n-BuLi/TsCl/*n*-BuLi ($n = 3$)	Syn 550 (1981)
TsOH, Δ ($n = 4$)	Org Syn Coll Vol *4* 534 (1963) JOC *37* 1947 (1972)
Me_2SO_4 ($n = 4$)	JACS *103* 7398 (1981)
TsCl, py ($n = 4, 5$)	JACS *72* 1593 (1950) TL 2731 (1975) JOC *45* 1828 (1980)
$(Me_2\overset{+}{N}{=}CCl_2)Cl^-$/NaOMe or MeLi ($n = 2$)	TL *27* 4697 (1986) (from cis diols)
$[(CH_3)_3CN{=}C{=}\overset{CH_3}{\overset{\vert}{N}}C(CH_3)_3]BF_4^-/Et_3N$, Δ	JACS *97* 464 (1975)
$EtO_2CN{=}NCO_2Et$, PPh_3 ($n = 2$–6)	BCSJ *49* 510 (1976) TL 5153 (1978) JOC *48* 5396 (1983)
CCl_4, PPh_3, (K_2CO_3) ($n = 2, 4, 5$)	JOC *46* 3361 (1981); *47* 3980 (1982); *48* 5396 (1983) TL *24* 661 (1983)
CCl_4, $P(NMe)_2)_3$/(NaOR) ($n = 2, 3$)	TL 4459 (1973); 3459 (1975) Tetr *32* 1283 (1976)
$P(OEt)_5$ ($n = 4$)	JACS *93* 4004 (1971)

$Ph_3P(OEt)_2$ ($n = 2, 4, 5$)

Phosphorus *1* 151 (1971)
JACS *93* 4004 (1971); *107* 5210 (1985)
JOC *48* 5396 (1983); *52* 525 (1987)
(1,4-oxathianes)
Phosphorus and Sulfur *26* 15 (1986)

$Ph_3P(OCH_2CMe_3)_2$ ($n = 2, 4, 5$)

JOC *51* 5490 (1986)

polymer-$PPh_2(OEt)_2$ ($n = 2, 4, 5$)

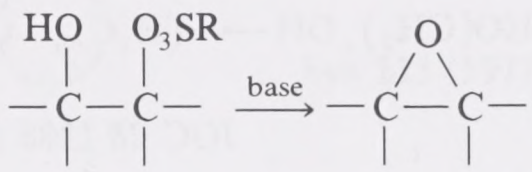
JOC *50* 5007 (1985)

$Ph_2S[OC(CF_3)_2Ph]_2$ ($n = 2, 4, 5$)

JACS *96* 4604 (1974)
Helv *61* 822 (1978)

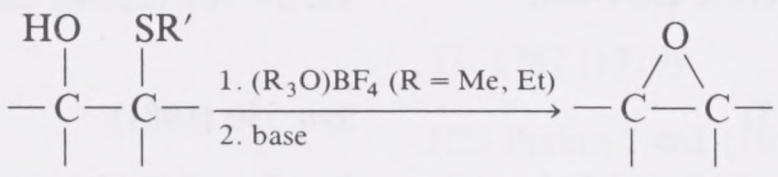
Al_2O_3 ($n = 4$–6)

BCSJ *53* 3031 (1980)

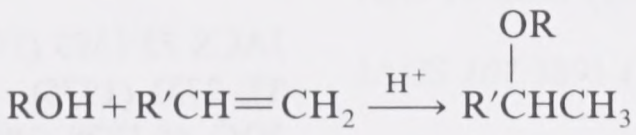


R = Me, *p*-Tol

Helv *30* 1929 (1947)
Angew Int *18* 958 (1979)
JACS *102* 7984 (1980); *109* 6205 (1987)
TL *24* 4539 (1983); *28* 2619, 2627, 2863, 6191 (1987)
JOC *50* 5687 (1985); *52* 2378 (1987)

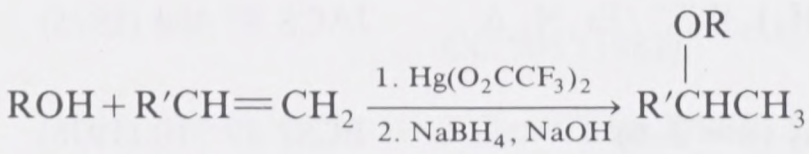


JOC *50* 5687 (1985)
TL *27* 6329 (1986); *28* 797, 5677 (1987)

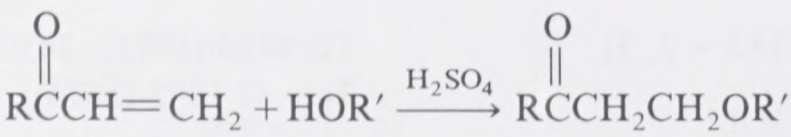


R = alkyl, aryl

Ind Eng Chem *43* 1596 (1951)
JOC *20* 1232 (1955); *21* 247 (1956)



TL 5165 (1967)
JACS *91* 5646 (1969); *105* 7407 (1983)
R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 3 (review)



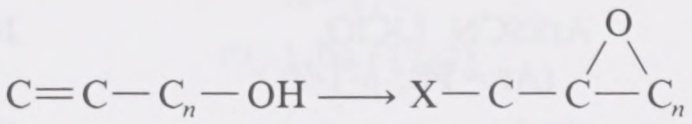
JOC *17* 962 (1952)

$$NCCH{=}CH_2 + ROH \xrightarrow{NaOR} NCCH_2CH_2OR$$

JCS 535 (1945)

$$RCH{=}CH_2 \xrightarrow{BH_3} \xrightarrow[NaClO_4,\ NaOCH_3,\ CH_3OH]{\text{electrolysis}} RCH_2CH_2OCH_3$$

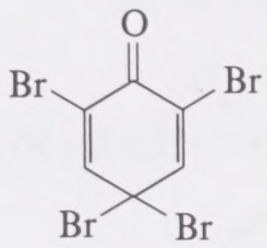
CL 1021 (1974)

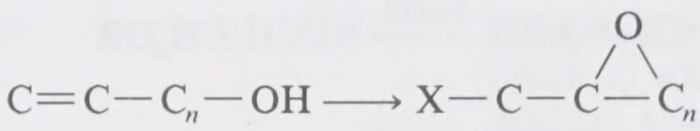


Review:

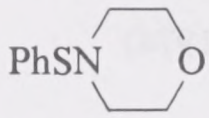
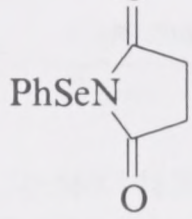
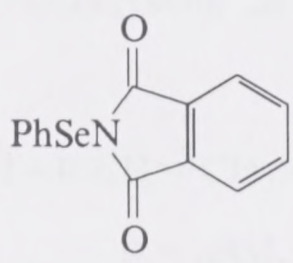
P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 6

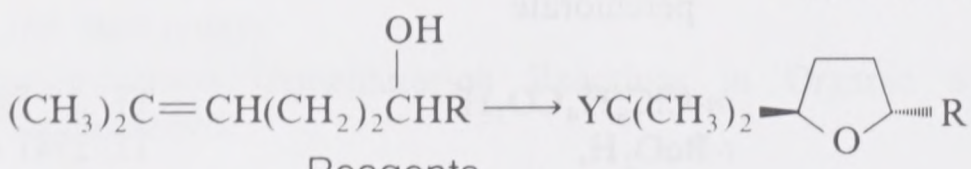
For intermolecular reactions see page 325, Section 4.

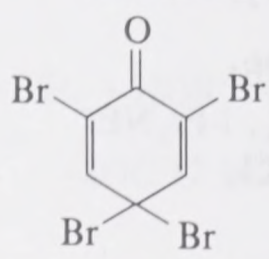
X	Reagent(s)	
Br	Br_2	JOC *52* 4191 (1987)
	NBS	CC 264 (1969)
		JACS *93* 5813 (1971); *101* 260 (1979); *106* 2668 (1984)
		JOC *52* 1686, 4191 (1987)
		TL *28* 3065 (1987)
		JACS *106* 2668 (1984)
I	I_2	JOC *51* 2230 (1986)
	I_2, $NaHCO_3$	JACS *103* 3963 (1981); *107* 3271 (1985)
		TL *26* 2885 (1985)
		JOC *52* 4062, 4191, 4449 (1987)
	I_2, KI	Proc Acad Sci USSR, Chem Sec *146* 787 (1962)
	I_2, KI, $NaHCO_3$	BCSJ *53* 3383 (1980)
	I_2, HgO, hν	TL *28* 4011 (1987)
	NIS	JOC *51* 2230 (1986)
	iodonium dicollidine perchlorate	JOC *52* 4062 (1987)
OH	*m*-$ClC_6H_4CO_3H$	TL *28* 5501 (1987)
	t-BuO_2H, cat $VO(acac)_2$/HOAc	TL 2741 (1978); *28* 5501, 5665 (1987)
MeS	MeSCl, *i*-Pr_2NEt	TL *28* 523 (1987)
	$(MeSSMe_2)BF_4$, *i*-Pr_2NEt	TL *26* 6159 (1985)
	$(MeSSMe_2)SbCl_6$	JCS Perkin I 3106 (1981)



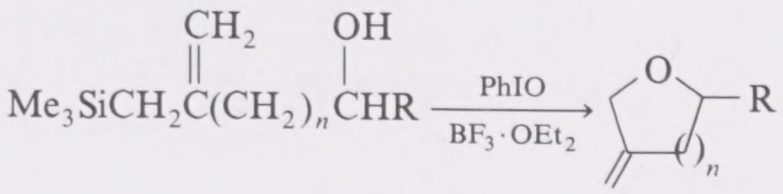
(*Continued*)

X	Reagent(s)	
ArS	*n*-BuLi/PhSCl	TL *28* 523 (1987)
	PhSCl, *i*-Pr_2NEt	TL *28* 523 (1987)
	 CF_3SO_3H	CC 1280 (1987)
	ArSSCN, $LiClO_4$ (Ar = Ph, *p*-Tol)	JOC USSR *14* 2265 (1978)
PhSe	$(PhSe)_2$, electrolysis	TL *28* 4343 (1987)
	PhSeCl	CC 725 (1977) TL 1257 (1977); *21* 129 (1980) (allenic alcohols) Can J Chem *55* 3894 (1977) JACS *102* 3784 (1980); *106* 3353 (1984); *109* 2082 (1987) Tetr *37* 4097 (1981) (review) JOC *51* 495 (1986); *52* 4191 (1987)
	PhSeBr	Helv *61* 3075 (1978)
	PhSeOTf	TL *28* 4297, 4415 (1987)
		Tetr *37* 4097 (1981) (review)
		Tetr *37* 4097 (1981) (review) JACS *107* 7792 (1985) JOC *52* 4191 (1987)
ArTe	$(ArTeO)_2O/NH_2NH_2$	TL *28* 1281 (1987)
$ArTeX_2$	$ArTeX_3$ (X = Cl, Br)	TL *28* 5611 (1987)
HgX	HgX_2	R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 3 (review) JOC *52* 4191 (1987)



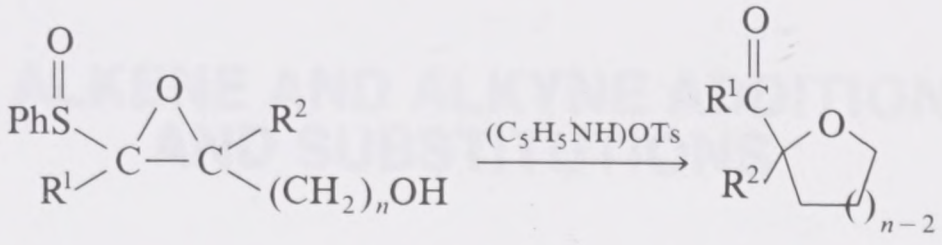
Y	Reagents	
OH	 /$AgBF_4$, MeOH	JACS *106* 2668 (1984)

OAc, OH, OCH_3, ONO_2 or NHAc	TlX_3 (X = O_2CCF_3, NO_3); HOAc, H_2O, CH_3OH, THF or CH_3CN	JOC *50* 2416 (1985)

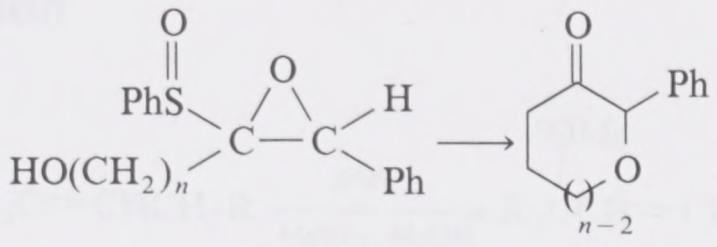


$n = 1, 2$

CC 1108 (1982)

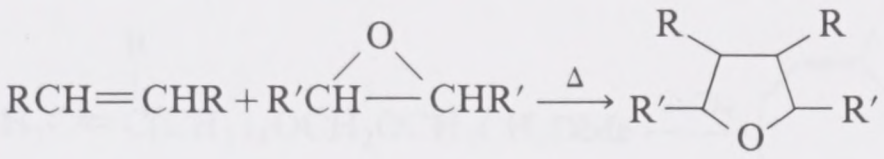


$n = 3, 4, 11$



$n = 3, 4$

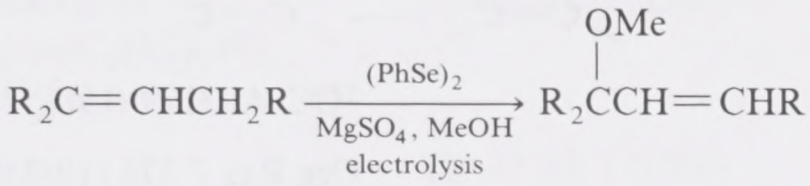
TL *28* 2603 (1987)



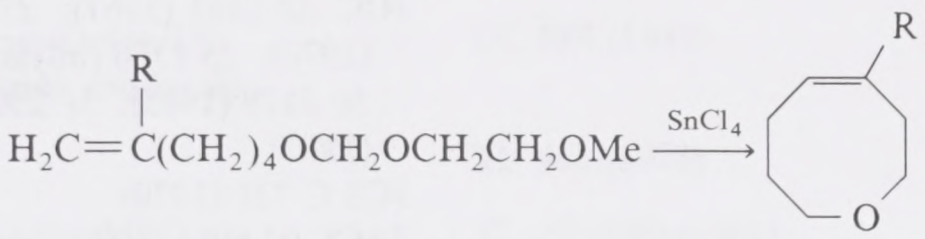
JACS *87* 3657, 3665 (1965)
CC 1190, 1192 (1971); 134 (1984)
JOC *41* 2654 (1976); *43* 4256 (1978)
Angew Int *16* 572 (1977) (review)
TL *21* 4909 (1980) (intramolecular); *23* 4665 (1982) (intramolecular); *25* 1137 (1984) (intramolecular); *28* 3155 (1987)
Ber *117* 2157 (1984)

3. ALKENE AND ALKYNE ADDITIONS AND SUBSTITUTIONS

1. Alkene Substitution



JACS *103* 4606 (1981)

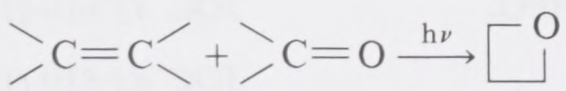


R = H, $SiMe_3$

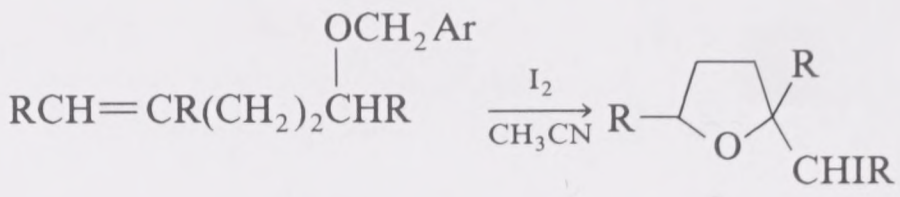
JACS *108* 3516 (1986)

2. Alkene Addition

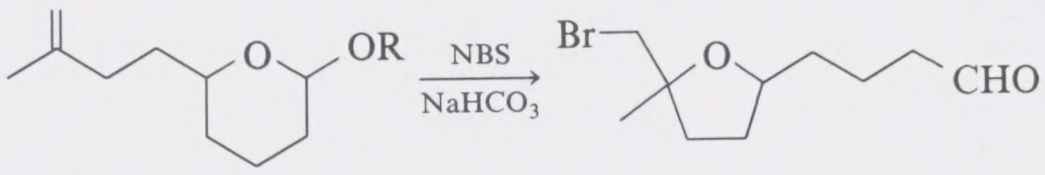
See also page 445, Section 2.



Adv Photochem *6* 301 (1968) (review)
Org Photochem *5* 1 (1981) (review)
TL *24* 3217 (1983); *28* 5933, 6151 (1987) (both intramolecular)
H. A. J. Carless, "Synthesis Organic Photochemistry," Ed. W. M. Horspool, Plenum Press, New York (1984), p 425 (review)
JACS *106* 4186, 7200 (1984)
CC 667 (1984)
Ber *118* 1485 (1985); *120* 307 (1987)
Science *227* 857 (1985)
Angew Int *24* 877 (1985)

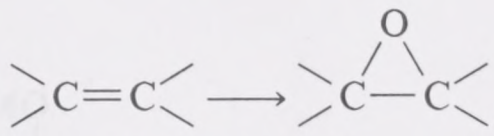


JACS *103* 3963 (1981)
TL *27* 2195 (1986)
JOC *52* 320, 5067 (1987)

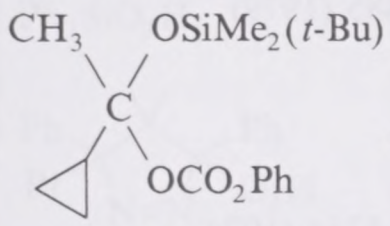
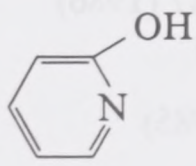
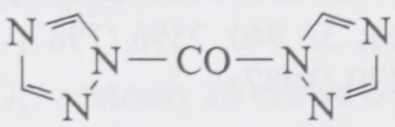


CC 1462 (1987)

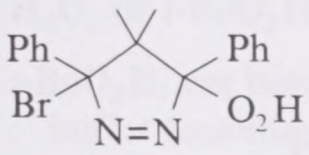
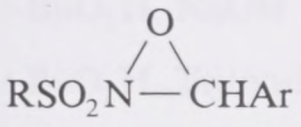
3. Epoxidation of Alkenes



enzymes	JOC *46* 3129 (1981)
RCO_3H	Org Rxs *7* 378 (1953) (review)
m-$ClC_6H_4CO_3H$	TL 849 (1965); 4347, 4733 (1979) JOC *32* 1363 (1967); *35* 251 (1970); *36* 3832 (1970); *38* 1380 (allylic alcohols), 1385 (1973); *50* 2179 (1985); *51* 2505 (1986); *52* 4495, 4511 (1987) JCS C 731 (1970) JACS *92* 6914 (1970); *96* 5254 (1974); *106* 7854 (1984); *109* 5437, 7838 (1987) CC 421 (1976) JCS Perkin I 2885 (1982)
m-$ClC_6H_4CO_3H$, $NaHCO_3$	JOC *38* 2267 (1973) TL 427 (1977)
m-$ClC_6H_4CO_3H$, Na_2CO_3	JOC *52* 4647 (1987)
m-$ClC_6H_4CO_3H$, K_2CO_3 or K_2HPO_4	JOC *43* 610 (1978)
m-$ClC_6H_4CO_3H$, phosphate	JOC *43* 610 (1978); *44* 1351 (1979)
m-$ClC_6H_4CO_3H$, KF	TL *22* 3895 (1981)
3,5-$(NO_2)_2C_6H_3CO_3H$	JOC *43* 3163 (1978) JACS *106* 7854 (1984) TL *28* 2771 (1987)
3,5-$(NO_2)_2C_6H_3CO_3H$, Na_2HPO_4	JACS *109* 5167, 5280 (1987)
o-$HO_2CC_6H_4CO_3H$	JACS *82* 6373 (1960)
CH_3CO_3H, NaOAc	JCS Perkin I 2909 (1982)

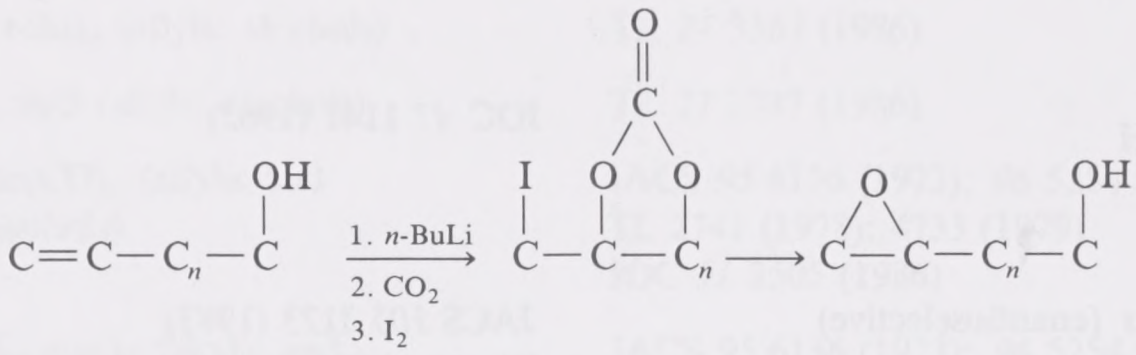
CF_3CO_3H	JACS *106* 7854 (1984)
$PhCH_2OCO_3H$	JOC *39* 3054 (1974)
 , cat $Cu(O_2CCF_3)_2$	TL *28* 1909 (1987)
H_2O_2, $ArSeO_2H$	JOC *42* 2035 (1977) Syn 299 (1978)
H_2O_2, cat $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$	Syn Commun *14* 865 (1984) (allylic alcohols)
H_2O_2, $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$	JOC *52* 1868 (1987)
H_2O_2, cat tungstic acid, Et_3N (allylic alcohols)	JACS *87* 734 (1965)
H_2O_2, cat tungstic acid, NaOAc or Me_3NO	TL *27* 707, 711 (1986)
H_2O_2, cat $Na_2WO_4 \cdot 2\ H_2O$, H_3PO_4, H_2SO_4, phase transfer catalyst	JOC *48* 3831 (1983)
H_2O_2; $[(n\text{-}C_8H_{17})_3NCH_3]HWO_4$ or $[(n\text{-}C_8H_{17})_3NCH_3]_2WO_4$; $(n\text{-}C_8H_{17})_3PO$, $PhPO_3H_2$ or $C_{12}H_{25}PO_3H_2$	TL *28* 2237 (1987)
H_2O_2, cat $(PhCH_2PPh_3)_2W_2O_{11}$	TL *27* 2617 (1986)
H_2O_2, cat $(n\text{-}Bu_4N)_2W_2O_{11}$	TL *27* 2617 (1986)
H_2O_2, cat chloromanganese(tetra-2,6-dichlorophenylporphyrin), imidazole	CC 888 (1985)
H_2O_2, $Fe(acac)_3$	TL 948 (1978)
H_2O_2, $Cl_2CHCOCHCl_2$, Na_2HPO_4	TL *22* 2089 (1981)
H_2O_2, CF_3COCF_3	JACS *101* 2484 (1979)
H_2O_2, RCN (R = Me, Ph)	JOC *26* 659 (1961); *32* 1363 (1967); *36* 3832 (1971); *50* 2179 (1985) Tetr *18* 763 (1962) JCS C 731 (1970) Org Syn *60* 63 (1981) JACS *106* 3539 (1984)
H_2O_2, $(EtO)_2POCN$, 	Chem Pharm Bull *29* 1774 (1981)
90% H_2O_2, $CH_3C(OEt)_3$	TL 1001 (1979)
H_2O_2, 	CC 711 (1974) JOC *43* 180 (1978); *44* 1485 (1979)
H_2O_2, EtO_2CCl, Na_2HPO_4 or $Na_3PO_4 \cdot 12\ H_2O$	JOC *44* 2569 (1979)

H_2O_2, ArNCO (Ar = Ph, *p*-ClC_6H_4)	TL 2029 (1970)
H_2O_2, PhCONCO	CC 711 (1974) JOC *43* 180 (1978); *44* 1485 (1979)
t-BuO_2H, $Al(O\text{-}t\text{-}Bu)_3$ (allylic alcohols)	TL *27* 3387 (1986)
t-BuO_2H, *n*-Bu_2SnO (allylic alcohols)	TL *27* 3387 (1986)
t-BuO_2H, cat $Mo(CO)_6$ (allylic and homoallylic alcohols)	JACS *95* 6136 (1973); *96* 5254 (1974) TL 2741 (1978); 4733 (1979) JOC *51* 2505 (1986)
t-BuO_2H, cat $VO(acac)_2$ (allylic and homoallylic alcohols)	JACS *95* 6136 (1973); *96* 5254 (1974); *103* 7690 (1981); *107* 256 (1985) CC 421 (1976) TL 2741 (1978); 4733 (1979); *27* 3353, 3387, 6035, 6071 (1986); *28* 1439, 2099, 6191 (1987) JOC *51* 4728 (1986); *52* 34, 4495, 4511, 4898 (1987)
$PhCMe_2O_2H$, cat $VO(acac)_2$, 2,6-lutidine (allylic alcohol)	JACS *109* 6187 (1987)
t-BuO_2H, cat $VOSO_4$ or $MoO_2(acac)_2$, (+)-3-trifluoroacetylcamphor	Z Chem *18* 218 (1978)
t-BuO_2H, $Ti(O\text{-}i\text{-}Pr)_4$ (allylic alcohols)	TL *27* 3387 (1986)
t-BuO_2H, $Ti(O\text{-}i\text{-}Pr)_4$, dialkyl tartrate (allylic alcohols, Sharpless, enantioselective)	JACS *102* 5974 (1980); *103* 464, 6237 (1981); *107* 1691, 7515, 7967 (1985); *108* 2776 (1986); *109* 1525, 2205, 4718 (1987) Tetr *37* 3873 (1981) Pure Appl Chem *55* 589 (1983) Org Syn *63* 66 (1984) JOC *49* 1707 (1984); *50* 3752 (1985); *51* 934, 1077, 4726, 4728 (1986); *52* 685, 940, 1106 (1987) "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1985), Vol 5, Chpts 7, 8 (reviews) CC 1759 (1985); 1237, 1732 (1986) TL *27* 3535, 4913 (1986); *28* 375, 1139, 2033, 3075, 4019, 4985, 6351 (1987) Syn 89 (1986) (review) Angew Int *25* 87 (1986) CL 1523 (1987)
t-BuO_2H, $Ti(O\text{-}i\text{-}Pr)_4$, diethyl tartrate, cat CaH_2, cat silica gel (enantioselective)	TL *26* 6221 (1985)
t-BuO_2H, cat $Ti(O\text{-}i\text{-}Pr)_4$, cat dialkyl tartrate, molecular sieves (allylic alcohols, enantioselective)	TL *27* 5791 (1986); *28* 131, 5129, 5205 (1987) JOC *51* 1922 (1986); *52* 940, 2596 (1987) JACS *109* 5765, 8120 (1987)
$PhCMe_2O_2H$, cat $Ti(O\text{-}i\text{-}Pr)_4$, cat diisopropyl tartrate, molecular sieves (allylic alcohols, enantioselective)	JOC *51* 3710, 5413 (1986); *52* 4973 (1987) JACS *109* 5765, 8120 (1987)

t-BuO_2H, $Zr(O\text{-}i\text{-}Pr)_4$, dicyclohexyltartramide (homoallylic alcohols, enantioselective)	CL 85 (1987)
Ph_3SiO_2H	TL 4337 (1979)
	JOC *47* 1141 (1982)
 (enantioselective)	JACS *105* 3123 (1983) TL *27* 5079 (1986)
O_2, CH_3CHO	Syn 711 (1977)
O_2, PhCOCHOHPh, hν	JACS *103* 2049 (1981)
O_2, cat $[Fe_3O(O_2CR)_6L_3]^+$	JACS *104* 6450 (1982)
O_2, cat Mn porphyrin	JACS *106* 6871 (1984)
$MO_5 \cdot HMPT$ (M = Mo, W)	JOC *51* 2374 (1986) TL *28* 6191 (1987) (homoallylic i-Pr_3Si ethers)
PhIO, Co catalyst	JOC *52* 4545 (1987)
NBS, H_2O/base	TL 121 (1962) JACS *85* 3295 (1963); *90* 5618 (1969) JOC *38* 1385 (1973); *51* 5447 (1986); *52* 4505 (1987) JCS Perkin I 2909 (1982)
NIS, H_2O/DBU	JOC *51* 2505 (1986)
$CH_3CONHBr$, H_2O/NaOH	JOC *51* 3407 (1986)
$CH_3CONHBr$, H_2O/K_2CO_3	JOC *52* 2860 (1987)
1,3-dibromo-5,5-dimethylhydantoin, H_2O/NaOH	TL *27* 4403 (1986)
I_2, H_2O, HI/NaOH	JCS C 928 (1970)
I_2, Ag_2O, H_2O	TL 207 (1976) JOC *51* 3023 (1986)
NaOCl, cat Mn porphyrin acetate, R_4NCl, py	JACS *106* 6668 (1984)
$KHSO_5$, acetone, 18-crown-6	JOC *45* 4758 (1980)
$KHSO_5$, CH_3COCH_3, Na_2(EDTA), 18-crown-6, CH_2Cl_2, H_2O	JOC *47* 2670 (1982)

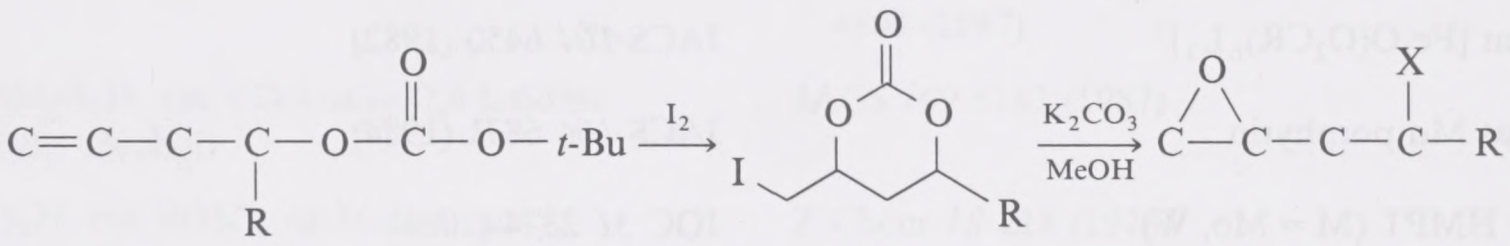
H_2O, NaBr, electrolysis — TL 4661 (1979)
JOC *46* 3312 (1981); *50* 3160 (1985)

H_2O, [polymer-$\overset{+}{N}R_3$]Br^-, electrolysis — JOC *47* 3575 (1982)



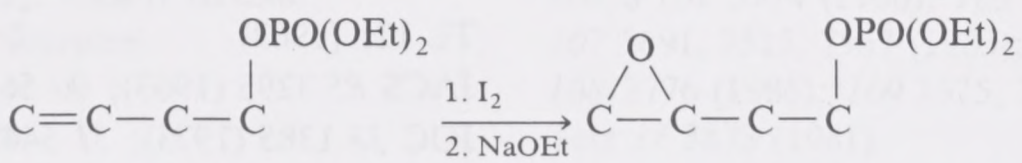
$n = 0, 1$

CC 465 (1981)
JOC *47* 4626 (1982); *52* 3560 (1987)

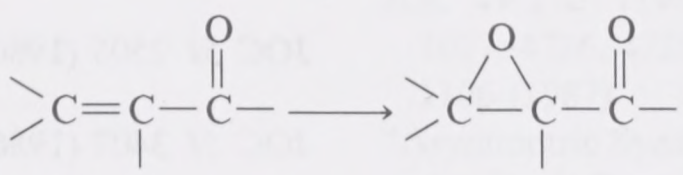


X = OH or OCO_2Me

JOC *47* 4013 (1982)



JACS *99* 4829 (1977)



H_2O_2, $NaHCO_3$ — JACS *103* 3460 (1981)
JOC *52* 4647 (1987)

H_2O_2, K_2CO_3 — JOC *52* 3560 (1987)

H_2O_2, LiOH — TL *28* 2099 (1987)

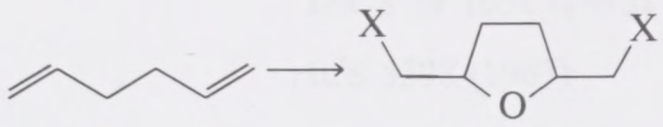
H_2O_2, NaOH — Ber *54* 2327 (1921)
Helv *25* 836 (1942)
JACS *79* 1488 (1957); *105* 2435 (1983); *109* 4690 (1987)
Org Syn Coll Vol *4* 552 (1963)
Tetr *19* 1091 (1963)
JOC *50* 2981, 3957 (1985); *51* 3098 (1986)

H_2O_2, NaOH, poly-L or D-alanine (enantioselective) — TL *28* 4857 (1987)

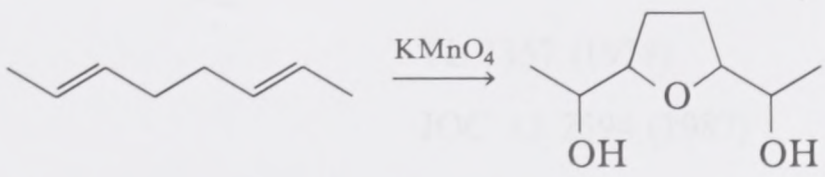
H_2O_2, cat $Na_2WO_4 \cdot 2\ H_2O$, H_2O — JOC *24* 54 (1959); *50* 1979 (1985)

H_2O_2 or *t*-BuO_2H, NaOH, R_4NCl (enantioselective)	TL 1831 (1976) Chimia *30* 445 (1976) CC 427 (1978) JOC *45* 2498 (1980)
H_2O_2 or *t*-BuO_2H, *n*-Bu_4F	CL 285 (1987)
t-BuO_2H, cat bovine serum albumin, buffer (enantioselective)	TL *28* 1577 (1987)
t-BuO_2H, NaOH	JACS *106* 4558 (1984)
t-BuO_2H, Triton-B	JACS *80* 5845 (1958); *99* 5773 (1977)
t-BuO_2H, DBU	JACS *107* 1777 (1987)
t-BuO_2H, RLi	CC 1378 (1986)
t-BuO_2H, KH	JACS *101* 2493 (1979); *106* 4038 (1984) TL *27* 1343, 6189 (1986) JOC *51* 3393 (1986)
NaOCl, py	JOC *28* 250 (1963)
NaOCl, (*n*-Bu_4N)HSO_4	Gazz Chim Ital *110* 267 (1980)
$KHSO_5$, CH_3COCH_3, $NaHCO_3$	JOC *51* 1925 (1986) (α,β-unsaturated acids)
$KHSO_5$, CH_3COCH_3, (18-crown-6)	JOC *45* 4758 (1980) (α,β-unsaturated acids)

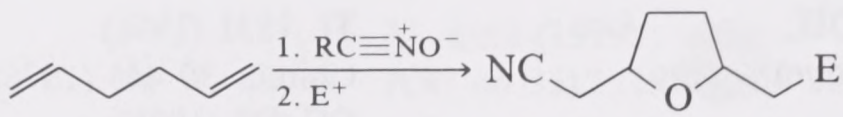
4. Diene Addition



X	Reagents	
PhSe	PhSeCl, H_2O	JOC *44* 1742 (1979) Tetr *41* 5301 (1985)
HgX	HgX_2, H_2O	R. C. Larock, "Solvomercuration/ Demercuration Reactions in Organic Synthesis", Springer, New York (1986), Chpt 2 (review)



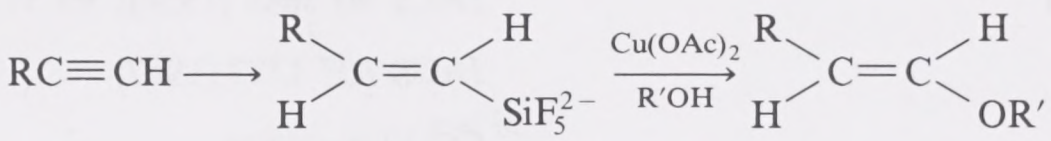
Tetr *21* 2353 (1965)
JACS *101* 4396 (1979)
TL *21* 3531 (1980); *28* 731 (1987)



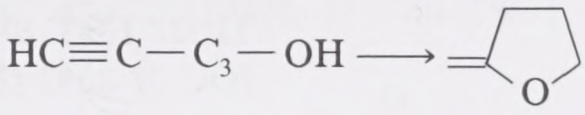
$R = Ph_3C, Me_3C, Me_3Si, R'CH(OSiMe_3)$; $E^+ = Br_2, I_2$, PhSeBr

JACS *109* 7577 (1987)

5. Alkyne Addition

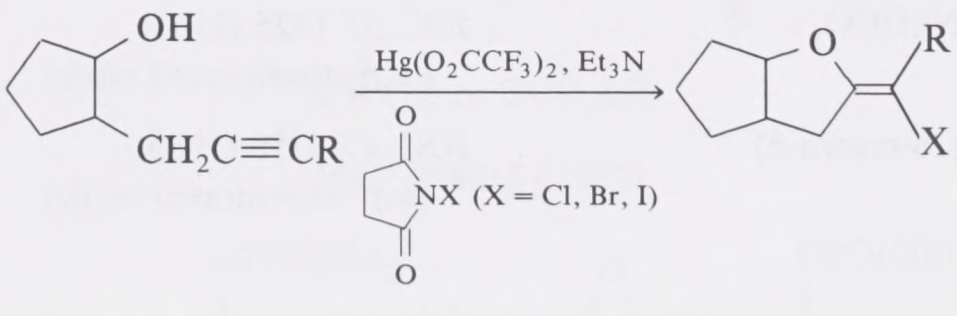


Organomet *1* 369 (1982)



Ag_2CO_3 TL *28* 6447 (1987)

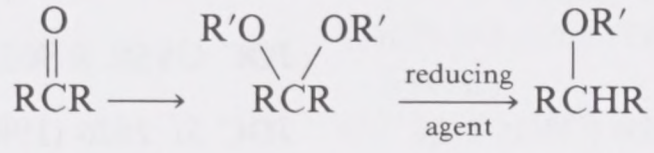
$HgCl_2$, Et_3N JACS *104* 5842 (1982)

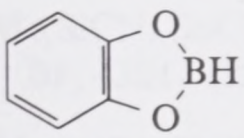


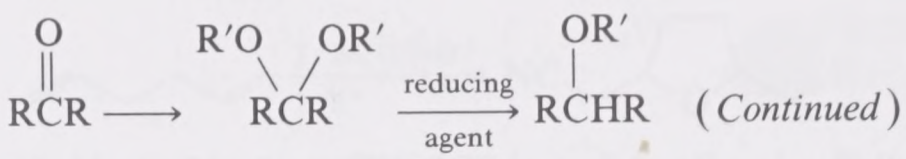
JACS *104* 5842 (1982)

4. ACETAL, CARBONYL AND ORTHO ESTER CONVERSIONS

1. Acetals



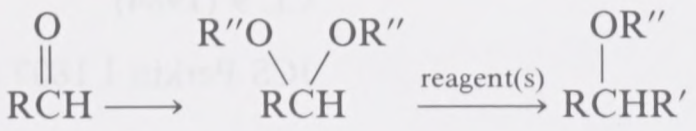
Reducing agent	
H_2, cat Rh-alumina, H^+	JOC *26* 1026 (1961)
H_2, cat Ni	JACS *54* 1651 (1932)
H_2, cat PtO_2, H^+	JCS 5598 (1963)
H_2, CO, cat $Co_2(CO)_8$ (R = aryl)	Can J Chem *54* 685 (1976)
BH_3	Curr Sci 404 (1963) Can J Chem *52* 888 (1974)
$ClBH_2 \cdot OEt_2$	CL 9 (1984)
Cl_2BH	JCS Perkin I 1807 (1981)
	JOC *42* 512 (1977)
$NaBH_4$, CF_3CO_2H (R = aryl)	Org Prep Proc Int *17* 11 (1985)
$NaBH_3CN$, HCl, CH_3OH	TL 1357 (1978)
$Zn(BH_4)_2$, Me_3SiCl	JOC *52* 2594 (1987)
i-Bu_2AlH	Izv Akad Nauk SSSR, Ser Khim 2255 (1959) [CA *54* 10837h (1960)] Ber *113* 3697 (1980) TL *24* 4581 (1983) (chiral); *27* 983 (1986) (chiral) JOMC *285* 83 (1985) (chiral)



(*Continued*)

Reducing agent

i-Bu_3Al	TL *28* 4181 (1987) (chiral)
Cl_2AlH	CC 334 (1987) (chiral)
Br_2AlH	Tl *24* 4581 (1983); *27* 983, 987 (1986) (all chiral) JOMC *285* 83 (1985) (chiral) CC 334 (1987) (chiral)
$LiAlH_4$, $AlCl_3$	JOC *23* 1088 (1958); *26* 4553 (1961); *27* 67 (1962) JACS *81* 6087 (1959); *84* 2371 (1962); *107* 3891 (1985) Org Syn Coll Vol *5* 303 (1973)
$LiAlH_4$, $TiCl_4$ (R = alkyl)	BCSJ *51* 2059 (1978)
$LiAlH_4/BF_3 \cdot OEt_2$	JOC *27* 67 (1962)
Et_3SiH, CF_3CO_2H	JOC USSR *8* 902 (1972)
Et_3SiH, Nalfion-H	JOC *51* 2826 (1986)
Et_3SiH, $BF_3 \cdot OEt_2$	Carbohydr Res *128* C9 (1984)
Et_3SiH, CF_3CO_2H, $BF_3 \cdot OEt_2$	JACS *104* 3539 (1982); *109* 8117 (1987)
R_3SiH (R = Me, Et), cat Me_3SiOTf	TL 4679 (1979) JOC *52* 892 (1987)
R_3SiH (R = Me, Et, n-Pr), cat $ZnCl_2$	Compt Rend *254* 1814 (1962)
Et_3SiH, $TiCl_4$	TL *27* 987 (1986) (chiral) JACS *109* 527 (1987) (chiral)

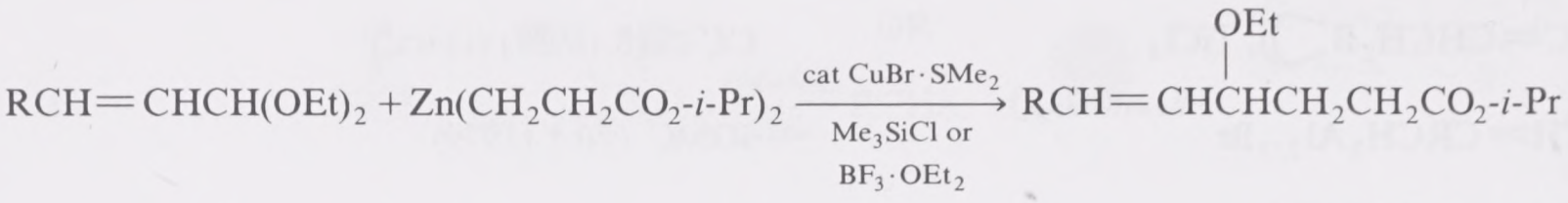


Reagent(s)

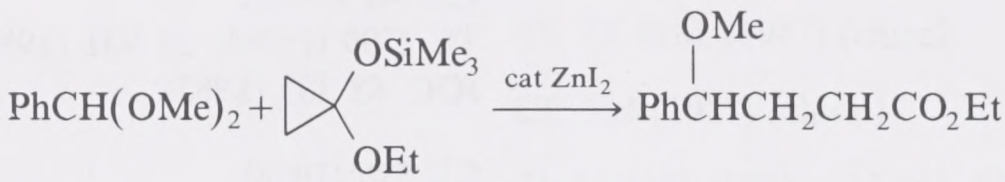
R'Li or $R'_2CuLi(MgX)$, $TiCl_4$	TL *25* 3947 (1984) (chiral)
R'MgX	JACS *73* 4893 (1951) Rec Trav Chim *81* 238 (1962) Organomet *1* 1670 (1982)
R'MgX, $TiCl_4$	BCSJ *54* 776 (1981) TL *25* 3947 (1984) (chiral)
$H_2C{=}CHCH_2M$ (M = B ◯, SnR_3), Lewis acid?	JACS *108* 7116 (1986) (chiral)

$H_2C{=}CHCH_2B$⟨⟩, $TiCl_4$	CC 1218 (1987) (chiral)
$RCH{=}CRCH_2Al_{2/3}Br$	JOMC *170* 1 (1979)
$RCH{=}CRCHRSiMe_3$,	
$BF_3{\cdot}OEt_2$	CL 941 (1976) TL 2589 (1978); *21* 951 (1980) JOC *48* 335 (1983)
$AlCl_3$	CL 575 (1978)
Me_3SiI	TL *22* 745 (1981)
Me_3SiOTf	TL *21* 71, 2527 (1980); *23* 723 (1982) JOC *52* 892 (1987)
$SnCl_4$	JCS Perkin I 251 (1981) (intramolecular) JACS *104* 7371 (1982) (chiral)
$TiCl_4$	CL 941 (1976); 575 (1978) TL 2589 (1978); 429 (1979); *21* 951, 2049 (1980); *23* 725 (1982); *28* 6343 (1987) JACS *105* 2088 (1983) (chiral); *108* 7116 (1986) (chiral) CC 1218 (1987) (chiral)
$TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$	TL *25* 3951 (1984) (chiral) JOC *50* 2598 (1985) (chiral)
$R'CH{=}CHCH{=}CHCH_2SiMe_3$; $TiCl_4$, $BF_3{\cdot}OEt_2$ or cat Me_3SiI	TL *21* 2049, 3783 (1980); *22* 745 (1981) Organomet *1* 1651 (1982)
$H_2C{=}C(CH_2){-}CH_2SiMe_3$, $TiCl_4$ or Me_3SiI	Tetr *39* 883 (1983)
$RC{\equiv}CSiMe_3$, $TiCl_4$	JACS *105* 2904 (1983) (chiral)
$RC{\equiv}CM$ ($M = Me_3Si$, $n\text{-}Bu_3Sn$), Lewis acid?	JACS *108* 7116 (1986) (chiral)
$n\text{-}Bu_3SnC{\equiv}CR$, $TiCl_4$	TL *28* 4589 (1987)
Me_3SiCN, $SnCl_2$ or $BF_3{\cdot}OEt_2$ ($R' = CN$)	TL *22* 4279 (1981) Tetr *39* 967 (1983)
Me_3SiCN, $TiCl_4$ ($R' = CN$)	JOC *48* 2294 (1983) (chiral) TL *25* 591 (1984) (chiral)
$H_2C{=}CHCH_2SnMe_3$, $(Et_2Al)_2SO_4$	CL 977 (1979)
$H_2C{=}CHCH_2Sn(n\text{-}Bu)_3$, $TiCl_4$	CC 1218 (1987) (chiral)
$RTiCl_3$	JOMC *285* 83 (1985)
RCu or R_2CuLi, $BF_3{\cdot}OEt_2$	TL *25* 3083 (1984) (chiral)

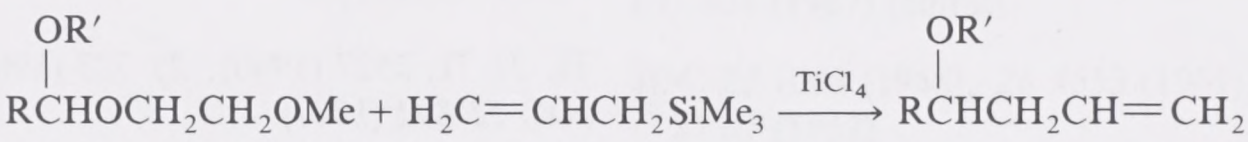
For reactions with enol silanes and Lewis acids see page 750, Section 7.2.



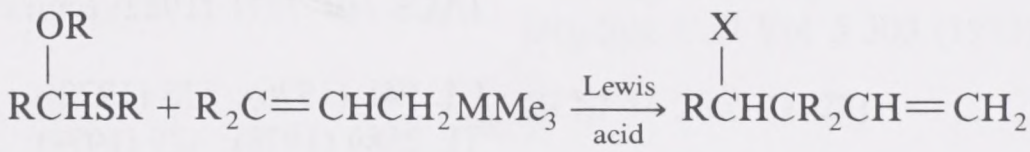
JACS *109* 8056 (1987)



JACS *109* 8056 (1987)



JOC *47* 2496 (1982)



X = OR or SR

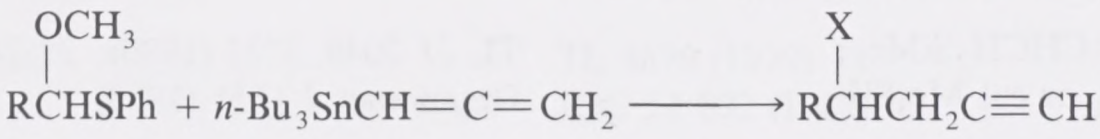
M

Si

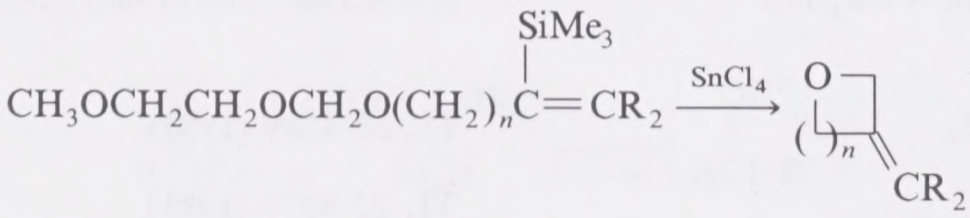
CC 459 (1982)

Sn

TL *28* 6299 (1987)

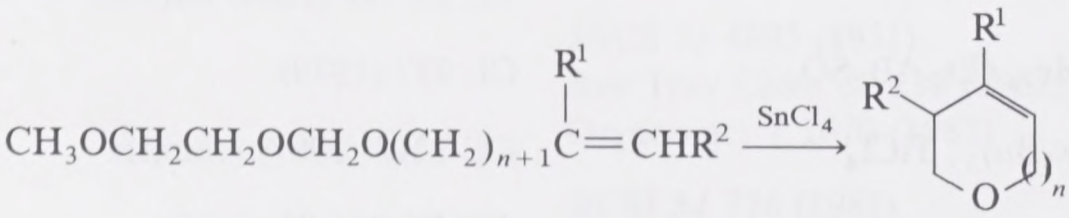


TL *28* 6299 (1987)



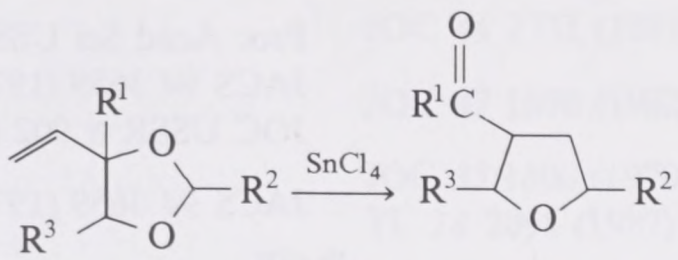
$n = 2$–4

JACS *108* 1303 (1986)

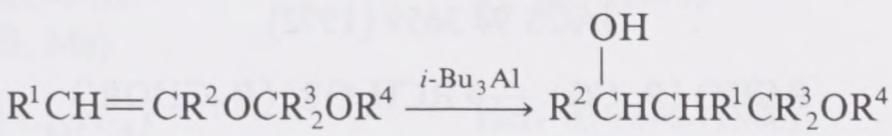


$R^1 = H, SiMe_3$; $R^2 = H, Me, n\text{-Bu}$; $n = 3, 4$

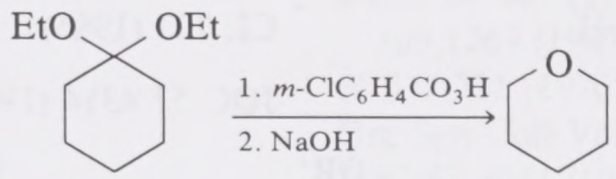
JACS *108* 3516 (1986)



JACS *109* 4748 (1987)

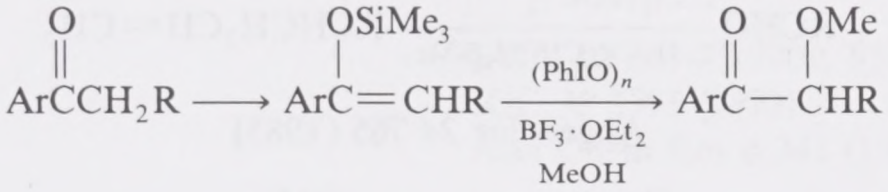


JOC *52* 5700 (1987)

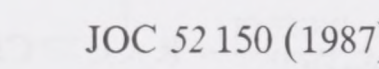


JOC *50* 3009 (1985)

2. Aldehydes and Ketones

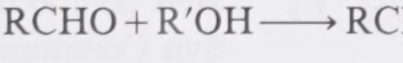


JOC *52* 150 (1987)



$BH_3 \cdot C_5H_5N$, CF_3CO_2H	CL 415 (1979) Chem Pharm Bull *27* 2405 (1979)
Et_3SiH, CF_3CO_2H	Proc Acad Sci USSR, Chem Sec *179* 328 (1968) JOC *39* 2740 (1974)
Et_3SiH, $BF_3 \cdot OEt_2$	JOMC *117* 129 (1976)
Et_3SiH, cat Ph_3CClO_4	CL 743 (1985)
Et_3SiH, cat Me_3SiOTf	JOC *52* 4314 (1987)

n-$BuSiH_3$, CF_3CO_2H	JOC *39* 2740 (1974)
Et_3SiH, cat Me_3SiOTf	JOC *52* 4314 (1987)



$BH_3 \cdot C_5H_5N$, CF_3CO_2H	Chem Pharm Bull *27* 2405 (1979)

Et_3SiH, CF_3CO_2H

Proc Acad Sci USSR, Chem Sec *179* 328 (1968)
JACS *94* 3659 (1972)
JOC USSR *8* 902 (1972)

Et_3SiH, H_2SO_4

JACS *94* 3659 (1972)

$$R_2CO + R'OH \xrightarrow[CF_3CO_2H]{Et_3SiH} R_2CHOR'$$

JACS *94* 3659 (1972)

$$RCHO\ (R_2CO) \longrightarrow RCH_2OR'\ (R_2CHOR')$$

$HC(OR')_3$, Nalfion-H/Et_3SiH, Nalfion-H

JOC *51* 2826 (1986)

Me_3SiOR', cat Ph_3CClO_4/Et_3SiH

CL 743 (1985)

Me_3SiOR', cat Me_3SiI/Me_3SiH

JOC *52* 4314 (1987)

$$RCHO \xrightarrow[2.\ R'X]{1.\ R_3SnLi} RCH(OR')SnR_3 \xrightarrow[2.\ E^+]{1.\ n\text{-BuLi}} RCH(OR')E$$

$E^+ = RX, Me_2SO_4, RCHO, R_2CO$

JACS *100* 1481 (1978); *106* 3376 (1984)

$$RCHO \xrightarrow[2.\ H_2C{=}CHCH_2SiMe_3]{1.\ Cl_2Ti(OR')_2} RCH(OR')CH_2CH{=}CH_2$$

Angew Int *24* 765 (1985)

$$RCR(=O) \xrightarrow[2.\ MeI]{1.\ R'C{\equiv}CLi} R_2CC(OMe){\equiv}CR'$$

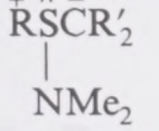
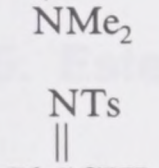
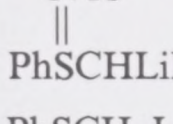
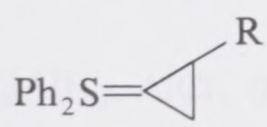
Syn 459 (1981)

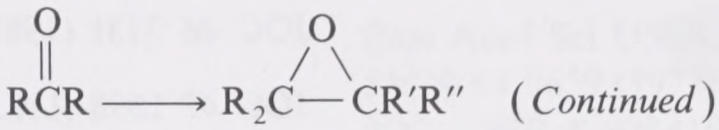
$$RCR(=O) \longrightarrow R_2C\text{—}CR'R''(O)$$

Review: Tetr *36* 2531 (1980)

$(CH_3)_2\overset{+}{S}\overset{-}{C}H_2$

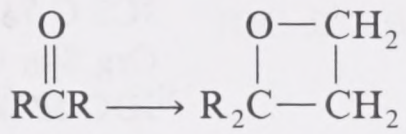
JACS *84* 3782 (1962); *87* 1353 (1965); *106* 723, 4038 (1984); *109* 3353 (1987)
TL 661 (1962); 169 (1963); *23* 5283 (1982); *28* 1877 (1987)
Ber *96* 1881 (1963)
JCS C 731 (1970)
Angew Int *12* 845 (1973)
Cancer Lett *1* 339 (1976)
Heterocycles *8* 397 (1977)
JOC *43* 3425 (1979); *46* 2731 (1981); *51* 3393, 5311 (1986); *52* 603 (1987)
Helv *63* 1665 (1980)
Syn Commun *12* 613 (1982)
CC 1642 (1986)

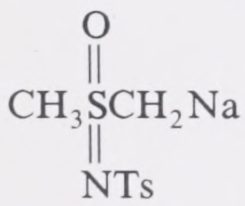
$Me_2\overset{+}{S}\overset{-}{C}HAr$	JOC *46* 2731 (1981)
$Me_2\overset{+}{S}\overset{-}{C}HCH{=}CHR$	JOC *47* 1698 (1982)
$Me_2\overset{+}{S}\overset{-}{C}HCO_2^-$	JOC *35* 1600 (1970) TL *28* 2095 (1987)
$PhEt\overset{+}{S}\overset{-}{C}HR'$ (intramolecular)	JOC *47* 5372 (1982)
$[Ar\overset{+}{S}(CH_2R')_2]O_3SF^-$, KO-*t*-Bu (Ar = polymer; R′ = H, Me)	TL 203 (1979)
$R\overset{+}{S}MeCH_2^-$ (R = Me, *n*-$C_{12}H_{25}$)	Helv *63* 1665 (1980)
$Ph_2\overset{+}{S}\overset{-}{C}R'_2$	TL 2325 (1967)
$(CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	JACS *84* 867 (1962); *87* 1353 (1965); *109* 1269 (1987) JCS C 731 (1970) Org Syn Coll Vol *5* 755 (1973) JOC *52* 4044 (1987)
PhSOCHClR′, base/*n*-BuLi/H_2O (R″ = H)	TL *27* 2379 (1986)
	JACS *92* 5753 (1970) Acct Chem Res *6* 341 (1973)
	JACS *92* 6594 (1970); *95* 7692 (1973) JOC *38* 1793 (1973) Acct Chem Res *6* 341 (1973)
	JOC *44* 2065 (1979)
$PhSCH_2Li/(Me_3O)BF_4/OH^-$	JACS *95* 3429 (1973)
$MeSCH_2Li$/MeI/KO-*t*-Bu	JOC *50* 3988, 5887 (1985)
$EtSCH{=}CHCH_2Ti(O\text{-}i\text{-}Pr)_3/(Me_3O)BF_4$/NaOH (R′ = CH=$CH_2$, R″ = H)	JACS *104* 7663 (1982)
$EtSCH{=}CHCH_2Ti(O\text{-}i\text{-}Pr)_3/MeO_3SCF_3$, 2,6-(*t*-Bu)$_2C_5H_3N/Cs_2CO_3$ (R′ = CH=CH_2, R″ = H)	TL *27* 5691 (1986)
$LiSCH{=}CHCH_2Li$, $MgBr_2$/MeI/NaOH (R′ = CH=CH_2, R″ = H)	Angew Int *15* 437 (1976)
 (R = H, Me)	JACS *95* 2038, 5311 (1973); *108* 4965 (1986)
$PhSeMeCH_2^-$	Angew Int *20* 671 (1981)
$MeSeCH_2Li/MeOSO_2F$/KOH	TL *23* 4389 (1982)
$Me_2SeC(Li)Me_2/MeOSO_2F$/KOH	CC 564 (1982)
MeSeCR′R″Li/MeI or Me_2SO_4/KO-*t*-Bu	Angew Int *14* 700 (1982)



(*Continued*)

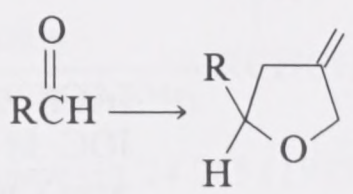
$Ph_3As{=}CHR'$	JACS *103* 1283 (1981)
$CH_3CH{=}CBrCO_2Et$, LDA ($R' = CH{=}CH_2$, $R'' = CO_2Et$)	JOC *51* 4746 (1986)
H_2CBr_2, Li	CC 1047 (1969) Tetr *27* 6109 (1971)
H_2CBr_2, Li(Hg)	Tetr *27* 6109 (1971)
H_2CBr_2, *n*-BuLi	Tetr *27* 6109 (1971)
H_2CBr_2, *sec*-BuLi, LiBr	TL *25* 835 (1984)
H_2CClI, MeLi	TL *27* 795 (1986)



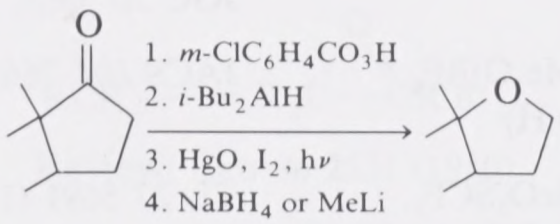


JACS *101* 6135 (1979)

$H_2C{=}CH_2$, hν See page 455, Section 2.

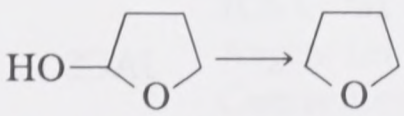


$R'_3SnCH_2C(=CH_2)CH_2OAc$, cat $Pd(OAc)_2$, cat PPh_3	JACS *107* 1778, 8277 (1985)
$Me_3SiCH_2C(=CH_2)CH_2OAc$, cat *n*-$Bu_3SnOAc$, cat $Pd(OAc)_2$, cat PPh_3	TL *27* 5971 (1986)



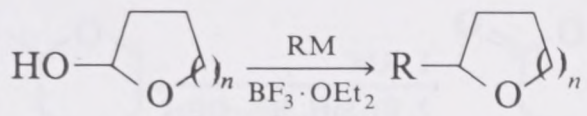
TL *25* 3995 (1984)
JOC *50* 2489 (1985)

3. Lactols



JOC *46* 2417 (1981)

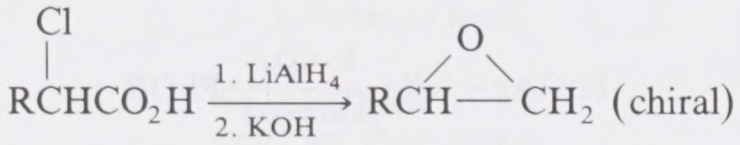
Et_3SiH, CF_3CO_2H	CC 1568 (1986)
Et_3SiH, $BF_3 \cdot OEt_2$	JOC *46* 2417 (1981) Carbohydr Res *128* C9 (1984) CC 1512 (1985)



$n = 1, 2$

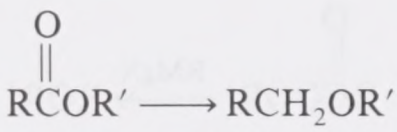
RM	
R_2Zn (R = Me, Et, Ph), R_3Al (R = Me, Et), $(H_2C{=}CHCH_2)_2SnBr_2$ or n-$Bu_2Sn(CH{=}CH_2)_2$	TL *28* 6339 (1987)
$H_2C{=}CHCH_2SiMe_3$	JACS *104* 4976 (1982) Angew Int *25* 556 (1986)
Me_3SiCN (R = CN)	Angew Int *25* 556 (1986)

4. Carboxylic Acids

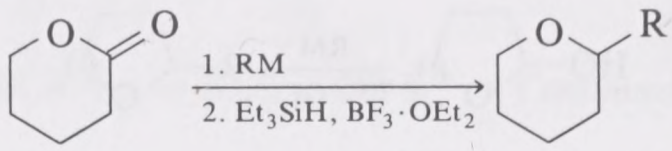


Syn 316 (1982)

5. Esters

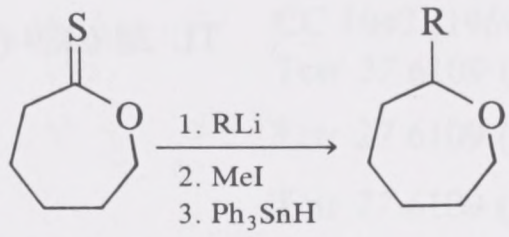


H_2, cat Pt oxide (δ-lactones)	Chem Ind 975 (1964)
BH_3	JOC *26* 1685, 4553 (1961); *27* 2127 (1962); *36* 3485 (1971) Can J Chem *44* 1097 (1966)
i-Bu_2AlH/Et_3SiH, $BF_3{\cdot}OEt_2$ (γ- and δ-lactones)	JOC *46* 2417 (1981)
$LiAlH_4$, $BF_3{\cdot}OEt_2$	JOC *25* 875 (1960) Tetr *18* 953 (1962)
$LiAlH_4$, $AlCl_3$ (lactones only)	Chem Ind 230 (1977)
$HSiCl_3$, hν	JACS *91* 4587 (1969) JOC *37* 76, 4349 (1972); *38* 795 (1973); *39* 2470 (1974); *40* 3885 (1975) BCSJ *47* 932 (1974)
$(ArPS_2)_2S$, Raney Ni	JOC *46* 831 (1981)



$RM = LiCH_2CO_2Et,\ H_2C{=}CHCH_2MgBr$

JACS *104* 4976 (1982)



JACS *109* 2504 (1987)

$$RCOR' \longrightarrow RCOR'$$
(O → CH_2)

CH_2N_2 TL *28* 3011 (1987)

$Cp_2Ti(CH_2)(Cl)AlMe_2$ JACS *102* 3270 (1980)

$$PhOAc + RX \xrightarrow[18\text{-crown-6}]{K_2CO_3} PhOR$$

R = 1° alkyl, allylic, benzylic

CC 815 (1982)

6. Peresters

$$RCOOR' \xrightarrow{RMgX} ROR'$$

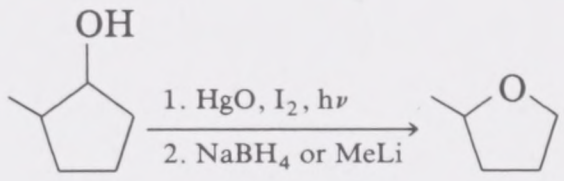
JACS *81* 4230 (1959)
Org Syn *43* 55 (1963)
Org Syn Coll Vol *5* 924 (1973)

7. Ortho Esters

$$RM + (PhO)_2CHOEt \longrightarrow R_2CHOEt$$

RM	
PhMgBr	Ber *103* 643 (1970)
$RCH{=}CR'CH_2Al_{2/3}Br$	JOMC *222* 1 (1981)

5. MISCELLANEOUS REACTIONS



CL 55 (1983)
JOC *49* 3753 (1984)

ALCOHOLS AND PHENOLS

GENERAL REFERENCES

"The Chemistry of the Hydroxyl Group," Ed. S. Patai, Interscience, New York (1971)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1c, Parts I and II, G. Thieme, Stuttgart (1976) (phenols)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1a, Parts I and II, G. Thieme, Stuttgart (1979 and 1980 respectively) (alcohols)

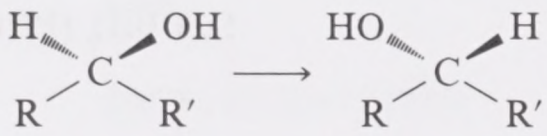
Syn 501 (1981) (preparation of acetals from alcohols or oxiranes and carbonyl compounds)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1b, Part III, G. Thieme, Stuttgart (1984) (alcohols)

1. ALCOHOL TRANSPOSITION

Resolution of alcohols by lipase-catalyzed transesterification:

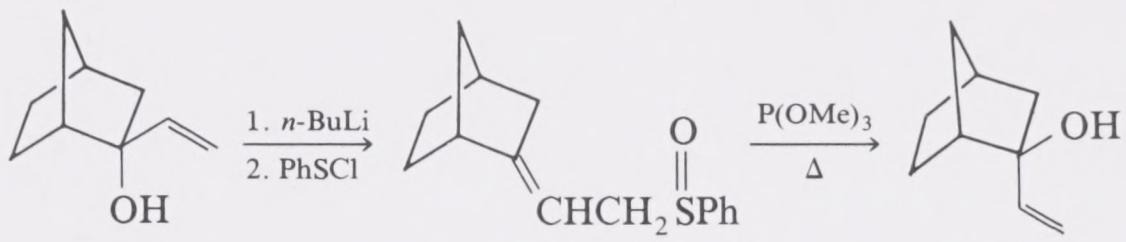
JACS *107* 7072 (1985)
JOC *52* 256 (1987)
TL *28* 1647 (1987)



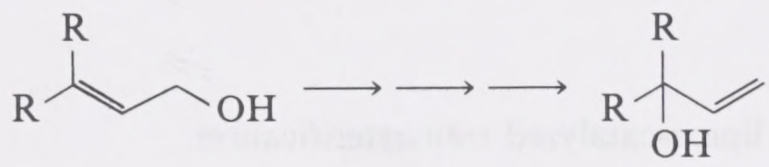
$TsCl/(n\text{-}Bu_4N)OAc/LiAlH_4$	JCS C 1605 (1969)
$TsCl/(Et_4N)OAc[O_2CH]$/saponify	TL 3265, 3269 (1972)
$TsCl/NaO_2CPh/K_2CO_3$	JACS *96* 5876 (1974)
$p\text{-}ClC_6H_4SO_2Cl/KO_2CH(OAc)$/saponify	Ann 901 (1974)
TsCl/DMF/saponify	JACS *80* 2906 (1958)
$p\text{-}XC_6H_4SO_2Cl$ (X = Cl, Me)/KNO_2	Ann 901 (1974) Syn 292 (1980)
TsCl or MsCl/$(n\text{-}Bu_4N)NO_3$/reduction	TL *26* 3369 (1985)
MsCl/KOH	JACS *107* 2138 (1985)
$MsCl/KO_2$	TL 3183 (1975)
MsCl, Et_3N/CsO_2CEt, DMF/hydrolysis	JOC *46* 4321 (1981)
mesylation/CsOAc, 18-crown-6/ hydrolysis	CL 1555 (1984)
$(Ms)_2O$, Et_3N/CsOAc, DMF/K_2CO_3, MeOH	TL *28* 503 (1987)
$PhCOCl/Al_2O_3$	Helv *42* 2177 (1959)
RCO_2H, $EtO_2CN{=}NCO_2Et$, R_3P/base	BCSJ *40* 2380 (1967); *44* 3427 (1971); *49* 510 (1976) TL 1619 (1973); *27* 3535 (1986); *28* 723, 1143, 3151 (1987) Helv *59* 2100 (1976); *60* 417 (1977)

Angew Int *18* 958 (1979)
Syn 1 (1981) (review)
JOC *48* 5083 (1983); *50* 2981 (1985); *52* 3468, 3883, 4235 (1987)
JACS *107* 4339 (1985); *109* 4690 (1987)

$HOAc, (Me_3CCH_2O)_2CHNMe_2$/saponify — Ann 821 (1974)



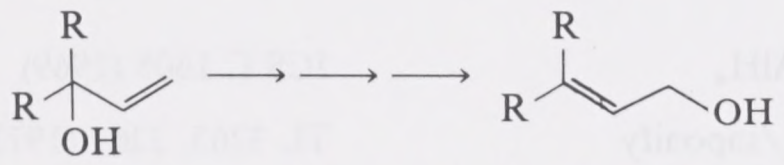
TL *26* 607 (1985)



t-BuO_2H, $VO(acac)_2$/$MeSO_2Cl$/Na, NH_3 — TL 2621 (1976)
BCSJ *52* 1757 (1979)

p-$NO_2C_6H_4SeCN$, n-Bu_3P/H_2O_2 — CC 770 (1978)

NaH, CS_2, MeI/n-Bu_3SnH/ m-$ClC_6H_4CO_3H$/HCl — Syn 1011 (1980)

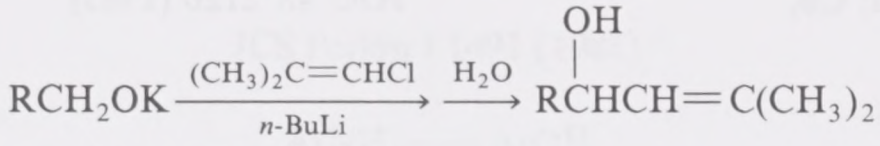


$ClCONMe_2$/$Hg(O_2CCF_3)_2$/PPh_3/cleavage — JACS *100* 4822 (1978)

H_2O, cat HCl or HOAc — JCS 396 (1946)

2. SUBSTITUTION

1. Hydrogen Substitution

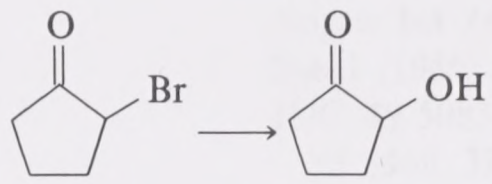


JACS *107* 2189 (1985)

2. Halide and Sulfonate Substitution

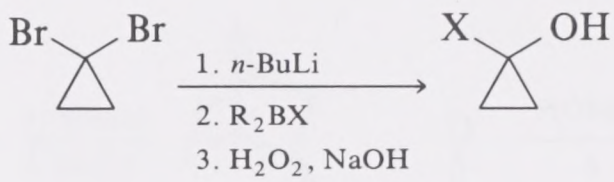
RX⟶ROH

H_2O	JOC *52* 4592 (1987) (2° benzylic bromide)
Al_2O_3, H_2O	CC 1136 (1987) (2° alkyl chloride)
$CaCO_3$, H_2O	JOC *51* 3762 (1986) (1° benzylic bromide)
polymer-supported carbonate	Syn 793 (1981) (1° alkyl chloride, bromide, iodide; 1° allylic bromide; 1° benzylic chloride, bromide)
(n-Bu_4N)OAc/$LiAlH_4$	JCS C 1605 (1969) (2° alkyl tosylates)
KO_2, 18-crown-6/H_2O	TL 3183 (1975) (1° alkyl, allylic, benzylic bromides; 2° alkyl tosylate; 2° allylic mesylate)
Li or Mg/O_2 or t-BuO_2Li	JOC *41* 1459 (1976) (2° cyclopropyl bromide)
Li/MoO_5·py·HMPA	JOMC *59* 293 (1973) (1° alkyl lithium)
Mg/MoO_5·py·HMPA	JOC *42* 1479 (1977) (aryl bromides) Austral J Chem *31* 2091 (1978) (1°, 2°, 3° alkyl bromides; aryl bromides)



NaOH, DMF — JOC *47* 4024 (1982)

N_2H_4, H_2O/H_2SO_4, MeOH — JOC *32* 3723 (1967)



X = H, R

JOC *50* 2401 (1985)

$RX \longrightarrow RCH_2OH$

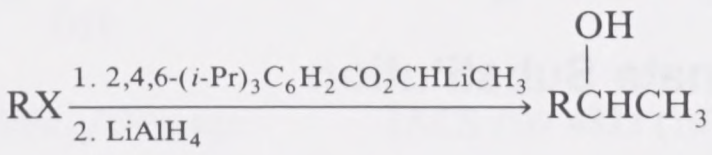
n-Bu_3SnCH_2OH, 2 *n*-BuLi/H_2O — Angew Int *15* 438 (1978); Ber *113* 1290 (1980)

(*i*-PrO)$_2$MeSiCH_2MgCl; Cu, Ni or Pd catalyst/ H_2O_2 or CH_3CO_3H — JOC *48* 2120 (1983)

$(Mes)_2BCH_2Li/[O]$ — Chem Soc Rev *11* 191 (1982)

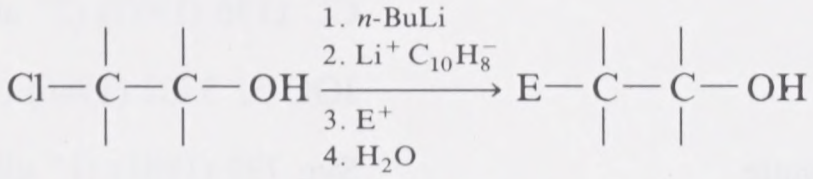

BCH_2Li/H_2O_2, NaOH — JACS *94* 6854 (1972)

2,4,6-(*i*-Pr)$_3C_6H_2CO_2CH_2Li/LiAlH_4$ — JACS *99* 5213 (1977)



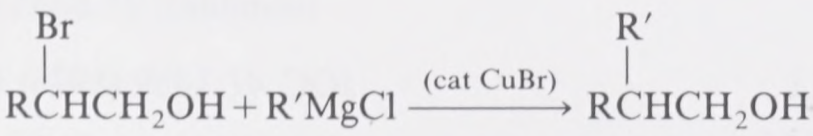
JOC *43* 4255 (1978)

For analogous conversions see page 553, Section 8.



$E^+ = D_2O$, RX, RCHO, R_2CO, CO_2, O_2, Me_2S_2

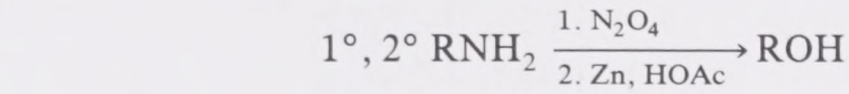
CC 1153 (1982)
JCS Perkin I 3019 (1983)



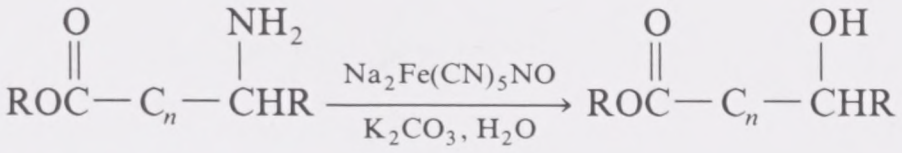
R′ = allyl, vinyl, aryl

BSCF II 289 (1980)

3. Amine Substitution

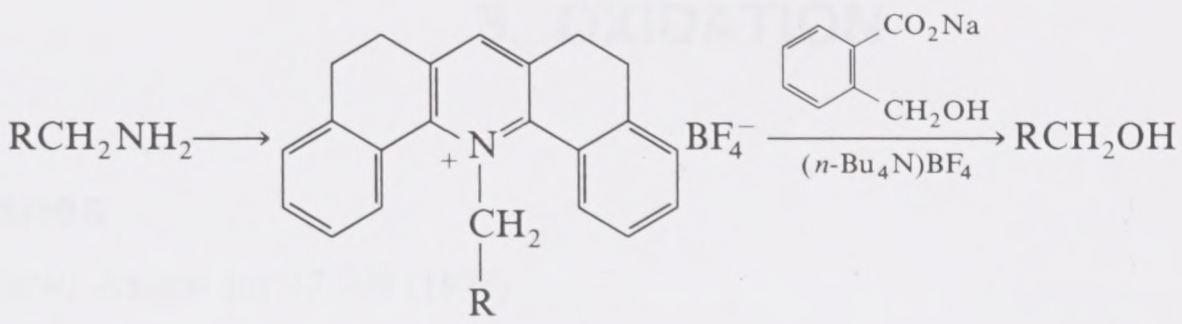


JCS Perkin I 1114 (1977)

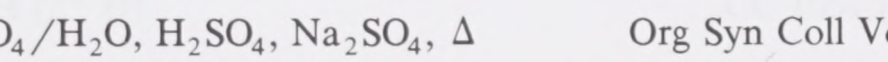


$n = 1, 3$

JOC *51* 3913 (1986)



JCS Perkin I 1492 (1981)

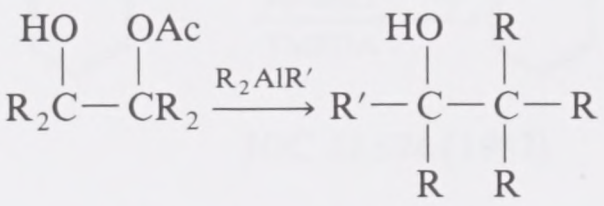


$NaHSO_3/NaOH/HCl$ JACS *83* 5015 (1961)

$NaNO_2$, H_2SO_4/H_2O, H_2SO_4, Na_2SO_4, Δ Org Syn Coll Vol *3* 130 (1955)

DMSO [on $(Ar\overset{+}{N}_2)BF_4^-$] Helv *59* 1427 (1976)

4. Acetate Substitution



BCSJ *55* 3941 (1982)

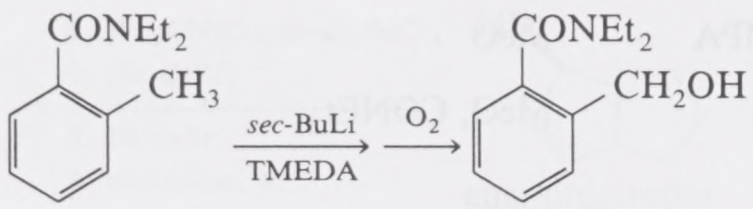
3. OXIDATION

1. Alkanes

Review: Angew Int *17* 909 (1978)

$$R_3CH \longrightarrow R_3COH$$

O_3, silica gel (3° H)	JOC *40* 2141 (1975); *50* 2759 (1985)
p-$NO_2C_6H_4CO_3H$, Δ (3° H)	Angew Int *18* 407 (1979)
CF_3CO_3H (2° H)	CC 1051 (1976)
$(PhNEt_3)MnO_4$ (3° H)	Angew Int *18* 68 (1979)
RuO_4 (3° H)	Acta Chem Scand B *40* 430 (1986)



JOC *52* 674 (1987)

2. Arenes

$$ArH \longrightarrow ArOH$$

Reviews:

Adv Org Chem *1* 103 (1960)
R. O. C. Norman, R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam (1965)
"Applications of Biochemical Systems in Organic Chemistry," Wiley, New York (1976), Part I, pp 69–106
"Comprehensive Organic Chemistry," Pergamon, Oxford (1979), Vol 1

H_2O_2, HF	JOC *35* 4028 (1970)
H_2O_2, HF, py	Syn 536 (1979)

ArH ⟶ ArOH (*Continued*)

H_2O_2, HF, BF_3	JOC *46* 4305 (1981)
H_2O_2, HF, SbF_5	Nouv J Chim *6* 477 (1982) TL *27* 4565 (1986)
H_2O_2, HSO_3F, SO_2ClF, (SbF_5)	JOC *43* 865 (1977)
H_2O_2, $AlCl_3$	JOC *36* 3184 (1971)
H_2O_2, $FeSO_4$ (on ArOH)	J Prakt Chem *152* 46 (1939)
t-BuO_2H, $AlCl_3$	BCSJ *43* 293 (1970)
CF_3CO_3H	JCS 1804 (1959); 5404 (1964) JOC *27* 627 (1962)
CF_3CO_3H, BF_3	JACS *85* 2177 (1963) JOC *29* 2397 (1964); *30* 331 (1965)
i-PrOCOOCO-*i*-Pr, $AlCl_3$	JACS *87* 1566, 4811 (1965)
$NaOH/K_2S_2O_8$ (on ArOH)	JCS 2303 (1948)
, $H_3PO_4/PdCl_2(CH_3CN)_2/H_2O_2$, HCl (on ArOH)	TL *22* 2327 (1981)
O_2, $HO_2CC(OH)=C(OH)CO_2H$, peroxidase catalyst (on ArOH)	JACS *103* 6263 (1981)

o-X—Ar—H ⟶ *o*-X—Ar—OH

Reagents	X	
n-BuLi/MoO_5·py·HMPA	MeO	TL *28* 2643 (1987)
sec-BuLi, TMEDA/O_2	MeO, $CONEt_2$	JOC *52* 674 (1987)

3. Alkenes

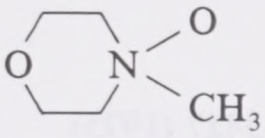
See page 493, Section 1, for addition to the double bond; and page 116, Section 5, for oxidation with allylic transposition.

$RCH_2CH=CH_2 \longrightarrow RCH(OH)CH=CH_2$

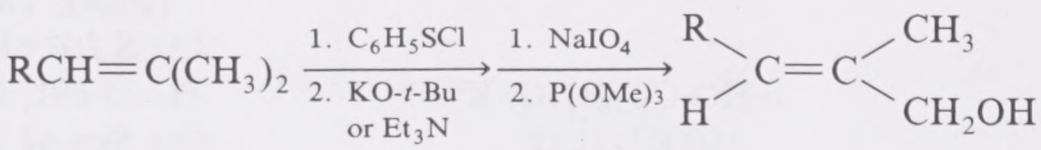
SeO_2	Org Rxs *5* 331 (1949); *24* 261 (1976) JOC *35* 1646, 1653 (1970); *44* 4683 (1979); *51* 256 (1986); *52* 3468 (1987) B. S. Thyagarajan, "Selective Organic Transformations," Vol 1 (1970), p 307 JACS *93* 4835 (1971) Syn 215 (1978) CL 85 (1986)

SeO_2, t-BuO_2H — JACS *99* 5526 (1977)
JOC *48* 1404 (1983); *50* 1602 (1985); *52* 3860 (1987)
TL *27* 2279 (1986); *28* 1561, 5945 (1987)

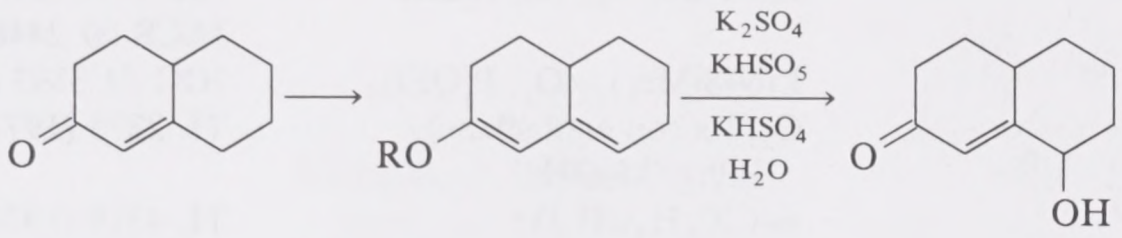
SeO_2, t-BuO_2H, silica gel — CL 1703 (1981)

SeO_2,  — JOC *51* 1635 (1986)

RLi, $TMEDA/O_2$ — JACS *94* 4298 (1972)
Chem Pharm Bull *32* 4632 (1984)
JOC *51* 4315 (1986)

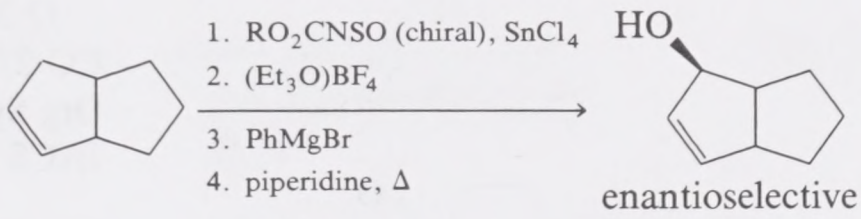


TL 4539, 5123 (1978)



R = Me, Ac, $SiMe_3$

TL *22* 4201 (1981)



JACS *109* 2839 (1987)

4. Alcohols

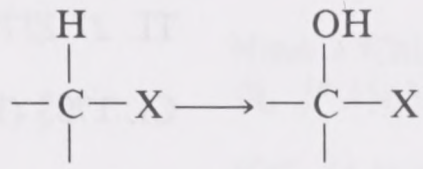
$ArCR_2OH \longrightarrow ArOH$

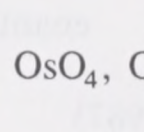
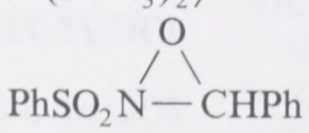
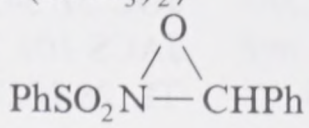
H_2O_2, HOAc, $HClO_4$ — JOC *15* 775 (1950)

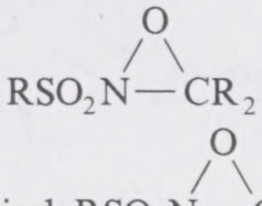
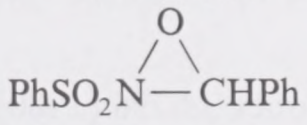
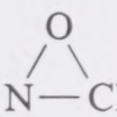
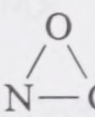
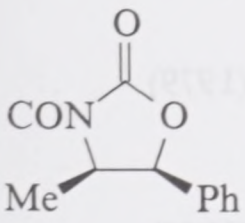
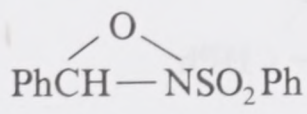
H_2O_2, TsOH — JOC *51* 5436 (1986); *52* 5283 (1987)

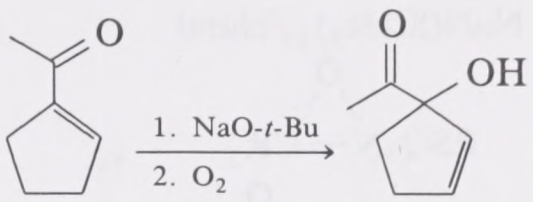
H_2O_2, $BF_3 \cdot OEt_2$ — JOC *51* 5436 (1986)
JACS *109* 2717 (1987)
TL *28* 1027 (1987)

5. Carbonyl Compounds

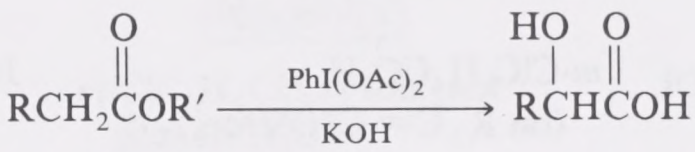


X	Reagent(s)	
CHO	*m*-$ClC_6H_4CO_3H$ (on enol silane)/H_3O^+	JOC *40* 3427 (1975)
COR	PhIO, NaOH, MeOH	TL *22* 1283 (1981) CC 641 (1981)
	$PhI(OAc)_2$, NaOH, MeOH	TL *22* 1283 (1981); *25* 4745 (1984); *28* 5709 (1987) JACS *103* 686 (1981)
	o-$HO_2CC_6H_4IO$, KOH, MeOH/H_3O^+	TL *25* 691, 4745 (1984) Org Syn *64* 138 (1985)
	NaH, $P(OEt)_3/O_2$	JOC *51* 1478 (1986)
	NaO-*t*-Bu, O_2, $P(OEt)_3$	JOC *33* 3294 (1968)
	KO-*t*-Bu, O_2/Zn, HOAc	JCS 1578 (1962) JACS *90* 2448 (1968)
	$LiN(SiMe_3)_2/O_2$, $P(OEt)_3$	JOC *51* 3393 (1986)
	O_2, hν (on enol silane)/PPh_3/MeOH	TL 2375 (1977)
	m-$ClC_6H_4CO_3H$ (on enol silane)/H_3O^+ or $(Et_3NH)F$	TL 4319 (1974); 2935 (1976); 4603 (1978); *28* 435, 581, 3723, 5017 (1987) JOMC *77* C19 (1974) JOC *40* 3427 (1975); *42* 1581 (1977); *43* 1599 (1978); *52* 3745 (1987) CC 27 (1977) Org Syn *64* 118 (1985) JACS *109* 7575 (1987)
	OsO_4,  (on enol silane)/H_3O^+	TL *22* 607 (1981) JACS *108* 5549 (1986)
	CrO_2Cl_2 (on enol silane)	TL *23* 2917 (1982)
	$(PhSeO)_2O$	CL 763 (1979) Tetr *37* 473 (1981)
	LDA/MoO_5·py·HMPA	JACS *96* 5944 (1974); *106* 3539, 4547 (1984) JOC *43* 188 (1978) Org Syn *64* 127 (1985)
	$NaN(SiMe_3)_2$/ 	JOC *52* 4592 (1987)
	$KN(SiMe_3)_2$/ 	JOC *49* 3241 (1984)

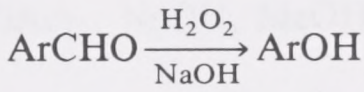
	$NaN(SiMe_3)_2$/chiral 	JOC *51* 4083 (1986)
	chiral $RSO_2N{-}CHAr$ (on enol silane)/H_3O^+	JOC *52* 954 (1987)
CO_2H	*m*-$ClC_6H_4CO_3H$ (on $R_2C{=}C(OSiMe_3)_2$)/H_3O^+	JOC *40* 3783 (1975)
	LDA/O_2	JOC *40* 3253 (1975) Syn Commun *9* 63 (1979) TL *27* 2199 (1986)
CO_2R	LDA/O_2	TL 1731 (1975) JOC *52* 3323 (1987)
	$LiNR_2/MoO_5 \cdot py \cdot HMPA$	JACS *96* 5944 (1974) JOC *43* 188 (1978); *46* 4825 (1981); *52* 1170, 3346 (1987) TL *26* 203 (chiral), 5631 (1985); *27* 1833 (1986); *28* 1147, 6381 (lactone) (1987)
	$KN(SiMe_3)_2$, KO-*sec*-Bu/$MoO_5 \cdot py \cdot HMPA$	TL *27* 3999 (1986) Helv *69* 615 (1986)
	(Li)$KN(SiMe_3)_2$/ 	JOC *49* 3241 (1984)
	chiral $RSO_2N{-}CHAr$ (on silyl ketene acetal)/H_3O^+ 	JOC *52* 954 (1987)
CO_2R, $CONR_2$	LDA/chiral $RSO_2N{-}CR_2$ 	JOC *51* 2402 (1986); *52* 5288 (1987)
$CONR_2$	LDA/O_2	TL 1731 (1975)
	$LDA/P(OEt)_3/O_2$	JOC *52* 4352 (1987)
	$LDA/MoO_5 \cdot py \cdot HMPA$	JOC *50* 2170 (1985)
	$NaN(SiMe_3)_2$/ 	JACS *107* 4346 (1985) (chiral)
CN	$LDA/O_2/SnCl_2$	JOC *40* 269 (1975)
	$LDA/MoO_5 \cdot py \cdot HMPA$	JOC *41* 740 (1976)



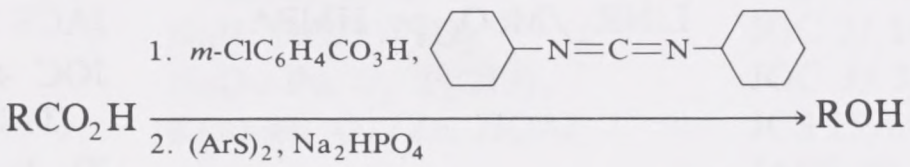
JOC *33* 3695 (1968)



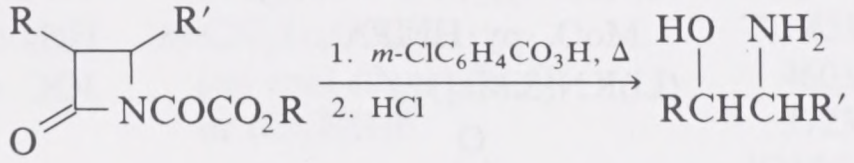
TL *22* 2747 (1981)



TL *28* 455 (1987)

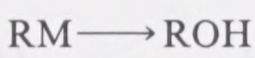


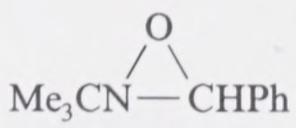
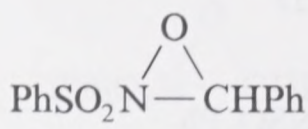
TL *28* 4489 (1987)

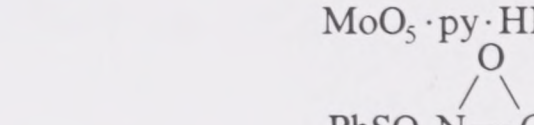


J Antibiotics *33* 796 (1980)

6. Organometallics



M	Reagent(s)	
Li	—	See also page 485, Section 1.
	$MoO_5 \cdot py \cdot HMPA$	JOC *50* 5660 (1985) (R = CH_2-oxazoline)
	$(Me_3SiO)_2/HCl$	Syn 633 (1986) (R = 1°, 2° alkyl; aryl)
		JACS *101* 1044 (1979) (R = aryl)
		JACS *101* 1044 (1979) (R = 1° alkyl, aryl) JOC *50* 5660 (1985) (R = CH_2-oxazoline) TL *28* 5115 (1987) (R = aryl)

MgX	$MoO_5 \cdot py \cdot HMPA$	JOC *42* 1479 (1977) (R = aryl)
		JACS *101* 1044 (1979) (R = 1° alkyl, aryl) TL *28* 5115 (1987) (R = 1°, 2° alkyl; aryl)
		TL *28* 5115 (1987) (R = aryl)
B	—	See page 497, Section 5.
$SiMe_2Ph$	KBr, CH_3CO_3H, NaOAc, HOAc	TL *28* 4229 (1987)
	$Hg(OAc)_2$, CH_3CO_3H, HOAc	TL *28* 4229 (1987)
	cat $Hg(OAc)_2$, cat $Pd(OAc)_2$, CH_3CO_3H, HOAc	TL *28* 4229 (1987)
	m-$ClC_6H_4CO_3H$, KF	TL *26* 397 (1985)
	HBF_4 / *m*-$ClC_6H_4CO_3H$, Et_3N	CC 29 (1984); 318 (1985)
	$BF_3 \cdot 2$ HOAc / *m*-$ClC_6H_4CO_3H$, Et_3N	CC 305 (1986)
	$BF_3 \cdot 2$ HOAc / CH_3CO_3H, Et_3N	CC 1198 (1986)
	$BF_3 \cdot 2$ HOAc / *m*-$ClC_6H_4CO_3H$, KF	CC 29 (1984)
$SiMe(OEt)_2$	H_2O_2, HCO_3^- or CO_3^{2-}	Organomet *2* 1694 (1983)
	H_2O_2, KF or KHF_2	Organomet *2* 1694 (1983)
	t-BuO_2H, KHF_2	Organomet *2* 1694 (1983)
	m-$ClC_6H_4CO_3H$	Organomet *2* 1694 (1983)
$SiMe_2OR$	H_2O_2, $NaHCO_3$	TL *27* 3377 (1986)
SiR_2OEt	*m*-$ClC_6H_5CO_3H$, KF	Tetr *39* 983 (1983)
SiR_nF_{3-n} ($n = 1, 2$)	*m*-$ClC_6H_4CO_3H$, KF	Tetr *39* 983 (1983)
SiF_5^{2-}	*m*-$ClC_6H_4CO_3H$	JACS *100* 2268 (1978) Tetr *39* 983 (1983)

4. ALKENE AND ALKYNE ADDITIONS

1. Alkenes

$$RCH{=}CH_2 \xrightarrow[H_2O]{\text{cat } H^+} RCH(OH)CH_3$$

JACS *40* 822, 1950 (1918); *46* 1512 (1924); *49* 873 (1927); *56* 460, 2138 (1934); *61* 940 (1939); *73* 3792 (1951); *74* 5372 (1952); *77* 1584 (1955); *79* 3724 (1957); *93* 4907 (1971)
JCS 4203 (1960)

$$RCH{=}CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} RCH(OH)CH_2HgOAc \xrightarrow[NaOH]{NaBH_4} RCH(OH)CH_3$$

Review:

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 2

JACS *89* 1522, 1524, 1525 (1967); *102* 7798 (1980) (diene regioselectivity)
JOC *35* 1844 (1970); *39* 1474 (1974); *44* 1910 (1979); *46* 531, 930, 3810 (1981)

$$RCH{=}CH_2 \longrightarrow RCH(OH)CH_2HgCl \xrightarrow{Li_2CuMe_3} RCH(OH)CH_2CH_3$$

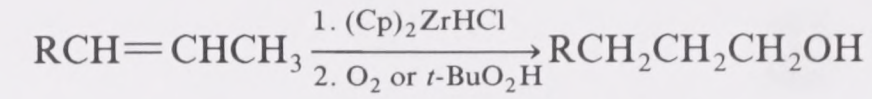
Organomet *1* 74 (1982)

$$RCH{=}CH_2 \longrightarrow RCH(OH)CH_2HgCl \longrightarrow RCH(OM)CH_2M \xrightarrow[2.\ H_2O]{1.\ E^+} RCH(OH)CH_2E$$

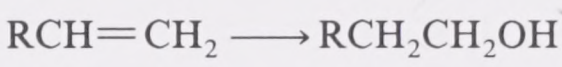
M = alkali metal

$E^+ = D_2O, O_2, CO_2, RCHO, R_2CO, Me_3SiCl, (MeS)_2, R_2C{=}NR$

TL 2015 (1978)
JOC *44* 4798 (1979); *47* 1560 (1982)

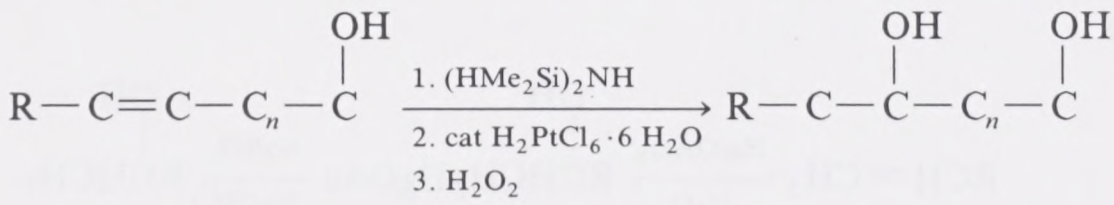


TL 3041 (1975); *23* 157 (1982)

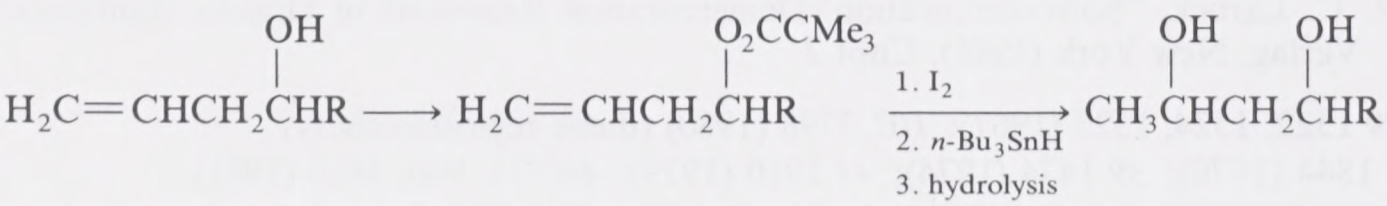


$NaBH_4$, $SnCl_4$	CC 796 (1979)
$NaBH_4$, $TiCl_4$	CC 414 (1980)
$NaBH_4$, cat Rh(III) porphyrin, O_2	JOC *52* 2555 (1987)
$LiBH_4$, Cp_2TiCl_2/H_2O_2, NaOMe	CL 1069 (1979)
Cl_2AlH, cat Et_3B/O_2	JACS *108* 6036 (1986)
$LiAlH_4$, $TiCl_4/O_2$	JOMC *142* 71 (1977)
$LiAlH_4$, Cp_2TiCl_2/O_2 or *m*-$ClC_6H_4CO_3H$	CL 1117 (1977)
Cl_3SiH, cat H_2PtCl_6/KF/*m*-$ClC_6H_4CO_3H$	JACS *100* 2268 (1978) Tetr *39* 983 (1983)
Cl_3SiH, cat $PdCl_2L_2$ (chiral)/CuF_2/ *m*-$ClC_6H_4CO_3H$	JOC *51* 3772 (1986)
$(EtO)_2SiMeH$, cat H_2PtCl_6/H_2O_2	Organomet *2* 1694 (1983)
$(EtO)_2SiMeH$, cat $ClRh(PPh_3)_3$/ Me_3NO, KHF_2	TL *27* 75 (1986)

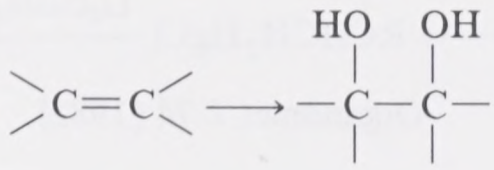
See also page 497, Section 5.



JACS *108* 6090 (1986)
TL *27* 3377 (1986)



JACS *106* 5304 (1984)

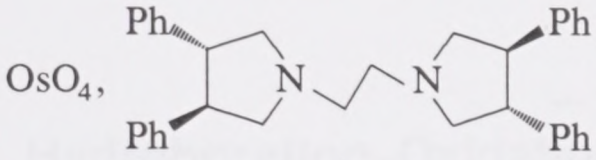
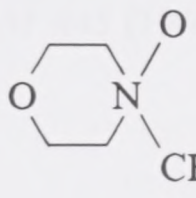


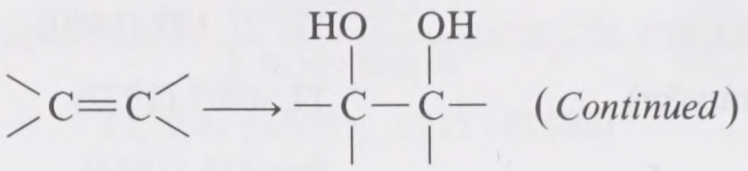
Reviews:

Adv Org Chem *1* 103 (1960)
Chem Rev *80* 187 (1980) (OsO_4)

cis hydroxylation

$KMnO_4$	Org Syn Coll Vol *2* 307 (1943) JACS *78* 5342 (1956)

$KMnO_4$ (phase transfer)	TL *21* 177 (1980)
$KMnO_4$, NaOH (phase transfer)	TL 4907 (1972)
$(n\text{-}C_{16}H_{33}NMe_3)MnO_4$	Syn 431 (1984)
$(Ph_3PMe)MnO_4$	Tetr *35* 1109 (1979)
OsO_4	JOC *25* 257 (1960)
OsO_4, py	Tetr *40* 2247 (1984) (on allylic alcohols) JOC *52* 2301 (1987) TL *28* 4955 (1987)
OsO_4, dihydroquinidine acetate (chiral)	JACS *102* 4263 (1980) TL *28* 3139 (1987)
OsO_4, dihydroquinine acetate (chiral)	JACS *102* 4263 (1980) TL *28* 3139 (1987)
OsO_4, quinuclidine (chiral)	TL *28* 3139 (1987)
OsO_4, (-)-(R,R)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-*trans*-diamine (chiral)	TL *27* 3951 (1986)
OsO_4, chiral diamines derived from tartaric acid	CL 131 (1986)
OsO_4, 	JACS *109* 6213 (1987)
cat OsO_4, H_2O_2	JACS *70* 1484 (1948)
cat OsO_4, *t*-BuO_2H, $(Et_4N)OH$	JACS *98* 1986 (1976)
cat OsO_4, *t*-BuO_2H, $(Et_4N)OAc$	JOC *43* 2063 (1978)
cat OsO_4, $Me_3NO \cdot 2\ H_2O$	JACS *109* 3402 (1987)
cat OsO_4, $Me_3NO \cdot 2\ H_2O$, py	JACS *109* 3353 (1987)
cat OsO_4,  $\cdot 2\ H_2O$	TL 1973 (1976); *28* 1603, 5473 (diene), 5755 (1987) Tetr *40* 2247 (1984) (on allylic alcohols) JACS *107* 2712, 3891 (1985); *108* 1094 (1986); *109* 5437 (1987) JOC *51* 2637 (1986); *52* 3745, 3784, 4505, 5624, 5700 (1987)
cat OsO_4, PhSeOR (R = Me, Ph)	TL *22* 2051 (1981)
NBS, H_2O or *m*-$ClC_6H_4CO_3H$-HBr/ $NCCH_2CO_2H$, TsCl, py/NaH/H_3O^+/ K_2CO_3, MeOH	TL *23* 4217 (1982)
I_2, AgOAc, H_2O, HOAc/KOH	JACS *80* 209 (1958) JCS 770 (1963)



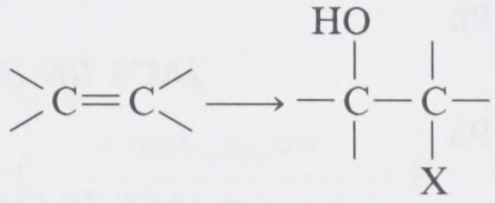
(*Continued*)

cis hydroxylation (*continued*)

I_2, AgOAc, H_2O, HOAc/$LiAlH_4$	JCS C 1327 (1966)
I_2, KIO_3, HOAc/KOH	TL 4485 (1973)
I_2, TlOAc, HOAc/H_2O, Δ/NaOH	Org Syn *59* 169 (1980)

trans hydroxylation

I_2, TlOAc, HOAc/NaOH	Org Syn *59* 169 (1980)
I_2, AgO_2CPh/KOH	Org Rxs *9* 350 (1957) (review)
RCO_3H/H_3O^+	Org Rxs *7* 378 (1953) (review)
HCO_2H, H_2O_2, H_2O	JCS 3634 (1950) Org Syn Coll Vol *3* 217 (1955) Syn 449 (1979)
CF_3CO_3H, $(Et_3NH)O_2CCF_3$/HCl	JACS *76* 3472 (1954)
$HO_2CCH_2CH_2CO_3H$, H_2O	BSCF 2800 (1963)
$KHSO_5$, $KHSO_4$, K_2SO_4, HOAc, H_2SO_4, H_2O	JOC *25* 1901 (1960)



X	Reagent(s)	
halogen	—	See page 325, Section 4.
OAc	I_2, AgOAc, H_2O, HOAc	JACS *109* 6403 (1987)
NHPh	$PhNH_2$, $HgO \cdot 2\ HBF_4$	Syn 376 (1981)

2. Alkynes

$$RC{\equiv}CH \xrightarrow[\text{cat Rh(III) porphyrin}]{NaBH_4,\ O_2} RCH_2CH_2OH$$

$$RC{\equiv}CR \longrightarrow RCHCH_2R \quad (OH)$$

JOC *52* 2555 (1987)

5. ORGANOBORANES

General References

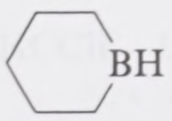
H. C. Brown, "Hydroboration," W. A. Benjamin, New York (1962)
Organomet Chem Syn *1* 305 (1972) (alkylation of halo compounds)
Angew Int *11* 692 (1972) (free radical reactions)
H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca, New York (1972)
G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York (1973)
See Intra-Science Chemistry Reports (1973)

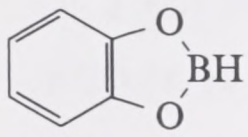
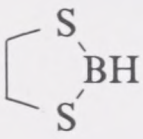
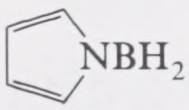
1. Hydroboration–Oxidation

$$RCH{=}CH_2 \xrightarrow{H-B\langle} RCH_2CH_2B\langle \xrightarrow[NaOH]{H_2O_2} RCH_2CH_2OH$$

Reviews:

H. C. Brown, "Hydroboration," W. A. Benjamin, New York (1962)
Org Rxs *13* 1 (1963)
JOC *51* 445 (1986) (cyclic dienes)

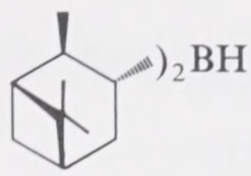
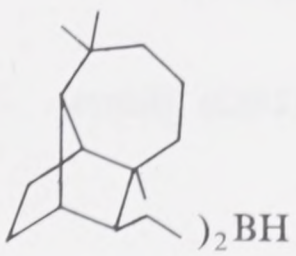
$BH_3 \cdot THF$	JACS *82* 4708 (1960); *88* 5851 (1966)
$BH_3 \cdot SMe_2$	JOC *39* 1437 (1976); *42* 1392 (1977) Org Prep Proc Int *13* 225 (1981) (review)
$MeBH_2$	JOC *51* 4925 (1986)
Me_2BH	JOC *51* 4925 (1986)
9-BBN	JACS *96* 7765 (1974) JOC *44* 2328 (1979); *46* 4599 (1981); *50* 5583 (1985)
$(Sia)_2BH$	JACS *83* 1241 (1961); *84* 190 (1962) (dienes) Org Syn *64* 164 (1985)
	JACS *106* 3768 (1984)

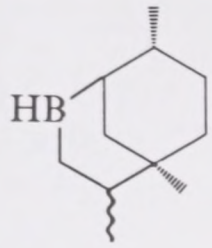
$Me_2CHCMe_2BHCl \cdot SMe_2$	JOC *45* 4540 (1980); *47* 863, 872 (1982)
$H_2BCl \cdot OEt_2$	JOC *38* 182 (1973) JACS *98* 1785 (1976)
$H_2BCl \cdot SMe_2$	JOC *42* 2533 (1977); *44* 2417 (1979); *51* 895 (1986)
$H_2BBr \cdot SMe_2$	Syn 695 (1977) JOC *44* 2417 (1979); *51* 895 (1986)
$H_2BI \cdot SMe_2$	JOC *44* 2417 (1979); *51* 895 (1986)
$HBCl_2 \cdot OEt_2$	JACS *98* 1798 (1976)
$HBCl_2 \cdot SMe_2$	JOC *42* 2533 (1977)
	JACS *93* 1816 (1971); *97* 5249 (1975) Tetr *32* 981 (1976)
	JOC *42* 3243 (1977)
	Syn 214 (1981)

1.1. Asymmetric Hydroboration

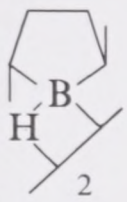
Reviews:

Tetr *37* 3547 (1981)
H. C. Brown, P. K. Jadhav in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Chpt 1

	JACS *99* 5514 (1977); *106* 1797 (1984) JOC *46* 5047 (1981); *52* 310 (1987)
	JACS *83* 486 (1961); *86* 397, 1071, 1076 (1964); *99* 5514 (1977); *108* 2049 (1986) Tetr *24* 6365 (1968) TL 1133 (1970) Israel J Chem *15* 12 (1977) JOC *47* 5065 (1982) Org Syn *63* 44 (1984)
	JOC *46* 2988 (1981)



Heterocycles *18* 169 (1982)



JACS *107* 4549 (1985)

$$RC{\equiv}CH \xrightarrow[\substack{2.\ OH^-\\3.\ [O]}]{1.\ BH_3} RCH_2CH_2OH$$

JACS *89* 291 (1967)

2. Carbonylation and Related Reactions

$$\rangle B-R \longrightarrow RCH_2OH$$

Organoborane	Reagents	
R_3B	$\bar{C}H_2\overset{+}{S}Me_2/[O]$	CC 505 (1967)
	$CO, NaBH_4/OH^-$	JACS *89* 2740 (1967)
	$CO, MHBR_3$ (M = Li, Na, K)$/OH^-$	JOC *44* 467 (1979)
	$CO, LiHAl(OMe)_3/OH^-$	JACS *91* 2144 (1969)
	$CO, LiHAl(OMe)_3/LiAlH_4/[O]$	JOC *45* 4067 (1980)
	$CO, KHB(O\text{-}i\text{-}Pr)_3/OH^-$	Syn 701 (1979)

$$R_3B \longrightarrow R_2CHOH$$

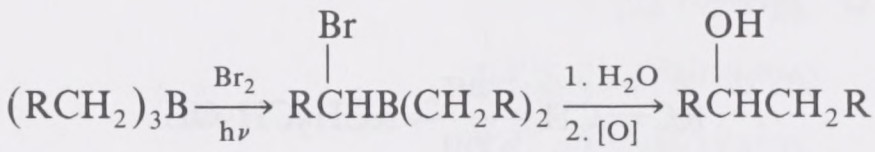
$CO, H_2O, \Delta/KOH$	JACS *89* 2738 (1967)
$CO, LiHAl(OMe)_3/HCl/H_2O_2, NaOH$	Syn 676 (1978)

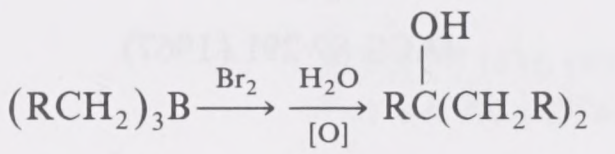
$$R_3B \longrightarrow R_3COH$$

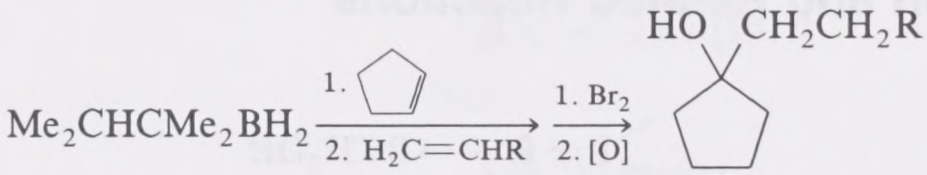
$CO, HOCH_2CH_2OH, \Delta/H_2O_2, NaOH$	JACS *89* 2737, 5478 (1967); *90* 5283 (1968); *91* 1224, 1226 (1969); *92* 2460, 6648 (1970); *93* 1818 (1971) JOMC *26* C67 (1971) Syn 197 (1972) CC 607 (1979) Tetr *37* 2441 (1981) JOC *51* 4925 (1986) TL *28* 3771 (1987)
$NaCN/(CF_3CO)_2O/[O]$	CC 1048 (1971); 186 (1973) JCS Perkin I 653 (1981)
$HCClF_2, LiOCEt_3/[O]$	JACS *93* 2070 (1971)

$HCCl_2OCH_3$, $LiOCEt_3$/[O]	JOC *38* 2422, 3968 (1973) Angew Int *20* 1038 (1981) Organomet *1* 212 (1982)
$LiC(SPh)_3/HgCl_2$ or $MeOSO_2F$/[O]	CC 1149 (1981)

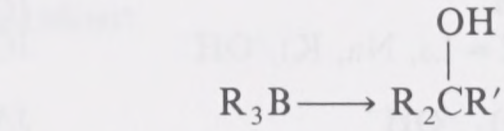
3. Other Reactions

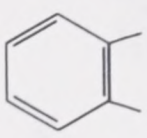


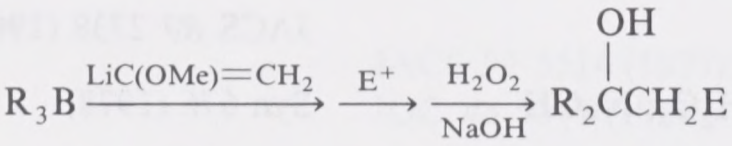




JACS *93* 1025, 2796 (1971)
Syn 303, 304 (1972)
JOC *44* 2417 (1979)



$LiCR'(SPh)_2/HgCl_2$, H_2O/H_2O_2, NaOH	CC 863 (1974)
 $CHR'Li/HgCl_2$, H_2O/H_2O_2, NaOH	JCS Perkin I 1172 (1977) TL 1895 (1979)



$E^+ = HCl, R'X$

JOMC *156* 123 (1978)

6. ETHER CLEAVAGE

Reviews:

Chem Rev *54* 615 (1954); *59* 737 (1959) (epoxides)
Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol 6/3, G. Thieme, Stuttgart (1965), p 143
"The Chemistry of the Ether Linkage," Ed. S. Patai, Interscience, New York (1967), pp 21–80
Syn 249 (1983); 629 (1984) (epoxides)
Pure Appl Chem *55* 589 (1983) (chiral 2,3-epoxy alcohols)

1. Cleavage of Acyclic Ethers

$$ROR' \longrightarrow ROH$$

See also page 349, Section 7.

Review: Chem Rev *54* 615 (1954)

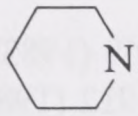
Reagent(s)	R	R′	
H_2, cat Raney Ni	1°, 2°, 3° alkyl; aryl	benzylic	Org Rxs *7* 263 (1953)
H_2, cat Pd-C	aryl	$2,4\text{-}Me_2C_6H_3CH_2$	Syn 987 (1982)
	1°, 2° alkyl	$PhCH_2$	CC 1234 (1980) JOC *47* 1373 (1982)
cat $Pd(OH)_2$, C,  , Δ	1°, 2° alkyl	$PhCH_2$	Syn 396 (1981) TL *28* 4131 (1987)
HCO_2H, cat Pd-C	1°, 2° alkyl	$PhCH_2$	Carbohydr Res *83* 175 (1980)
$(NH_4)O_2CH$, cat Pd-C, MeOH or CH_3COCH_3	1°, 2° alkyl	$PhCH_2$, Ph_3C	Syn 76 (1985)

ROR′ ⟶ ROH (*Continued*)

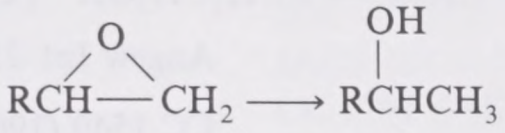
Reagent(s)	R	R′	
$(NH_4)O_2CH$, cat Pd-C, MeOH, HOAc	serine or threonine	$PhCH_2$	Syn 929 (1980)
N_2H_4, H_2O, cat Pd-C	1°, 2° alkyl	$PhCH_2$	Syn 317 (1986) TL *28* 6381 (1987)
Na-K	aryl	$PhCH_2$	JOC *30* 1610 (1965)
Na, NH_3	aryl	alkyl	JCS 102 (1947)
i-Bu_2AlH or *i*-Bu_3Al	aryl	Me	Syn 617 (1975)
$LiAlH_4$, C_6H_6	aryl	Me	CC 507 (1980)
$LiAlH_4$, CCl_4, THF	3° alkyl	Me	JOC *51* 1620 (1986)
HCl	aryl	$MeOCH_2$	JACS *104* 5551 (1982)
HBr, HOAc	aryl	Me	JACS *109* 3098 (1987)
CF_3CO_2H	aryl	$MeOCH_2CH_2OCH_2$	JACS *100* 8031 (1978)
$BF_3 \cdot OEt_2$, *n*-Bu_4NI	1°, 2° alkyl; aryl	Me, $PhCH_2$, $CH_2CH{=}CH_2$	Syn 274 (1985)
BCl_3	aryl	Me	JCS 2929 (1960) TL 4153 (1966)
BBr_3	1°, 2° alkyl; aryl	1°, 2° alkyl; $PhCH_2$	JACS *64* 1128 (1942) JCS 2929 (1960) Chem Ind 1658 (1963) Tetr *24* 2289 (1968) JOC *41* 170 (1976); *44* 4444 (1979); *51* 1620 (1986) J Med Chem *20* 164 (1977); *24* 773 (1981) Syn Commun *9* 341, 407 (1979)
BBr_3, NaI, 15-crown-5	1°, 2° alkyl	Me	TL *22* 4239 (1981)
BI_3	aryl	Me	Syn Commun *9* 341 (1979)
$BX_3 \cdot SMe_2$ (X = Cl, Br)	aryl	Me, CH_2	TL *21* 3731 (1980)
$BF_3 \cdot OEt_2$, Me_2S	1°, 2° alkyl; aryl	$PhCH_2$	Chem Pharm Bull *28* 3662 (1980) CC 1802 (1987)
$BF_3 \cdot OEt_2$, RSH	1°, 2° alkyl; aryl	Me, $PhCH_2$	JCS Perkin I 2237 (1976); 611 (1977) CL 97 (1979) JOC *44* 1661 (1979) Chem Pharm Bull *28* 3662 (1980)

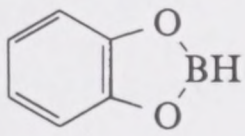
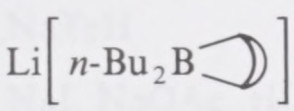
$BF_3 \cdot OEt_2$, PhSH	2° alkyl	$MeOCH_2$	JACS *100* 1938 (1978)
$BF_3 \cdot OEt_2$, $HSCH_2CH_2SH$, HCl	2° alkyl	Me	JACS *106* 3539 (1984)
Me_2BBr	1°, 2° alkyl; aryl 1°, 2°, 3° alkyl	Me, $PhCH_2$ $MeOCH_2$, $MeOCH_2CH_2OCH_2$, $MeSCH_2$	TL *24* 2969 (1983) TL *24* 3969 (1983) JOC *49* 3912 (1984)
Ph_2BBr	1° alkyl	$EtOCH_2$, $MeOCH_2CH_2OCH_2$	TL *24* 3969 (1983) JOC *49* 3912 (1984)
AlX_3 (X = Cl, Br), EtSH	1°, 2° alkyl; aryl	Me, CH_2	CL 97 (1979) JOC *45* 4275 (1980)
R_2AlCl (R = Et, *i*-Bu)	1° alkyl	Ph_3C	TL *23* 2641 (1982)
Me_3SiSR (R = Me, Ph), ZnI_2, *n*-Bu_4NI	1°, 2° alkyl; aryl	Me, $PhCH_2$	TL *21* 2305 (1980)
H_2SiI_2	1° alkyl, aryl	Me	JOC *52* 4846 (1987)
$SiCl_4$, NaI	1°, 2° alkyl; aryl	1°, 2° alkyl; allyl; benzyl	Syn 1048 (1982)
$MeSiCl_3$, NaI	1°, 2° alkyl	Me, Et, $PhCH_2$, Ph_3C, THP	Angew Int *20* 690 (1981) JOC *48* 3667 (1983)
Me_3SiCl, NaI	1°, 2° alkyl; aryl	Me, Et, $PhCH_2$, Ph_3C	CC 874 (1978) JOC *44* 1247 (1979) Ann 1416 (1983) Chem Ind 34 (1984)
Me_3SiI	1°, 2° alkyl; aryl	Me, *t*-Bu	Angew Int *15* 774 (1976) JOC *42* 3761 (1977); *44* 4444 (1979) Org Syn *59* 35 (1980) CC 876 (1987)
$(Me_3Si)_2$, I_2	2° alkyl, aryl	Me, $PhCH_2$, Ph_3C	Angew Int *18* 612 (1979) Ann 1416 (1983)
$PhSiMe_3$, I_2	aryl	1° alkyl, $PhCH_2$	Syn 417 (1977)
P_2I_4	aryl	$MeOCH_2$, $MeOCH_2CH_2$, $Me_3SiCH_2CH_2OCH_2$	TL *27* 1607 (1986)
$FeCl_3$	1°, 2° alkyl	$ArCH_2$	TL *28* 3823 (1987)
$ZnBr_2$ or $TiCl_4$	2°, 3° alkyl; allylic; aryl	$MeOCH_2CH_2OCH_2$	TL 809 (1976) JACS *100* 8034 (1978)
$HgCl_2$ or $AgNO_3$, H_2O	1° alkyl, 1° allylic, 1° benzylic	$MeSCH_2$	TL 3269 (1975)

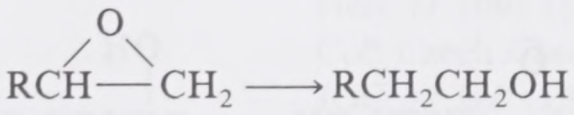
ROR′ ⟶ ROH (*Continued*)

Reagent(s)	R	R′	
n-Bu_4NF	1°, 2° alkyl; allylic; aryl	$Me_3SiCH_2CH_2OCH_2$	TL *21* 3343 (1980)
n-Bu_4NI, $BF_3 \cdot OEt_2$	1°, 2° alkyl; aryl	Me, allyl, benzyl	Syn 274 (1985)
LiI; 2,4,6-collidine	aryl	Me	CC 616 (1969)
$NaNH_2$, 	aryl	1° alkyl, $PhCH_2$	Chem Ind 80 (1957)
PhNMeNa, HMPA	aryl	Me	Syn 638 (1980)
NaCN, DMSO	aryl	Me	TL 5183 (1978)
Na_2S, *N*-methyl-pyrrolidone	aryl	Me	JACS *98* 3237 (1976)
MeSLi, DMF	aryl	Me	TL 3859 (1977) JACS *101* 1353 (1979) JOC *45* 4407 (1980)
MeSNa, DMF or HMPA	aryl	9-anthrylmethyl	JACS *96* 590 (1974)
EtSNa, DMF	aryl	Me	TL 1327 (1970) Austral J Chem *25* 1719, 1731 (1972) JACS *98* 3237 (1976); *108* 1311, 2662, 3040 (1986) JOC *43* 2553 (1978); *52* 1072 (1987)
PrSNa, DMF	aryl	Me	TL *28* 4015 (1987)
n-PrSLi, HMPA	aryl	Me	TL 4459 (1970)
n-BuSLi, HMPA	aryl	Me	TL 505 (1977)
t-BuSLi, HMPA	aryl	Me	JACS *107* 2712 (1985)
PhSLi, HMPA	aryl	Me	TL *27* 2687 (1986)
p-MeC_6H_4SNa, HMPA	aryl	Me, $PhCH_2$	Syn 191 (1976)
$PhCH_2SeNa$, DMF	aryl	Me	JOC *42* 1228 (1977)
Ph_2PLi	aryl	Me, $PhCH_2$, allyl	Chem Ind 1386 (1964) JCS 4120 (1965) TL 1071 (1976) JACS *107* 7967 (1985)
DDQ, H_2O	1° alkyl or allylic, 2° alkyl	4-$MeOC_6H_4CH_2$ or 3,4-$(MeO)_2C_6H_3CH_2$	TL *23* 885 (1982); *28* 5125 (1987)
$(NH_4)_2Ce(NO_3)_6$, H_2O, CH_3CN	1°, 2° alkyl	*p*-$MeOC_6H_4$	CC 201 (1984)

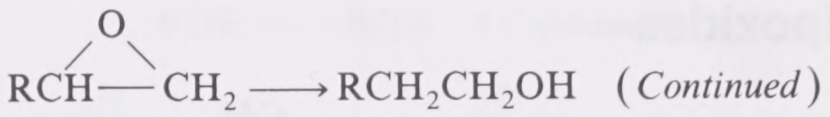
2. Reduction of Epoxides



H_2, Raney nickel, NaOH	JACS *71* 3362 (1949)
Li, RNH_2	Quart Rev *12* 22–23 (1958)
Li, NH_3	JACS *107* 1015 (1985) JOC *51* 5450 (1986)
Li, $H_2NCH_2CH_2NH_2$	JOC *35* 3243 (1970); *51* 3391 (1986) JACS *92* 6914 (1970); *107* 1015 (1985)
Ca, $H_2NCH_2CH_2NH_2$	JOC *51* 3391 (1986)
Li, biphenyl/H_2O	Angew Int *25* 653 (1986)
Li or Mg, naphthalene/H_2O	Angew Int *25* 653 (1986)
	JOC *42* 512 (1977)
BH_3, $NaBH_4$	JOC *45* 3836 (1980)
$LiBH_4$	JCS C 928 (1970)
$LiBH_4$, MeOH	JOC *51* 4000 (1986)
$NaH_2B[(OCH_2CH_2)_nOH]_2$ ($n = 8, 9$)	JOC *52* 671 (1987)
$LiHBEt_3$	JACS *95* 8486 (1973); *106* 3252 (1984); *109* 8117 (1987) Angew Int *18* 958 (1979) JOC *45* 1 (1980) TL *28* 4959 (1987)
$KHBPh_3$	JOC *52* 5564 (1987)
	CC 672 (1976)
i-Bu_2AlH	JOC *50* 2443 (1985)
$LiAlH_4$	JACS *70* 3738 (1948); *71* 1675 (1949); *74* 923, 5917 (1952) Org Rxs *6* 469 (1951)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	JOC *38* 1385 (1973)
$LiHAl(i\text{-}Bu)_2(n\text{-}Bu)$	JOC *49* 1717 (1984)
NaTeH/Ni boride	TL *26* 6197 (1985)

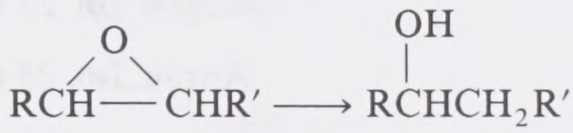


H_2, Raney nickel	JACS *71* 3362 (1949)
Li, naphthalene/H_2O (R = Ph)	Angew Int *25* 653 (1986)

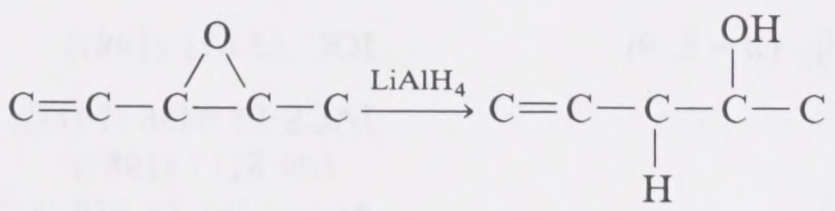


(Continued)

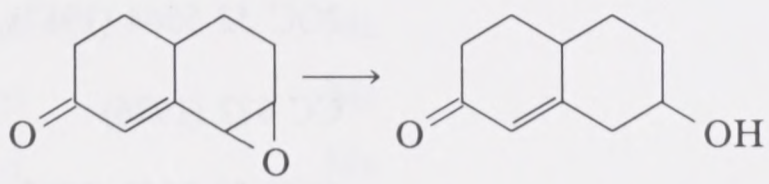
K, biphenyl/H_2O (R = CO_2Et)	Angew Int *25* 653 (1986)
BH_3, $BF_3 \cdot OEt_2$	CC 1549 (1968)
BH_3, $NaBH_4$	JACS *90* 2686 (1968)
$NaBH_3CN$, $BF_3 \cdot OEt_2$	JOC *46* 5214 (1981) TL *27* 6071 (1986)
$KHBPh_3$, cat Ph_3B	JOC *52* 5564 (1987)
$LiAlH_4$, $AlCl_3$	JACS *78* 3226 (1956); *84* 2356 (1962); *90* 6495 (1968) Rec Chem Prog *22* 129 (1961) TL 981 (1978)



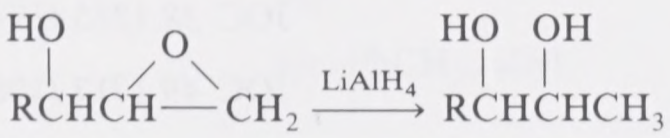
Li, NH_3	BCSJ *52* 2640 (1979); *53* 2642 (1980)
Li, K or Mg; naphthalene or biphenyl/H_2O	Angew Int *25* 653 (1986)
i-Bu_2AlH	JACS *107* 1015 (1985) TL *28* 2021 (1987)



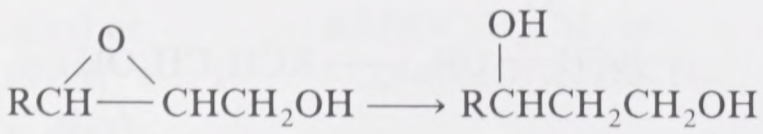
JACS *74* 5917 (1952); *81* 1643 (1959); *86* 2657 (1964); *107* 7978 (1985)
JOC *33* 423 (1968); *50* 5910 (1985); *52* 4898 (1987)



cat Pd-$BaSO_4$, 	Helv *54* 2775, 2785 (1971)
Al(Hg), H_2O, HCl	Steroids *27* 603 (1976)

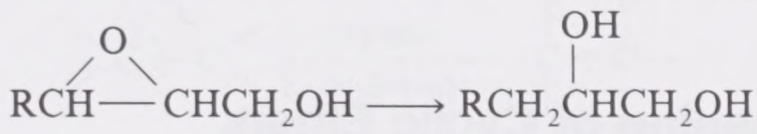


JOC *50* 5687 (1985)

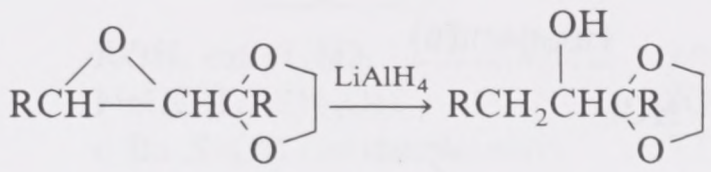


$NaBH_3CN$, $BF_3 \cdot OEt_2$	TL *28* 4569 (1987)
$LiAlH_4$	JOC *47* 1378 (1982) TL *28* 2629 (1987)

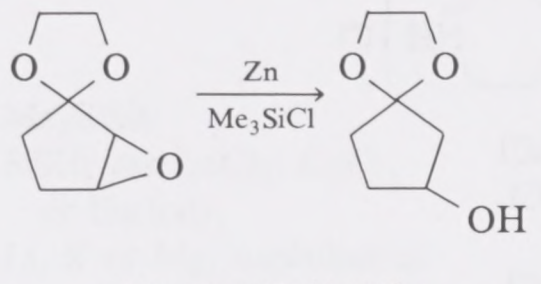
$NaH_2Al(OCH_2CH_2OCH_3)_2$	TL *23* 2719, 4541 (1982); *27* 3535 (1986); *28* 703 (1987) JOC *47* 1378 (1982) JACS *104* 1109, 5521 (1982); *109* 2205 (1987) CC 1292 (1982); 1408 (1986); 311 (1987) CL 175 (1983)



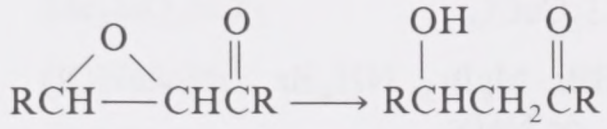
$LiBH_4$, $Ti(O\text{-}i\text{-}Pr)_4$	TL *27* 4343 (1986)
$i\text{-}Bu_2AlH$	TL *23* 2719, 3597 (1982)



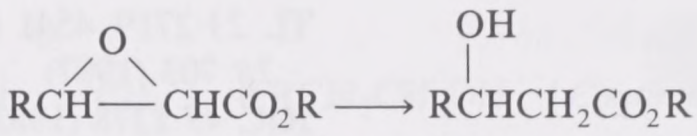
JOC *50* 5696 (1985)
TL *28* 551 (1987)



TL *28* 551 (1987)

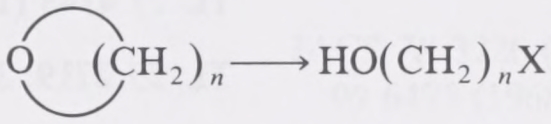


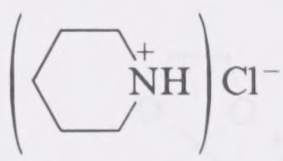
PhSeNa, HOAc, EtOH	TL *28* 4293 (1987)
NaTeH	CL 271 (1984)
NaI, NaOAc, HOAc	TL 4377 (1974)
Al(Hg)	CC 254 (1973) JOC *38* 3187 (1973); *43* 3942 (1978); *52* 3560 (1987) Helv *57* 781 (1974) JACS *100* 4618 (1978) Steroids *34* 683 (1979)
$CrCl_2$	JOC *19* 131 (1954)
$Cr(OAc)_2$	JACS *77* 4601 (1955) Helv *41* 1667 (1958) Coll Czech Chem Commun *26* 1207 (1961) JOC *37* 565 (1972); *43* 3946 (1978)
Zn, CH_3OH, HOAc	Chem Pharm Bull *24* 2810 (1976)
SmI_2, CH_3OH	JOC *51* 2596 (1986)
electrolysis	JOC *46* 5017 (1981)



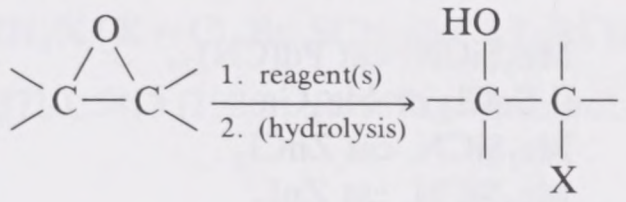
K, biphenyl/H_2O	Angew Int *25* 653 (1986)
MgI_2 / *n*-Bu_3SnH	TL *28* 4435 (1987)
SmI_2, $Me_2NCH_2CH_2OH$, THF, HMPA	TL *28* 4437 (1987)

3. Nucleophilic Opening of Cyclic Ethers



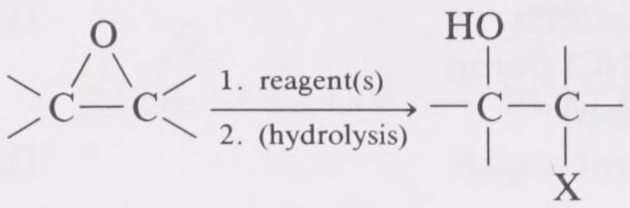
X	n	Reagent(s)	
Cl	2	HCl	Ber *49* 477, 2778, 2782 (1916) JACS *63* 2541 (1941); *76* 1235, 1259 (1954) JCS 915 (1963); 644 (1965)
			Syn Commun *11* 287 (1981)
		NaCl	JCS 915 (1963); 644 (1965)
		$AlCl_3$	Tetr *25* 1807 (1969) BCSJ *49* 1063 (1976)
		$SnCl_4$	JACS *76* 1235 (1954)
		$FeCl_3$	JOC *42* 343 (1977)
		Li_2CuCl_4	TL *27* 3697 (1986)
Br	2	HBr, $MgBr_2$, NH_4Br or NaBr	JACS *76* 1259 (1954)
		$(Me_2N)_2BBr$	TL *27* 827 (1986)
		Me_3SiBr, Et_3N (forms silyl ether)	Nouv J Chim *3* 705 (1979)
		Li_2NiBr_4	TL *25* 2061 (1984)
	2–4	Me_2BBr	TL *24* 2969 (1983) JOC *52* 1680 (1987)
		Me_3SiBr (forms silyl ether)	Ber *95* 174 (1962) TL 4483 (1978) Syn 383 (1981)
	2, 4–6	BBr_3	Heterocycles *18* 163 (1982)
	3	$MgBr_2$	JACS *73* 124 (1951)
	4	R_4NBr (R = Et, *n*-Bu)	JOC *51* 3372 (1986)
I	2	HI	JACS *76* 1259 (1954)
		Me_3SiI, Et_3N (forms silyl ether)	Nouv J Chim *3* 705 (1979)
		MgI_2	TL *28* 4435 (1987)
	2, 4	*n*-Bu_4NI, $BF_3 \cdot OEt_2$	Syn 274 (1985)
	4	NaI, $AlCl_3$	TL *25* 219 (1984)
		Me_3SiI (forms silyl ether)	Ber *95* 174 (1962) TL 4483 (1978)

Cl, Br, I	2	R_3SiX, cat PPh_3 or *n*-Bu_4NCl (forms silyl ether)	TL *22* 3803 (1981)
		X_2, PPh_3	TL *24* 1307 (1983); *26* 2011 (1985)



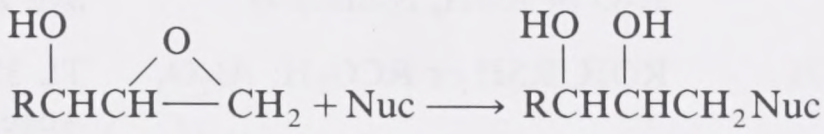
Review: Chem Rev *59* 737 (1959)

X	Reagent(s)	
RO	ROH, cat H_2SO_4	JACS *108* 3040 (1986)
	$NaOCH_3$, CH_3OH	JOC *52* 4812 (1987)
	n-Bu_3SnOR (intramolecular)	TL 2249 (1976)
OH, OR	H_2O or ROH, Nalfion-H	Syn 280 (1981)
OR, SR, O_2CR	ROH, RSH or RCO_2H; Al_2O_3	TL 3597 (1975) Angew Int *17* 487 (1978) (review)
SR	Me_3SiSR	TL *21* 1485 (1980)
	RSH; cat $SmCl_3$, $CeCl_3$ or $Eu(fod)_3$	TL *28* 6065 (1987)
	Li, K or Mg; naphthalene or biphenyl/RSSR	Angew Int *25* 653 (1986)
O_3SCF_3	$Me_3SiO_3SCF_3$	JACS *101* 2738 (1979)
SePh	(K)NaSePh	JACS *95* 2697 (1973); *99* 8208 (1977); *106* 7854 (1984); *107* 1691, 1777 (1985) TL 5087 (1978) Tetr *34* 1049 (1978) JOC *51* 2148 (1986)
	$Me_3SiSePh$, cat ZnI_2 or *n*-BuLi	CL 909 (1979)
	i-$Bu_2AlSePh$	JOC *50* 5897 (1985)
NHR	RNH_2	TL *28* 1603 (1987)
	Me_3SiNHR	TL *27* 2451 (1986) (aryl epoxides only)
NR_2	Et_2AlNR_2	TL *22* 195 (1981)
	R_2NH, Al_2O_3	Angew Int *17* 487 (1978) (review)
	Me_3SiNR_2	JOC *32* 2210 (1967)
	n-Bu_3SnNR_2, cat $LiNR_2$	JOMC *8* 255 (1967)
N_3	Me_3SiN_3	Ann 266 (1975)
	Me_3SiN_3, cat $Ti(O\text{-}i\text{-}Pr)_4$	TL *27* 4423 (1986)
NRCOR	$Me_3SiNRCOR$, cat $NaOSiMe_3$	Ber *102* 14 (1969)



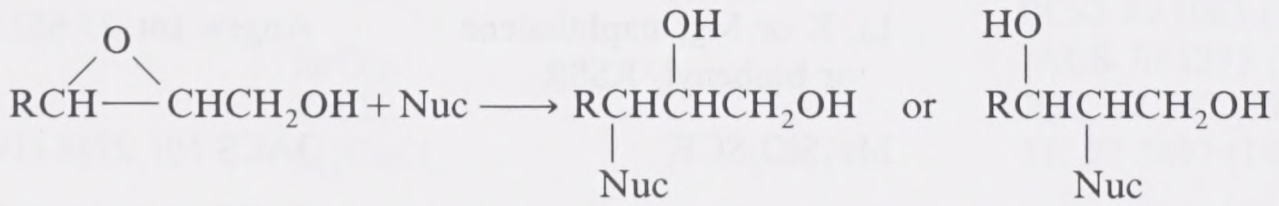
(*Continued*)

X	Reagent(s)	
$-N\equiv C$	Me_3SiCN; cat $Pd(CN)_2$, $SnCl_2$ or Me_3Ga	JOC *52* 1013 (1987)
	Me_3SiCN, cat $ZnCl_2$	TL *24* 655 (1983)
	Me_3SiCN, cat ZnI_2	JACS *104* 5849 (1982); TL *25* 3259 (1984); *27* 6307 (1986)
$-C\equiv N$	Me_3SiCN; $Al(O\text{-}i\text{-}Pr)_3$, $i\text{-}Bu_2AlO\text{-}i\text{-}Pr$ or Et_2AlCl	JOC *52* 1013 (1987)
	Me_3SiCN, cat $AlCl_3$	TL 1449 (1973)
	Me_3SiCN, cat Et_2AlCl	JOC *47* 2873 (1982)



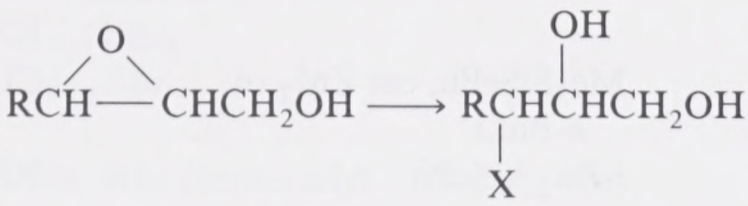
Nuc = NaN_3; *t*-BuSH, NaOH; KCN

JOC *50* 5687 (1985)

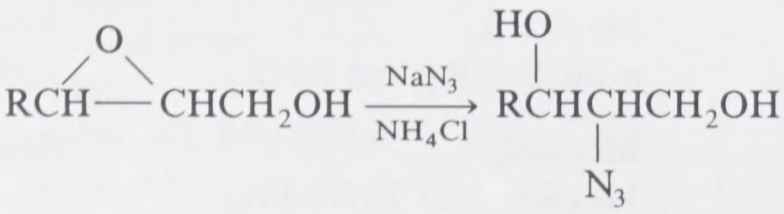


Nuc = NaN_3, NaSPh, NaSePh

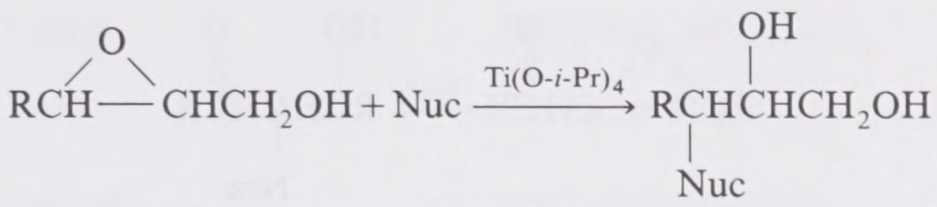
JOC *50* 5696 (1985)



X	Reagents	
Cl	$(i\text{-PrO})_2TiCl_2$, diethyl tartrate	TL *27* 6031 (1986)
N_3	NaN_3, zeolite	CL 1327 (1986)

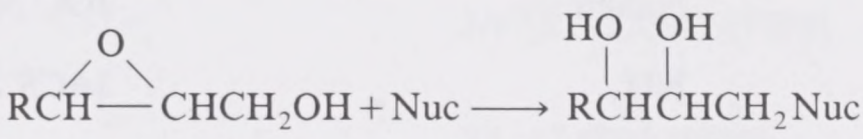


JOC *52* 3337 (1987)

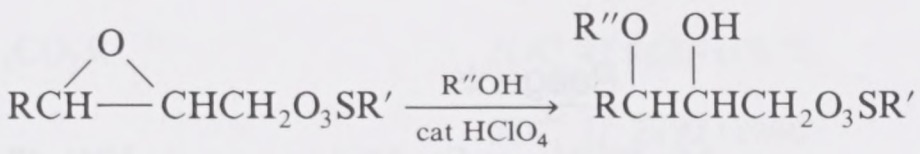


Nuc = R_2NH, ROH, NaOAr, PhSH, PhSeH, PhSNa, N_3^-, CN^-,
NH_4X (X = Cl, Br, SCN, O_2CR), RCO_2H

JOC *50* 1557 (1985); *51* 3710, 5413 (1986); *52* 667 (on *p*-nitrobenzoate ester), 4973 (1987)
TL *27* 4987, 4991 (1986)

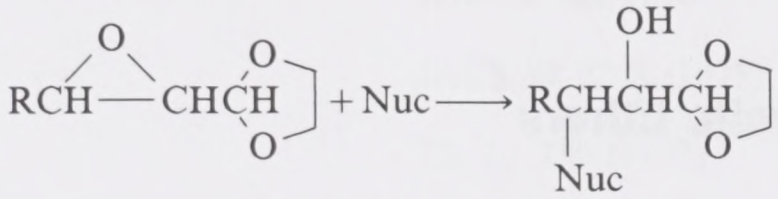


Nuc	
RSH, NaOH; R_2NH	JOC *50* 5687 (1985)
$RC{\equiv}CLi$, $BF_3 \cdot OEt_2$	CC 202 (1984)



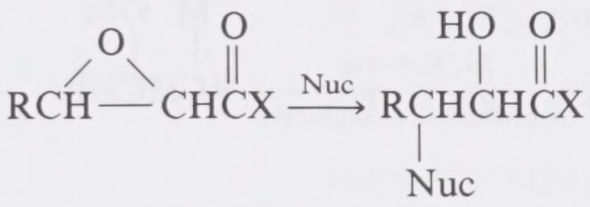
R′ = Me, *p*-C_6H_4Me; R″ = H, Me

JOC *50* 5687 (1985)

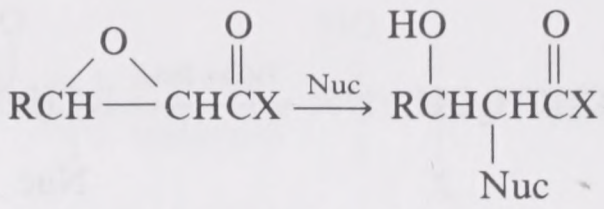


Nuc = NaN_3, NaSPh

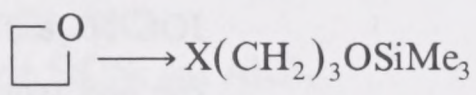
JOC *50* 5696 (1985)



X	Nuc	
OH	R_2NH, Ti(O-*i*-Pr)$_4$	JOC *50* 1560 (1985)
	PhSH or PhSNa, Ti(O-*i*-Pr)$_4$	JOC *50* 1560 (1985)
OR	NH_3	Arch Pharm *307* 871 (1974); *308* 135 (1975) JCS Perkin I 1618 (1980)
NR_2	NaN_3, $MgSO_4$	JOC *50* 5696 (1985)
	R_2NH	BCSJ *54* 2136 (1981) Arch Pharm *314* 464 (1981)
	PhSH or PhSNa, Ti(O-*i*-Pr)$_4$	JOC *50* 1560 (1985)
OH, OR, NR_2	$ArNH_2$	Arch Pharm *312* 26 (1979)
	R_2NH	Arch Pharm *312* 138 (1979)



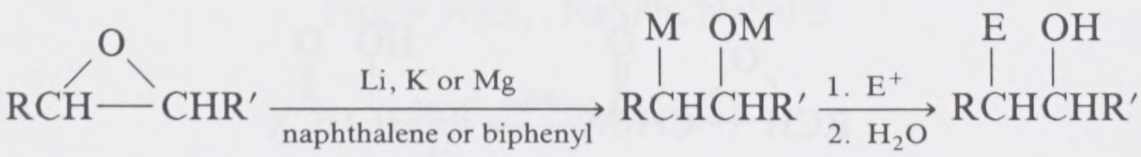
X	Nuc	
OH	$PhCH_2NH_2$ or NH_3	JCS 1116 (1962)
	R_2NH	JOC *50* 1560 (1985)
	NaSPh	JOC *50* 1560 (1985)
OR	NH_3	JACS *80* 187 (1958)
NR_2	NaSPh	JOC *50* 1560, 5696 (1985)



X	Reagents	
—CN	Me_3SiCN, cat Et_2AlCl	JOC *47* 2873 (1982)
—N≡C	Me_3SiCN, cat ZnI_2	Syn Commun *15* 775 (1985)

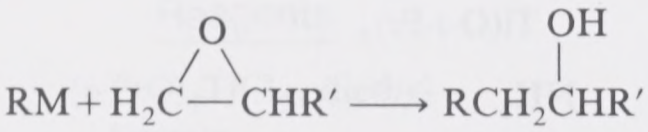
4. Alkylation of Cyclic Ethers

4.1. Epoxides

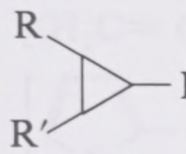
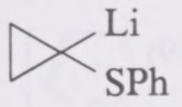
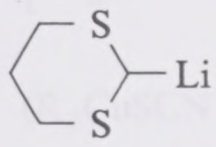


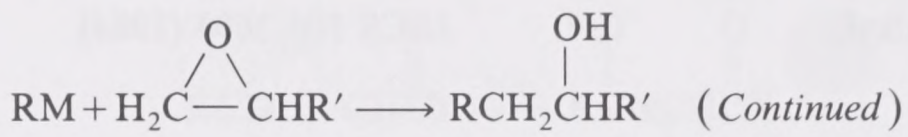
$E^+ = H_2O, D_2O, RX, CO_2, RSSR$

Angew Int *25* 653 (1986)



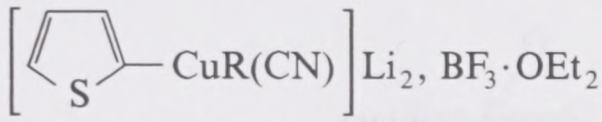
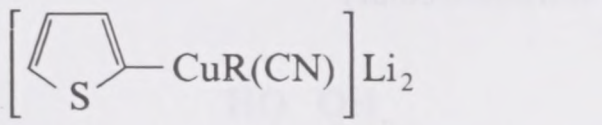
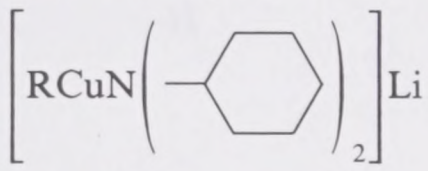
RM	
Li, naphthalene/*n*-$Bu_3P \cdot CuI$/RX (R = 1° alkyl, aryl)	JOC *52* 5057 (1987)
CH_3Li	JACS *92* 4979 (1970)
CH_3Li, CH_3MgCl	TL *27* 5335 (1986) JOC *52* 4505 (1987)

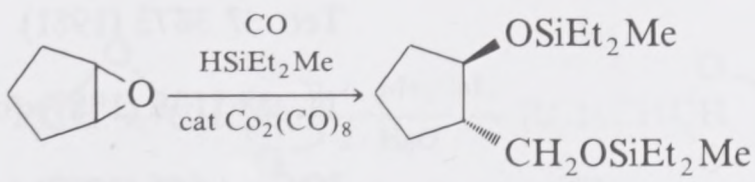
RLi, $BF_3 \cdot OEt_2$ (R = 1° alkyl, aryl, vinylic)	JACS *106* 3693 (1984)
	JOC *47* 3211 (1982)
	TL *23* 2379 (1982)
	JACS *106* 2949 (1984)
$PhSCH(Li)SiMe_3$	TL *27* 4403 (1986)
$RCHLiSO_2Ph$, $BF_3 \cdot OEt_2$	TL *27* 6345 (1986) CC 1226 (1987)
$RC(Li)_2SO_2Ph$	JACS *109* 6205 (1987)
$LiCH_2CO_2Li$ or $LiCH_2CO_2R$	JOC *42* 1688 (1977)
$LiCH_2CN$	JOC *51* 2230 (1986) TL *28* 1611 (1987)
$H_2C{=}CHCH_2Li$	JACS *108* 8015 (1987) JOC *52* 862 (1987)
$Me_3SiC{\equiv}CCH_2Li$	JACS *97* 3258 (1975)
$(i\text{-}Pr)_3SiC{\equiv}CCH_2Li$	TL *23* 719 (1982)
ArLi	JOC *52* 5668 (1987) TL *28* 861 (1987)
PhLi, CuCN	TL *28* 1783 (1987)
$RCH{=}CHLi$, $MgBr_2$	JOC *52* 4495 (1987)
$RCH{=}CHLi$, cat CuI	JACS *109* 5437 (1987)
$HC{\equiv}CLi$(EDA), DMSO	Compt Rend C *265* 839 (1967) JCS D 674 (1969) CC 223 (1973) JACS *101* 5364 (1979); *103* 7520 (1981) JOC *51* 4840 (1986)
$RC{\equiv}CLi$	Syn 26 (1978); 490 (1981) Helv *65* 385 (1982) TL *23* 1331 (1982) JACS *106* 3548 (1984); *109* 6176 (1987)
$LiO_2CC{\equiv}CLi$	TL 3173 (1976)
$RC{\equiv}CLi$, $BF_3 \cdot OEt_2$	TL *24* 391 (1983); *27* 4991 (1986); *28* 391, 5457 (1987) JOC *52* 622, 2860 (1987) JACS *109* 7495 (1987)



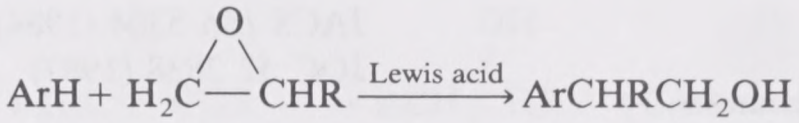
(*Continued*)

RM	
RMgX	Org Syn Coll Vol *1* 306 (1941) Chem Rev *49* 413 (1951); *59* 737 (1959) JOC *16* 673 (1951); *46* 4608 (1981) Rec Trav Chim *87* 1249 (1968) JACS *92* 4979 (1970) J Chem Res (S) 162 (1982) TL *27* 6071 (1986)
$H_2C{=}CHCH_2MgCl$	TL *27* 5335, 6071 (1986)
Me_2Mg	TL *23* 1763 (1982)
RMgX, cat CuCN	TL *27* 2679 (1986)
MeMgCl, cat $CuCl{\cdot}SMe_2$	TL *28* 3835 (1987)
RMgX, cat CuI	TL 1503 (1979); *23* 1267 (1982) Can J Chem *61* 1166 (1983) CC 620 (1986)
RMgX, CuI	CC 836 (1986); 429 (1987) JOC *51* 2230 (1986) TL *27* 6071 (1986); *28* 2627 (1987)
$H_2C{=}CHCH_2MgX$, CuI	TL *27* 6071 (1986)
$H_2C{=}CHMgBr$, CuI	TL *27* 4485, 5791 (1986) CC 877 (1987)
R_2CuMgX	TL *28* 1781, 1993 (1987)
$(RCH{=}CH)_2CuMgX$	TL *28* 1993 (1987)
R_2CuLi	JACS *92* 3813, 4979 (1970); *109* 8105 (1987) JOC *38* 4263 (1973); *40* 2263 (1975) (α-silyl epoxides); *48* 546 (1983); *52* 4495 (1987) Org Rxs *22* 253 (1975) JCS Perkin I 2885 (1982) TL *27* 6071 (1986); *28* 1781, 1993, 6191 (1987)
$R_2CuLi{\cdot}2\ RLi$	TL *21* 4365 (1980)
$(R_2C{=}CR)_2CuLi$	TL *26* 5837 (1985); *27* 2519, 5277 (1986); *28* 1781, 1993 (1987)
$[(RC{\equiv}C)Cu(\mathbf{CH{=}CHR})]Li$	JCS Perkin I 2954 (1979), 852 (1980)
$(Me_3SiC{\equiv}CCu\mathbf{CH_2CH{=}CROSiMe_3})Li$	JACS *107* 5495 (1985)
(RCuCN)Li	TL 3407 (1977); 2399 (1978)
$(R_2CuCN)Li_2$	JACS *104* 2305 (1982); *109* 6176 (1987) JOC *49* 3928 (1984)

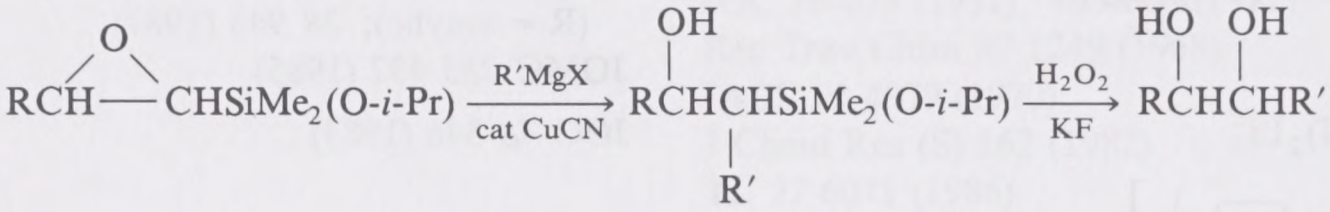
$[(H_2C{=}CH)_2CuCN]Li_2$	JACS *106* 5304 (1984) JOC *52* 2838 (1987)
$[(H_2C{=}CH)_2CuCN]Li_2$, $BF_3{\cdot}OEt_2$	TL *27* 5791 (1986)
	TL *25* 5959 (1984)
	TL *25* 5959 (1984); *27* 4825 (1986) (R = vinylic); *28* 945 (1987) JOMC *285* 437 (1985)
$(R_2CuSCN)_2Li_2$	JOC *48* 546 (1983)
	JACS *104* 5824 (1982)
$(RCuPPh_2)Li$	JACS *104* 5824 (1982)
$Et_2Al\mathbf{CH_2CO_2}$-*t*-**Bu**	JOC *41* 1669 (1976) Syn 284 (1983)
E-*i*-$Bu_2Al\mathbf{CH{=}CHR}$	JOC *42* 2712 (1977)
$(R_3Al\mathbf{CH{=}CRR'})Li$	Syn 632 (1975); 1034 (1980) CC 17 (1976)
$\mathbf{RC{\equiv}C}AlR'_2$ (R′ = Me, Et)	CC 634 (1968); 287 (1975); 907 (1976) TL 1379 (1969); 2695 (1970); 3899 (1973); 1769 (1976) JACS *94* 4342, 4343 (1972); *95* 7171 (1973); *100* 3950 (1978); *103* 7520 (1981); *108* 5559 (1986); *109* 2205 (1987) JOC *41* 1669 (1976); *42* 394 (1977); *43* 353 (1978); *50* 3923 (1985) JCS Perkin I 2954 (1979); 852 (1980)
$(t\text{-}\mathbf{Bu})\mathbf{Me_2SiCH_2C{\equiv}C}AlEt_2$	JOC *52* 4495 (1987)
$MeOAl(Me)\mathbf{C{\equiv}CR}$	TL 3899 (1973)
$[Me_2Al(\mathbf{C{\equiv}CR})_2]Li$	JOC *50* 3923 (1985)
$RSiMe_3$ (R = allylic), $TiCl_4$	Syn 446 (1978) TL *24* 5661 (1983) CC 585 (1984) (intramolecular)
$RSiMe_3$ (R = allylic), $BF_3{\cdot}OEt_2$	Can J Chem *61* 214 (1983) (intramolecular) TL *28* 2753 (1987) (intramolecular)
R_3MnLi	TL *27* 5351 (1986)



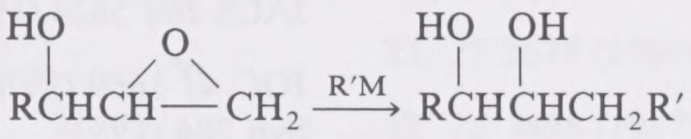
JACS *106* 6093 (1984)



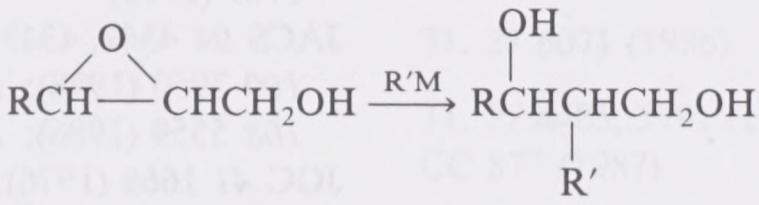
JCS 5404 (1964) (intramolecular)
Tetr *25* 1807 (1969)
JOC *48* 2449, 4572 (1983); *52* 425 (1987) (all intramolecular)

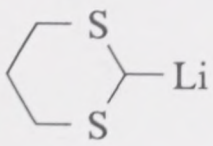


JOC *52* 4412 (1987)

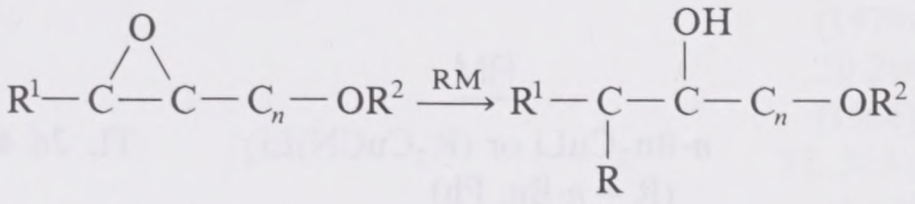


R′M	
Me_2CuLi, $LiC{\equiv}CCH_2OTHP$	JOC *50* 5687 (1985)
$PhSe\bar{C}HSiMe_3$, $LiC{\equiv}CCH_2OTHP$	TL *24* 4539 (1983)

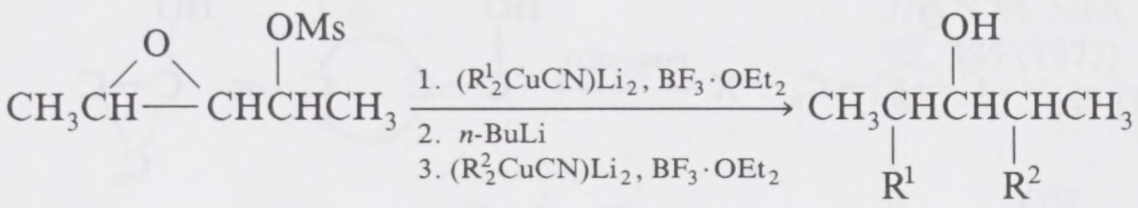


R′M	
$LiC{\equiv}CH{\cdot}EDA$	CC 874 (1986) (mixture)
	TL *27* 4825 (1986)
RMgX, cat CuI	JOC *48* 3131 (1983) JACS *108* 1035 (1986)
R'_2CuLi	JOC *38* 4346 (1973) (cyclohexyl system); *52* 2596 (1987) TL 4343 (1979); *23* 707 (1982); *24* 1377 (1983); *28* 5009 (1987) Tetr *37* 3873 (1981)
Me_2CuLi, $BF_3{\cdot}OEt_2$	TL *28* 1139 (1987) (on trityl ether)
Me_3CuLi_2	JOC *52* 685 (1987) (mixture)
$(CH_3CuCN)Li$	JOC *51* 956 (1986) (mixture)

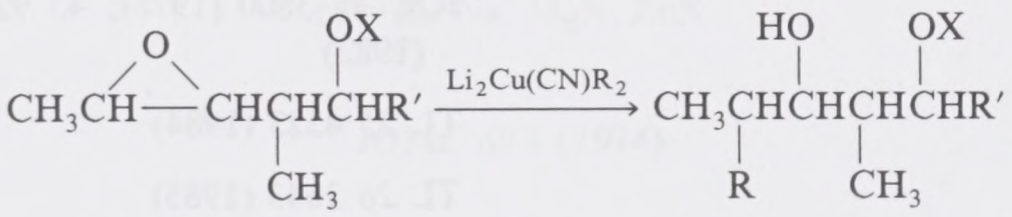
$(Me_2CuCN)Li_2$ JACS *108* 2776 (1986)
TL *28* 5009 (1987)
JOC *52* 3784 (1987)



n	R^2	RM	
1	H	R_3Al	TL *23* 3597 (1982); *24* 1377 (1983); *27* 3369, 4601 (1986); *28* 1139 (1987) JOC *52* 2596 (1987)
		$\mathbf{RC{\equiv}C}AlEt_2$	TL *23* 3597 (1982)
		Me_3CuLi_2	JOC *52* 685 (1987) (mixture)
		(MeCuCN)Li	JOC *51* 956 (1986) (mixture)
		$(Me_2CuCN)Li_2$, $BF_3 \cdot OEt_2$	TL *28* 5009 (1987)
	H, Me	Me_2CuLi	JOC *38* 4346 (1973) (cyclohexyl system)
	CH_2OCH_3, CH_2Ph	$Me_2AlC{\equiv}\mathbf{CR}$	JOC *48* 409 (1983)
	SiR_3	RLi, CuCN	CC 1237 (1986)
1,2	CH_2Ph	Me_3Al, cat *n*-BuLi or LiOMe	Angew Int *21* 71 (1982)

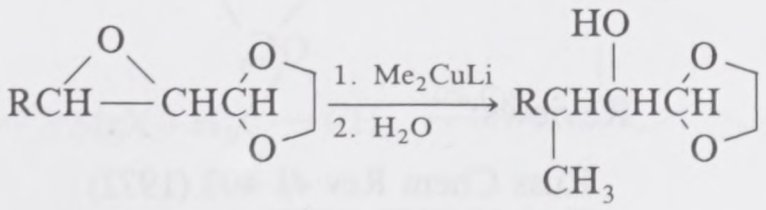


TL *28* 5631 (1987)

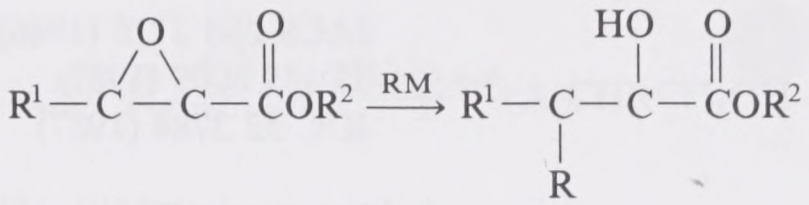


X = H, SiR_3

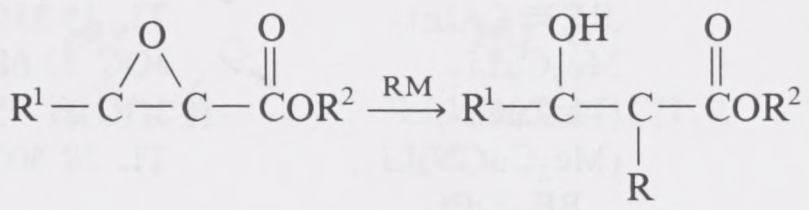
TL *28* 6195 (1987)



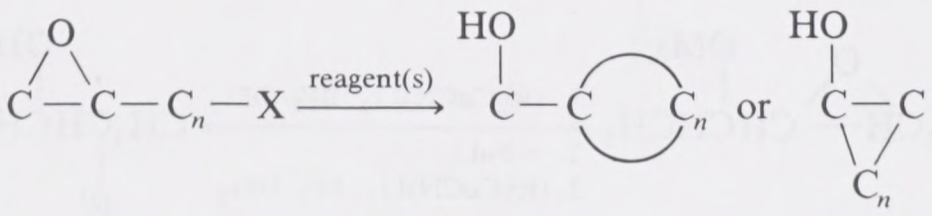
JOC *50* 5696 (1985)



R^2	RM	
H	*n*-Bu_2CuLi or $(R_2CuCN)Li_2$ (R = *n*-Bu, Ph)	TL *26* 4683 (1985)
Et	Me_2CuLi	JACS *106* 2949 (1984) ($R^1 = CO_2Et$)
alkyl	$Et_2AlC{\equiv}CR$	TL *23* 2331 (1982); *27* 5397 (1986) JOC *47* 3941 (1982) JACS *108* 5559 (1986)

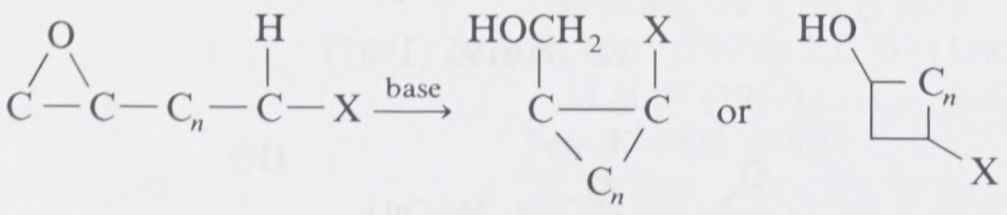


R^2	RM	
H	*n*-Bu_2CuLi, $(R_2CuCN)Li_2$ (R = *n*-Bu, Ph)	TL *26* 4683 (1985)
alkyl	R_2CuLi	JACS *92* 3813 (1970); *106* 2949 (1984) ($R^1 = CO_2Et$) JOC *38* 4263, 4346 (1973)



X = Br, I

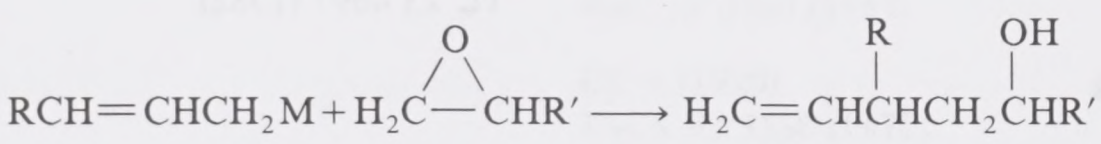
Reagent(s)	
n-BuLi	JOC *43* 3800 (1978); *45* 922 (1980); *47* 3211 (1982)
sec-BuLi	TL *25* 4323 (1984)
t-BuLi	TL *26* 3643 (1985)
Cu, *n*-Bu_3P	JOC *52* 5057 (1987)



Reviews:

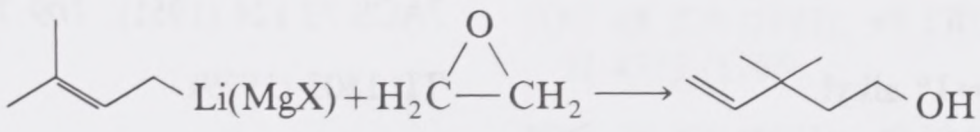
Russ Chem Rev *41* 403 (1972)
Tetr *39* 2323 (1983)
Syn 629 (1984)

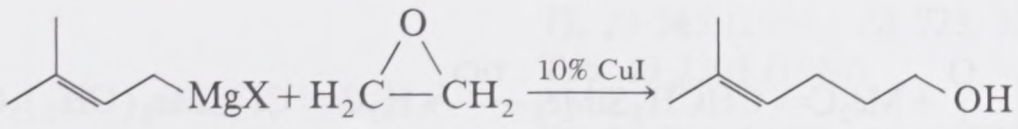
X	Ring size	
Ph_2	3	JOC *41* 885 (1976)
SO_2Ph	3–6	JOC *41* 3648 (1976); *44* 4603 (1979); *47* 2564 (1982); *50* 2943 (1985); *51* 5311 (1986); *52* 4614 (1987) TL 503 (1976); *22* 4339 (1981); *26* 6301 (1985) Can J Chem *56* 505 (1978); *59* 1415 (1981)
$(SO_2Ph)_2$	3, 5–7	CC 406 (1987)
COR	3–6	JCS 2988 (1951) JACS *79* 3519 (1957); *86* 3162 (1964); *94* 7132 (1972); *107* 1438 (1985) (β-lactam) TL 3731 (1970); 3683 (1972) Tetr *28* 5525, 5533 (1972) JOC *37* 2911 (1972) Can J Chem *55* 1629 (1977)
CO_2R	3	JOC *41* 885 (1976) TL 2441 (1976)
$(CO_2R)_2$	5	JOC *34* 4060 (1969)
$CONR_2$	3	TL *23* 1343 (1982) JOC *49* 2682 (1984)
	6	JOC *52* 4044 (1987)
CN	3–6	JACS *96* 5268, 5270 (1974) TL 585 (1975) JOC *41* 3648 (1976)



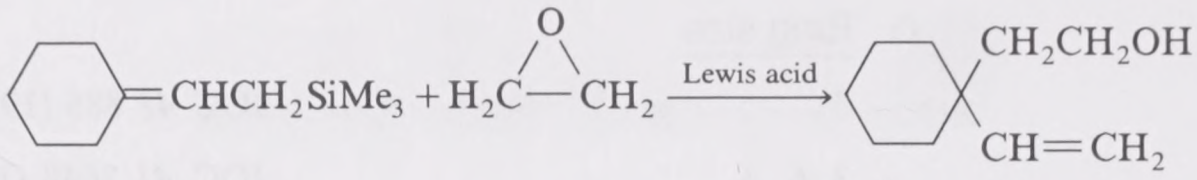
M = Li, Na, MgX, ZnX

JOMC *69* 1 (1974)



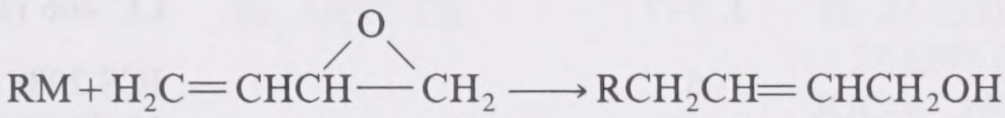


TL 4069 (1978)

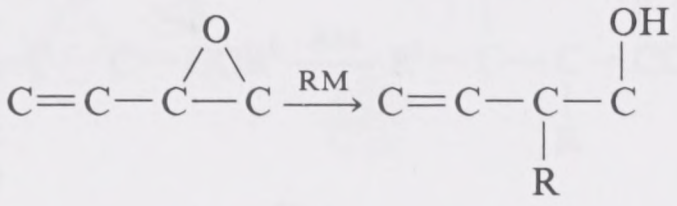


Lewis acid

$BF_3 \cdot OEt_2$	Can J Chem *61* 214 (1983) (intramolecular) TL *28* 2753 (1987) (intramolecular)
$TiCl_4$	Syn 446 (1978) TL *24* 5661 (1983) CC 585 (1984) (intramolecular)



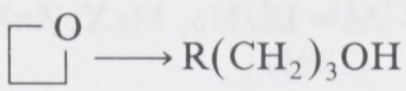
See page 119, Section 8.



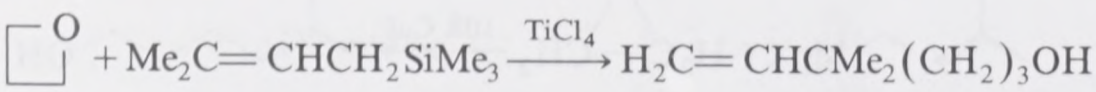
RM

RMgX	CC 248 (1969) BSCF 2556 (1970) TL 2005 (1971) JOC *51* 1687 (1986)
$Et_2AlCH_2CO_2$-*t*-Bu (R = CH_2CO_2-*t*-Bu)	Syn 284 (1983)
$LiAlR_4$	TL *23* 4697 (1982)
R_2CuLi	TL *23* 4697 (1982)
$(R_2CuCN)Li_2$	TL *23* 4697 (1982)

4.2. Oxetanes



RLi	JACS *73* 124 (1951)
RMgX	JACS *73* 124 (1951); *109* 7280 (1987)
RMgX, cat CuI (R = 1° alkyl, allylic, aryl)	TL 1503 (1979)
RLi, $BF_3 \cdot OEt_2$ (R = 1° alkyl, aryl, vinylic)	JACS *106* 3693 (1984)



JOC *50* 2782 (1985)

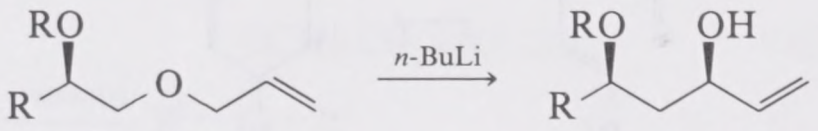
5. Rearrangement

$$R_2CHOR \xrightarrow[2.\ H_2O]{1.\ R'Li} R_3COH$$

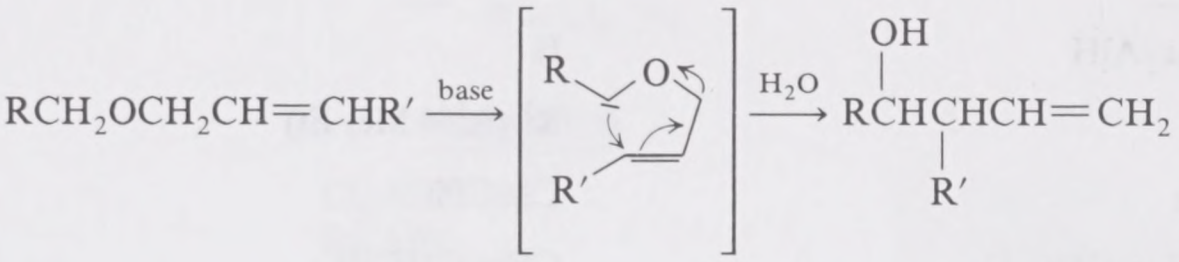
Angew Int *9* 763 (1970)

$$ArOH \longrightarrow ArOCH_2SiMe_3 \xrightarrow[2.\ KOH]{1.\ RLi} ArCH_2OH$$

JOC *47* 5051 (1982)



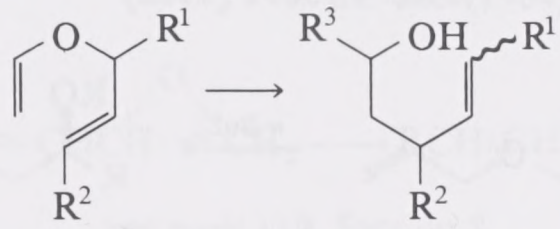
TL *28* 1043 (1987)



Reviews:
Angew Int *18* 563 (1979) (stereochemistry of 2,3-sigmatropic rearrangements)
Chem Rev *86* 885 (1986)

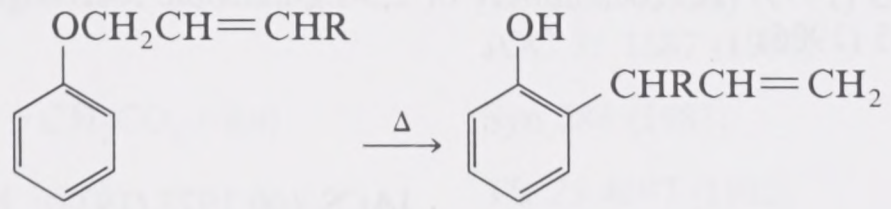
R	
—	JACS *100* 1927 (1978); *108* 3841 (1986); *109* 3017, 6199 (1987) TL *26* 5013, 5017 (1985); *28* 2099, 4993 (1987) JOC *52* 2960 (1987)
aryl	CC 4 (1970) JACS *93* 3556 (1971) JOC *48* 279 (1983); *49* 1842 (1984)
vinylic	CC 4 (1970) CL 557 (1977) JACS *103* 6492 (1981); *107* 3915 (1985) TL *23* 3931 (1982) JOC *48* 279 (1983); *49* 1707, 1842 (1984); *51* 4315 (1986)
alkynyl	JOC *48* 279 (1983); *49* 1842 (1984); *51* 4316 (1986); *52* 3860, 3883 (1987) CL 1379 (1983) TL *25* 565 (1984); *28* 723, 3323 (1987) Tetr *40* 2303 (1984)
heterocyclic	TL *24* 513 (1983); *25* 6011 (1984)
COR	Helv *57* 2084 (1974)

R	
CO_2^-	TL *22* 69 (1981) JOC *51* 4090 (1986)
CO_2R	TL *27* 4511 (Me_3SiOTf added), 4581 (Cp_2ZrCl_2 added) (1986); *28* 803 (1987) (Cp_2ZrCl_2 added)
$CONR_2$	CL 1729 (1985) TL *27* 4577 (1986) (Cp_2ZrCl_2 added)
CN	TL *24* 2077 (1974)

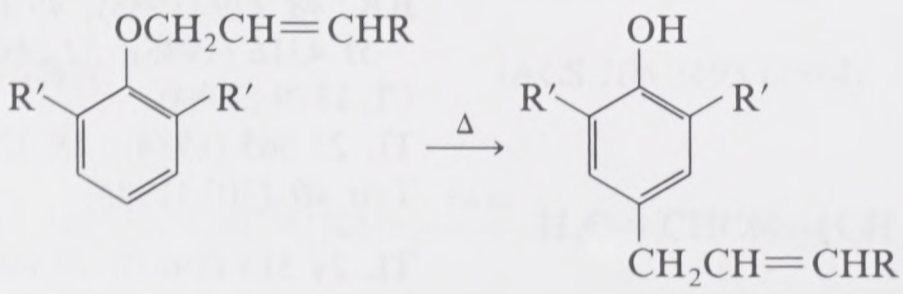


Reagent	R^3
i-Bu_3Al or *i*-Bu_2AlH	H
R^3_3Al	R^3 (R^3 = Me, Et)
$Et_2AlC{\equiv}CPh$	$C{\equiv}CPh$
E-(*i*-Bu)$_2$AlCH=CHC_6H_{13}	$CH{=}CHC_6H_{13}$

TL *22* 3985 (1981)

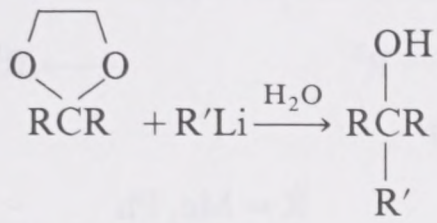


Org Rxs *2* 1 (1944) (review)
Org Syn Coll Vol *3* 418 (1955)
Helv *52* 337 (1967)
Adv Heterocyclic Chem *8* 143 (1967) (review, nitrogen heterocycles); *42* 203 (1987) (review, heteroaromatics)
Chimia *24* 89 (1970) (review)
Austral J Chem *34* 819, 1079 (1981)
CL 1131 (1982)
CC 1120 (1982); 182, 750 (1986)
TL *23* 4407 (1982), *27* 4945 (1986) (in microwave ovens); *28* 3075 (1987)
Tetr *38* 3079 (1982)
Chem Rev *84* 205 (1984) (review, catalysis)
JACS *107* 3891 (1985)

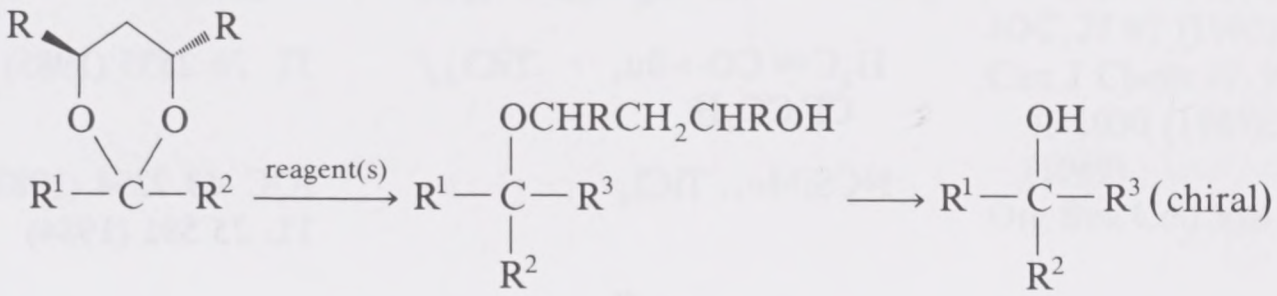


Org Rxs *2* 1 (1944) (review)
JACS *70* 1747 (1948)

6. Acetal Cleavage

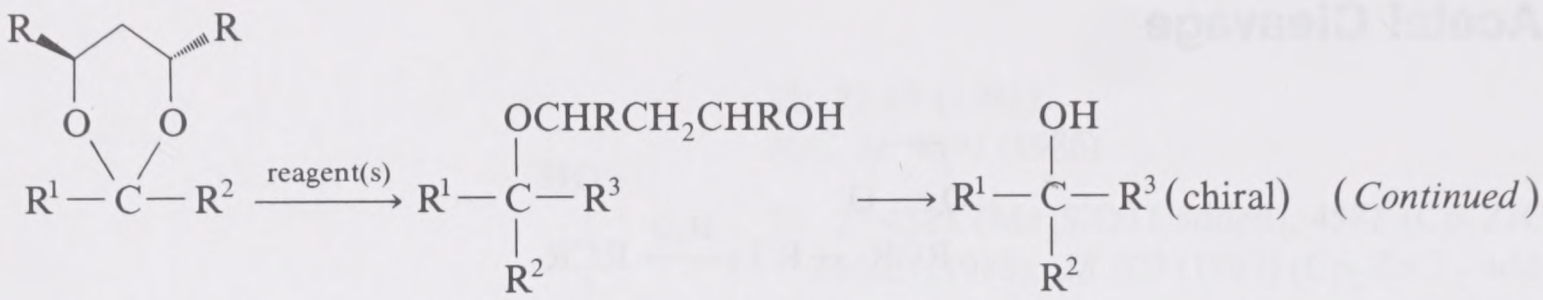


Syn Commun *13* 769 (1983)



R = Me, Ph

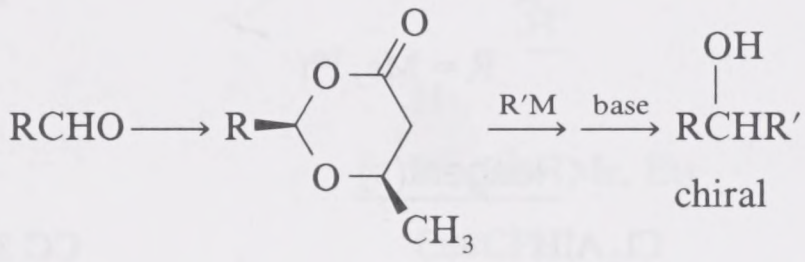
R^3	Reagent(s)	
H	Cl_2AlH	CC 334 (1987)
	Br_2AlH	TL *24* 4581 (1983); *27* 983, 987 (1986)
		JOMC *285* 83 (1985)
		CC 334 (1987)
	i-Bu_2AlH	TL *24* 4581 (1983); *27* 983 (1986)
		JOMC *285* 83 (1986)
	$TiCl_4$, Et_3SiH	TL *27* 987 (1986)
1° alkyl, Ph	$R_2CuLi \cdot BF_3$	TL *25* 3083 (1984)
1° R, $H_2C{=}CHCH_2$	RMgX or RLi or $R_2CuLi(MgX)$, $TiCl_4$	TL *25* 3947 (1984)
$H_2C{=}CHCH_2$	$H_2C{=}CHCH_2SiMe_3$, $SnCl_4$	JACS *104* 7371 (1982)
	$H_2C{=}CHCH_2SiMe_3$, $TiCl_4$	JACS *108* 7116 (1986)
	$H_2C{=}CHCH_2M$ (M = B⟨ ⟩, *n*-Bu_3Sn, Ph_3Sn), Lewis acid?	JACS *108* 7116 (1986)
$H_2C{=}CRCH_2$	$H_2C{=}CRCH_2SiMe_3$ (R = H, Me), $TiCl_4$, Ti(O-*i*-Pr)$_4$	JACS *105* 2088 (1983)
		TL *25* 3951 (1984)
		JOC *50* 2598 (1985)
$RC{\equiv}C$	$RC{\equiv}CSiMe_3$, $TiCl_4$	JACS *105* 2904 (1983)
	$RC{\equiv}CM$ (M = Me_3Si, *n*-Bu_3Sn), Lewis acid?	JACS *108* 7116 (1986)
$CH_3CH_2COCH_2$	$CH_3CH_2COCH_2SiMe_3$, $SnCl_4$	JACS *104* 7371, 7372 (1982)
$RCOCH_2$	$RC(OSiMe_3){=}CH_2$, $TiCl_4$	JACS *104* 7371, 7372 (1982); *106* 7588 (1984)
		JOC *52* 180 (1987)



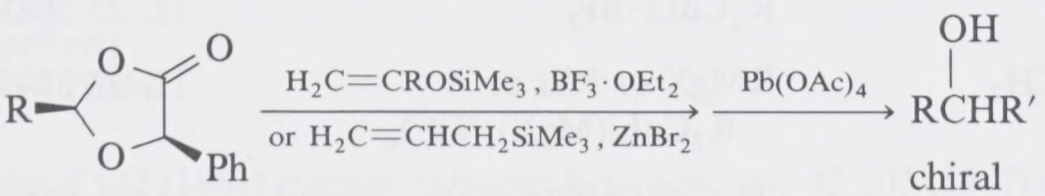
(*Continued*)

R = Me, Ph

R^3	Reagent(s)		
CH_2CO_2H	$H_2C{=}C(OSiMe_2\text{-}t\text{-}Bu)CO\text{-}t\text{-}Bu$, CF_3CO_2H	$TiCl_4$/	TL *26* 2535 (1985)
CN	$NCSiMe_3$, $TiCl_4$		JOC *48* 2294 (1983) TL *25* 591 (1984)

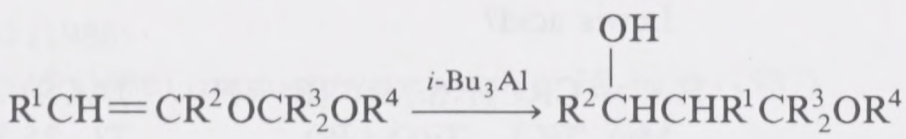


R′M		
R′Li (R′ = 1° alkyl, aryl, vinyl), $CuBr\cdot SMe_2$		TL *27* 2945 (1986)
$H_2C{=}CHCH_2Li$, CuBr, $BF_3\cdot OEt_2$		TL *27* 2945 (1986)
Me_3SiR' (R′ = allyl, alkynyl, CN), Cl_3TiX (X = Cl, O-*i*-Pr)		Angew Int *25* 178 (1986)

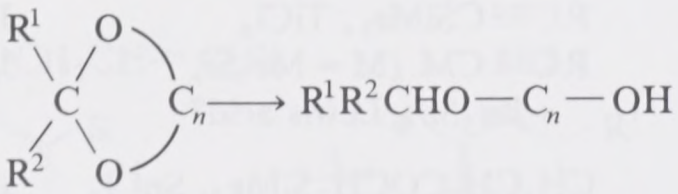


R′ = CH_2COR or $CH_2CH{=}CH_2$

JOC *49* 2513 (1984)

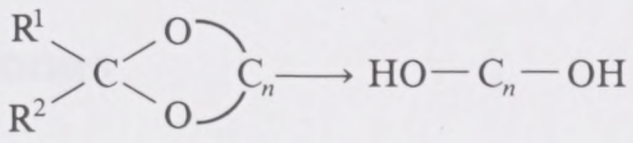


JOC *52* 5700 (1987)



R^1	R^2	Reagent(s)	n	
Ph	H	*i*-Bu_2AlH	2,3	CL 1593 (1983) Chem Pharm Bull *32* 791 (1984)

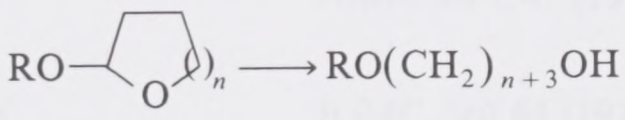
Ph	H	$LiAlH_4$, $AlCl_3$	2–4	JACS *84* 2371 (1962) JOC *27* 67 (1962) Can J Chem *47* 1195 (1969) Carbohydr Res *44* 1 (1975); *51* C19 (1976) TL 3551 (1976); *22* 3919 (1981); *23* 3507 (1982)
p-$MeOC_6H_4$	H	$NaBH_3CN$, CF_3CO_2H or Me_3SiCl	3	CC 201 (1984)
H or alkyl	H or alkyl	$LiAlH_4$, $AlCl_3$	2,3	JACS *84* 2371 (1962) JOC *27* 67 (1962) Can J Chem *42* 990 (1964); *43* 1030 (1965); *47* 1195 (1969) Org Syn Coll Vol *5* 303 (1973)



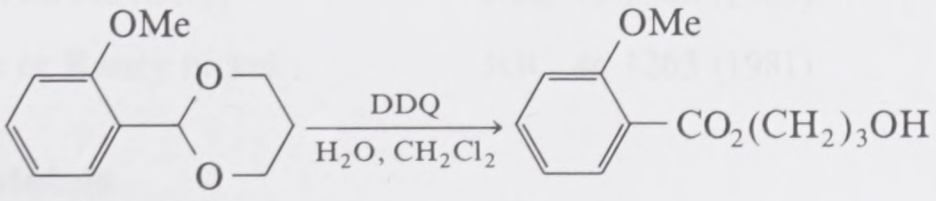
Review:

T. W. Greene, "Protective Groups in Organic Synthesis," Wiley-Interscience, New York (1981), pp 72–86

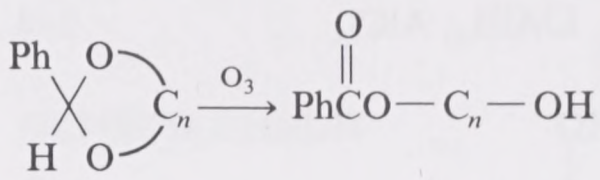
R^1	R^2	Reagent(s)	n	
Ph	H	N_2H_4, H_2O, cat Pd-C	2	Syn 317 (1986)
Ph	H	HCO_2H, cat Pd-C	3	Carbohydr Res *83* 175 (1980)
Ph	H	 , cat $Pd(OH)_2$—C	3	Syn 396 (1981)
p-$CH_3OC_6H_4$	CH_3	$SnCl_4$/*n*-Bu_4NOH	2,3	JOC *46* 2419 (1981)



n	Reagents	
1,2	$LiAlH_4$, $AlCl_3$	JOC *30* 2441 (1965) Can J Chem *45* 2547 (1967)
2	$LiAlH_4$, HCl	JACS *73* 5917 (1951)

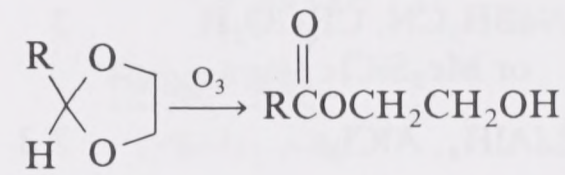


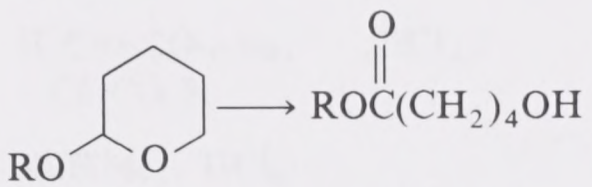
TL *23* 889 (1982)



$n = 2,3$

Can J Chem *53* 1204 (1975)





Can J Chem *49* 2465 (1971)

7. REDUCTION OF CARBONYL COMPOUNDS

1. Aldehydes and Ketones

Review: Syn 605 (1982) (stereoselectivity of reduction of chiral aminocarbonyl compounds)

1.1. Hydrogenation

Reviews:

C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley Interscience, New York (1970), p 201

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 14

H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York (1972), p 1

M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley and Sons, New York (1978), Chpt 9

P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 4

H_2, $FeCl_2$ (δ-hydroxy-β-keto ester)	Helv *69* 803 (1986)
H_2, cat [Rh(1,5-hexadiene)Cl]$_2$ + R_3P (chiral) (asymmetric)	JOMC *94* C47 (1975)
H_2, cat [Rh(1,5-hexadiene)L_2]X (L_2 = 2,2′-bipyridine, phenanthrolines; X = PF_6, BPh_4) (C=O > C=C)	JOMC *140* 63 (1977)
H_2, cat [Rh(bipy)S_2]$^+$ or [Rh(bipy)$_2$]$^+$ (S = solvent) (C=O > C=C)	JOMC *157* 345 (1978)
H_2, cat $RuCl_2(CO)_2(PPh_3)_2$, Δ (aldehydes only)	JOMC *145* 189 (1978)
H_2, cat NaH-NaO-*t*-Am-Ni(OAc)$_2$	JOC *45* 1946 (1980)
H_2, cat nickel boride or Raney nickel	JOC *46* 1263 (1981)

1.2. Reduction by Metals

Review: Tetr *42* 6351 (1986) (alkali metals in protic solvents)

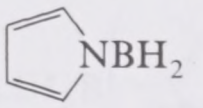
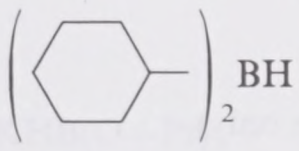
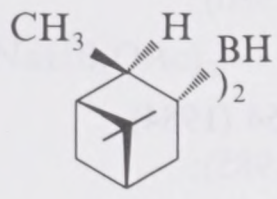
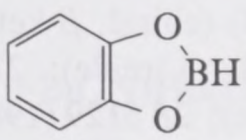
Li, NH_3	JACS *90* 6486 (1968); *108* 800 (1986) JCS C 968 (1969) Helv *64* 2109 (1981) Acct Chem Res *16* 399 (1983)
Li, Na, or K; NH_3	BSCF 4399 (1970) JCS Perkin I 999 (1972)
Li, Na or K; NH_3; NH_4Cl	BSCF 4404 (1970) JCS Perkin I 999 (1972) Helv *64* 2109 (1981) CC 1558 (1986)
Li, NH_3, ROH	BSCF 4404 (1970) Pure Appl Chem *49* 1049 (1977) JACS *108* 3443 (1986)
Li(Na), ROH	JCS C 968 (1969)
Na, H_2O, EtOH	JACS *106* 4547 (1984)
Na, *i*-PrOH	JOC *51* 4779 (1986) Org Syn *65* 203 (1987)
Al(Hg), H_2O	Arch Pharm *280* 361 (1942)
Fe, HOAc	Org Syn Coll Vol *1* 304 (1932) JACS *61* 2134 (1939)

1.3. Metal Hydride Reduction

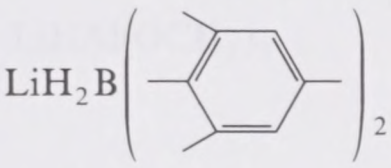
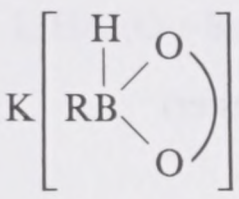
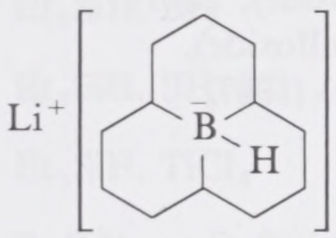
Reviews:

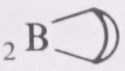
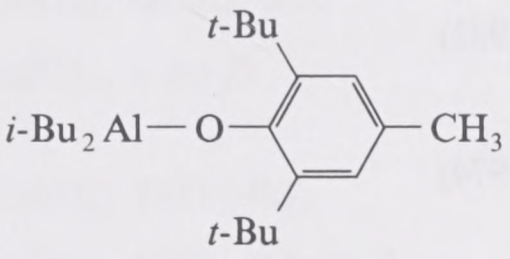
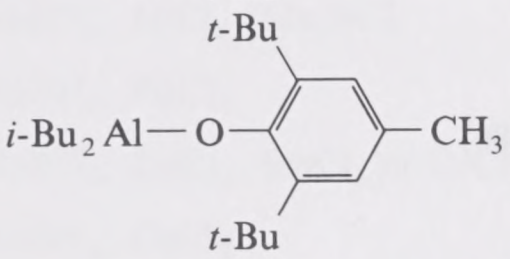
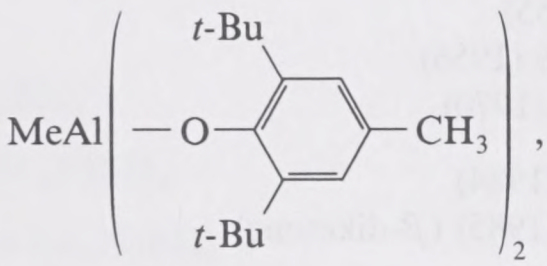
N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York (1956)
H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca, NY (1972), pp 209–250
H. O. House, "Modern Synthetic Reactions," Benjamin, New York (1972), p 49
Chem Soc Rev *5* 23 (1976)
Tetr *35* 449 (1979) (stereochemistry and mechanism)
Topics Stereochem *11* 53 (1979) (stereochemistry)
JACS *103* 4540 (1981) (stereochemistry of cyclohexanone reductions)

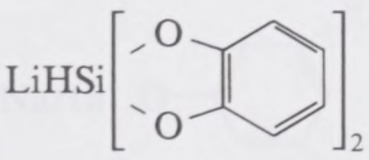
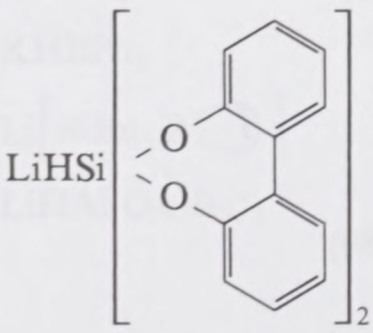
LiH	JOC *52* 4299 (1987) (ynal)
MgH_2	JOC *43* 1557 (1978)
ROMgH	JOC *43* 1560 (1978)
ArOMgH	JOC *43* 1557, 1560 (1978)
$ROMg_2H_3$ (R = Me, Ar)	TL 3133 (1977)
R_2NMgH	JOC *43* 1564 (1978)
BH_3	JACS *92* 1637 (1970)
$BH_3 \cdot py$	JOC *23* 1561 (1958)
$BH_3 \cdot$pyridine polymer	JOC *45* 2724 (1980)
$BH_3 \cdot py$, CF_3CO_2H	Chem Pharm Bull *27* 2405 (1979)

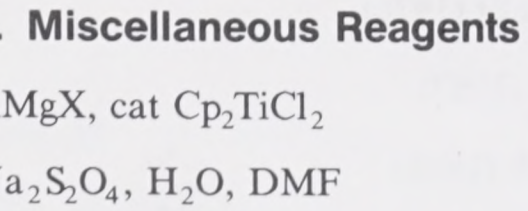
$BH_3 \cdot NH_3$	TL *21* 693 (1980)
$BH_3 \cdot t\text{-}BuNH_2$	TL *21* 693 (1980)
$BH_3 \cdot NMe_3$	CL 61 (1986) (ketone on silica gel)
	Syn 214 (1981)
$BH_3 \cdot SMe_2$	Syn 733 (1982)
$(CH_3)_2CHC(CH_3)_2BH_2$	JOC *37* 2942 (1972); *39* 1631 (1974)
$(CH_3)_2CHC(CH_3)_2BHCl \cdot SMe_2$	JOC *51* 5264 (1986)
$(Sia)_2BH$	JACS *92* 7161 (1970) JOC *39* 1631 (1974)
	JOC *39* 1631 (1974)
	JACS *88* 2871 (1966) JOC *39* 1631 (1974)
9-BBN	JOC *40* 1864 (1975); *41* 1778 (1976); *42* 1197 (1977)
9-BBN · py	JOC *42* 4169 (1977)
	JOC *42* 512 (1977)
$(CF_3CO_2)_2BH$	JOC *46* 355 (1981)
SiaB 	JOC *43* 1470 (1978)
$LiBH_4$	JACS *107* 6046 (1985) (ynone) Ber *118* 722 (1985) (β-diketone) JOC *52* 5067 (1987)
$NaBH_4$	JACS *71* 122 (1949); *75* 1286 (1953); *84* 373 (1962); *88* 2811 (1966) Tetr *26* 2411 (1970); *40* 2233 (1984) (on B chelate of β-hydroxy ketones) Ber *118* 722 (1985) (β-diketone) TL *26* 2951 (1985) (on β-chelate of δ-keto-β-hydroxy ester); *28* 155 (1987) (on B chelate of β-hydroxy ketone) Helv *69* 803 (1986) (on B chelate of δ-hydroxy-β-keto ester) JOC *52* 4062 (1987) (β-hydroxy ketone)
$NaBH_4$, alumina	Syn 891 (1978)
$NaBH_4$, Fontainebleau sand	CC 1066 (1981)

$NaBH_4$, HOAc	CC 535 (1975) (RCHO only) TL *28* 4725 (1987)
$NaBH_4$, tartaric acid	Syn Commun *14* 955 (1984)
$NaBH_4$, *n*-Bu_3B	CL 1415 (1980) (β-hydroxy ketone diastereoselectivity)
$NaBH_4$, $Ti(O\text{-}i\text{-}Pr)_4$	TL *28* 703 (1987) (β-hydroxy ketone)
$NaBH_4$, $NiCl_2/Me_3SiCl$	TL *28* 5741 (1987) (aldehydes only)
$NaBH_4$, $PdCl_2$	CL 1029 (1981) (hindered ketones)
$NaBH_4$; $LnCl_3$, $SmCl_3$ or $CeCl_3$	JACS *100* 2226 (1978)
$NaBH_4$, $CeCl_3$	Syn Commun *10* 623 (1980) JOC *51* 5320 (1986) (ynones)
KBH_4	JOC *50* 2668 (1985)
$(Et_4N)BH_4$	TL *21* 3963 (1980) (aldehyde only)
$(n\text{-}Bu_4N)BH_4$	JOC *41* 690 (1976); *45* 216 (1980) TL *28* 5661 (1987)
$Zn(BH_4)_2$	JACS *82* 6074 (1960); *106* 1154 (1984) (β-keto imide); *107* 1421 (1985); *108* 4603 (1986) (β-keto ester) Proc Natl Acad Sci USA *72* 3355 (1975) TL *21* 1641 (1980) (β-keto ester); *22* 4723 (1981) (α,β-epoxy ketone); *24* 2653 (α-hydroxy ketone), 4805 (β-keto imide), 5385 (β-keto amide) (1983); *25* 6015 (1984) (chiral, β-keto amides); *26* 6465 (1985) (β-keto imide); *27* 6341 (1986) (α-hydroxy ketone); *28* 5129 (1987) Syn Commun *13* 901 (1983) (α,β-epoxy ketones) Acct Chem Res *17* 338 (1984) (review) Chem Pharm Bull *32* 1411 (1984) (β-hydroxy or alkoxy ketone) Ber *118* 722 (1985) (β-diketone) Helv *69* 803 (1986) (δ-hydroxy-β-keto ester)
$Zn(BH_4)_2$, $ZnCl_2$	JACS *109* 7488 (1987) (β-keto ester)
$Cp_2ZrClBH_4$	TL 4985 (1978)
$(Ph_3P)_2CuBH_4$; HCl, $AlCl_3$, $BF_3 \cdot OEt_2$ or $ZnCl_2$	TL *22* 675 (1981)
$NaBH_4$, $PhCHOHCO_2H$	Ind J Chem B *21* 212 (1982) (ketones only?)
$NaBH_3OH$	JOC *42* 3963 (1977)
$NaBH_2S_3$	Syn 526 (1972)
$NaBH_3CN$	JOC *40* 2530 (1975) Syn 135 (1975)
$NaBH_3CN$, CF_3CO_2H	JOC *45* 216 (1980)
$NaBH_3CN$, $ZnCl_2$	JOC *50* 1927 (1985)
$LiBH_3CN$	JACS *91* 3996 (1969)

$[(Ph_3P)_2CuBH_3CN]_2$	TL *21* 813 (1980)
LiH_3BMe	Syn Commun *12* 723 (1982)
$LiH_3B(n\text{-Bu})$	JOC *47* 3311 (1982)
	JACS *96* 274 (1974)
	JOC *51* 337 (1986)
$NaHB(OR)_3$ (R = Me, *i*-Pr, *t*-Bu)	JCS 3426 (1955) JACS *78* 3616 (1956) Tetr *26* 2411 (1970)
$KHB(O\text{-}i\text{-}Pr)_3$	JOC *49* 885 (1984) Ber *118* 722 (1985) (β-diketone)
$NaHB(OAc)_3$	CC 535 (1975) (aldehydes only) TL *24* 273 (1983) (β-hydroxy ketones); *25* 5449 (1984) (β-hydroxy ketones) JACS *108* 2476 (1986) CC 880 (1987)
$KHB(OAc)_3$	TL 4851 (1979) (aldehydes only)
$(Me_4N)HB(OAc)_3$	TL *27* 5939 (1986) (β-hydroxy ketone) JOC *52* 3211 (1987) (β-hydroxy ketone)
$(n\text{-}Bu_4N)HB(OAc)_3$	TL *24* 4287 (1983) (aldehydes only)
$LiHBEt_3$	JOC *45* 1 (1980); *52* 5700 (1987) JACS *108* 3385 (1986) TL *27* 6233 (1986)
$KHBEt_3$	TL *26* 4643 (1985) (β-keto amides)
	JACS *92* 709 (1970) JOC *52* 4898 (1987)
$LiHB(sec\text{-}Bu)_3$	JACS *94* 7159 (1972); *95* 4100 (1973) TL 141 (1973); 4487 (1978); *28* 35 (1987) JOC *50* 3957 (1985)
$KHB(sec\text{-}Bu)_3$	JACS *95* 4100 (1973) TL 4487 (1978); *28* 2999 (1987) CC 1239 (1982)
$LiHB(Sia)_3$	JACS *98* 3383 (1976) TL 4487 (1978)
$KHB(Sia)_3$	JOC *51* 238 (1986)
$KHBPh_3$	JOC *51* 226 (1986); *52* 5564 (1987)

$Li(n\text{-}Bu)_2B$ 	JACS *98* 1965 (1976)
$(n\text{-}Bu_4N)B_3H_8$	TL *23* 3337 (1982)
	JOC *44* 1363 (1979) JACS *108* 284 (1986)
	JACS *109* 7488 (1987) (β-keto ester)
	TL *26* 3853 (1985) (gives equatorial alcohols)
$(HAlN\text{-}i\text{-}Pr)_6$	TL 2369 (1977) Z Chem *17* 18 (1977)
AlH_3	JACS *88* 1464 (1966); *90* 2927 (1968) JCS B 581 (1967)
$i\text{-}Bu_2AlH$	Ann *623* 9 (1959) JOC *24* 627 (1969); *47* 2590 (1982); *50* 2443 (1985) CC 213 (1970) Syn 617 (1975) (review); 732 (1982) JACS *107* 2730, 7524 (1985) Ber *118* 722 (1985) (β-diketone) TL *26* 435 (1985) (α-sulfoxide); *27* 3009 (β-hydroxy ketone), 6233 (1986); *28* 4861, 4865 (1987) (both α-sulfoxide)
$i\text{-}Bu_2AlH$, $ZnCl_2$	TL *26* 435 (1985) (α-sulfoxide); *28* 797 (α-sulfoxide), 4861 (α-sulfoxide), 6481 (β-hydroxy ketone) (1987) JOC *52* 304 (1987)
$i\text{-}Bu_3Al$	Ann *623* 9 (1959)
$i\text{-}Bu_3Al$, amine	BCSJ *51* 2664 (1978)
$LiAlH_4$	JACS *71* 1675 (1949); *78* 2579 (1956); *88* 1458 (1966); *98* 8114 (1976) Org Rxs *6* 469 (1951) Tetr *26* 2411 (1970); *35* 449, 567 (1979) JOC *43* 2173 (1978); *44* 2760 (1979); *52* 1425 (β-diketones), 4062 (β-hydroxy ketones) (1987) TL 4487 (1978); *26* 435 (1985) (α-sulfoxide) Ber *118* 704 (1,2-; 1,3-; 1,4-; and 1,5- diketones), 722 (1,2- and 1,3-diketones) (1985)
$LiAlH_4$, silica gel	TL *23* 4585 (1982) (α,β,γ and δ-keto ester to hydroxy ester)

$LiAlH_4$, py	JACS *84* 1756 (1962)
$LiAlH_4$, $AlCl_3$	JOC *30* 3809 (1965)
$LiAlH_4$, $TiCl_4$	JOC *52* 1425 (1987) (β-diketones)
$LiHAl(OCH_3)_3$	JACS *87* 5614, 5620 (1965); *106* 6414 (1984) Tetr *26* 2411 (1970) Ber *118* 722 (1985) (β-diketone)
$LiHAl(O\text{-}t\text{-}Bu)_3$	JACS *80* 5372 (1958); *87* 5620 (1965); *107* 686, 2730 (1985) Coll Czech Chem Commun *24* 2284 (1959) Tetr *24* 2039 (1968); *26* 2411 (1970) JOC *52* 1425 (β-diketones), 1429, 4495 (1987) TL *28* 1439, 3839 (1987)
$LiHAl(O\text{-}t\text{-}Bu)_3$, $TiCl_4$	JOC *52* 1425 (1987) (β-diketones)
$LiHAl(OCEt_3)_3$	JOC *46* 4628 (1981)
$LiHAl(i\text{-}Bu)_2(t\text{-}Bu)$	Syn 171 (1977) JOC *47* 4581 (1982)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	TL *24* 2653 (1983) (α-silyloxy ketones)
$PhMe_2SiH$, cat $n\text{-}Bu_4NF$	JACS *106* 4629 (1984) JOC *51* 2267 (1986) (mechanism); *52* 3218 (1987) (α-fluoro-β-keto ester)
$PhMe_2SiH$, CF_3CO_2H or $[(Et_2N)_3S]F_2SiMe_3$	JACS *107* 8294 (1985) (β-keto amides)
Ph_2SiH_2; KF, CsF, KO_2CH or $(PhCH_2NMe_3)F$	JOMC *172* 143 (1979)
Ph_3SiH, $AlCl_3$	JOC *52* 3218 (1987) (α-fluoro-β-keto ester)
Et_3SiH, HCl or H_2SO_4	JOC *39* 2740 (1974)
Et_3SiH, BF_3	JOC *43* 374 (1978)
Et_3SiH, $BF_3 \cdot OEt_2$	JOMC *117* 129 (1976)
Et_3SiH, $TiCl_4$	TL *28* 6331 (1987)
R_2SiH_2 or R_3SiH (R = Et, Ph), cat $RuCl_2(PPh_3)_3$	JOC *47* 2469 (1982)
	JOC *52* 948 (1987)
	JOC *52* 948 (1987)

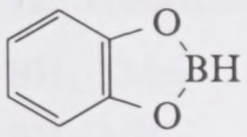
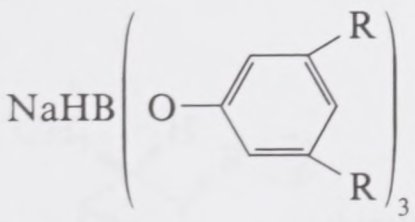
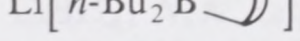
$(MeO)_3SiH$, LiOMe	CC 1411 (1986)
$(MeO)_3SiH$, $LiOCMe_2CMe_2OLi$	CC 1411 (1986)
$(EtO)_3SiH$, KF or CsF	CC 121 (1981) Tetr *37* 2165 (1981); *39* 999 (1983)
$(EtO)_2SiMeH$ or  KF or KO_2CH	Syn 981 (1982)
$(MeHSiO)_n$, *n*-$Bu_2Sn(OAc)_2$	JOC *38* 162 (1973)
R_2SnH_2 or R_3SnH (R = *n*-Bu, Ph)	JACS *80* 3798 (1958); *83* 1246 (1961)
n-Bu_3SnH, pressure	JOC *51* 1672 (1986)
n-Bu_3SnH, silica	JOC *43* 3977 (1978)
n-Bu_3SnH, $ZnCl_2$	TL *27* 3009 (1986) (*β*-hydroxy ketone)
Ph_3SnH	JOC *50* 2149 (1985)
cat Cp_2ZrH_2, *i*-PrOH	JOC *51* 240 (1986) (ketones only)
LiH, VCl_3	JOC *43* 4804 (1978)
NaH, $FeCl_2$ or $FeCl_3$	JOC *41* 1667 (1976)
NaH, NaO-*t*-Am, $Ni(OAc)_2$	TL 1069 (1977)
$LaNi_5H_6$	CC 163 (1984) JOC *52* 5695 (1987)
Li_nCuH_{n+1} (n = 1–5)	JOC *43* 183 (1978)
$[(Ph_3P)_2N]HM(CO)_4L$ [M = Cr, W; L = CO, $P(OMe)_3$]/CH_3CO_2H or C_6H_5OH	JACS *107* 2428 (1985)

1.4. Miscellaneous Reagents

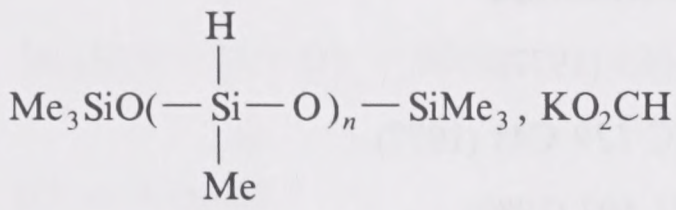
RMgX, cat Cp_2TiCl_2	TL *21* 2171 (1980)
$Na_2S_2O_4$, H_2O, DMF	TL *22* 179 (1981)
SmI_2, H_2O, THF	JACS *109* 6187 (1987)
SmI_2, MeOH	JACS *102* 2693 (1980)
LiO-*i*-Pr	JCS C 804 (1969)
cat LiO-*i*-Pr, cat $NiCl_2$, *i*-PrOH	JOC *50* 3082 (1985)
$Al(O\text{-}i\text{-}Pr)_3$	Org Rxs *2* 178 (1944) JACS *78* 2579 (1956)
H_2Se, hν	Angew Int *19* 1008 (1980)

$NaH_2PO_2 \cdot H_2O$, Na_2CO_3, cat Pd-C, H_2O	JOC *50* 3408 (1985) (aryl aldehydes only)
NaO_2CH, KH_2PO_4 1-methyl-2-pyrrolidinone	JOC *46* 3367 (1981)
HCO_2H, cat $RuCl_2(PPh_3)_3$	BCSJ *55* 2441 (1982)

1.5. Reduction of Aldehydes in the Presence of Ketones

H_2, cat $RuCl_2(PPh_3)_3$	CL 1085 (1977)
H_2, cat $H_3Ir(PPh_3)_3$, HOAc	JOMC *129* C43 (1977)
$BH_3 \cdot t$-$BuNH_2$	TL *21* 697 (1980) JOC *51* 4047 (1986)
9-BBN·py	JOC *42* 4169 (1977)
	JOC *42* 512 (1977)
SiaB 	JOC *43* 1470 (1978)
BH_4 exchange resin	TL *24* 5367 (1983)
$NaBH_4$	Austral J Chem *28* 1383 (1975)
$NaBH_4$, n-Bu_4NBr, H_2O, C_6H_6	Ind J Chem B *25* 626 (1986)
$NaBH_4$, t-BuSH	TL 263 (1977)
$NaBH_4$, $NiCl_2/Me_3SiCl$	TL *28* 5741 (1987)
$NaBH_4$, $ErCl_3$, aq EtOH	TL *22* 4077 (1981)
$LiBH_4$	Austral J Chem *28* 1383 (1975)
$LiBH_4$, molecular sieves	JOC *44* 3969 (1979)
$(Et_4N)BH_4$	TL *21* 3963 (1980)
$(Ph_3P)_2CuBH_4$, HCl	TL *22* 675 (1981)
$(n$-$Bu_4N)BH_3CN$	JACS *95* 6131 (1973)
$NaHB(OAc)_3$	CC 535 (1975)
$KHB(OAc)_3$	TL 4851 (1979)
$(n$-$Bu_4N)HB(OAc)_3$	TL *24* 4287 (1983)
 (R = Me, t-Bu)	CL 461 (1981)
$KHBPh_3$	JOC *51* 226 (1986)
	JACS *98* 1965 (1976)
$LiHAl(O$-t-$Bu)_3$	Austral J Chem *28* 1383 (1975) JACS *108* 4586 (1986)

$LiHAl(OCEt_3)_3$	JOC *46* 4628 (1981)
$(MeO)_3SiH$, LiOMe	CC 1411 (1986)
$(EtO)_3SiH$, KF or CsF	CC 121 (1981) Tetr *37* 2165 (1981); *39* 999 (1983)
$(EtO)_2SiMeH$ or	Syn 981 (1982)



n-Bu_3SnH, silica	JOC *43* 3977 (1978)
$EtCH(OMgBr)_2$	TL *22* 621 (1981)
SmI_2, MeOH	Nouv J Chim *1* 5 (1977) JACS *102* 2693 (1980)
i-PrOH or $(i\text{-Pr})_2CHOH$, alumina	TL 3601 (1975) JOC *42* 1202 (1977)

1.6. Reduction of Ketones in the Presence of Aldehydes

$NaBH_4$, $MCl_3 \cdot 6\ H_2O$ (M = Ce, Er, Cr, La), EtOH	JACS *101* 5848 (1979) JOC *44* 4187 (1979) TL *22* 4077 (1981)
t-$BuNH_2$ / $LiHAl(O\text{-}t\text{-}Bu)_3$ / H_3O^+ or alumina	TL *21* 5085 (1980) Tetr *38* 1827 (1982)
$Ti(NEt_2)_4$ / $LiAlH_4$ / H_2O	CC 406 (1983)

1.7. Selective Reduction between Aldehydes

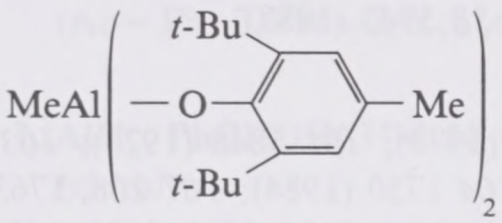
BH_4 exchange resin	TL *24* 5367 (1983)

1.8. Reduction of Conjugated Aldehydes in the Presence of Non-conjugated Aldehydes

$NaBH_4$, $ErCl_3$	TL *22* 4077 (1981)

1.9. Selective Reduction between Ketones

$BH_3 \cdot t\text{-}BuNH_2$	TL *21* 697 (1980)
$KHBPh_3$	JOC *51* 226 (1986)
$Li[n\text{-}Bu_2B$ $]$	JACS *98* 1965 (1976)
$NaBH_4$	JACS *74* 2814 (1952)
$NaBH_4$, $ErCl_3 \cdot 6\ H_2O$	JOC *44* 4187 (1979)

BH_4 exchange resin	TL *24* 5367 (1983)
 , *t*-BuMgCl	TL *26* 3853 (1983) (cyclic > acyclic)

1.10. Reduction of Enones in the Presence of Aldehydes

$NaBH_4$, $CeCl_3$, EtOH	JOC *47* 381 (1982)

1.11. Reduction of Enones in the Presence of Ketones

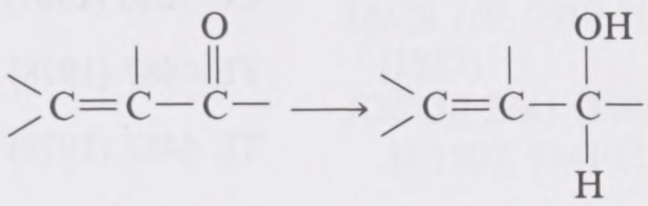
$(HAlN\text{-}i\text{-}Pr)_6$	TL 2369 (1977)
$NaBH_4$, $CeCl_3$	JOC *44* 4187 (1979)

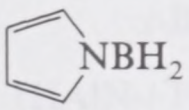
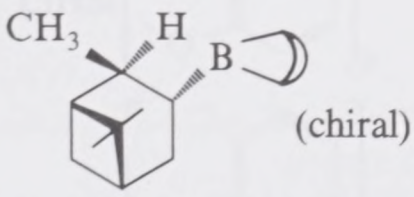
1.12. Reduction of Ketones in the Presence of Enones

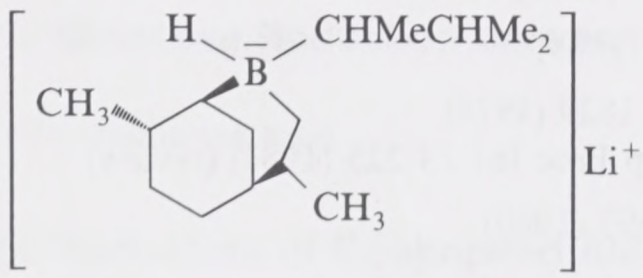
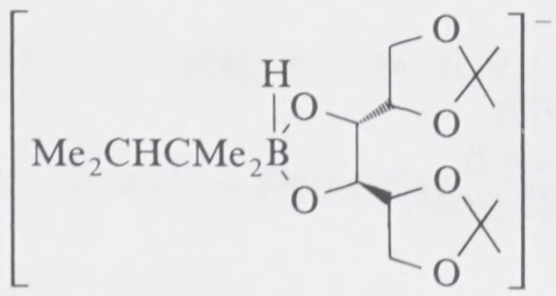
$BH_3 \cdot SMe_2$	TL *22* 4929 (1981)
$BH_3 \cdot NH_3$	TL *21* 693 (1980)
$NaBH_4$	JCS 3426 (1955); 2680 (1960) TL *21* 693 (1980); *27* 4461 (1986)
$LiHAl(O\text{-}t\text{-}Bu)_3$	Tetr *24* 2039 (1968)

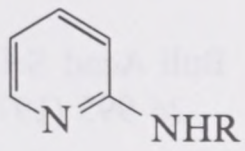
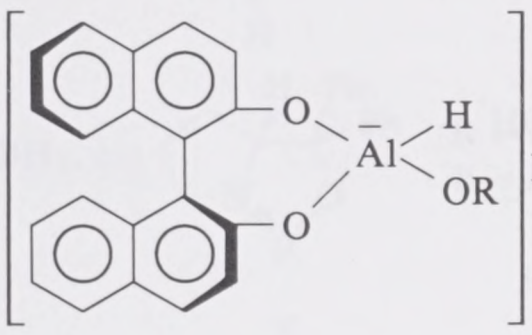
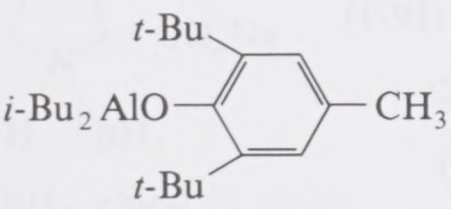
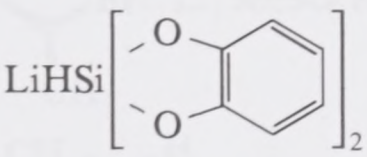
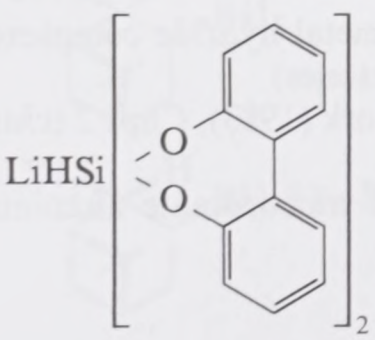
1.13. Reduction of Enones to Allylic Alcohols

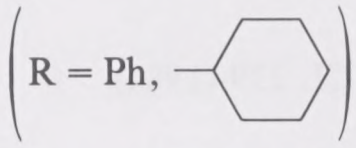
For enone to saturated ketone reductions see page 8, Section 3.6.



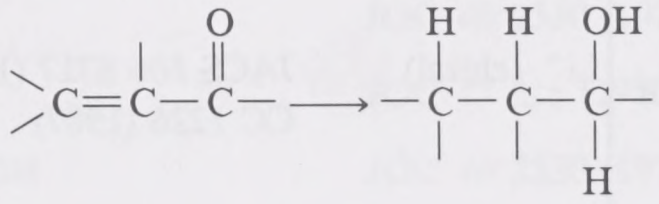
H_2, cat Pt-Ge	CC 1729 (1986)
H_2, cat $[H_2Ir(Et_2PPh)_4]^+$	CC 746 (1986)
$BH_3 \cdot SMe_2$	JOC *43* 1829 (1978) Org Prep Proc Int *13* 225 (1981) (review)
$BH_3 \cdot t\text{-}BuNH_2$	TL *21* 693 (1980)
	Syn 214 (1981)
9-BBN	JOC *40* 1864 (1975); *41* 1778 (1976); *42* 1197 (1977) TL *23* 3405 (1982) JACS *108* 4561 (1986)
 (chiral)	JOC *50* 1384 (1985)
$LiBH_4$, *N*,*N*′-dibenzoylcystine, *t*-BuOH (chiral)	CC 413 (1984)
$LiBH_4$, $TbCl_3$	TL *27* 4759 (1986)

$NaBH_4$	JOC *35* 1041 (1970); *52* 5560 (1987) TL 2441 (1976); *28* 5945 (1987)
$NaBH_4$, $CeCl_3$	CC 601 (1978) JACS *100* 2226 (1978); *101* 5848 (1979); *103* 5454 (1981); *104* 1750 (1984); *107* 268, 1763, 5219 (1985); *108* 2090, 3110, 3731, 3739 (1986); *109* 2082, 3017, 3025, 3987, 4690, 6199, 8119 (1987) JOC *44* 689, 4187 (1979); *47* 381, 1855 (1982); *49* 2152 (1984); *50* 2981 (1985); *51* 491, 789, 1622 (1986); *52* 943, 3250, 3541, 4135, 5233, 5457, 5624 (1987) Syn Commun *12* 167 (1982) TL *27* 6341 (1986); *28* 333, 4951, 5655, 5977, 6253, 6485 (1987)
$Zn(BH_4)_2$	JACS *109* 3981 (1987)
$NaBH_3CN$, H^+, MeOH	JOC *40* 2530 (1975)
$NaBH_3CN$, CF_3CO_2H	JOC *45* 216 (1980)
(n-Bu_4N)BH_3CN, H^+, MeOH	JOC *40* 2530 (1975)
LiH_3B(n-Bu)	JOC *47* 3311 (1982)
$LiHBEt_3$	JOC *52* 4665 (1987)
$LiHB$(*sec*-Bu)$_3$	TL 4487 (1978) CC 1226 (1987)
$LiHB(Sia)_3$	TL 4487 (1978)
KHB(*sec*-Bu)$_3$	TL 4487 (1978)
$KHBPh_3$	JOC *52* 5564 (1987)
	JACS *94* 8616 (1972)
	JOC *52* 4020 (1987)
$NaHB(OAc)_3$	TL *28* 5755 (1987)
$LiAlH_4$	JCS 5280 (1965) JOC *34* 2206 (1969); *35* 1041 (1970)
$LiAlH_4$, LiBr or $MgBr_2$	TL *28* 5681 (1987)
$LiAlH_4$; 2S, 3R-Darvon alcohol	TL *27* 4759 (1986)

$LiAlH_4$, $ArNHCH_2CH(NHCH_3)CH_2CH_2OH$ (Ar = Ph; 2,6-$Me_2C_6H_3$) (chiral)	TL *24* 4123 (1983)
$LiAlH_4$, $PhCHOHCHMeNMe_2$,  (chiral)	CL 239 (1984)
$LiAlH_4$, $PhCHOHCHMeNMe_2$, EtNHPh (chiral)	CC 1026 (1980)
$LiAlH_4$, $PhCH_2COHPhCHMeCH_2NMe_2$ (chiral)	TL *27* 4759 (1986)
$LiHAl(i\text{-}Bu)_2(n\text{-}Bu)$	JACS *102* 7910 (1980) JOC *49* 1717 (1984)
$LiHAl(OMe)_3$	JOC *34* 2206 (1969)
 (chiral)	JACS *106* 6717 (1984) CC 1226 (1987)
AlH_3	JOC *34* 2206 (1969); *38* 1380 (1973) TL *28* 503 (1987)
$i\text{-}Bu_2AlH$	CC 213 (1970) JACS *102* 7910 (1980); *109* 3017, 3025, 3981 (1987) JOC *50* 2443 (1985); *51* 5232 (1986); *52* 1907, 3841 (1987)
$i\text{-}Bu_2AlH$, $ZnCl_2$	TL *28* 61 (1987)
$i\text{-}Bu_3Al$	JOC *47* 4640 (1982)
	JOC *44* 1363 (1979) BCSJ *54* 3033 (1981)
$(HAlN\text{-}i\text{-}Pr)_6$	TL 2369 (1977)
$PhMe_2SiH$ or Ph_2MeSiH, cat $n\text{-}Bu_4NF$	JACS *106* 4629 (1984)
	JOC *52* 948 (1987)
	JOC *52* 948 (1987)

R_2SiH_2 (R = Et, Ph), cat $ClRh(PPh_3)_3$, MeOH	Organomet *1* 1390 (1982)
$RSiH_3$, cat $ClRh(PPh_3)_3$ (R = Ph, )	Bull Acad Sci USSR, Div Chem Sci *26* 995 (1977)
LiH, VCl_3	JOC *45* 1041 (1980)
NaH, NaO-*t*-Am, $ZnCl_2$	JOC *44* 2203 (1979)
NaH, $ZnCl_2$, $MgBr_2$	JOC *44* 2203 (1979)
Li_4CuH_5	JOC *43* 183 (1978)
i-PrOH, alumina (enals only)	TL 3601 (1975)

1.14. Reduction of Enones to Saturated Alcohols



H_2, cat Rh-alumina	TL *28* 5615 (1987)
Li, NH_3/Li, MeOH/NH_4Cl	JACS *108* 800 (1986)
Li, NH_3, EtOH	JOC *50* 2981 (1985)
Li, NH_3, NH_4Cl	CC 1044 (1987)
$NaBH_4$, MeOH	JACS *108* 3443 (1986)
KHB(*sec*-Bu)$_3$	Austral J Chem *34* 745 (1981)
$KHBPh_3$	JOC *52* 5564 (1987)
Et_3SiH, CF_3CO_2H	JOC USSR *7* 2145 (1971)
$HFe(CO)_4^-$	BCSJ *55* 1329 (1982)
$LaNi_5H_6$	JOC *52* 5695 (1987)
$LaNi_{4.5}Al_{0.5}H_5$	JOC *52* 5695 (1987)

1.15. Asymmetric Reduction of Aldehydes and Ketones

Reviews:

Syn 329 (1978) (asymmetric hydrogenation and hydrosilation)
Tetr *37* 3547 (1981) (organoboron reagents); *42* 5157 (1986) (chiral metal hydride complexes)
JACS *105* 3725 (1983) (Cram and anti-Cram reduction of α-chiral ketones)
"Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Chpt 2 (chiral boron reagents), Chpt 3 ($LiAlH_4$ derived reagents)
Topics Stereochem *14* 231 (1983) (complex aluminum hydrides and tricoordinate aluminum reagents)
JOC *52* 5406 (1987) (reagent comparison)

H_2, chiral Rh catalyst

CC 428 (1977) (α-keto esters)
Org Syn *63* 18 (1984) (α-keto lactones)
CL 1603 (1984) (α-keto esters, amides and lactones)
TL *27* 4477 (1986) (α-keto lactone); *28* 3675 (1987) (α-keto lactone)

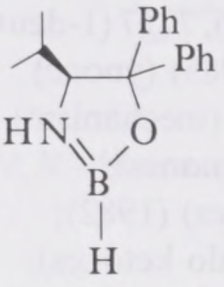
H_2, cat RuX_2(BINAP) (X = Cl, Br)

JACS *109* 5856 (1987) (β-keto esters)

H_2, Raney Ni, tartaric acid

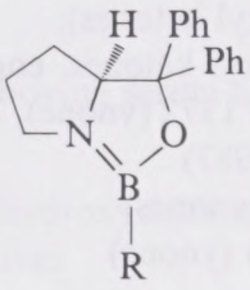
BCSJ *36* 155 (1963) (β-keto ester); *53* 3367 (1980) (β-diketone to diol); *55* 2186 (1982) (β-keto ester); *56* 1414 (1983) (β-keto ester)

BH_3, cat



JACS *109* 5551 (1987)

BH_3, cat

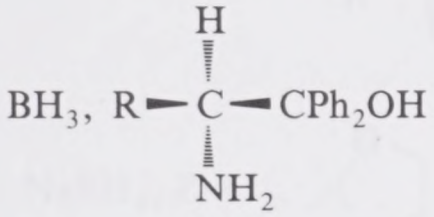


R = H
R = Me

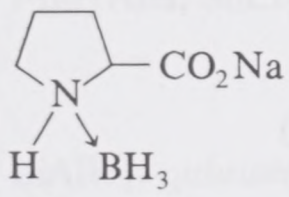
JACS *109* 5551 (1987)
JACS *109* 7925 (1987)

BH_3, various chiral β-amino alcohols

CC 315 (1981) (aryl ketones)
JCS Perkin I 1673 (1983) (aryl ketones)



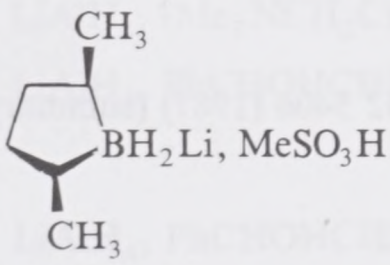
CC 469 (1983) (aryl ketones)
JOC *49* 555 (1984) (aliphatic ketones); *52* 5406 (1987) (summary)
JCS Perkin I 2039 (aliphatic and aryl ketones, α-halo, α-OH, α-$OSiMe_3$, α-OAc ketones, α-keto ester); 2615 (polymer-supported reagent, aryl and α-halo ketones) (1985)



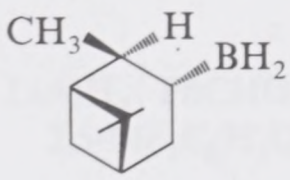
Chem Pharm Bull *27* 1479 (1979)

BH_3, chiral Li amide

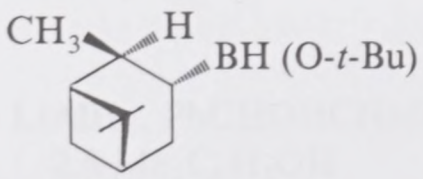
TL *27* 635 (1986)



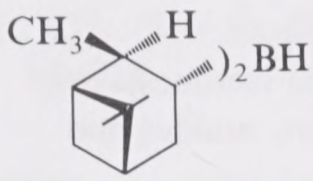
JACS *108* 7402, 7404 (1986) (alkyl ketones)



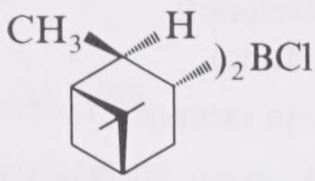
JOC *49* 2558 (1984) (low ee's)



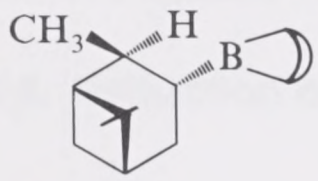
JOC *49* 3646 (1984) (low ee's)



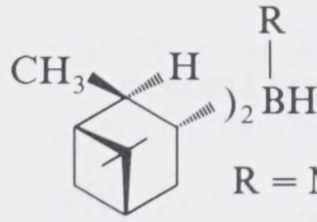
JACS *83* 3166 (1961)
Tetr *24* 6365 (1968)
JOC *42* 2996 (1977)



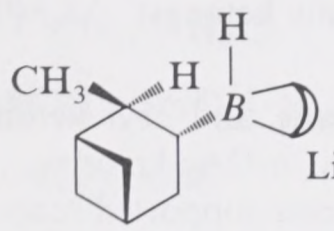
JOC *50* 5446 (1985) (aryl ketones); *51* 3394 (1986) (3° alkyl ketones); *52* 5406 (1987) (summary)



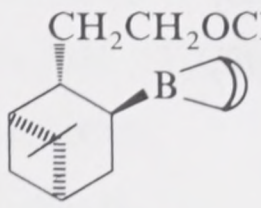
JACS *99* 5211 (1977) (1-deuteroaldehydes); *101* 2352 (1979) (1-deuteroaldehydes); *102* 867 (1980) (ynones); *106* 1531 (α-keto esters), 3548 (ynone), 4192 (ynone), 7217 (1-deuteroaldehyde) (1984); *107* 3915 (1985) (ynone)
JOMC *156* 203 (1978) (mechanism)
JOC *46* 4107 (1981) (ynones); *47* 1606 (alkyl ketones) (1982); *48* 1784 (1983) (α-halo ketones); *49* 1316 (1984) (alkyl ketones); *50* 1384 (1985) (alkyl ketones, enones, ynones, α-halo ketones); *52* 1372 (ynone), 2860 (ynone), 5406 (summary) (1987)
Tetr *40* 1371 (1984) (ynones)
Org Syn *63* 57 (1985) (ynone)



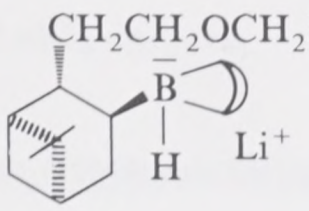
JCS C 2557 (1971)
JACS *93* 1491 (1971)



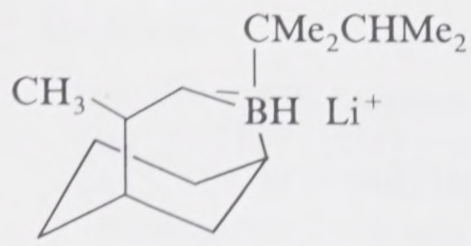
JOC *42* 2534 (1977)



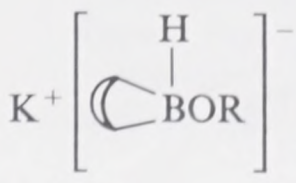
JOC *47* 2814 (1982) (ynones)
Tetr *40* 1371 (1984) (ynones)



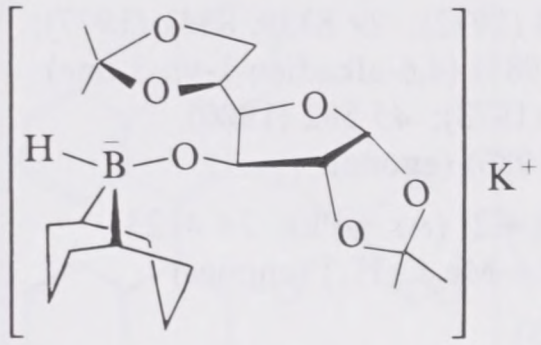
JOC *47* 2495 (1982); *52* 5406 (1987) (summary)



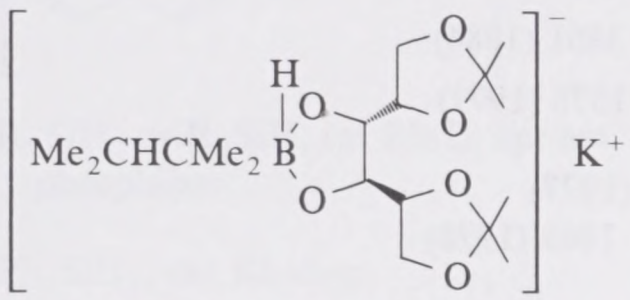
JACS *93* 1491 (1971)



JOC *51* 3278 (1986)



JOC *51* 1934 (RCOAr, hindered RCOR), 3278 (aliphatic and aryl ketones), 3396 (α-keto esters) (1986); *52* 5406 (1987) (summary)



JOC *52* 4020 (1987) (ketones, enones)

$LiBH_4$; *N*,*N*′-dibenzoylcystine; ROH

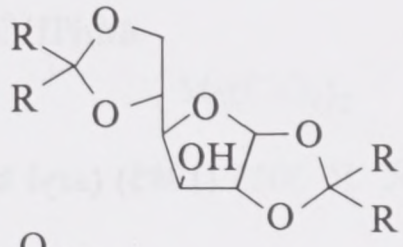
CC 413 (1984) (aryl ketones and enones); 138 (1985) (3-aryl-3-oxo esters); 801 (1987) (acetylpyridines, α- and β-amino ketones)
TL *28* 2837 (1987) (β-keto ester)

$NaBH_4$, bovine serum albumin

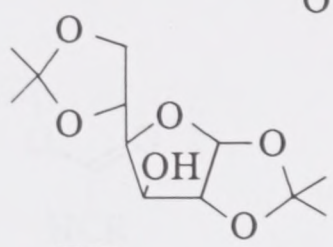
CC 926 (1978)
JOC *51* 5423 (1986) (δ-keto acids)

$NaBH_4$, hydroxymonosaccharide derivatives

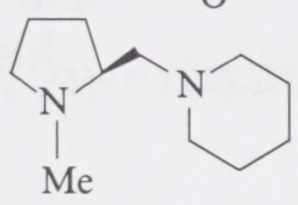
JOC *44* 1720 (1979)

$NaBH_4$, $R'CO_2H$, 

JOC *45* 4229 [$R_2 = (CH_2)_5$], 4231 (R = Me) (1980)
JCS Perkin I 900 (1981) [R = Me; $R_2 = (CH_2)_5$]

$NaBH_4$, $ZnCl_2$, 

CC 807 (1979)
BCSJ *54* 1424 (1981) (aryl ketones)

i-Bu_2AlH, $SnCl_2$, 

CL 2071 (1984); 813 (1985) (α-, β- and γ-keto esters)

$LiAlH_4$, quinine

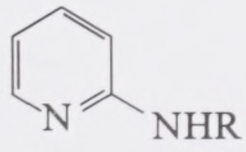
Coll Czech Chem Commun *30* 2487 (1965); *32* 3897 (1967); *39* 1869 (1974)

$LiAlH_4$, $(Me_2NCH_2CHOH)_2$

Ber *107* 1748 (1974); *113* 1691 (1980)

$LiAlH_4$, $PhCHOHCHMeNMe_2$, EtNHPh

CL 981 (1980)
CC 1026 (1980) (enones only)

$LiAlH_4$, $PhCHOHCHMeNMe_2$, 

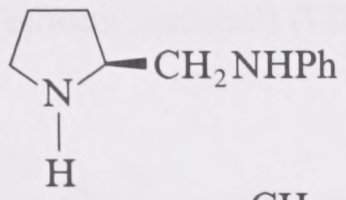
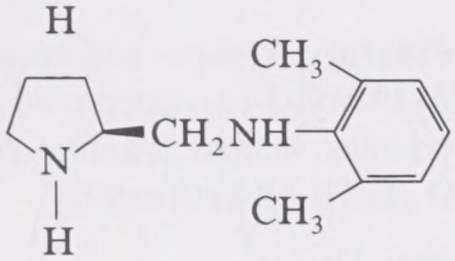
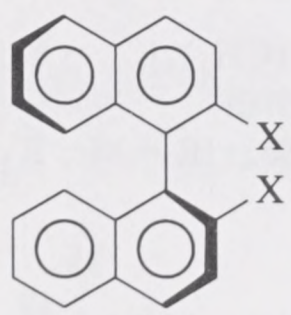
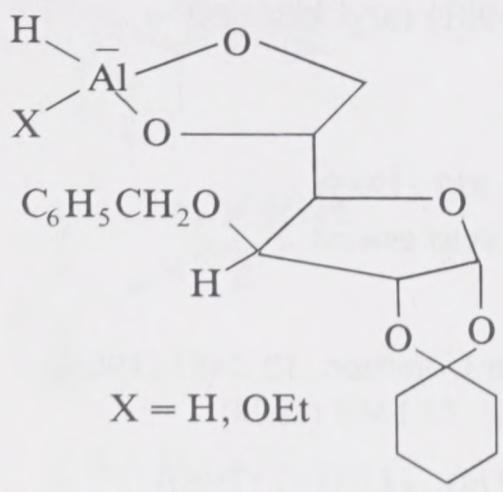
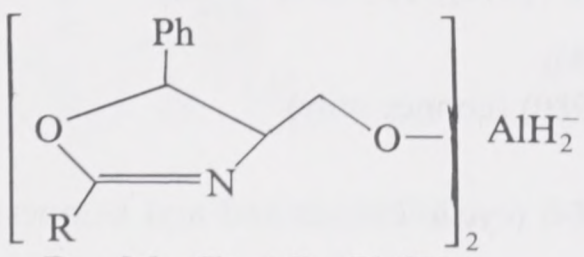
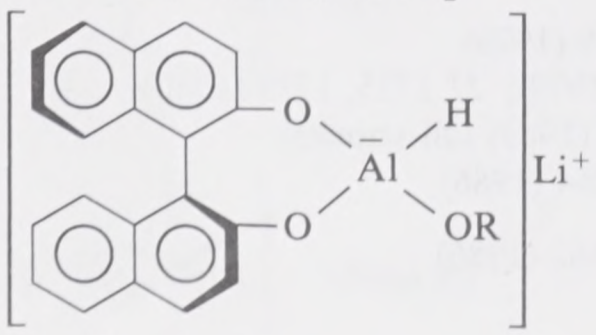
CL 239 (1984) (cyclic enones and aryl ketones)

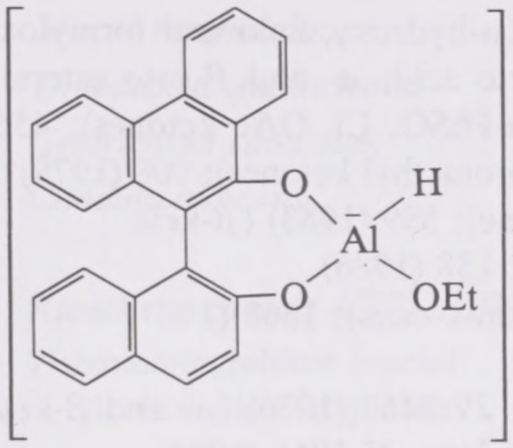
$LiAlH_4$, $PhCHOHCHMeNMe_2$, $2,5\text{-}Me_2C_6H_3OH$

Tetr *32* 939 (1976)
TL 2683 (1979); *21* 1735, 1739 (1980); *24* 4477 (1983) (all ynones)
JOC *51* 1264 (1986)

$LiAlH_4$, $PhCHOHCHMeNMeCH_2$-polymer, $2,5\text{-}Me_2C_6H_3OH$

JOC *51* 3462 (1986)

$LiAlH_4$, $PhCH_2COHPhCHMeCH_2NMe_2$	JACS *94* 9254 (1972); *99* 8339, 8341 (1977); *107* 1034 (1985) (4,6-alkadien-1-yn-3-one) JOC *38* 1870 (1973); *45* 582 (1980) TL *27* 4759 (1986) (enone)
$LiAlH_4$, $ArNHCH_2CH(NHMe)CH_2CH_2OH$	TL *23* 4111 (1982) (Ar = Ph); *24* 4123 (Ar = Ph; 2,6-$Me_2C_6H_3$) (enones)
$LiAlH_4$, $PhCHMeNHMe \cdot HCl$	TL 3195 (1973)
$LiAlH_4$, $O_2S(NHCHMePh)_2$, MeNHPh	JOC *49* 3861 (1984)
$LiAlH_4$, *o*-$Me_2NC_6H_4CH_2NHCHMePh$	JOC *42* 1578 (1977)
$LiAlH_4$, 	CL 783 (1977) BCSJ *51* 1869 (1978)
$LiAlH_4$, 	Heterocycles *12* 499 (1979)
$LiAlH_4$, terpenic glycols	JOC *42* 2073 (1977)
$LiAlH_4$, *cis*-2,3-pinanediol	Ber *106* 1312 (1973) (low ee's)
$LiAlH_4$; 1,4:3,6-dianhydro-D-mannitol or 1,3:4,6-di-O-benzylidene-D-mannitol	JCS Perkin I 1123 (1977) (very low ee's)
$LiAlH_4$,  (X = NH_2, NHR)	JOC *50* 3013 (1985) (aryl ketones)
	JCS C 1822, 2280 (1966); 197 (1967)
	TL 1337 (1974)
	JACS *101* 3129, 5843 (1979); *106* 6709, 6717 (1984) (enones, ynones and aryl ketones); *108* 6384 (1986) Pure Appl Chem *53* 2315 (1981) (review) TL *22* 247 (1981) (ynones) JOC *52* 5406 (1987) (summary) CC 1226 (1987)



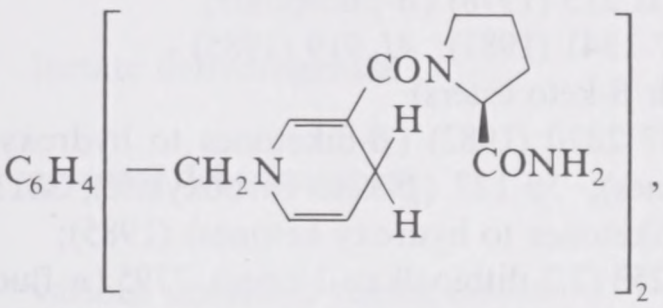
CC 1490 (1984)

R_2SiH_2 or R_3SiH, cat Rh(I), opt act phosphines

J Chem Res (S) 320 (1980)
CC 1238 (1982)

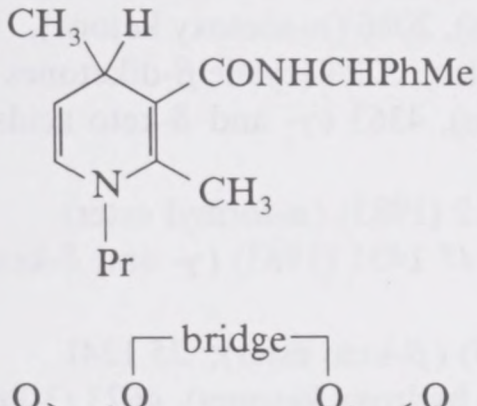
Ph_2SiH_2, cat Rh-diop

CC 1238 (1982)



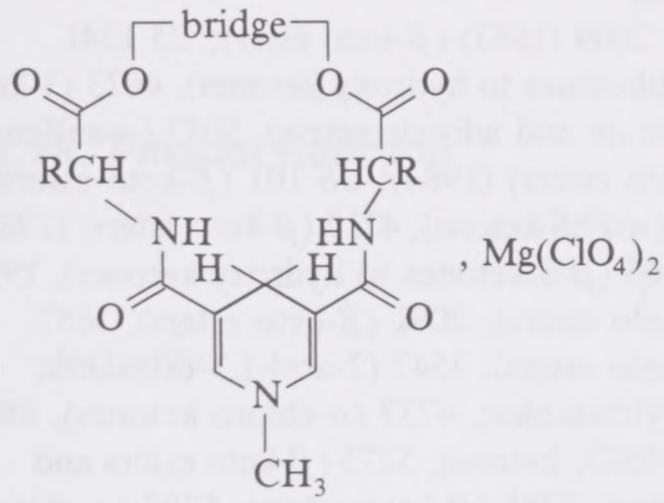
$Mg(ClO_4)_2$ *o*, *m*, or *p*

JACS *103* 4613 (1981)



, $Mg(ClO_4)_2$

JACS *101* 7036 (1979) (α-keto esters, aryl ketones)



, $Mg(ClO_4)_2$

JACS *101* 2759 (1979); *103* 2091 (1981); *107* 3981 (1985)

bakers yeast

Adv Carbohydr Chem *4* 75 (1949) (review)
Org Syn Coll Vol *2* 545 (1949) (α-hydroxy ketone)
Can J Chem *29* 678 (1951) (β-keto carboxylates)
Biochem *3* 838 (1964) (ketones)
Biochem J *95* 633 (1965) (5-oxodecanoic acid)
Coll Czech Chem Commun *31* 2615 (1966) (methyl ketones)
JACS *88* 3595 (1966) (1-deuteroaldehydes); *102* 870 (1980) (β-keto ester); *104* 4251 (β-keto ester), 5473 (ketone) (1982); *105* 5925 (1983) (β-keto ester); *108* 4912 (1986) (ketone); *109* 8102 (1987) (β-keto ester)

bakers yeast (*continued*)	CC 400 (1975) (α-hydroxy, halo and formyloxy ketones; α-keto acid; α- and β-keto esters); 315 (1977) (α-PhSO, Cl, OAc ketones); 456 (1978) (trifluoromethyl ketones); 908 (1979) (bicyclic ketone); 599 (1983) (β-keto carboxylates); 138 (1986) (2,2-dithioalkan-1-ones); 1368 (1987) (β-keto ester) Austral J Chem *29* 2459 (1976) (α- and β-keto esters and amides); *31* 1965 (1978) (α-RS, α-RSO, α-RSO_2 ketones) Helv *60* 1175 (1977); *62* 2829 (1979); *63* 1383 (1980); *65* 495 (1982); *66* 485 (1983); *67* 1843 (1984) (all β-keto esters) BSCF II 215 (1978) (α-phosphate) Tetr *37* 1341 (1981); *41* 919 (1985) (both β-keto esters) JOC *47* 2820 (1982) (β-diketones to hydroxy ketones); *50* 127 (β-keto carboxylate), 3411 (β-diketones to hydroxy ketones) (1985); *51* 1253 (2,2-dithioalkan-1-ones), 2795 (α-fluoro ketones) (1986); *52* 192 (β-keto esters), 256, 1141, 1359 (β-keto esters) 2036 (β-diketones to hydroxy ketones), 2086 (α-acetoxy ketone), 2244 (β-keto ester), 3223 (cyclic β-diketones to hydroxy ketones), 4363 (γ- and δ-keto acids) (1987) Angew Int *22* 1012 (1983) (α-formyl ester) Agric Biol Chem *47* 1431 (1983) (γ- and δ-keto esters) TL *24* 2009 (1983) (β-keto ester); *25* 1241 (β-diketones to hydroxy ketones), 4623 (3-keto glutarate and adipate esters), 5083 (α-sulfenyl-β-keto esters) (1984); *26* 101 (β-keto esters), 771 (α-PhS ketone), 4213 (β-keto esters) (1985); *27* 565 (β-diketones to hydroxy ketones), 1915 (α-keto esters); 2091 (β-keto esters), 2657 (β-keto esters), 3547 (2-acyl-1,3-dithianes; 2-acylthiazoles), 4737 (α-chloro ketones), 4817 (α-$PhSO_2$ ketone), 5275 (β-keto esters and amides), 5281 (β-keto esters), 5397 (α-chloro ketone, β-keto ester), 5405 (β-keto thioester) (1986); *28* 2709 (β-chloro-α-keto ester), 3189 (β-keto ester) (1987) Syn 897 (1983) (CH_3 and CF_3 ketones) Chem Pharm Bull *31* 4384 (1983) ($MeO_2CCOCHMeCO_2Me$) Org Syn *63* 1 (1984) (β-keto esters) CL 1475 (1985) (δ-keto acids)
Corynebacterium equi IFO 3730	JOC *52* 2735 (1987) (α-PhS, α-PhSO and α-$PhSO_2$ ketone)
Sporobolomycetes pararoseus	JOC *43* 2357 (1978) (aryl ketones)
Cryptococcus macerans	JOC *45* 3352 (1980) (α-halo aryl ketones)

Mucor rammanianus	JACS *97* 865 (1975)
Dipodascus uninucleatus	JACS *97* 865 (1975)
Geotrichum candidum	TL *28* 5037 (1987) (β-diketone to hydroxy ketone)
Candida albicans	Chem Pharm Bull *31* 4384 (1983) ($MeO_2CCOCHMeCO_2Me$)
Kloeckera corticis ATCC 20109	TL *23* 5489 (1982) (2,2-dithia-1-alkanone)
Thermoanaerobium brockii alcohol dehydrogenase	Angew Int *23* 151 (1984) (β-keto esters) JACS *108* 162, 3474 (4,5 and 6 chloro ketones) (1986) JOC *52* 256 (1987)
horse liver alcohol dehydrogenase	JACS *98* 8476 (1976) Can J Chem *59* 1574 (1981) (3-thiacycloalkanones) TL *28* 3059 (1987)
lactate dehydrogenase	JACS *104* 4458 (1982) (α-keto acid) JOC *52* 2608 (1987) (α-keto acid)
glycerol dehydrogenase	JOC *51* 25 (1986); *52* 2608 (1987) (both α-hydroxy ketones)
various enzymes, yeasts, molds, fungi or bacteria	Adv Carbohydr Chem *4* 75 (1949) (review) Appl Microbiol *11* 389 (1963) (γ- and δ-keto acids) BSCF 4217 (1972) Angew Int *23* 570 (1984); *24* 539 (1985) (both reviews) JACS *107* 2992, 4028 (1985); *108* 284 (1986) TL *27* 2631 (β-keto esters), 2657 (β-keto esters), 4453 (α-diketones to diol) (1986); *28* 1487 (aryl ketone), 3939 (β-keto esters), 5033 (4-*O*-benzyl-2-methyl-3-oxo-butyrate esters) (1987) JOC *52* 256 (1987)

1.16. Pinacol Reaction

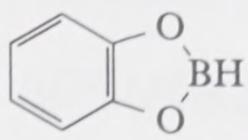
$$2\,R_2CO \longrightarrow \underset{\displaystyle R_2C-CR_2}{\overset{\displaystyle HO\quad OH}{|\quad\quad|}}$$

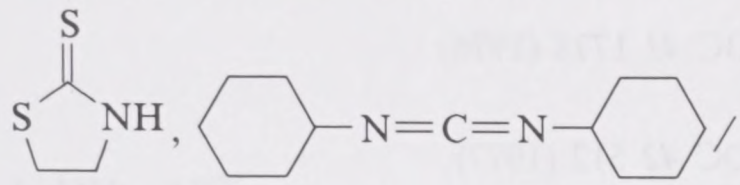
electrolysis	JACS *72* 3797 (1950); *74* 4260 (1952) JOC *15* 435 (1950); *31* 3755 (1966); *33* 294, 2145 (1968); *34* 2807 (1969) Acta Chem Scand *11* 283 (1957) JCS 863 (1958) Chem Rev *62* 19 (1962) (review) JCS C 653 (1966); 2388 (1968)
photolysis	Chem Rev *40* 181 (1947) (review)
Li, THF	TL *28* 1813 (1987)
Li, NH_3	TL *28* 1813 (1987)
Na	TL 3613 (1970) JACS *108* 1265 (1986)
Na(Hg)	JCS 2423 (1928) JACS *55* 1179, 2827 (1933); *73* 2586 (1951); *108* 4561 (1986) TL 1879 (1964)

Mg-graphite	CC 1802 (1986)
Mg, MgI_2	JACS *49* 236 (1927); *51* 306 (1929) Chem Rev *57* 417 (1957) (review)
Mg, Me_3SiCl, HMPA	TL 75 (1972)
Mg, $HgCl_2$	Org Syn Coll Vol *1* 459 (1941)
Me_8Sn_3	TL 2847 (1978)
Cp_2TiCl_2, *sec*-BuMgCl	TL *28* 5717 (1987)
$TiCl_3$, NaOH	TL *23* 3517 (1982)
$TiCl_3$, K	TL *23* 5485 (1982)
$TiCl_4$, *n*-BuLi	Chimia *40* 12 (1986) (ArCHO)
$TiCl_4$, Mg(Hg)	JOC *41* 260 (1976); *47* 1657 (1982); *51* 2969 (1986) TL *28* 4965 (1987)
$TiCl_4$, Zn	CL 1041 (1973) TL *26* 1983 (1985) (intramolecular); *28* 1799 (1987) (intramolecular)
Ce, I_2	TL *23* 1353 (1982)
SmI_2	JOMC *250* 227 (1983) TL *24* 765 (1983)
Zn, HCl	JACS *107* 686 (1985)
Zn, Me_3SiCl, lutidine	TL *24* 2821 (1983) (intramolecular)

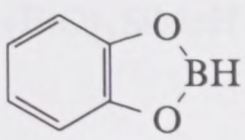
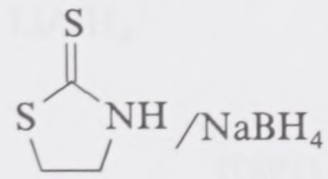
2. Carboxylic Acids and Derivatives

$$RCO_2H \longrightarrow RCH_2OH$$

BH_3	JACS *92* 1637 (1970); *106* 2160 (1984); *109* 3098 (1987) J Med Chem *13* 203 (1970) JOC *38* 2786 (1973) Org Syn *64* 104 (1985)
$BH_3 \cdot SMe_2$	JACS *101* 6710 (1979) Org Prep Proc Int *13* 225 (1981) (review)
$BH_3 \cdot SMe_2$, $BF_3 \cdot OEt_2$	TL 3527 (1977) (amino acid) Org Syn *63* 136 (1984) (amino acids)
$BH_3 \cdot SMe_2$, $B(OMe)_3$	JOC *39* 3052 (1974)
9-BBN	JOC *41* 1778 (1976)
	JOC *42* 512 (1977)
$LiBH_4$, MeOH, diglyme, Δ	JOC *51* 4000 (1986)

$NaBH_4$, $AlCl_3$	JACS *78* 2582 (1956)
$NaBH_4$, $TiCl_4$	Syn 695 (1980)
$NaBH_4$, $MeSO_3H$, DMSO	JOC *46* 2579 (1981) (R = alkyl only)
i-Bu_2AlH	Syn 617 (1975)
$LiAlH_4$	Org Rxs *6* 469 (1951) JACS *81* 610 (1959); *108* 4138 (1986); *109* 7816 (1987) JOC *51* 5019 (1986); *52* 2337 (1987)
$LiAlH_4$, $AlCl_3$	JACS *81* 610 (1959)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	JOC *47* 5201 (1982)
 $NaBH_4$	JCS Perkin I 2470 (1980)

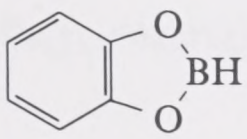
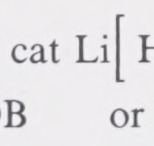
$$RCOCl \longrightarrow RCH_2OH$$

9-BBN	JOC *41* 1778 (1976)
	JOC *42* 512 (1977)
$NaBH_4$	JACS *71* 122 (1949)
$NaBH_4$, alumina	Syn 912 (1979)
$NaBH_4$, $AlCl_3$	JACS *78* 2582 (1956)
$NaBH_4$, $TiCl_4$	Syn 695 (1980)
$Zn(BH_4)_2$, TMEDA	TL *27* 4213 (1986)
$LiH_3B(n\text{-Bu})$	JOC *47* 3311 (1982)
$LiHBEt_3$	JOC *45* 1 (1980)
$NaBH_3CN$, $ZnCl_2$	JOC *50* 1927 (1985)
$(n\text{-}Bu_4N)B_3H_8$	TL *23* 3337 (1982)
i-Bu_2AlH	JOC *50* 2443 (1985)
$LiAlH_4$	Org Rxs *6* 469 (1951) JACS *81* 610 (1959) Syn 901 (1981)
$LiAlH_4$, $AlCl_3$	JACS *81* 610 (1959)
$LiHAl(i\text{-}Bu)_2(n\text{-Bu})$	JOC *49* 1717 (1984)
	JCS Perkin I 2470 (1980)

$$RCO_2R' \longrightarrow RCH_2OH$$

electrolysis, NH_3	TL *28* 1173 (1987)

$RCO_2R' \longrightarrow RCH_2OH$ (*Continued*)

Li or Na, NH_3	JOC *44* 2810 (1979)
Na, NH_3, EtOH	Ann 1532 (1982)
Na, EtOH	Org Syn Coll Vol *2* 372 (1943)
Na, *t*-BuOH, HMPA	CC 567 (1978)
$BH_3 \cdot SMe_2$	Syn 439 (1981) JOC *47* 3153 (1982) TL *28* 1147 (lactone), 3091 (1987)
$BH_3 \cdot SMe_2$, cat $NaBH_4$	CL 1389 (1984) (α-hydroxy ester) CC 992 (1987) (α-hydroxy ester)
9-BBN	JOC *41* 1778 (1976)
	JOC *42* 512 (1977)
$LiBH_4$	Carbohydr Res *4* 504 (1967) JOC *47* 4702 (1982) TL *23* 4991 (1982); *28* 535, 4681 (lactone), 5458 (lactone) (1987) JACS *109* 1186 (1987)
$LiBH_4$, MeOH	JOC *51* 4000 (1986)
$LiBH_4$; cat Li[], $LiHBEt_3$, MeOB or $B(OMe)_3$	JOC *47* 1604 (1982); *49* 3891 (1984)
$NaBH_4$, H_2O, THF	TL *28* 1147 (1987) (lactone)
$NaBH_4$, polyethylene glycols, Δ	JOC *46* 4584 (1981)
$NaBH_4$, MeOH	JOC *28* 3261 (1963); *52* 3777 (1987) TL *28* 6069 (1987)
$NaBH_4$, EtOH	Chem Pharm Bull *13* 995 (1965) (amino acid ester hydrochloride salts) TL *28* 2709 (1987) (α-hydroxy ester)
$NaBH_4$, MeOH, *t*-BuOH, Δ	Syn Commun *12* 463 (1982)
$NaBH_4$, LiCl, ROH	JOC *52* 1252 (1987) TL *28* 3671 (1987)
$NaBH_4$, $AlCl_3$	JACS *78* 2582 (1956)
$NaBH_4$, $MeSO_3H$, DMSO (R = alkyl)	JOC *46* 2579 (1981)
$Ca(BH_4)_2$	JOC *47* 4702 (1982) TL *28* 5161 (1987)
$NaBH_3OH$	JOC *42* 3963 (1977)
$LiH_3B(n\text{-Bu})$	JOC *47* 3311 (1982)
$LiHBEt_3$	JOC *45* 1 (1980); *52* 4352 (1987) CC 1786, 1797 (1987)
AlH_3	BCSJ *55* 3555 (1982)

i-Bu_2AlH	Ann *623* 9 (1959) Syn 617 (1975) (review) JOC *49* 1707 (1984); *50* 2443 (1985); *52* 1201 (1987) TL *27* 5799 (1986) (lactone)
$LiHAl(i\text{-}Bu)_2(n\text{-}Bu)$	JOC *49* 1717 (1984) JACS *109* 5280 (1987)
$LiAlH_4$	JACS *69* 1197 (1947); *107* 2730 (1985); *108* 468, 1019 (1986) Helv *31* 1617 (1948); *32* 1156 (1949) (both α-amino esters) Org Rxs *6* 469 (1951) Org Syn *63* 140 (1984) JOC *50* 2026 (1985); *52* 5419, 5480 (1987)
$LiAlH_4$, $AlCl_3$	JACS *81* 610 (1959); *105* 3252 (1983); *109* 6719 (1987) JOC *51* 2863 (1986)
$HSi(OEt)_3$, CsF/H_3O^+	Syn 558 (1981)
$(EtO)_2SiMeH$ or $Me_3SiO(-\underset{\underset{Me}{\vert}}{\overset{\overset{H}{\vert}}{Si}}-O)_n-SiMe_3$, KF or KO_2CH	Syn 981 (1982)
i-BuMgBr, cat Cp_2TiCl_2	TL *21* 2175 (1980)
LiH, VCl_3	JOC *45* 1041 (1980)

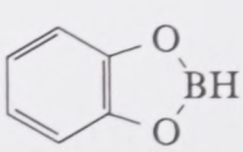
$$RCH{=}CHCO_2R \xrightarrow[EtOH]{Li,\ NH_3} RCH_2CH_2CH_2OH$$

JOC *37* 2871 (1972)

$$R\overset{\overset{O}{\|}}{C}SR' \longrightarrow RCH_2OH$$

$NaBH_4$	CC 330 (1978) Syn Commun *11* 599 (1981) TL *23* 3151 (1982)
$LiAlH_4$	JACS *108* 4603 (1986)

$$(RCO)_2O \longrightarrow RCH_2OH$$



JOC *42* 512 (1977)

$LiH_3B(n\text{-Bu})$ JOC *47* 3311 (1982)

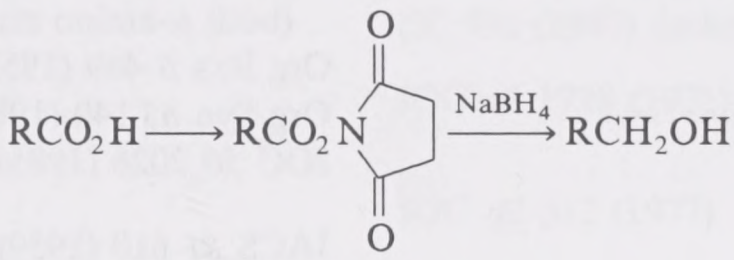
$LiHAl(i\text{-Bu})_2(n\text{-Bu})$ JOC *49* 1717 (1984)

$$RCO_2H \longrightarrow RCO_2CO_2Et \longrightarrow RCH_2OH$$

$NaBH_4$ J Med Chem *7* 483 (1964)
Chem Pharm Bull *16* 492 (1968); *27* 816 (1979)
TL *27* 6349 (1986)

$NaBH_4$, SmI_3 TL *28* 5977 (1987)

$LiBH_4$ Z Naturforsch B *10* 252 (1955)



CL 981 (1979)

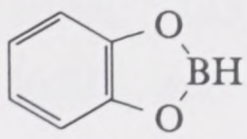
$$RCONR'_2 \longrightarrow RCH_2OH$$

9-BBN JOC *41* 1778 (1976)

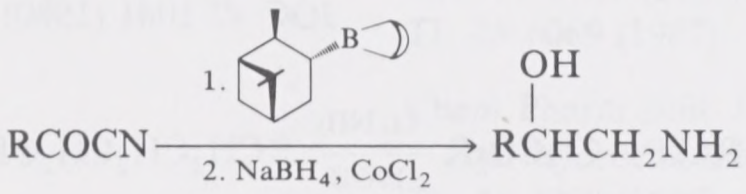
$LiHBEt_3$ Syn 635 (1977)
JOC *45* 1 (1980)

$$RCO_2Na \longrightarrow RCH_2OH$$

$BH_3 \cdot THF$ TL *23* 2475 (1982)



JOC *42* 512 (1977)



chiral

JOC *50* 3237 (1985)

8. ALKYLATION OF CARBONYL COMPOUNDS

1. Addition to Carbon Monoxide

$$2\,ArLi + RBr + CO \xrightarrow{H_2O} Ar_2C(OH)R$$

JOC *46* 4625 (1981)

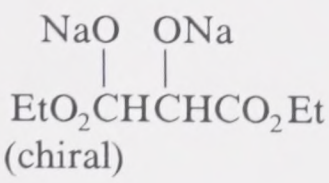
2. Addition to Aldehydes and Ketones

2.1. Organometallic Additions

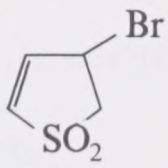
$$RX + M + R'_2CO \xrightarrow{H_2O} RCR'_2(OH)$$

Review: Syn 18 (1977) (M = Mg, Li, Ca, Zn)

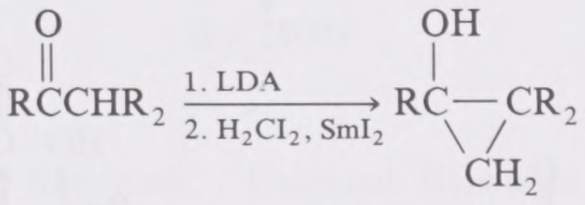
M	RX	
Li	1°, 2°, 3° alkyl; allylic; benzylic; vinylic; aryl halides	JACS *102* 7926 (1980) (ultrasound)
	1°, 2°, 3° alkyl; allylic; aryl halides	JCS Perkin I 1655 (1972)
	1° alkyl, allylic, aryl halides	CC 1160 (1970)
	2° alkyl chloride	CC 1319 (1986) (ultrasound)
	2° alkyl chloride, bromide, iodide	TL *28* 2013 (1987) (ultrasound)
	3° benzylic chloride	CC 225 (1987) (4,4′-*t*-BuC_6H_4-*t*-Bu added)
	$H_2C{=}CHCH_2Br$	JACS *102* 7926 (1980) (ultrasound)
	bromobenzene	JCS Perkin II 378 (1976)

M	RX	
Mg	1° alkyl, allylic, benzylic, propargylic, aryl halides	Syn 18 (1977) (review)
	$Me_2N(CH_2)_3Cl$	Syn Commun *11* 241 (1981)
Ca	1° alkyl iodides	JOMC *66* 219 (1974)
Al, Sn	$RCH{=}CHCH_2X$ (X = Cl, Br)	Organomet *2* 191 (1983) TL *26* 6121 (1985)
	$RCH{=}C(CO_2Et)CH_2Br$	CL 541 (1986)
Al, $SnCl_2$, H_2O	$RCH{=}CHCH_2Cl$	JOC *50* 5396 (1985) TL *27* 2395 (1986)
Al, $BiCl_3$, H_2O	$RCH{=}CHCH_2Br$	CC 708 (1987)
Sn	XCR_2CO_2R (X = Cl, Br) $RCOCR_2Br$ allylic bromides and iodides	CL 161, 929 (1982) CL 467 (1982); 1727 (1983) CL 1527 (1981); 541 (1986)
Sn, ultrasound	$H_2C{=}CHCH_2Br$	TL *26* 1449 (1985)
Sn, electrolysis	$H_2C{=}CHCH_2Br$	TL *25* 6017 (1984)
Sn, H_2O	$H_2C{=}CXCH_2Br$ (X = H, Br, OAc)	Organomet *2* 191 (1983) JOC *49* 172 (1984)
	$RCH{=}C(CO_2Et)CH_2Br$	CL 541 (1986)
SnF_2	$H_2C{=}CHCH_2I$	CL 1507 (1980); 1109 (1981); 929 (1982)
	CBr_4	CL 1505 (1981)
$SnCl_2$	$H_2C{=}CHCH_2I$	Tetr *37* 3873 (1981)
$SnCl_2$,  (chiral)	$H_2C{=}CHCH_2Br$	CC 685 (1986) JOC *52* 5447 (1987)
Sb	$H_2C{=}CHCH_2I$	TL *28* 3707 (1987)
Sb, LiI	$H_2C{=}CHCH_2X$ [X = Br, $OPO(OPh)_2$]	TL *28* 3707 (1987)
Bi	$H_2C{=}CHCH_2X$ (X = Br, I)	TL *26* 4211 (1985)
$BiCl_3$, Zn or Fe	$R_2C{=}CHCH_2X$ (X = Cl, Br, I)	TL *27* 4771 (1986)
$CrCl_2$	$RSCH_2Cl$	JOC *51* 5045 (1986)
	ArI, $RCH{=}CRX$ (X = Br, I)	TL *24* 5281 (1983)
	$RC{\equiv}CX$ (X = Br, I)	TL *26* 5585 (1985)

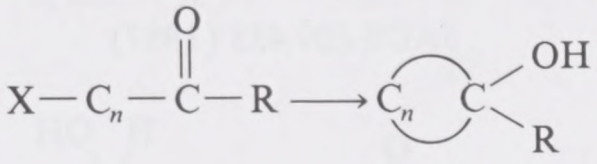
$CrCl_2$, cat $NiCl_2$	$RCH{=}CRO_3SCF_3$ $RCH{=}CHI$ $RC{\equiv}CI$	JACS *108* 6048 (1986) JOC *52* 4823 (1987) TL *28* 3463 (1987)
$CrCl_2$, cat $NiCl_2$ or $Pd(OAc)_2$	$RCH{=}CHI$	JACS *108* 5644 (1986)
$CrCl_2$ or $CrCl_3$-$LiAlH_4$	allylic bromides, iodides and tosylates	JACS *99* 3179 (1977); *107* 5219 (1985) TL 1685 (1978); *22* 1037 (1981); *23* 2343 (1982); *27* 4957, 5091 (1986); *28* 5615 (1987) Tetr *37* 3873 (1981) BCSJ *55* 561 (1982) CL 85 (1986) (intramolecular) JOC *52* 316 (1987)
Mn	$RCH{=}CHCH_2Br$	Organomet *1* 1249 (1982)
Mn, I_2	$H_2C{=}CHCH_2Br$	CL 1237 (1983)
cat $NiBr_2$(bipy), electrolysis	$ClCH_2CO_2Me$, $H_2C{=}C(Me)CH_2Cl$	TL *28* 55 (1987)
Zn	review	"Methods of Elemento-Organic Chemistry," North-Holland, Amsterdam (1967), Vol 3
	$RCHBrCOR$	JACS *89* 5727 (1967)
	$RCHXCO_2R$	Org Rxs *1* 1 (1942); *22* 423 (1975) (both reviews) Org Syn Coll Vol *4* 444 (1963) JOC *34* 3689 (1969); *35* 3966 (1970) [$B(OMe)_3$ added]; *39* 269 (1974); *46* 4323 (1981); *47* 5030 (1982) (ultrasound); *48* 4108 (1983); *52* 4796 (Me_3SiCl added), 5745 (intramolecular) (1987) Organomet Chem Rev A *8* 183 (1972) (review) Syn 452 (1975) BSCF II 145 (1980) Acta Chem Scand B *35* 273 (1981) (chiral RO_2CCH_2Br) JACS *107* 3891 (1985) [$B(OMe)_3$ added]; *108* 1617 (1986) TL *28* 6145 (1987)
	$BrCF_2CO_2Et$	TL *25* 2301 (1984)
	$RCHBrCONR_2$	JOC *52* 5745 (1987) (intramolecular)
	$BrCH_2C(Me){=}CHCO_2R$	TL *27* 5193 (1986)
	CF_3Br	CC 642 (1987)
	CF_3I	CL 1679 (1981) (ultrasound)

M	RX	
	allylic halides	JOC *41* 551 (1976); *47* 3148 (1982); *48* 4108 (1983); *50* 2011 (1985) TL *28* 3151, 4551 (1987)
	$RCH{=}C(SO_2Ph)CH_2Br$	TL *27* 5091 (1986)
	$H_2C{=}CHCH{=}CHCH_2Br$	TL *27* 5211 (1986)
	propargylic halides	Syn Commun *10* 637 (1980)
Zn, ultrasound	$H_2C{=}CHCH_2Br$	TL *26* 1449 (1985)
Zn, ultrasound, H_2O	$R_2C{=}CHCH_2X$ (X = Cl, Br)	JOC *50* 910 (1985)
Zn, ultrasound, (Cp_2TiCl_2)	perfluoroalkyl bromides and iodides	JACS *107* 5186 (1985)
Zn, cat $MCl_2(PPh_3)_2$ (M = Ni, Pd)	perfluoroalkyl iodides	CL 517 (1984)
Zn, cat $Pd(PPh_3)_4$	$H_2C{=}CHCH_2OAc$	JOC *52* 3702 (1987) (RCHO only)
Zn-Cu	$BrCH_2CO_2Et$	Syn 698 (1977)
	$BrCH_2CH{=}CHCO_2R$	JOC *52* 4397 (1987)
Zn-CuCl or Zn-AgOAc-Et_2AlCl	$ClCF_2COR$	TL *28* 6481 (1987)
Zn-Ag, ultrasound		CC 1552 (1987)
Zn-Ag graphite	$RCHXCO_2R$ (X = Cl, Br)	CC 775 (1986)
Zn-Ag, Et_2AlCl	$BrCH_2CO_2R$	BCSJ *53* 3301 (1980)
Zn, cat $HgCl_2$	$RC{\equiv}CCF_2Br$	TL *28* 659 (1987)
Ce(Hg)	benzylic and propargylic iodides	JOC *49* 3904 (1984)
	allylic bromides and iodides	TL *22* 4987 (1981) JOC *49* 3904 (1984)
Sm	CH_2I_2	TL *27* 3243 (1986)
SmI_2	1° alkyl iodides, bromides, tosylates; allylic; propargyl; benzylic halides; $RCHBrCO_2R$	JACS *102* 2693 (1980)
	benzylic bromides, allylic halides	JOMC *250* 227 (1983)
	allylic bromides and iodides, benzylic bromides	TL *23* 3497 (1982)
	CH_2X_2 (X = Br, I)	TL *27* 3891 (1986)

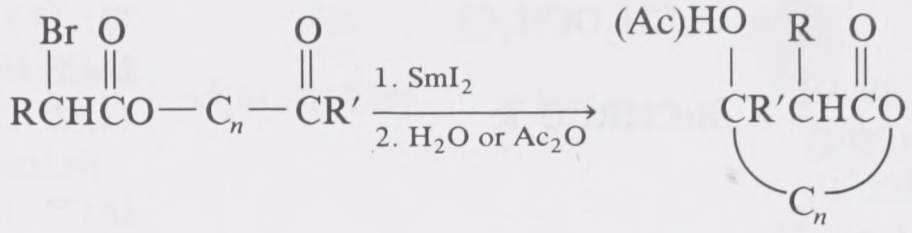
	$PhCH_2OCH_2Cl$	TL *25* 3225 (1984) JACS *109* 4424 (1987)
	$BrCHRCO_2R$	TL *27* 3889 (1986) (intramolecular) JACS *109* 6559 (1987) (intramolecular)
	RCOCl	TL *25* 2869 (1984)
SmI_2, cat $Pd(PPh_3)_4$	allylic acetates	TL *27* 1195 (1986)



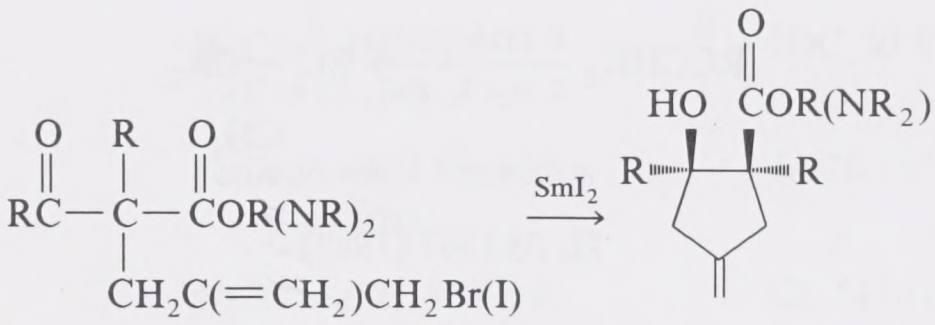
TL *28* 1307 (1987)



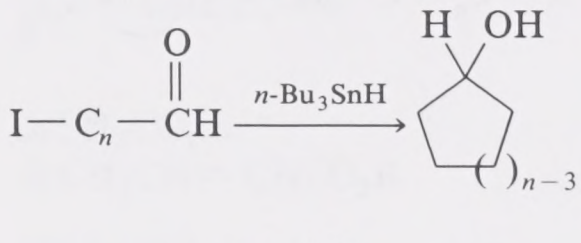
n	X	Reagent(s)	
3	Br	Mg	CC 890 (1968) BSCF 359 (1968)
3, 4	Br	Mg(Hg)	Compt Rend C *265* 1472 (1967)
4	Br	Mg or Ca, NH_3	Can J Chem *58* 2524 (1980)
	I	Mg	Ber *35* 2684 (1902) JOC *47* 5368 (1982)
		Mg, $HgCl_2$	TL *28* 3963 (1987)
		n-BuLi	TL *28* 3963 (1987)
		n-Bu_2CuLi	TL *28* 5071 (1987)
		SmI_2	TL *28* 3963 (1987) Syn Commun *17* 901 (1987)
4, 5	I	SmI_2, [cat $Fe(PhCOCHCOPh)_3$]	TL *25* 3281 (1984) JOC *51* 1778 (1986) JACS *109* 453 (1987)
5	Br	Mg	CC 1287 (1968) Angew Int *20* 576 (1981)
		SmI_2	JACS *109* 6559 (1987)
	I	*n*- or *t*-BuLi	TL *26* 4987 (1985) JOC *51* 1778 (1986)
		SmI_2	JOC *50* 2759 (1985)
5, 6	I	nickel tetraphenyl-porphine, Li naphthalenide	JACS *92* 395 (1970)



n	
2	JACS *109* 6556 (1987)
8–14	TL *27* 3889 (1986)

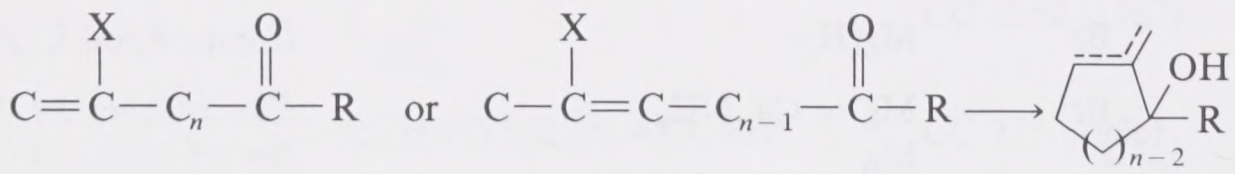


JACS *109* 453 (1987)



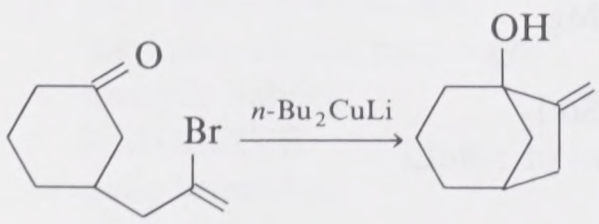
$n = 4, 5$

JACS *108* 2116, 8102 (1986); *109* 3484 (1987)

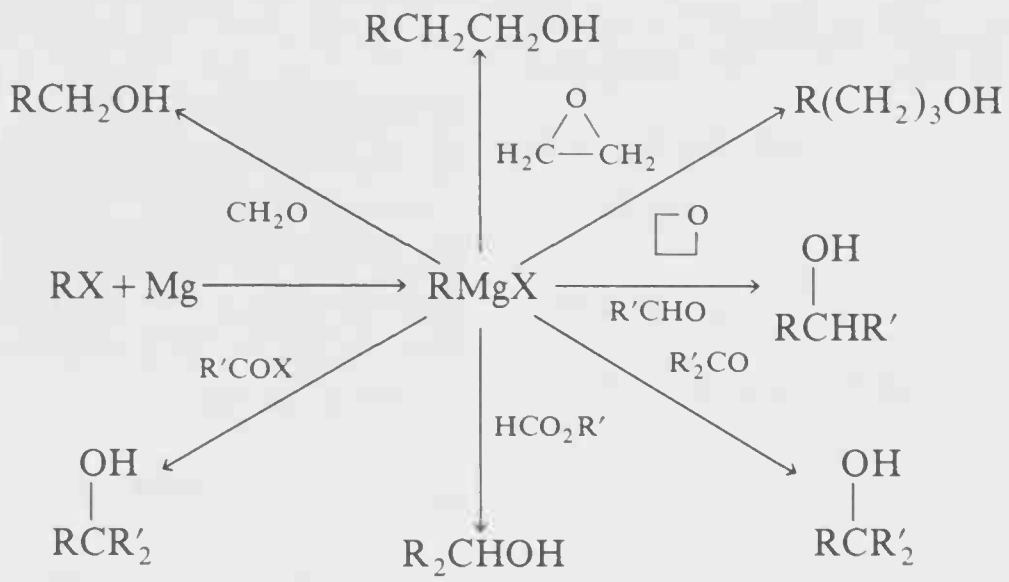


JOC *51* 3405 (1986)

X	Ring Size	Reagent	
Br	6	Li	JACS *104* 6879 (1982)
I	5	*n*-BuLi	TL *23* 4987 (1985)
		R_2CuLi	JACS *92* 395 (1970)
	6	Mg	JOC *51* 3405 (1986)

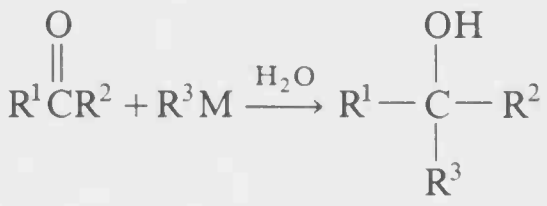


JACS *92* 396 (1970)
TL *23* 3291 (1982)



Review:

M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954)



Reviews:

M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954)
JOC *39* 3258 (1974) (organometallic "ate" complexes of Li, B, Al, Mg, Zn)
Chem Rev *75* 521 (1975) (stereochemistry)
"Organometallic Chemistry Reviews," Vol 3 (1977)
J. C. Stowell, "Carbanions in Organic Synthesis," J. Wiley, New York (1979)
R. L. Augustine, "Carbon-Carbon Bond Formation," Vol 1, Marcel Dekker, New York (1979)
E. Negishi, "Organometallics in Organic Synthesis," J. Wiley, New York (1980)
Pure Appl Chem *52* 545 (1980) (mechanism of Grignard addition to ketones)
JACS *103* 4540 (1981) (stereochemistry of cyclohexanone additions)
Syn 605 (1982) (stereoselectivity of addition to chiral aminocarbonyl compounds)
CC 452 (1982) (stereoselectivity of various R^3M on α-chiral ketone)
E. L. Eliel in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York, Vol II, Part A (1983), p 125
Angew Int *23* 556 (1984) (chelation and non-chelation control in addition reactions of chiral α- and β-alkoxy carbonyl compounds)

R^3M

RLi

JACS *81* 2748 (1959) (stereochemistry); *97* 5280 (1975) (stereochemistry); *101* 1455 (1979) (asymmetric); *103* 4540 (stereochemistry); 4585 (chiral catalysis) (1981); *107* 6411 (1985) (stereochemistry)
CC 1160 (1970); 1600 (1986) (α-alkoxy or -siloxy ketone diastereoselectivity)
JCS Perkin I 1655 (1972)
JOC *38* 904 (1973); *40* 1469 (1975) (stereochemistry); *43* 1064, 2173 (stereochemistry) (1978); *46* 2798 (1981) (chiral catalysis)

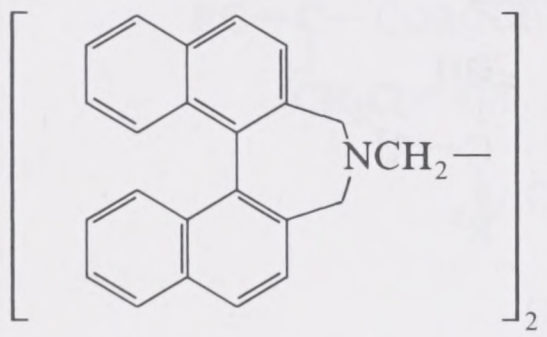
$\underline{R^3M}$

JCS Perkin II 378 (1976)
TL 2659 (1976) (stereochemistry); 1709 (1977) (stereochemistry); *28* 2629 (1987)
CL 219 (1978) (asymmetric)
Helv *62* 1701, 1710, 2695 (1979)
Tetr *38* 2725 (1982) (stereoselectivity using chiral ligand)

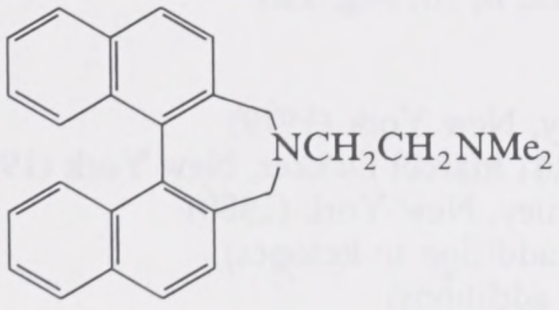
RLi, $LiClO_4$ — JOC *44* 4371 (1979)

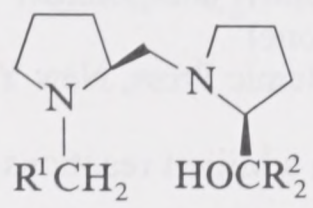
RLi, *n*-Bu_4NBr — CC 923 (1987) (Cram selective)

RLi, crown ether — JACS *107* 6411 (1985) (stereochemistry)

RLi, chiral  — JACS *103* 4585 (1981) (enantioselective)

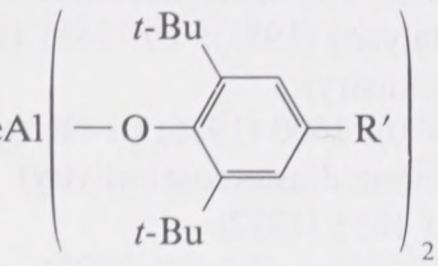
or



RLi, chiral  — JACS *101* 1455 (1979) (enantioselective)

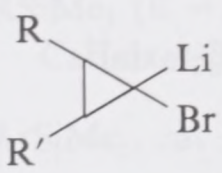
n-BuLi, chiral lithium amides — TL *25* 5187 (1984) (enantioselective)

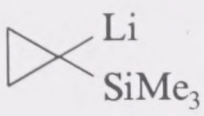
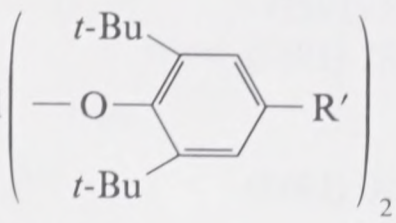
MeLi — JACS *107* 4573 (1985) (stereochemistry)
JOC *50* 422 (1985)

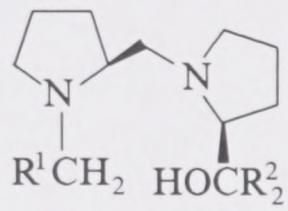
MeLi, MeAl  — JACS *107* 4573 (1985) (aldehydes and cyclic ketones only, axial addition)
TL *28* 1439 (1987)

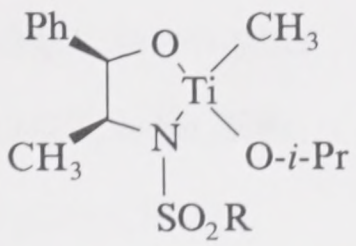
($R' = Me,\ t\text{-}Bu$)

$R_2C(OR')Li$ — TL *21* 1285 (1980); *28* 4131 (1987)
JACS *106* 3376 (1984); *107* 3285 (1985)

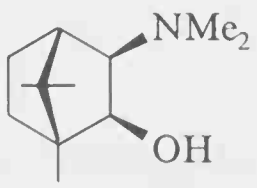
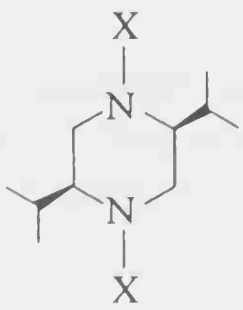
$LiCH_2OLi$	Angew Int *15* 738 (1978) Ber *113* 1290, 2055 (1980)
$Li(CH_2)_3OLi$	Ber *113* 1290 (1978)
$(EtO)_2CHCH_2CH_2Li$	CC 425 (1987)
$LiCH_2CN$	JACS *109* 613 (1987) (diastereoselective)
$RCH{=}CRLi$	TL 4839 (1976); *22* 3745 (1981) Ber *111* 2785 (1978)
$LiCH{=}CHCH_2OLi$	Ber *113* 1290 (1978)
$H_2C{=}C(Li)CHO$	JOC *52* 2625 (1987)
$HC{\equiv}CLi$	CC 363 (1981) (stereochemistry) JACS *107* 1034 (1985)
$R_3SiC{\equiv}CLi$	CL 929 (1982) JOC *52* 4191 (1987)
$RC{\equiv}CLi$	JACS *87* 5632 (1965); *107* 3915 (1985) JOC *38* 3588 (1973); *50* 2390 (1985); *52* 3241 (enediones), 3662, 3798, 4124 (1987) CL 447 (1979) (asymmetric); 255 (1980) (asymmetric) TL *28* 1019 (1987)
$EtOC{\equiv}CLi$	JOC *52* 2332 (1987)
$LiO_2CC{\equiv}CLi$	Syn Commun *12* 977 (1982)
$RO_2CC{\equiv}CLi$	JOC *45* 28 (1980); *52* 3342 (1987) Syn Commun *12* 977 (1982)
$R_3SiC{\equiv}CCH_2Li$	TL *23* 719 (1982)
RCHLiSOAr	JOC *46* 4101, 5452 (1981) JCS Perkin I 1278 (1981)
$LiCH_2Cl$	TL *25* 835 (1984); *27* 795 (1986)
$LiCHX_2$ (X = Cl, Br, I)	JACS *96* 3010 (1974); *104* 4708 (1982); *106* 3030 (1984); *108* 3102 (1986) TL *22* 3745 (1981) Topics Curr Chem *106* 55 (1982) (review)
$LiCX_3$ (X = Cl, Br)	JACS *96* 3010 (1974) Topics Curr Chem *106* 55 (1982) (review)
$LiCF_2CF_3$	TL *26* 5243 (1985) JOC *52* 2481 (1987)
	Ber *115* 1990 (1982)
$Me_3SiCH_2CH_2M$ (M = Li, MgBr)	JOC *47* 1983 (1982)

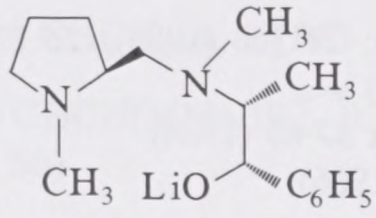
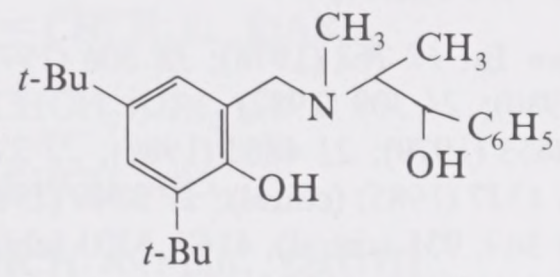
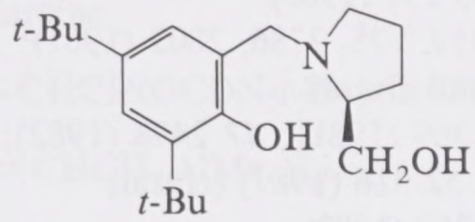
R^3M	
	TL *23* 259 (1982)
$H_2C{=}C(Li)SiMe_3$	TL *23* 259 (1982)
$HC{\equiv}CNa$	Org Syn Coll Vol *3* 416 (1955) Syn 211 (1982)
$RC{\equiv}CNa$	JOC *38* 3588 (1973)
$RC{\equiv}CH$, NaOH (phase transfer)	Ann 1750 (1982)
NCNa	Org Syn Coll Vol *2* 7 (1943)
O_2NCH_2Na	Org Syn Coll Vol *4* 221 (1963)
O_2NCH_2K	Org Syn Coll Vol *5* 833 (1973)
RMgX	Org Syn Coll Vol *1* 188 (1941); *3* 200 (1955) JACS *73* 4462 (1951); *74* 4954 (1952); *81* 2748 (1959) (stereochemistry); *103* 4540 (1981) (stereochemistry); *107* 4573, 6411 (1985) (both stereochemistry) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954) (review) JOC *27* 3860 (1962) (stereochemistry); *37* 1918 (1972) (stereochemistry); *50* 2179 (1985) (bicyclic ketones); *51* 5353 (1986) (2-alkoxy aldehyde stereoselectivity) BSCF 219 (1971) (stereochemistry) TL 4383 (1979); *21* 1031 (1980) (asymmetric); *23* 5211 (1982) (δ-keto ester stereoselectivity); *28* 2629 (1987) JCS Perkin II 597 (1981) (stereochemistry) JCS Perkin I 197 (stereochemistry using chiral alkoxide ligand), 979 (stereochemistry) (1982) CC 1600 (1986) (α-alkoxy or -siloxy ketone diastereoselectivity)
RMgX, crown ether	JACS *107* 6411 (1985) (stereochemistry)
RMgX, *n*-Bu_4NBr	CC 923 (1987) (Cram selective)
$R_2C{=}CRMgX$	JOC *52* 3798 (1987)
RMgX, MeAl()$_2$ ($R' = Me$, *t*-Bu)	JACS *107* 4573 (1985) (aldehydes and cyclic ketones only, axial addition, anti-Cram)
$RMgOR'$ or $RMgNR'_2$	JOC *43* 4094 (1978) (stereoselective)

R_2Mg	JOC *37* 1918 (1972) (stereochemistry) CL 601 (1978) (asymmetric) JACS *101* 1455 (1979) (asymmetric); *107* 6411 (1985) (stereochemistry)
Me_2Mg, ($LiClO_4$)	JOC *44* 4371 (1979)
R_2Mg, chiral 	JACS *101* 1455 (1979) (enantioselective)
Me_3SiCH_2MgCl	TL *23* 3249 (1982) Ber *115* 1132 (1982)
$XMgCX_2CO_2R$	JCS Perkin I 2063 (1982)
$H_2C{=}CHCH{=}CHMgBr$	JOC *52* 4416 (1987)
$RC{\equiv}CMgBr$	TL *28* 1019 (1987)
$BrMgC{\equiv}CMgBr$	CC 363 (1981)
RCaX	JOMC *66* 219 (1974)
R_nAlX_{3-n} (X = halogen, OR, NR_2)	JOC *44* 4792 (1979)
R_3Al	JOC *37* 1918 (1972); *40* 1469 (1975) BCSJ *47* 1971 (1974)
$RC{\equiv}CAlR_2$	Compt Rend *261* 1992 (1965) BSCF 205 (1968)
$(RC{\equiv}C)_3Al$	Compt Rend C *262* 289 (1966)
$LiAlR_4$	JOC *39* 3258 (1974) TL *26* 4181 (1985) (on menthyl phenylglyoxalate)
$RSiR'_3$, cat $[(Me_2N)_3S]Me_3SiF_2$ (R = $CHCl_2$, CCl_3, CCl_2Me, $CF_2CH{=}CH_2$, $CF{=}CF_2$, $CF{=}CF$-*n*-Bu, $CF{=}CFSEt$, $CCl{=}CF_2$, $CF{=}CFH$)	JACS *107* 4085 (1985)
$HC{\equiv}CCH_2SiMe_3$, *n*-Bu_4NF (allenic product))	TL *22* 455 (1981)
$ArCH_2SiMe_3$, *n*-Bu_4NF	TL *24* 4217 (1983) BSCF II 90 (1985) JOC *52* 4381 (1987)
$RSiMe_3$ (R = benzylic, 4-picolyl, phenylallyl), KF-18-crown-6 or *n*-Bu_4NF-silica	TL *23* 577 (1982)
$RSiMe_3$ (R = benzyl, allyl, heterocyclic); CsF or *n*-Bu_4NF-silica	TL 5079 (1982)
$ArSiMe_3$, cat KO-*t*-Bu	Angew Int *20* 265 (1981)
$ArSiMe_3$, CsF	TL *28* 2933 (1987) (intramolecular)

R^3M	
$Cr(CO)_3 \cdot ArSiMe_3$, cat CsF	Angew Int *20* 266 (1981)
$RCH{=}C(SiMe_3)CO_2R$, *n*-Bu_4NF ($R^3 = RCH{=}CCO_2R$)	Syn 734 (1986)
$Me_3SiC{\equiv}CSiMe_3$, $AlCl_3$	TL 2449 (1976)
$Me_3SiC{\equiv}CSiMe_3$, KF, 18-crown-6	CC 840 (1979)
$RC{\equiv}CSiMe_3$, *n*-Bu_4NF	Angew Int *15* 498 (1976) Tetr *39* 975 (1983)
$PhCOSiMe_3$, *n*-Bu_4NF/H_2O ($R^3 = PhCO$)	TL *22* 1881 (1981)
R_fSnX_2I (X = F, Cl)	CL 1337 (1981)
n-$Bu_3SnCH_2CH_2COX$ (X = OMe, NHPh), $TiCl_4$	JOC *50* 5907 (1985)
$RC{\equiv}CSn(n\text{-}Bu)_3$, $TiCl_4$	CC 102 (1986)
$RC{\equiv}CSnEt_3$, $ZnCl_2$	TL 495 (1967)
R_4Pb, $TiCl_4$	JACS *109* 4395 (1987) (aldehydes only)
RTi review	Topics Curr Chem *106* 1 (1982)
$RTiCl_3$	Angew Int *19* 1011 (1980); *22* 989 (1983) Syn Commun *11* 647 (1981) JACS *105* 4833 (1983) CC 1600 (1986) (α-alkoxy or -siloxy ketone diastereoselectivity) Tetr *42* 2931 (1986)
$RO_2CCH_2CH_2TiCl_3$	JACS *99* 7360 (1977); *105* 651 (1983); *108* 3745 (1986)
$RO_2CCH_2CH_2TiCl_3$, $Ti(O\text{-}i\text{-}Pr)_4$	JACS *107* 2138 (1985); *108* 3745 (1986)
R_2TiCl_2	Angew Int *19* 1011 (1980) Ber *118* 1441 (1985)
	TL *27* 5711 (1986) (enantioselective)
$RTi(OR')_3$	Angew Int *19* 1011 (1980); *21* 135 (1982); *22* 31 (1983) Helv *63* 2451 (1980); *64* 357, 2485 (1981); *65* 249 (1982) JACS *105* 4833 (1983); *107* 4577 (1985) Ber *118* 1421, 1441 (1985) JOC *50* 422 (1985)

	CC 1600 (1986) (α-alkoxy or -siloxy ketone diastereoselectivity) Tetr *42* 2931 (1986) TL *27* 5351 (1986) (β-Me_2N ketone); *28* 2959 (1987)
$R_2Ti(OR')_2$	Angew *21* 135 (1982) Ber *118* 1421 (1985)
Me_4Ti	Angew *21* 135 (1982) Ber *118* 1421 (1985)
$RZr(OR')_3$	Helv *64* 1552 (1981) Angew Int *21* 135 (1982); *22* 31 (1983)
Me_4Zr	Angew Int *21* 135 (1982)
$MeHfX_3$ (X = Cl, OEt)	TL *27* 5351 (1986) (α-hydroxy ketone)
Me_2VOCl	TL *27* 5351 (1986) (β-hydroxy ketone)
$(CH_3)_2Nb(OEt)_3$	TL *23* 2301 (1982) (RCHO > R_2CO)
CH_3NbCl_4	TL *23* 2301 (1982) (RCHO > R_2CO)
$(CH_3)_2Ta(OEt)_3$	TL *23* 2301 (1982) (RCHO > R_2CO)
$CH_3Ta(OEt)_4$	TL *23* 2301 (1982) (RCHO > R_2CO)
CH_3TaCl_4	TL *23* 2301 (1982) (RCHO > R_2CO)
MeCrCl	TL *27* 5351 (1986) (β-hydroxy ketone)
$MeCrCl_2$	TL *27* 5355 (1986)
Me_2CrCl	TL *27* 5351 (1986) (β-Me_2N ketone)
MeMnCl	TL *27* 5351 (1986) (α-Me_2N ketone)
RMnX	TL 3383 (1977) (RCHO > R_2CO); *27* 4445 (1986)
$(Cl_2CH)_3MnLi$	TL *27* 5351 (1986) (α-Me_2N ketone)
$RCu \cdot BF_3$	JOC *47* 119 (1982)
$RCu \cdot MgBr_2$	JOC *50* 422 (1885)
R_2CuLi	JOC *31* 3128 (1966); *40* 1460 (1975); *50* 422 (1985) CC 320 (1973) TL 3128 (1974); *21* 1035 (1980) (asymmetric); *27* 3059, 5351 (β-Me_2N ketone) (1986) JACS *107* 6411 (1985) (stereoselectivity)
$\left(H_2C{=}\overset{\overset{CH_3}{\vert}}{C}{-} \right)_2 CuLi$	TL *28* 4147 (1987)
R_2CuLi, crown ether	JACS *107* 6411 (1985) (anti-Cram)
R_2CuLi, *n*-Bu_4NBr	CC 923 (1987) (anti-Cram)

R^3M	
$Me_3SiI/R_2CuLi/H_2O$	Syn Commun *13* 213 (1983)
$\left[H_2C{=}C(CO_2Me)CuC{\equiv}C(CH_2)_3CH_3\right]Li$	TL 3897 (1975)
R_3CuLi_2	JACS *97* 5280 (1975) (stereochemistry) TL 2659 (1976) (stereochemistry); 1709 (1977) (stereochemistry); *28* 5547 (1987)
$(RC{\equiv}C)_3CuLi_2$	CC 892 (1975) (on enones)
$R_5Cu_3Li_2$, crown ether	JACS *107* 6411 (1985) (anti-Cram)
$Me_2Cu(CN)Li_2$	JACS *106* 6414 (1984) (on RCHO)
$R_2Cu(CN)Li_2$, crown ether	JACS *107* 6411 (1985) (anti-Cram)
RZnX	"Methods of Elemento-organic Chemistry," Vol 3, North-Holland, Amsterdam (1967) (review) Adv Organometal Chem *12* 83 (1974) (review)
CF_3CX_2ZnX (X = Cl, Br)	TL *27* 2135, 2139 (1986)
$RO_2CCHRZnX$	See the earlier equation in this section under Zn
$(RO_2CCHRCH_2)_2Zn$, Me_3SiCl	JACS *109* 8056 (1987)
$BrZnCH_2CR{=}CHCO_2SiMe_3$	JOMC *219* C1 (1981) (α or γ)
R_2Zn, $TiCl_4$	Syn Commun *11* 261 (1981) Angew Int *22* 989 (1983) JACS *105* 4833 (1983) JOC *52* 320 (1987)
R_2Zn, cat bis[(−)-camphorquinone-α-dioximato) cobalt(II) or palladium(II)]	CL 841 (1983) (ArCHO only, enantioselective)
R_2Zn, cat cinchona alkaloids	JOC *52* 135 (1987) (ArCHO only, enantioselective) TL *28* 6163 (1987)
R_2Zn, 	JACS *108* 6071 (1986) (RCHO only, enantioselective)
R_2Zn, cat  (X = H, Li)	TL *28* 4841 (1987) (ArCHO only, enantioselective)
R_2Zn, cat $PhCHOHCHMeNR_2$	CC 1690 (1987) (enantioselective) TL *28* 3013 (1987) (ArCHO only, enantioselective)
R_2Zn, chiral polymeric amino alcohol	JOC *52* 4140 (1987) (ArCHO only, enantioselective)

R_2Zn, several chiral amino alcohols	TL *25* 2823 (1984) (PhCHO only, enantioselective); *28* 6163 (1987) (ArCHO only, enantioselective)
R_2Zn, chiral pyrrolidinylmethanols	CC 467 (1987) (enantioselective) JACS *109* 7111 (1987) (enantioselective)
R_2Zn, cat 	TL *28* 5233 (1987) (RCHO only, enantioselective)
R_2Zn, cat $PhCHCH(CH_3)NCH_2CH_2N(CH_3)_2$ (OLi, CH_3)	TL *28* 5233 (1987) (ArCHO only, enantioselective)
R_2Zn, cat 	TL *28* 5237 (1987) (ArCHO only, enantioselective)
R_2Zn, cat 	TL *28* 5237 (1987) (ArCHO only, enantioselective)
$RC{\equiv}CZnX$	TL *28* 1019 (1987)
$(ArCH_2)_2Cd$, MgX_2	TL 1581 (1979)
$RCeX_2$ (X = Cl, I)	CC 1042 (1982) TL *25* 4233 (1984); *27* 3329 (1986); *28* 31 (1987) JOC *49* 3904 (1984); *52* 281, 4142 (1987) JACS *108* 7873 (1986); *109* 7908 (1987)
$RC{\equiv}CCeCl_2$	CL 1543 (1984) TL *26* 1549 (1985); *27* 195 (1986); *28* 3971, 4583 (1987) CC 1290, 1474 (1987) JOC *52* 4135 (1987)
$(RC{\equiv}C)_3Ce$	CL 1543 (1984)
RYbI	JOC *52* 3524 (1987)

$$R^1\overset{\overset{O}{\|}}{C}H\,(R_2CO) \longrightarrow R^1\overset{\overset{OH}{|}}{C}HCHR^2CH{=}CHR^3$$

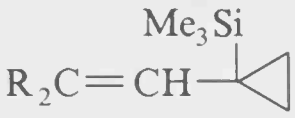
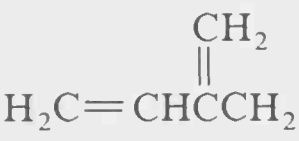
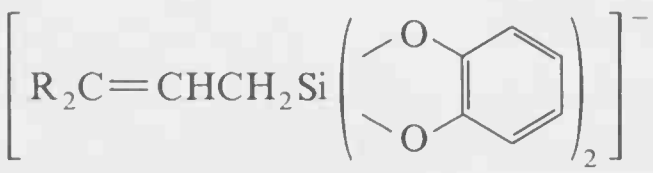
See also the direct reaction of aldehydes and ketones with allylic halides plus metals, as well as page 119, Section 8, for ene-type reactions

Reviews:

JOMC *69* 1 (1974) (Li, Na, Mg, Zn, Cd, Al)
Heterocycles *18* 357 (1982)
Angew Int *21* 555 (1982) (diastereoselectivity)
Topics Curr Chem *106* 55 (1982) (Ti)
JOMC *285* 31 (1985)

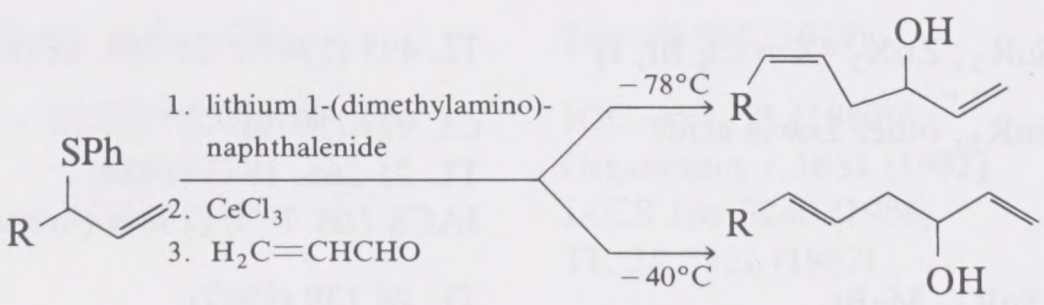
allylic lithium compounds	Tetr *42* 2803 (1986)
$ClCH{=}CHCH_2Li$ (no rearrangement)	JOMC *236* 139 (1982)
$Me_3SiCH{=}CHCH_2Li$ (no rearrangement)	CL 713 (1979)
$R_2C{=}CHCH(Li)SO_2Ph$ (no rearrangement)	CL 1331 (1982)
$R^2CH{=}CHCHR^3MgX$	TL 3829 (1975); *21* 365 (1980); *26* 823 (1985); *28* 869 (1987) Austral J Chem *37* 65 (1984) JOC *51* 3290 (1986)
$H_2C{=}C(Me)CH_2MgCl$	JOC *52* 1603 (1987)
$(H_2C{=}CHCH_2)_2Mg$	BSCF 4038 (1969)
$H_2C{=}CHCH_2MgCl, ZnCl_2$	TL *27* 4961 (1986)
$R^2CH{=}CHCHR^3B(OR)_2$	Angew Int *17* 768 (1978); *18* 306 (1979); *19* 218 (1980); *21* 309 (1982) TL 4653 (1979); *21* 4883 (1980); *22* 2751 (1981); *26* 4327 (1985) (chiral); *27* 3349 (1986) (chiral); *28* 869, 931 (chiral), 4169, 5303 (chiral) (1987) JOMC *195* 137 (1980) Ber *114* 359, 375, 2786, 2802 (1981); *115* 2357 (1982) (all chiral) JOC *46* 1309 (1981); *47* 2498 (1982); *49* 3429 (1984); *52* 316 (1987) (chiral) Helv *65* 1258 (1982) JACS *107* 8186 (1985) (chiral); *108* 294 (chiral), 3422 (chiral aldehydes) (1986); *109* 953 (chiral), 8117 (chiral) (1987)
$RCH{=}CHCHClB(OR)_2$	Angew Int *23* 437 (1984); *25* 189 (1986)
$H_2C{=}CHCHXB(OR)_2$ (X = Cl, Br, OMe, SR)	TL *24* 3209 (1983)
$H_2C{=}CHCH(SiMe_3)B(OR)_2$	Organomet *2* 236 (1983)
$R'OCH{=}CHCH_2B(OR)_2$	TL *23* 845 (1982); *24* 2227 (1983); *27* 3353 (1986) JOC *47* 2498 (1982) Syn Commun *12* 779 (1982) JACS *109* 7575 (1987)
$R^2CH{=}CHCHR^1BR^1OH$	JACS *104* 2330 (1982)
$RCH{=}CHCH_2BR_2$	JOC *42* 2292 (1977); *49* 4089 (1984) (chiral); *51* 432 (chiral), 886 (1986); *52* 319 (chiral), 3701 (chiral), 4831 (chiral) (1987) CL 993 (1980) JACS *105* 2092 (1983) (chiral); *107* 2564 (1985); *108* 293, 5919 (chiral) (1986); *109* 7553 (chiral), 8120 (chiral) (1987) TL *25* 1215, 5111 (1984) (both chiral); *27* 5135 (1986) CC 877 (1987) (chiral)

$CH_3CH{=}CHCHXB\langle\rangle$ (X = H, Me_3Si, Me_3Sn)	CC 191 (1983)
$Me_3SiCH_2\overset{SiMe_3}{\overset{\vert}{C}}{=}CHCH_2B\langle\rangle$	JOC *51* 4733 (1986)
$Me_3SiCH{=}CHCH_2Li$, R_2BCl	CC 1326 (1982)
$CH_3CH{=}CHCH(MMe_3)B\langle\rangle$ (M = Si, Sn)	JACS *103* 3229 (1981)
$R^2CH{=}CHCH_2\bar{B}R_3$	CC 1072 (1980) JACS *103* 1969 (1981)
$RCH{=}CHCH_2AlX_2$	BSCF 1475 (1963)
$Me_3SiCH{=}CHCH_2Li$, $EtAlCl_2$	CC 1326 (1982)
$R^2CH{=}CHCH_2AlEt_2$	JACS *102* 2118 (1980)
$ROCH{=}CHCH_2AlEt_2$	CC 845 (1982)
$H_2C{=}CHCH_2Al(i\text{-}Bu)_2$, $Sn(OTf)_2$, chiral diamine	CL 97 (1986) (chiral)
$CH_3CH{=}CHCH(OCON\text{-}i\text{-}Pr_2)Al(i\text{-}Bu)_2$	Angew Int *21* 372 (1982)
$(CH_3CH{=}CHCH_2AlMe_3)Li$	JACS *108* 4943 (1986)
$(XCH{=}CHCH_2AlEt_3)Li$ (X = Me_3Si, PhSe)	TL *23* 4597 (1982)
$(ROCH{=}CHCH_2AlEt_3)Li$	JOC *45* 195 (1980) TL *23* 4959 (1982)
$(RSCH{=}CHCH_2AlEt_3)Li$	JOC *45* 195 (1980) TL *23* 4959 (1982); *27* 5947 (1986)
$Me_2C{=}CHCH_2SiF_3$, CsF	TL *28* 4081 (1987)
$R^2CH{=}CHCH_2SiMe_3$, $BF_3{\cdot}OEt_2$	TL 3513 (1978) (intramolecular); *26* 823 (1985); *28* 4959 (1987) Helv *66* 1655 (1983) (intramolecular) JOC *49* 4214 (1984) CC 396 (1986) JACS *109* 2512 (1987)
$R^2CH{=}CHCHR^3SiMe_3$, $AlCl_3$	JOMC *84* 199 (1975) TL 2449 (1976); 429 (1979) Helv *66* 1655 (1983) (intramolecular)
$H_2C{=}CRCH_2SiMe_3$, $EtAlCl_2$	JACS *104* 6879 (1982) (intramolecular)
$R^2CH{=}CHCH_2SiMe_3$, SnX_4 (X = Cl, Br)	TL 3513 (1978) (intramolecular); *24* 4765 (1983) Helv *66* 1655 (1983) (intramolecular) JOC *49* 4214 (1984); *51* 3290 (1986); *52* 316 (1987) JACS *109* 2512 (1987)
$R^2CH{=}CHCHR^3SiMe_3$, $TiCl_4$	CC 927 (1976); 102 (1986)

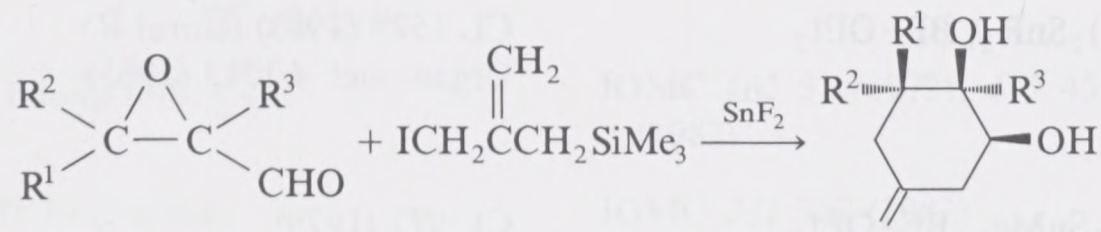
$R^2CH{=}CHCHR^3SiMe_3$, $TiCl_4$ (*continued*)	TL 1295 (1976); 1385 (1977); 2589 (1978); 429 (1979); *23* 723 (1982); *24* 2865, 5661 (1983); *26* 823 (1985); *27* 4485 (1986); *28* 655 (intramolecular), 969 (chiral) (1987) JACS *101* 3340 (1979); *104* 4962, 4963 (1982); *105* 4833 (1983) CL 961 (1982) JOC *48* 281 (1983) (chiral); *49* 4214 (1984); *51* 3290 (1986); *52* 5492 (1987) Angew Int *22* 989 (1983)
$H_2C{=}CBrCH_2SiMe_3$, $TiCl_4$	JACS *104* 6879 (1982)
$R^2CH{=}CHCHR^3SiMe_3$, R_4NF	TL 3043, 3513 (intramolecular) (1978); *23* 577 (1982) Helv *66* 1655 (1983) (intramolecular)
	TL *23* 3227 (1982)
$Me_3SiCH{=}CHCH_2SiMe_3$, *n*-Bu_4NF	JOMC *264* 207 (1984)
	Tetr *39* 883 (1983)
$R^2CH{=}CHCH{=}CHCHR^3SiMe_3$, $TiCl_4$	JOC *45* 1721 (1980) Organomet *1* 1651 (1982) JACS *106* 3240 (1984) TL *28* 5921 (1987)
	CC 1517 (1987) (RCHO only)
$RCH{=}CHCH_2SnCl_n(n\text{-}Bu)_{3-n}$	JOMC *162* 37 (1978); *197* 45 (1980); *226* 149 (1982)
$H_2C{=}CHCHMeSnCl(n\text{-}Bu)_2$	JOMC *231* 307 (1982)
$(R^2_2C{=}CHCH_2)_2SnBr_2$ (R^2 = H, Me)	JOMC *280* 307 (1985)
$R^2CH{=}CHCH_2SnR_3$, Δ (R = Et, *n*-Bu)	TL 495 (1967); *28* 5343 (1987) JOMC *35* C20 (1972) JACS *102* 4548 (1980); *106* 7970 (1984) (intramolecular) Pure Appl Chem *53* 2401 (1981) (review)
$R^2CH{=}CHCH(OR)Sn(n\text{-}Bu)_3$, Δ	CC 1115 (1982); 800 (1984) TL *28* 527 (1987)
$R^2CH{=}CHCH(OR)Sn(n\text{-}Bu)_3$, $BF_3{\cdot}OEt_2$	TL *28* 527 (1987) (intramolecular)
$Me_3SiCH{=}CHCH_2Li$, *n*-Bu_3SnCl, BF_3	CC 1326 (1982)
$R^2CH{=}CHCH_2SnR_3$, MgX_2 (X = Br, I)	TL *25* 265, 1879, 3927 (1984); *28* 4381 (1987) JOC *51* 5478 (1986); *52* 316 (1987) JACS *109* 7553 (1987)

$R^2CH{=}CR^4CHR^3SnR_3$, $BF_3{\cdot}OEt_2$	CL 919, 977 (1979); 1297, 1299 (1982) JACS *102* 4548, 7107 (1980); *106* 6835, 7970 (intramolecular) (1984); *107* 1778 (1985); *108* 4645 (1986) CC 683 (1980) TL *23* 4959 (1982); *25* 265, 1879, 1883, 3927 (1984); *26* 6235 (1985); *27* 5423 (1986); *28* 139, 2629, 3939, 5343 (1987) Tetr *40* 2239 (1984) Organomet *4* 1213 (1985) (chiral) JOC *51* 863, 886, 1856, 2621, 5478 (1986); *52* 316 (1987)
$R^2CH{=}CR^4CH_2SnR_3$, $SnCl_4$	TL *25* 3927 (1984); *26* 6235 (1985); *28* 2629 (1987) JACS *106* 7970 (1984) (intramolecular) JOC *51* 3290, 5478 (1986); *52* 316 (1987)
$R^2CH{=}CR^4CH_2SnR_3$, $TiCl_4$	TL *25* 265, 1879, 1883, 3927 (1984); *28* 2629 (1987) JACS *106* 7970 (1984) (intramolecular) CC 102 (1986) JOC *51* 863, 1856, 3290, 5478 (1986)
$R^2CH{=}CHCH_2SnR_3$, ZnX_2 (X = Cl, Br, I)	TL 495 (1967); *25* 265, 1879, 1883, 3927 (1984)
$R^2CH{=}CHCH_2SnR_3$, other Lewis acids	CL 977 (1979) TL *25* 265, 1883 (1984) JACS *106* 7970 (1984) (intramolecular)
$ROCH{=}CHCH_2SnR_3$, $MgBr_2$	TL *28* 139 (1987)
$ROCH{=}CHCH_2SnR_3$, $BF_3{\cdot}OEt_2$	TL *28* 143 (1987)
$(H_2C{=}CHCH_2)_2SnR_2$, $BF_3{\cdot}OEt_2$	CL 1529 (1983) (chiral R) Organomet *4* 1213 (1985)
$H_2C{=}C(CH_2)CH_2SnMe_3$, $BF_3{\cdot}OEt_2$	CL 977 (1979)
$R^2CH{=}CHCH_2TiCp_2$	TL *23* 4589 (1982) JOMC *224* 327 (1982) CC 921 (1983)
$R^2CH{=}CHCH_2TiCp_2X$ (X = Br, I)	CC 342, 1140 (1981); 98 (1986) TL *22* 243 (1981)
$R^2CH{=}CHCH_2Ti(OR)_3$	Angew Int *19* 1011 (1980); *21* 135 (1982) Helv *65* 1085, 1972 (1982) JACS *104* 7663 (1982); *107* 1691 (1985) Ber *118* 1441 (1985) Tetr *42* 2803 (1986) TL *28* 869 (1987)
$R^2CH{=}CHCH_2Ti(NEt_2)_3$	Ber *118* 1441 (1985)
$CH_3CH{=}CHCH(OCON\text{-}i\text{-}Pr_2)Ti(NEt_2)_3$	Angew Int *21* 372 (1982)

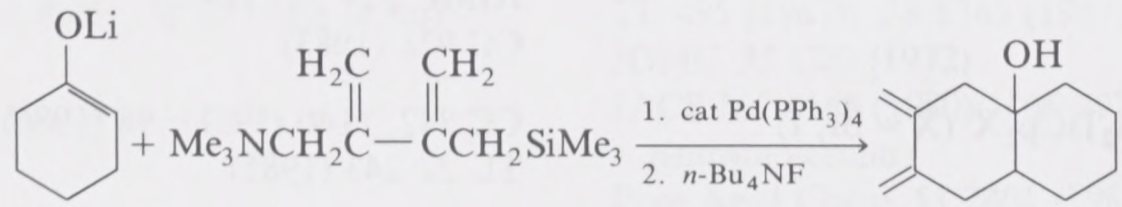
$[Me_3SiCH{=}CHCH_2Ti(O\text{-}i\text{-}Pr)_4]Li$	Ber *118* 1441 (1985)
$[H_2C{=}CHCH_2Ti(O\text{-}i\text{-}Pr)_4]MgCl$	TL *23* 5259 (1982) ($RCHO > R_2CO$) Ber *118* 1441 (1985)
$[H_2C{=}CHCH_2Ti(NMe_2)_4]Li$	TL *23* 5259 (1982) ($R_2CO > RCHO$)
$R^2CH{=}CHCH_2ZrCp_2Cl$	TL *22* 2895 (1981)
$(H_2C{=}CHCH_2)_4Zr$	JACS *105* 4833 (1983)
$H_2C{=}CHCH_2CrCl_2$	TL *27* 5351 (1986) (β-hydroxy ketone)
$H_2C{=}CHCH_2Cu\cdot SMe_2/MgBr_2$	TL *28* 869 (1987)
$R^2CH{=}CHCHR^3ZnX$	BSCF 1475 (1963) TL 3829 (1975) (with and without rearrangement)
$(H_2C{=}CHCH_2)_2Zn$	BSCF 974 (1962); 4038 (1969) Pure Appl Chem *53* 1163 (1981) JOC *51* 3742 (1986); *52* 1141 (1987) TL *28* 869 (1987)
$H_2C{=}CHC(=CH_2)CH_2ZnBr$	Syn 742 (1979)
$(H_2C{=}CHCH_2)_2Cd$	BSCF 4038 (1969)



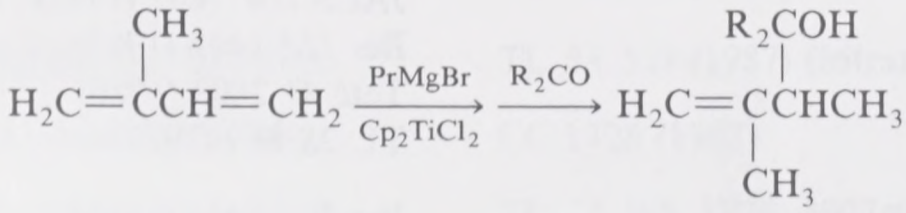
JACS *109* 4710 (1987)



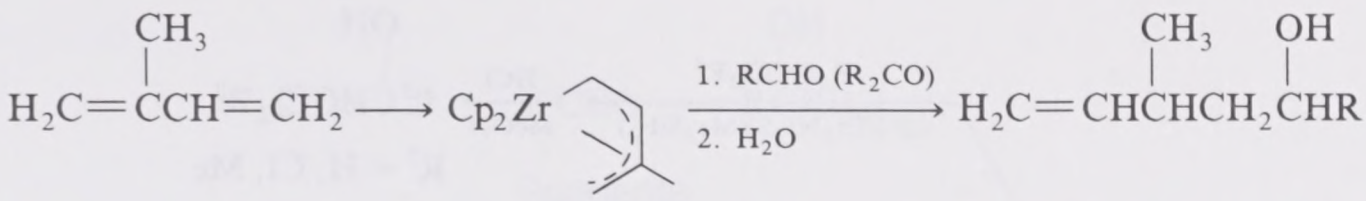
JACS *109* 576 (1987)



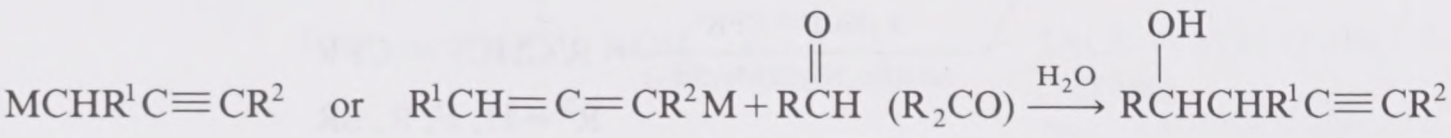
CC 570 (1987)

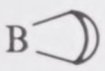


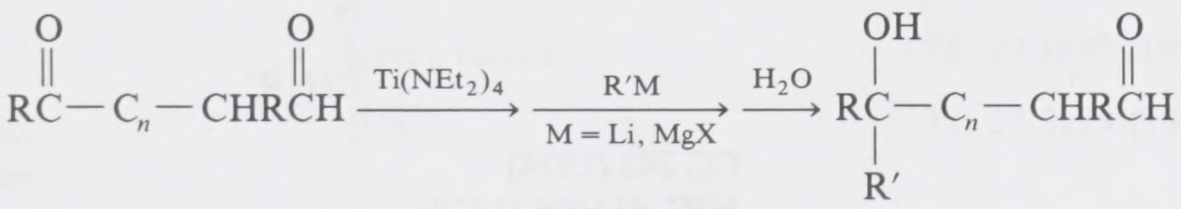
TL *21* 365 (1980)
CC 342 (1981)



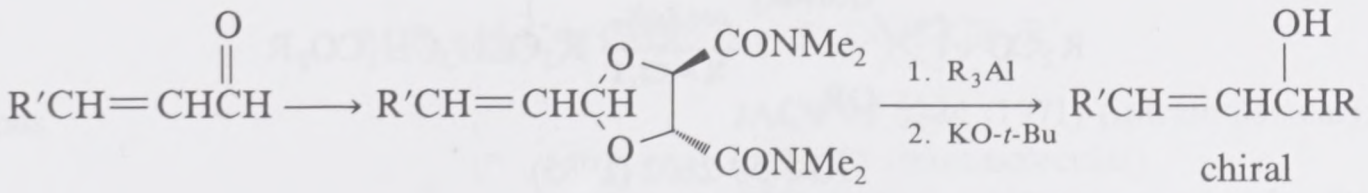
CL 671 (1981)



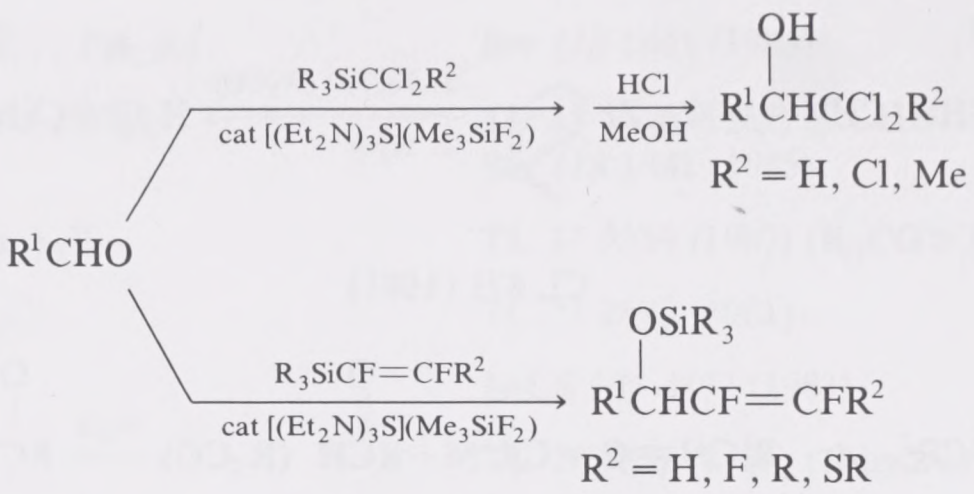
M	
Li	JOC *47* 2225 (1982)
MgX	JACS *90* 6141 (1968); *109* 8051 (1987) Compt Rend C *269* 342 (1969) TL 37 (1972); *27* 3311 (1986) BSCF 3371 (1973) JOC *47* 2225 (1982)
$B(OR)_2$	JOMC *92* 17 (1975); *195* 137 (1980) JACS *104* 7667 (1982); *108* 483 (1986) (both chiral) TL *27* 1175 (1986) JOC *51* 886 (1986)
BEt_2	JACS *106* 3875 (1984)
B 	JOC *50* 1577 (1985) (RCHO > R_2CO)
$Al_{2/3}Br$	Ann *682* 62 (1965) TL 37 (1972) BSCF 3371 (1973)
$SiMe_3$, ($TiCl_4$)	JOC *45* 3925 (1980); *51* 3870 (1986)
$Ti(OR)_3$	JOC *47* 2225 (1982); *51* 886 (1986)
Cu	JACS *109* 5437 (1987)
ZnBr	BSCF 3371 (1973); 1248 (1975) TL *22* 1579 (1981) JOC *47* 2225 (1982)



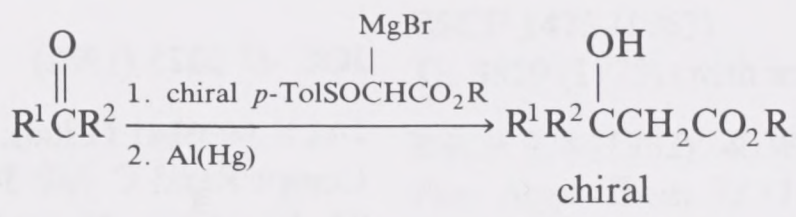
CC 406 (1983)



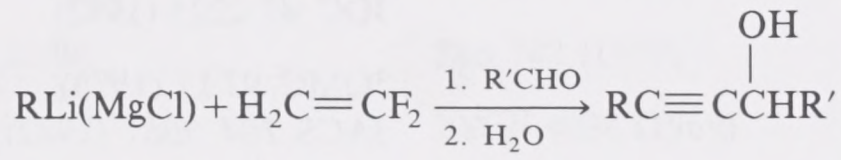
JACS *106* 5004 (1984)



JACS *107* 4085 (1985)



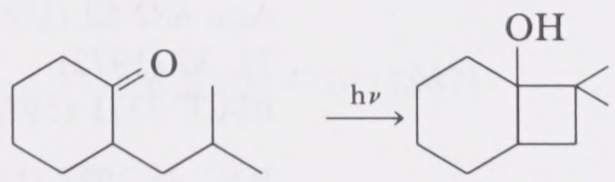
CC 162 (1977)



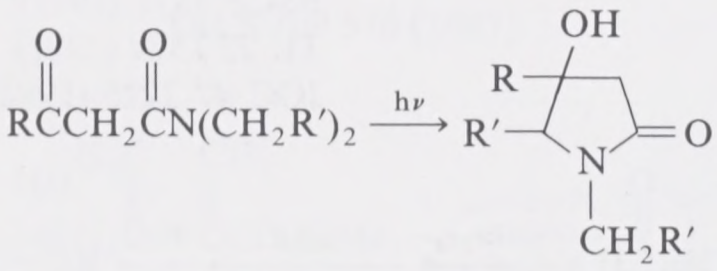
R = 1°, 2°, 3° alkyl; allyl; vinyl

TL *23* 4325 (1982)

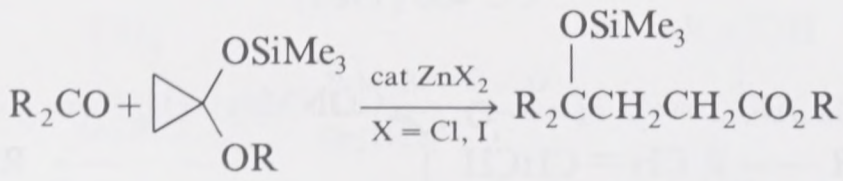
2.2. Miscellaneous Additions



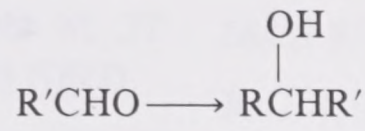
JCS Perkin II 7, 14 (1976)
JACS *108* 3841 (1986); *109* 3017 (1987)
JOC *52* 5521 (1987)

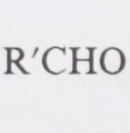
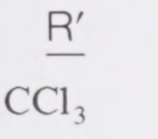
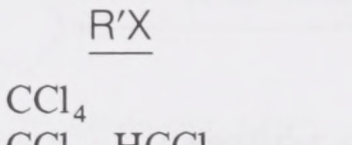


CC 743 (1974)
JOC *43* 1005 (1978)

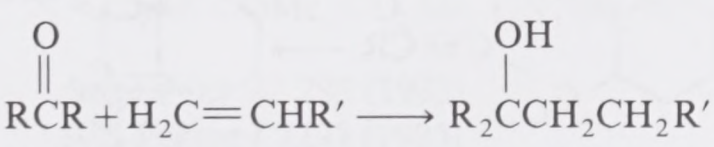


JOC *50* 2802 (1985)
JACS *109* 8056 (1987)
TL *28* 337 (1987)



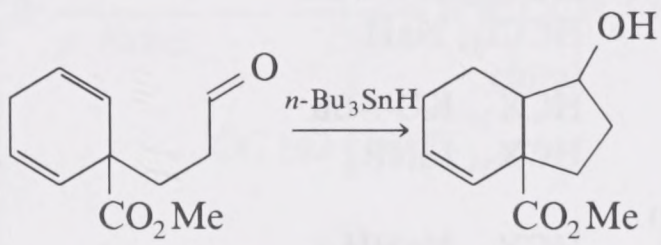
R	Reagents	
CHX_2 (X = Cl, Br, I)	H_2CX_2, $LiNR_2$	JACS *96* 3010 (1974) BCSJ *50* 1588 (1977)
CCl_3	$HCCl_3$, KOH	JACS *70* 1189 (1948); *72* 5012 (1950) JOC *50* 2527 (1985); *52* 944 (1987)
	$HCCl_3$, NaOH, $(PhCH_2NEt_3)Cl$	Ber *110* 96 (1977)
	$HCCl_3$, KO-*t*-Bu	JOC *50* 2527 (1985)
	$HCCl_3$, NaH	JOC *50* 2527 (1985)
CX_3 (X = Cl, Br)	HCX_3, KO-*t*-Bu	Ber *91* 2664 (1958)
	HCX_3, $LiNR_2$	JACS *96* 3010 (1974) BCSJ *50* 1588 (1977)
	HCX_3, $NaNH_2$	Ber *96* 420 (1963)
	 , PhI, SmI_2	TL *28* 5877 (1987)
	 , PhI, SmI_2	TL *28* 5877 (1987)

R′	R′X	
CCl_3	CCl_4	TL 1521 (1978)
	CCl_4, $HCCl_3$	TL *22* 871 (1981) JACS *106* 259 (1984) JOC *50* 2527 (1985)
CCl_2CO_2Me	Cl_3CCO_2Me, $HCCl_2CO_2Me$	JACS *106* 259 (1984) JOC *50* 2527 (1985)
$CHPhCO_2Me$	$BrCHPhCO_2Me$, $PhCH_2CO_2Me$	JOC *50* 2527 (1985)
$CH(CO_2Me)_2$	$BrCH(CO_2Me)_2$, $H_2C(CO_2Me)_2$	JOC *50* 2527 (1985)
allylic	allylic chloride	TL *22* 1895 (1981)
allylic, benzylic, α-chloro ester, CF_3, CCl_3, aryl	R′X	TL *27* 3129 (1986)

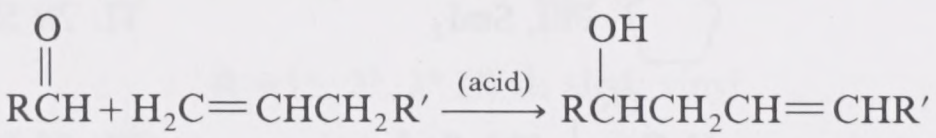


electrolysis	JACS *93* 5284 (1971) (intramolecular); *100* 545 (1978) (intramolecular) JOC *50* 2202 (1985) (intramolecular, R′ = CO_2Et); *51* 1041 (1986) (intramolecular)

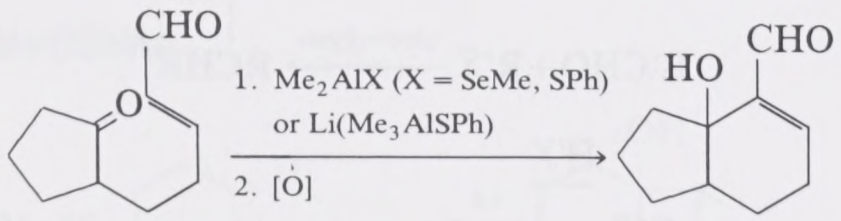
hν, Et_3N	TL *26* 4591 (1985) (intramolecular); *28* 4545 (1987) (intramolecular)
hν, HMPA	TL *26* 4591 (1985) (intramolecular) JOC *51* 4196 (1986) (intramolecular)
Li, NH_3	JCS 3154 (1965) (intramolecular)
Na, moist ether	CC 206 (1965) (intramolecular)
Na, *t*-BuOH	JOC *44* 2369 (1979)
Mg, Me_3SiCl	JOC *50* 5193 (1985) (intramolecular)
Zn, Me_3SiCl, lutidine	TL *24* 2821 (1983) (intramolecular)
SmI_2	TL *28* 4367 (1987) (intramolecular)



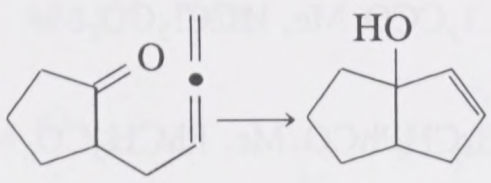
JACS *108* 5893 (1986)



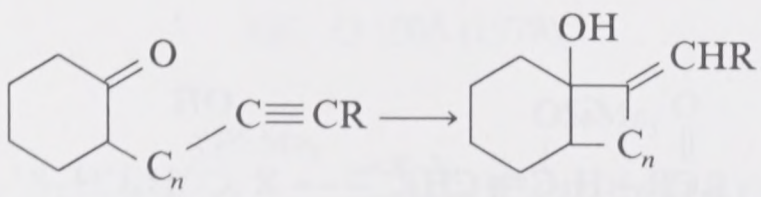
See page 119, Section 8.



TL *21* 361 (1980)
BCSJ *54* 274 (1981)
JACS *109* 8017 (1987)

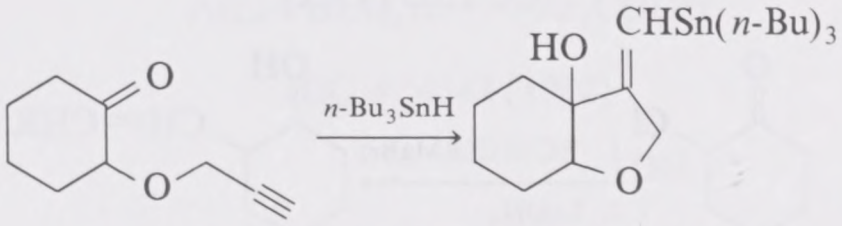


electrolysis	Tetr *41* 4001 (1985)
Na, naphthalene	Tetr *41* 4001 (1985) TL *27* 2243 (1986)

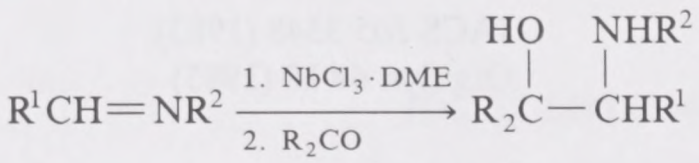


electrolysis	CL 1233 (1976)
hν, HMPA	JOC *51* 4196 (1986)
hν, Et_3N	TL *28* 4545, 4547 (1987)

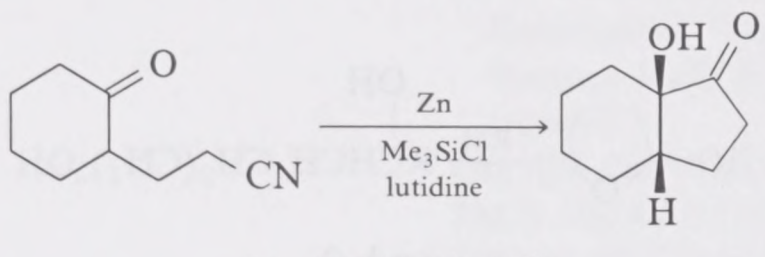
Li, NH_3, $(NH_4)_2SO_4$	JACS *87* 1148 (1965)
Na	JOC *46* 2622 (1981)
Na, naphthalene	JOC *41* 1943 (1976); *46* 2622 (1981) TL *23* 5471 (1982); *27* 399 (1986); *28* 5945 (1987)
K, NH_3, $(NH_4)_2SO_4$	JACS *101* 7107 (1979)
Zn, Me_3SiCl	TL *24* 2821 (1983); *28* 2001 (1987)



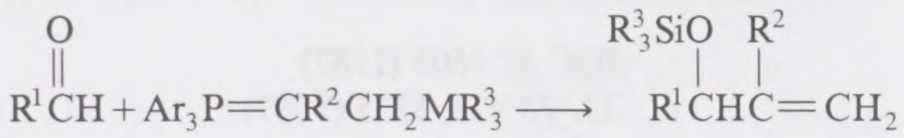
TL *28* 2001 (1987)



JACS *109* 6551 (1987)

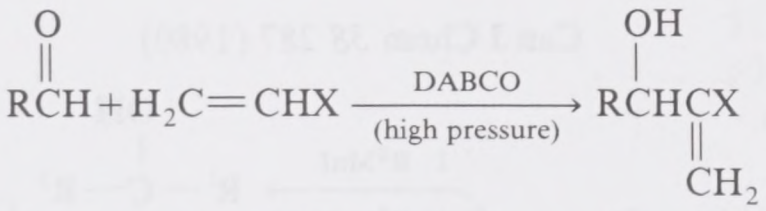


TL *24* 2821 (1983)



M

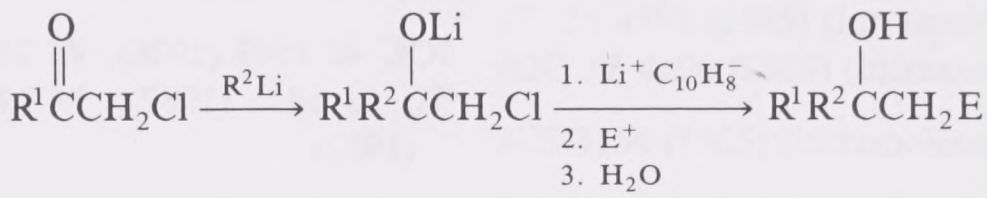
Si	TL *26* 4471 (1985); *27* 6373 (1986); *28* 2379, 4561 (1987) CC 880 (1986)
Sn	TL *28* 4561 (1987)



X = CHO, COMe, CO_2Me, CN, SO_2Ph

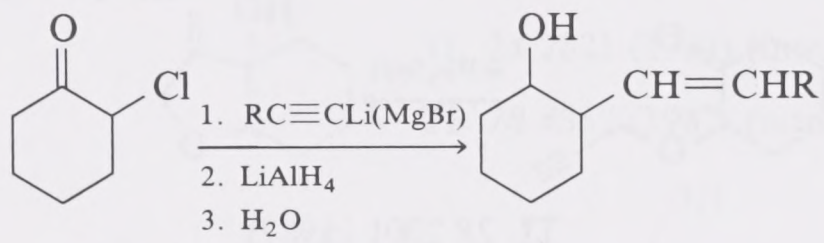
Angew Int *22* 795 (1983)
JCS Perkin I 2293 (1983)
Helv *67* 413 (1984)
JOC *50* 3849 (1985)
TL *27* 2031, 4307, 5007, 5095 (1986)
Syn Commun *17* 587 (1987)

3. Alkylation of α-Haloketones



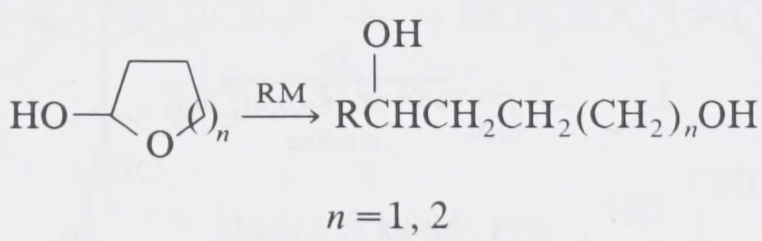
$E^+ = D_2O, RCHO, R_2CO, CO_2, O_2, (MeS)_2$

CC 1153 (1982)



JACS *105* 3348 (1983)
Org Syn *64* 10 (1985)

4. Addition to Acetals

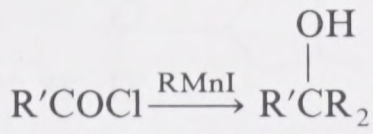


$n = 1, 2$

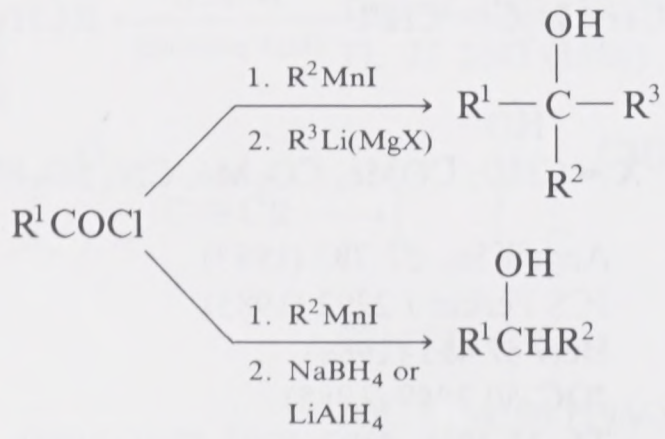
$RM = MeLi, RMgX, Me_3Al, MeTiCl_3, MeTi(O\text{-}i\text{-}Pr)_3$

JOC *52* 4603 (1987)
TL *28* 423, 6335 (1987)

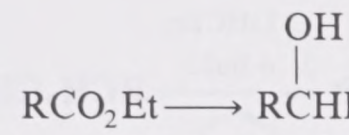
5. Addition to Carboxylic Acid Derivatives



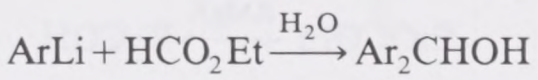
Can J Chem *58* 287 (1980)



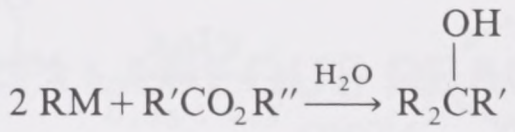
TL *27* 4441 (1986)



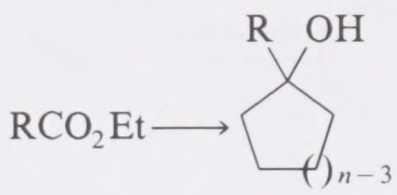
i-$Bu_2AlH/R'MgX$	JOC *48* 2775 (1983) TL *28* 3905 (1987)
$R'MgX$, $LiBH_4$	TL *25* 1321 (1984); *28* 3905, 4143 (1987)
2 $R'MgX$, Cp_2TiCl_2	TL *21* 2175 (1980)



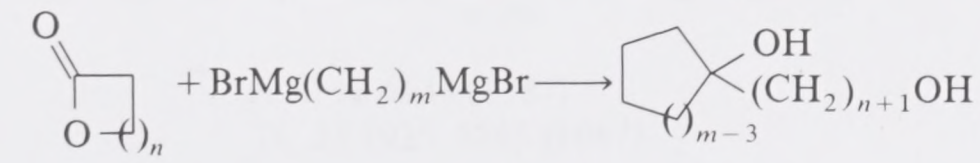
JOC *47* 4347 (1982)



RM	
CF_3CF_2Li	JOC *52* 2481 (1987)
ArLi	JACS *108* 3762 (1986)
RMgX	M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice Hall, New York (1954), pp 549–708 (review) Org Syn Coll Vol *3* 839 (1955) JACS *108* 4119 (1986) JOC *52* 4511 (1987) (lactone)
Me_3SiCH_2MgCl, $CeCl_3$	TL *28* 6261 (1987)

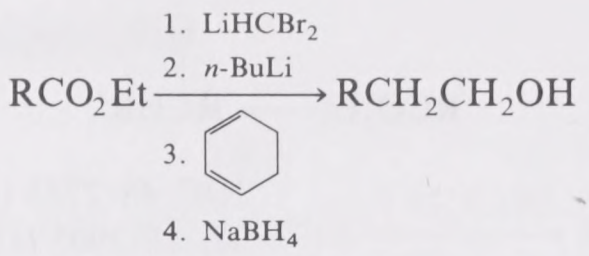


Reagent(s)	n	
$Br(CH_2)_5Br$, Li, ultrasound	5	TL *28* 2013 (1987)
BrMg-C_n-MgBr	4, 5	Compt Rend *144* 1358 (1907) JACS *72* 3483 (1950) TL *22* 4995 (1981) JOC *51* 2147 (1986); *52* 4025 (1987)

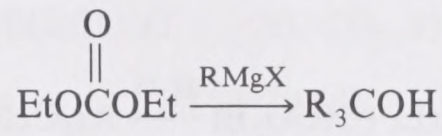


$n = 1$–4 $m = 4, 5$

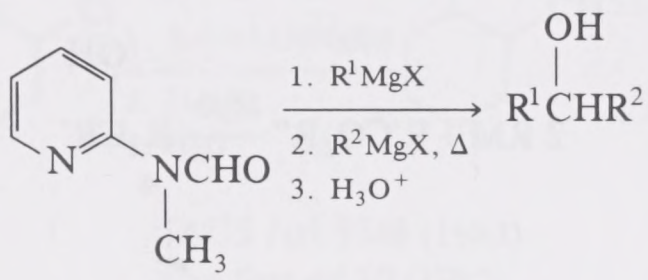
JOC *45* 1828 (1980); *52* 569 (1987)
Tetr *40* 865 (1984)
TL *28* 4997 (1987)



JACS *108* 1324 (1986)

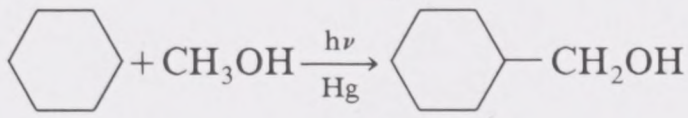


Org Syn Coll Vol *2* 602 (1943)

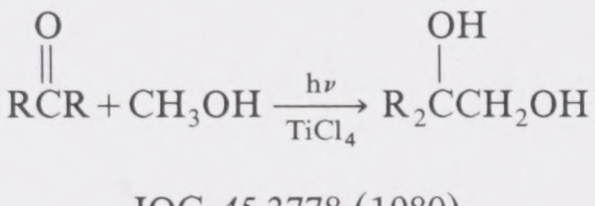


TL *22* 1085 (1981)

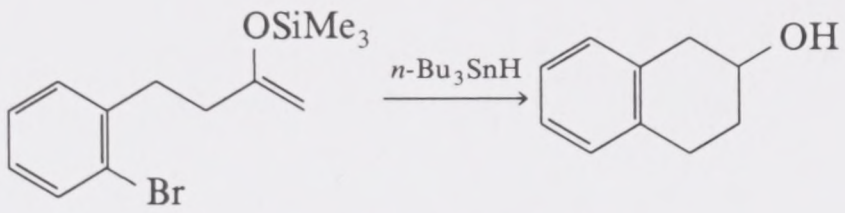
9. MISCELLANEOUS REACTIONS



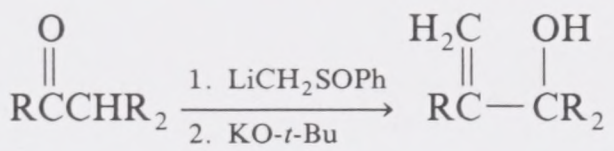
CC 970 (1987)
TL *28* 5599 (1987)



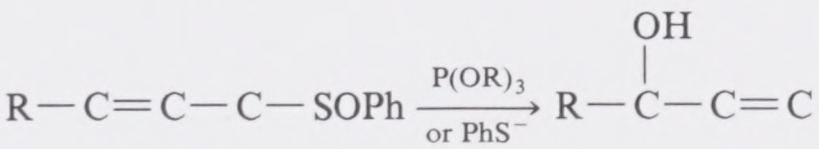
JOC *45* 3778 (1980)



TL *27* 1355 (1986)

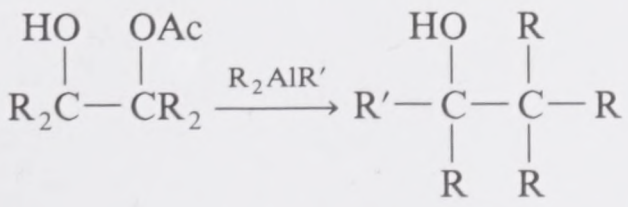


Syn 640 (1980)



JOC *52* 4634 (1987)
TL *28* 1925, 5865 (1987)

See also page 185, Section 1.



BCSJ *55* 3941 (1982)

ALDEHYDES AND KETONES

GENERAL REFERENCES

Chem Rev *38* 227 (1946)

Quart Rev *20* 169 (1966)

"The Chemistry of the Carbonyl Group," Ed. S. Patai, Interscience, New York (1966–70)

C. D. Gutsche, "The Chemistry of Carbonyl Compounds," Prentice Hall, Englewood Cliffs, New Jersey (1967)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VII/2a, G. Thieme, Stuttgart (1973) (ketones)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VII/2b, G. Thieme, Stuttgart (1976) (ketones)

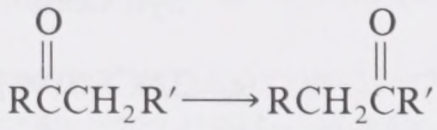
Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VII/2c, G. Thieme, Stuttgart (1977) (ketones)

Syn 633 (1979) (Synthesis of aldehydes, ketones and carboxylic acids from lower carbonyl compounds by C—C coupling reactions)

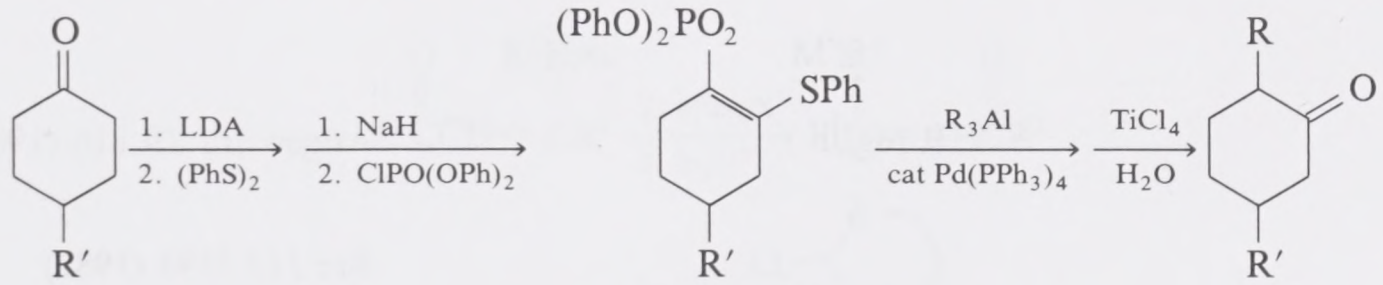
Tetr *36* 2531 (1980) (Carbonyl homologation and masked homoenolate equivalents)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E3, G. Thieme, Stuttgart, New York (1983) (aldehydes)

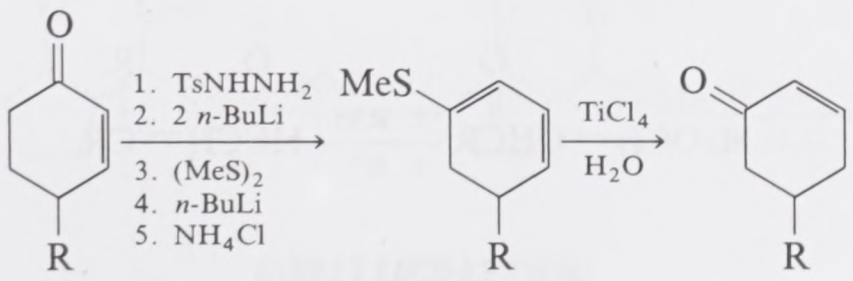
1. CARBONYL TRANSPOSITION



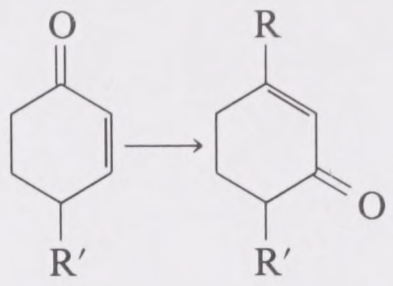
PhCHO, $OH^-/LiAlH_4$, $AlCl_3/O_3$	CC 898 (1967) JCS C 244 (1970)
PhCHO, $OH^-/NaBH_4/Ac_2O/O_3$/Li, NH_3	JACS *104* 1907 (1982)
t-$BuONO_2$, KO-*t*-Bu/$NaBH_4$/Zn, HOAc	JOC *33* 1733 (1968)
AmONO, KO-*t*-Bu/N_2H_4, KOH/$NaHSO_3$	CC 1350 (1968)
LiN(*i*-Pr)(*c*-C_6H_{11})/$(PhS)_2/NaBH_4$/MsCl-py or TsOH/$HgCl_2$-H_2O or $TiCl_4$-HOAc	JACS *97* 438 (1975)
$TsNHNH_2$/2 *n*-BuLi/$(MeS)_2$/*n*-BuLi/NH_4Cl/H_2O, $HgCl_2$	TL 531 (1979) CL 931, 1099 (1980)
$PhSO_2NHNH_2$/2 *n*-BuLi/Me_3SiCl/*m*-$ClC_6H_4CO_3H$/$LiAlH_4$/$Na_2Cr_2O_7$, H_2SO_4	JOC *43* 1620 (1978); *45* 3028 (1980)



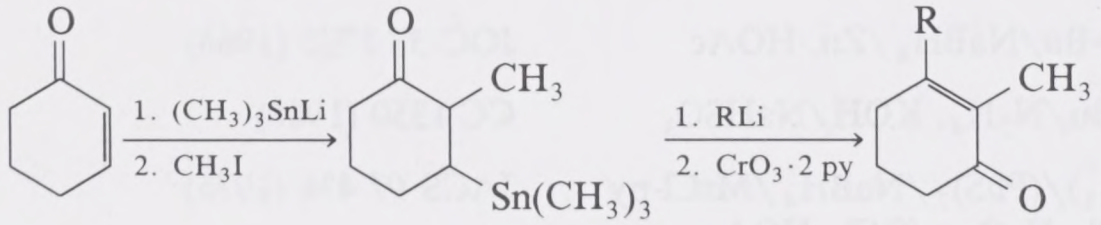
TL *22* 1609 (1981)



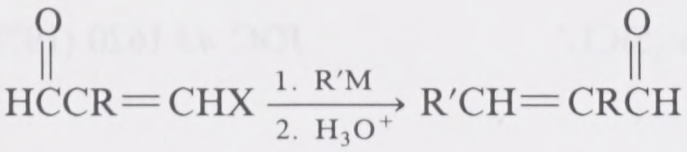
CL 1099 (1980)

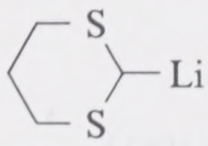


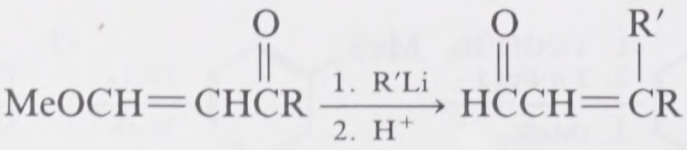
RMgX/PCC	JACS *108* 3443 (1986)
RLi/PCC	Syn Commun *6* 649 (1976) JOC *42* 682, 813 (1977); *50* 2557 (1985); *51* 4497 (1986) JACS *105* 7352 (1983) CC 358 (1987)
$RC{\equiv}CLi$/PDC	TL *28* 1069 (1987)
RLi/CrO_3, H_2SO_4	JOC *36* 2021 (1971); *39* 2317 (1974) Syn Commun *11* 7 (1981)
RMgX/CrO_3, H_2SO_4	JACS *108* 3385 (1986)
RLi/PhSeCl/O_3/$Hg(OAc)_2$ or HCl or HCO_2H	JOC *45* 2551 (1980), *47* 1258 (1982)
RLi/PhSCl/$(PhS)_2$/H_2O, $HgCl_2$	JACS *97* 4018 (1975)



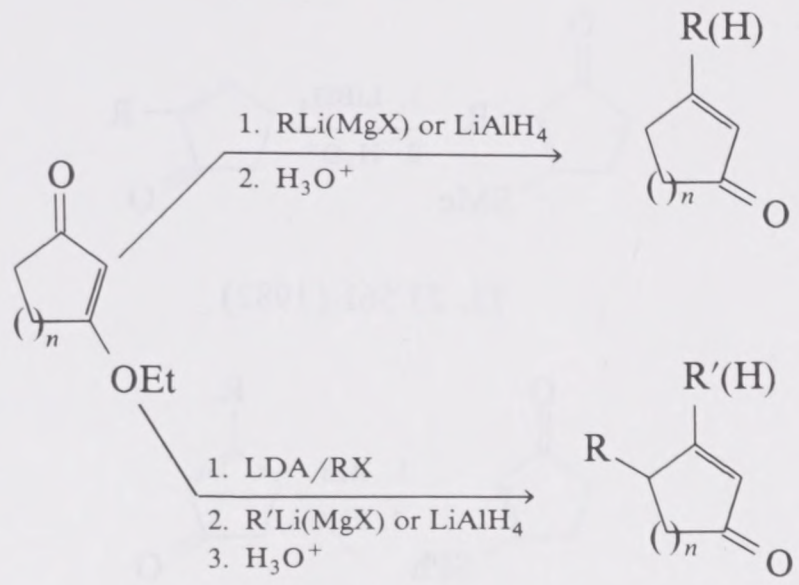
JACS *99* 4836 (1977)



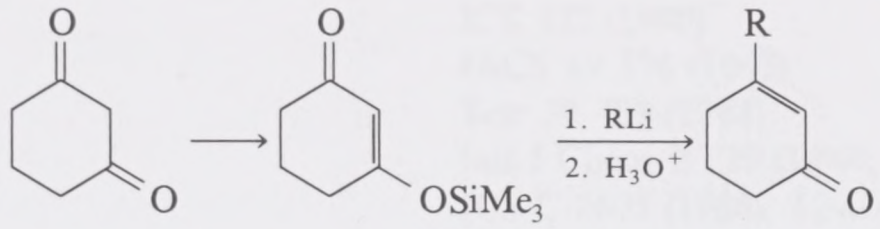
X	R′M	
OEt	R′MgBr	Angew Int *19* 816 (1980)
OEt		Ber *115* 3898 (1982)
NMe_2	RLi	JOC *51* 879, 1631 (1986)



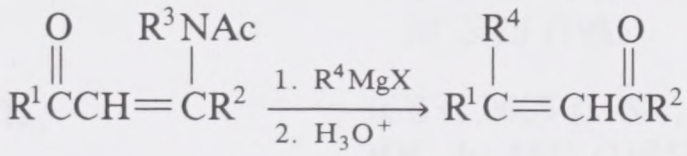
JOC *51* 4743 (1986)



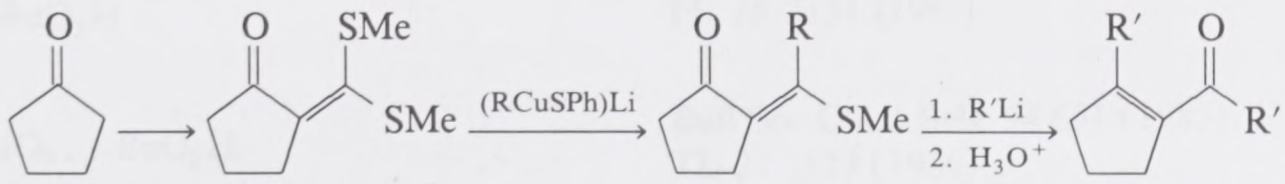
JACS *72* 1645 (1950); *103* 82 (1981); *105* 1292 (1983); *106* 2115, 3353 (1984); *107* 268, 7732, 7745 (1985); *108* 806, 1106, 3110, 6276 (1986); *109* 4690, 5491 (1987)
JCS 1779 (1953)
JOC *38* 1451, 1775 (1973); *43* 3968 (1978); *46* 2400 (1981); *47* 381, 3297, 4820, 5096 (1982); *48* 2318 (1983); *49* 2152 (1984); *50* 3155, 5550, 5727 (1985); *51* 879, 1490, 4323 (1986); *52* 120, 3491 (1987)
TL *22* 15, 97 (1981); *23* 3283 (1982); *27* 2087, 5232 (1986); *28* 1329, 3065, 3107 (1987)
Tetr *38* 3527 (1982)
Syn Commun *12* 167, 521 (1982)
Can J Chem *60* 2965 (1982)
Org Syn *64* 68, 73 (1985)
CC 75 (1986)



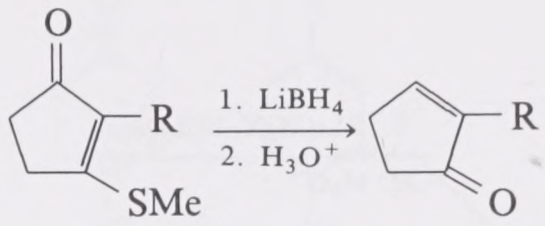
Syn Commun *12* 795 (1982)



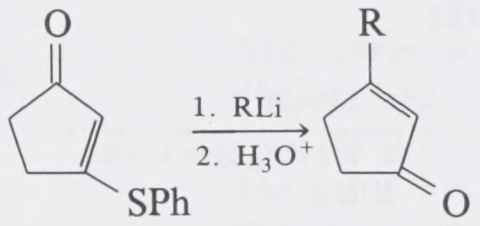
Heterocycles *19* 1211 (1982)



TL *23* 3751 (1982)



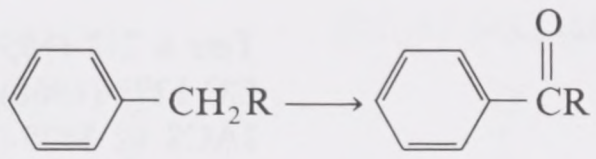
TL *23* 561 (1982)



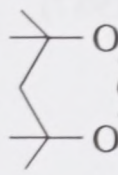
Organomet *1* 1240, 1243 (1982)
JOC *52* 110 (1987)

2. OXIDATION

1. Alkanes



(R = H or alkyl)

CrO_3, HOAc	JCS 727 (1940) JACS *69* 576 (1947) Tetr *20* 409 (1964) Ind J Chem *2* 229 (1964) JCS C 2603 (1968); 1240 (1969) Acta Chem Scand *24* 2252 (1970) Steroids *18* 593 (1971); *22* 327 (1973) Org Prep Proc Int *4* 67 (1972) Syn Commun *3* 89 (1973) JOC *39* 1416 (1974); *46* 1752 (1981); *50* 2435 (1985)
CrO_3, H_2SO_4, H_2O, CH_3COCH_3	JCS C 2603 (1968); 1240 (1969) JOC *50* 2435 (1985)
CrO_3, 3,5-dimethylpyrazole	JACS *108* 3040 (1986)
CrO_3, HCl, bipy	JOC *50* 2435 (1985)
cat CrO_3, *t*-BuO_2H	TL *28* 2131 (1987)
cat  CrO_2, *t*-BuO_2H	Bull Soc Chim Belg *94* 651 (1985) TL *27* 3139 (1986)
PCC, Celite	Syn Commun *16* 1493 (1986)
PCC, *t*-BuO_2H, Celite	JOC *52* 5048 (1987)

cat $Cr(CO)_6$, *t*-BuO_2H	JOC *50* 2791 (1985)
$Ce(O_3SCH_3)_3 \cdot 2\ H_2O$, electrolysis	TL *28* 1067 (1987) (ArCHO > ArCOR)
$K_2S_2O_8$, $CuSO_4$, H_2O	TL *22* 2605 (1981) (electron-rich arenes)
$(PhSeO)_2O$	TL 3331 (1979)
O_2, cat $ClRh(PPh_3)_3$	TL 3665 (1967); 2917 (1968)
DDQ	Syn 144 (1979) (requires *p*-MeO)

2. Alkenes

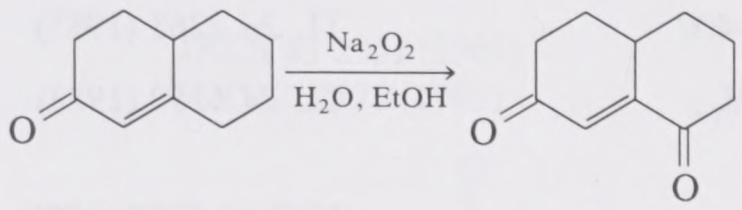
See also page 325, Section 4.

$$RCH{=}CHCH_2R \longrightarrow RCH{=}CHC(=O)R$$

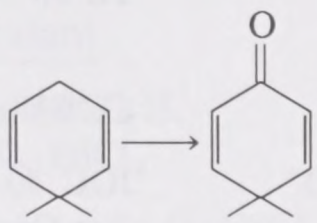
SeO_2	Tetr *6* 217 (1959) CC 1277 (1968) JACS *92* 3429 (1970); *93* 4835, 5311 (1971) Org Rxs *24* 261 (1976) (review)
t-BuO_2H, cat $Cr(CO)_6$	TL *25* 1235 (1984) JCS Perkin I 267 (1985)
t-BuO_2H, PCC, Celite	JOC *52* 5048 (1987)
t-BuO_2H, cat CrO_3	TL *28* 4665 (1987)
Na_2CrO_4, HOAc, Ac_2O	JOC *35* 192, 4068 (1970) JACS *106* 6690 (1984)
t-$C_4H_9OCrO_3H$	JOC *34* 3587 (1969)
CrO_3, *t*-BuOH	JACS *79* 6308 (1957) Helv *35* 284 (1962)
CrO_3, py, Celite	JOC *52* 3346 (1987)
$CrO_3 \cdot 2$ py	JOC *34* 3587 (1969); *52* 3573 (1987) Syn Commun *6* 217 (1976) JACS *107* 7724 (1985); *108* 6276 (1986)
$CrO_3 \cdot 1$ py	J Chem Res (S) 42 (1979)
$CrO_3 \cdot$ 3,5-dimethylpyrazole	JOC *43* 2057 (1978); *52* 1686, 2960 (1987) JACS *108* 2090, 3513 (1986) TL *27* 3411, 5245 (1986)
CrO_3, HOAc	JACS *63* 758 (1941) BCSJ *52* 184 (1979)

CrO_3, HOAc, Ac_2O

BCSJ *52* 184 (1979)
(4-oxo-2-alkenoates)
JOC *47* 5093 (1982)
(4-oxo-2-alkenoates)



TL *22* 5127 (1981)



$(C_5H_5NH)_2Cr_2O_7$

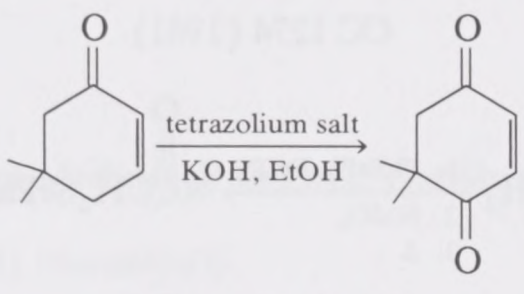
TL *27* 1481 (1986)
JACS *109* 3991 (1987)

Na_2CrO_4, HOAc, Ac_2O

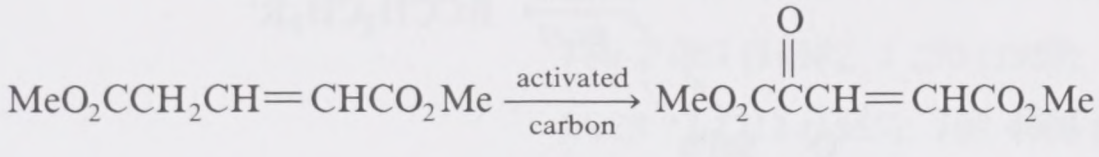
JACS *109* 3991 (1987)

CrO_3, HOAc, Ac_2O

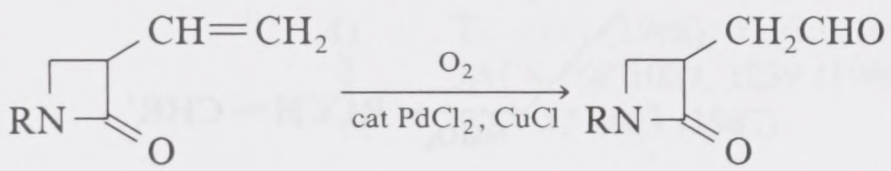
JACS *109* 3991 (1987)
JOC *52* 5482 (1987)



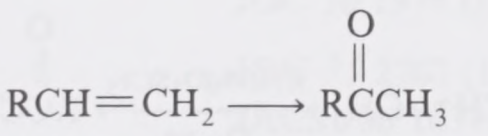
TL *28* 4323 (1987)



CC 882 (1987)



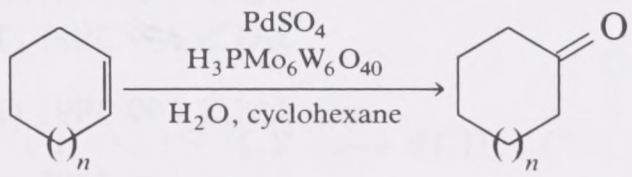
TL *27* 5955 (1986)



cat $PdCl_2$, CuCl or $CuCl_2$, O_2

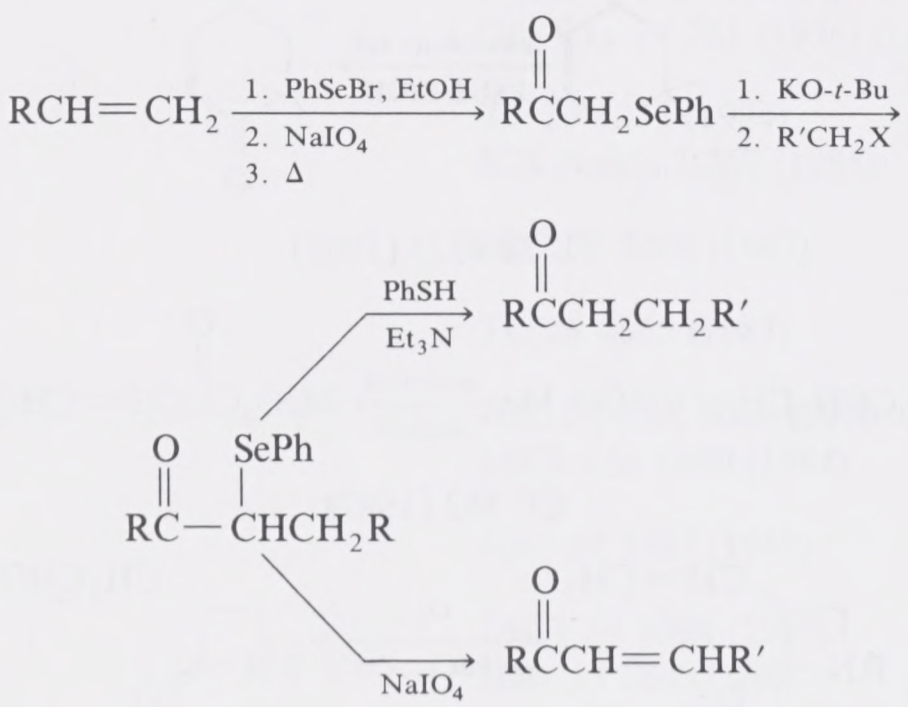
Angew Int *1* 80 (1962) (review)
JOC *29* 241 (1964); *39* 3276 (1974); *52* 4592 (1987)
TL 2975 (1976); *21* 955 (1980); *27* 2529, 4431 (1986)
JACS *101* 5070, 5072 (1979); *105* 7352 (1983); *108* 3474 (internal alkene), 8015 (1987)
Syn Commun *10* 273 (1980)

	Topics Curr Chem *91* 29 (1980) (review) Syn 369 (1984) (review) Israel J Chem *24* 153 (1984) CC 1578 (1987)
cat $PdCl_2$, $CuCl_2$, O_2, PEG-400	TL *26* 2263 (1985)
cat $PdCl_2$, $CuCl_2$, H_2O, C_6H_6, (n-$C_{16}H_{33}NMe_3$)Br	TL *24* 5159 (1983)
cat $Pd(OAc)_2$, H_2O_2	JOC *45* 5387 (1980)
cat $Pd(OAc)_2$, cat benzoquinone, electrolysis	TL *28* 3683 (1987)
$Hg(OAc)_2$, CH_3OH/cat Li_2PdCl_4, $CuCl_2$	CC 818 (1971)
cat $Hg(O_2CEt)_2$, CrO_3 or $Na_2Cr_2O_7$, H_3O^+	JOC *40* 3577 (1975) Syn Commun *11* 7 (1981)

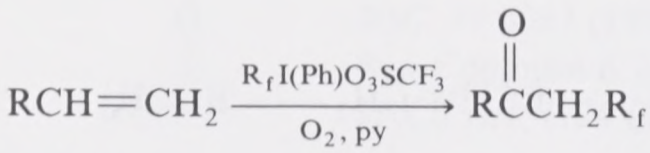


$n = 0, 1$

CC 1274 (1981)



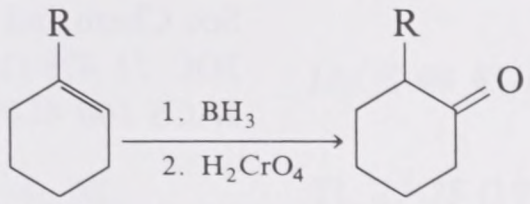
TL 799 (1978)



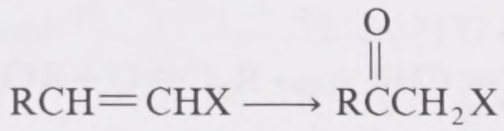
TL *23* 4101 (1982)

$RCH{=}CH_2 \longrightarrow RCH_2CHO$

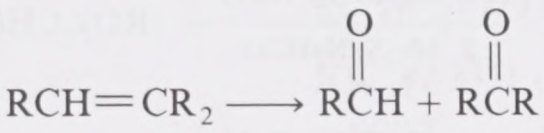
BH_3 or R_2BH/PCC	JOMC *172* C20 (1979) Syn 151 (1980)
PhSH, AIBN/NCS/CuO, $CuCl_2$, H_2O	JOC *41* 3261 (1976)



JACS *83* 2951 (1961)
JOC *50* 2179 (1985)



X	Oxidant	
COR, CO_2R	H_2O_2 or *t*-BuO_2H, cat Na_2PdCl_4	CL 257 (1980)
CH_2OR, CH_2OAc	benzoquinone or O_2-CuCl, cat $PdCl_2$	TL *23* 2679 (1982)
CH_2COCH_3, CH_2CO_2R	O_2, CuCl, cat $PdCl_2$	CL 859 (1982)



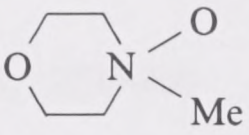
Reviews:

Acct Chem Res *1* 313 (1968)
W. Carruthers, "Some Modern Methods of Organic Synthesis," Cambridge Univ. Press (1971), Chpt 6
Russ Chem Rev *50* 636 (1981) (ozonolysis)

O_3, reducing agent	Chem Rev *58* 925 (1958) (review)
O_3/H_2, cat Pd-C	Tetr *2* 203 (1958); *3* 230 (1958)
O_3/Zn, HOAc	JACS *77* 1212 (1955); *108* 4603 (1986)
O_3/I^-, HOAc	Org Syn *41* 41 (1961)
O_3/Me_2S	TL 4273 (1966); 1391 (1969); 2417 (1973) JACS *108* 1039, 1239 (1986) JOC *52* 1603 (1987)
$O_3/SC(NH_2)_2$	Tetr *38* 3013 (1982)
O_3/Ph_3P	JOC *30* 1976 (1965)
$O_3/(MeO)_3P$	JOC *25* 2703 (1963) JACS *108* 1039 (1986)
O_3/py	JACS *80* 915 (1958) Compt Rend *250* 1078 (1960)
$KMnO_4$	JOC *51* 3213 (1986)
$NaIO_4$, cat $KMnO_4$	Can J Chem *33* 1710, 1714 (1955)
$NaIO_4$, cat $RuCl_3 \cdot (H_2O)_n$	JOC *51* 3247 (1986)
$NaIO_4$, cat RuO_2	JOC *52* 2875 (1987)

$NaIO_4$, cat OsO_4

Soc Chem Ind *62* 90 (1943)
JOC *21* 478 (1956)
JACS *108* 4149 (1986)

$NaIO_4$, cat OsO_4, 

TL *28* 3225 (1987)

$(bipy)H_2CrOCl_5$

Org Prep Proc Int *14* 362 (1982) (aryl alkenes)

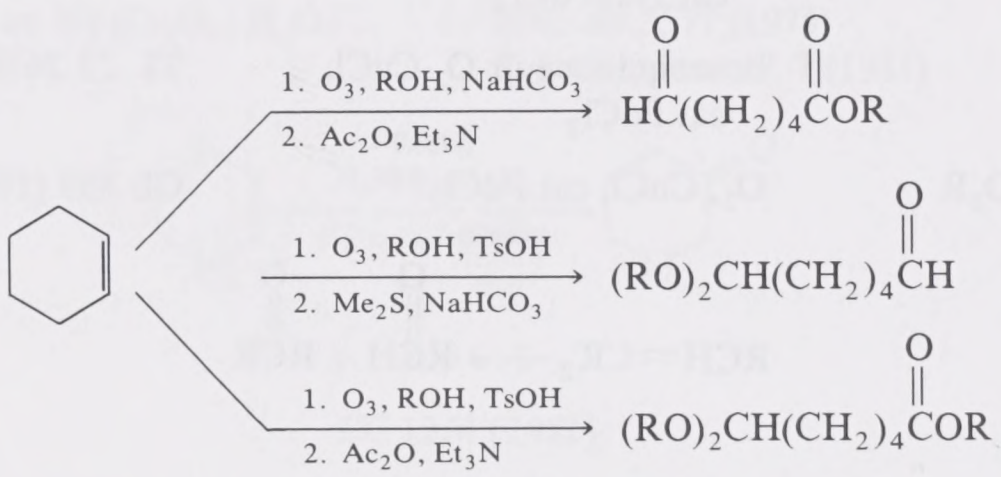
$$R_2C{=}CHR \longrightarrow R_2C{=}O + RCO_2H$$

$KMnO_4$, $NaIO_4$

Can J Chem *33* 1714 (1955)
Syn Commun *12* 1063 (1982)

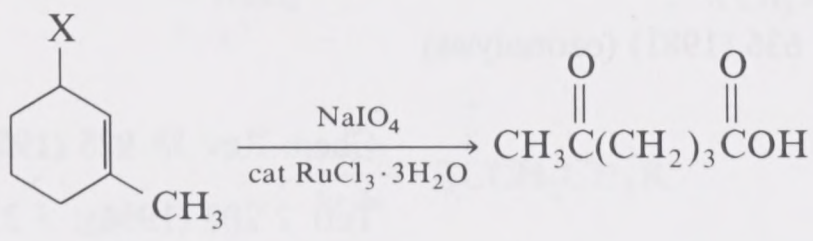
$KMnO_4$, silica gel

JOC *52* 3698 (1987)

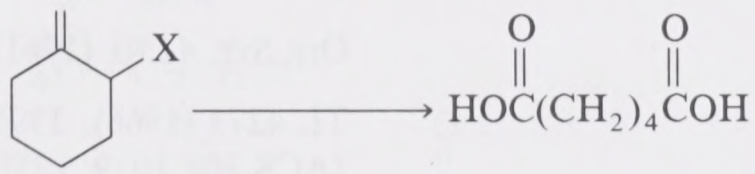


TL *23* 3867 (1982)

Org Syn *64* 150 (1985)



X = OH, =O



X = OH, =O

JOC *52* 689 (1987)

3. Alkynes

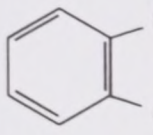
$$RC{\equiv}CR' \longrightarrow RCH_2\overset{O}{\overset{\|}{C}}R'$$

BH_3 or R_2BH/H_2O_2, NaOH

JACS *83* 3834 (1961); *89* 5086 (1967); *91* 4771 (1969)
Org Rxs *13* 1 (1963)
TL 41 (1970)
Organomet Chem Syn *1* 249 (1971)

$ClBH_2/H_2O_2$, NaOH or NaOAc

JOC *38* 1617 (1973)



BH/H_2O_2, NaOH — JACS *94* 4370 (1972)

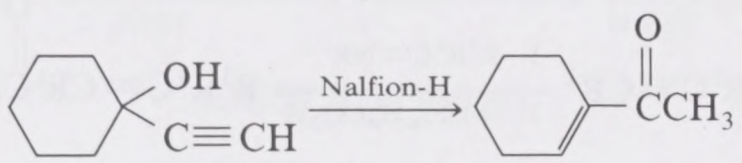
$HSiMe(OEt)_2$, cat $ClRh(PPh_3)_3/Me_3NO$, KHF_2 ($R' = H$) — TL *27* 75 (1986)

cat $PdCl_2(CH_3CN)_2$, H_2O, ultrasound — TL *28* 3127 (1987) (1,4- and 1,5-diketones)

cat $NaAuCl_4 \cdot 2H_2O$, H_2O, ultrasound — TL *28* 3127 (1987) (1,5-diketone)

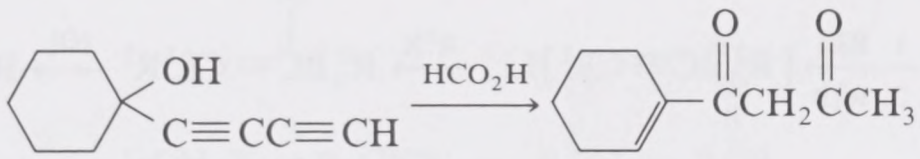
H_2O, H_2SO_4, Hg(II) — JCS 3257 (1954)
JACS *76* 525 (1954); *86* 935, 936 (1964) (both diketones)
Can J Chem *50* 1105 (1972)
JOC *40* 2250 (1975); *47* 3331, 3707 (1982)
Syn 671 (1978)
Z Chem *22* 185 (1982)
R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986) (review)
TL *28* 5709 (1987)

$PhHgOH/H_2O$ — JOC *47* 3331 (1982) ($RC{\equiv}CH \rightarrow RCOCH_3$ only)



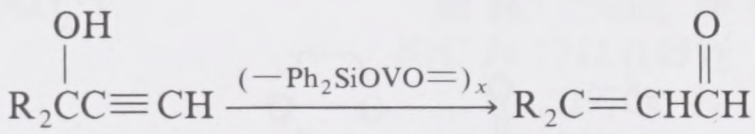
Nalfion-H

Syn 473 (1981)



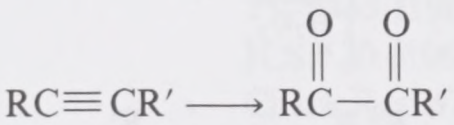
HCO_2H

TL *23* 1051 (1982)



$(-Ph_2SiOVO=)_x$

TL 2981 (1976); *23* 3193 (1982)



$KMnO_4$, $NaHCO_3$, $MgSO_4$, H_2O, CH_3COCH_3 — JOC *44* 1574 (1979)

$KMnO_4$, HOAc, CH_2Cl_2, phase transfer agent — Syn 462 (1978)
JOC *44* 2726 (1979)

$KMnO_4$, H_2O, HOAc, CH_2Cl_2, phase transfer agent — Syn 462 (1978)
JOC *44* 2726 (1979)

$Zn(MnO_4)_2$, silica gel — JACS *105* 7755 (1983)

MoO_5(HMPA), cat $Hg(OAc)_2$ — TL *27* 5139 (1986)

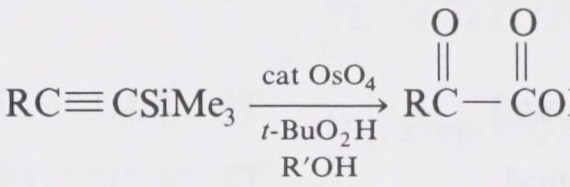
NaOCl, cat RuO_2 — TL 2941 (1971)

$NaIO_4$, cat RuO_2

TL 2941 (1971); *27* 6133 (1986)
JACS *109* 6176 (1987)

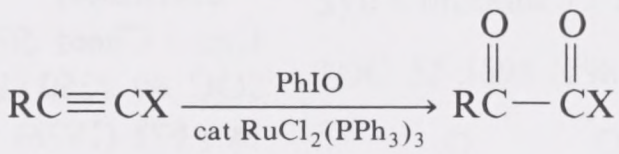
PhIO, cat $RuCl_2(PPh_3)_3$

Helv *64* 2531 (1981)



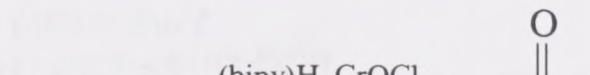
$R' = H$ or alkyl

TL *27* 1947 (1986)

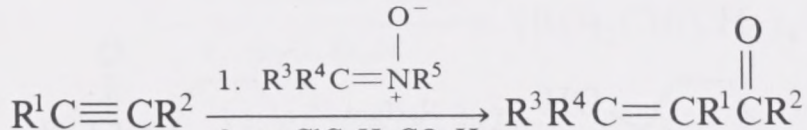


$X = OR, NR_2$

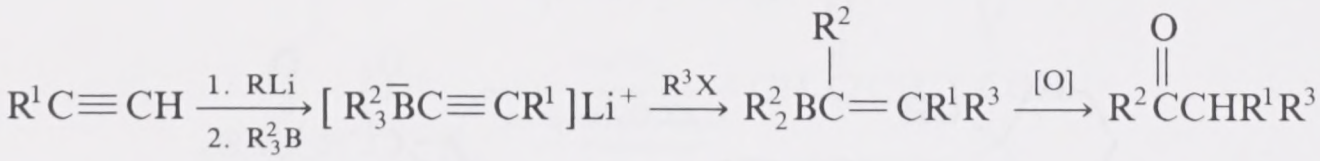
TL *23* 3661 (1982)



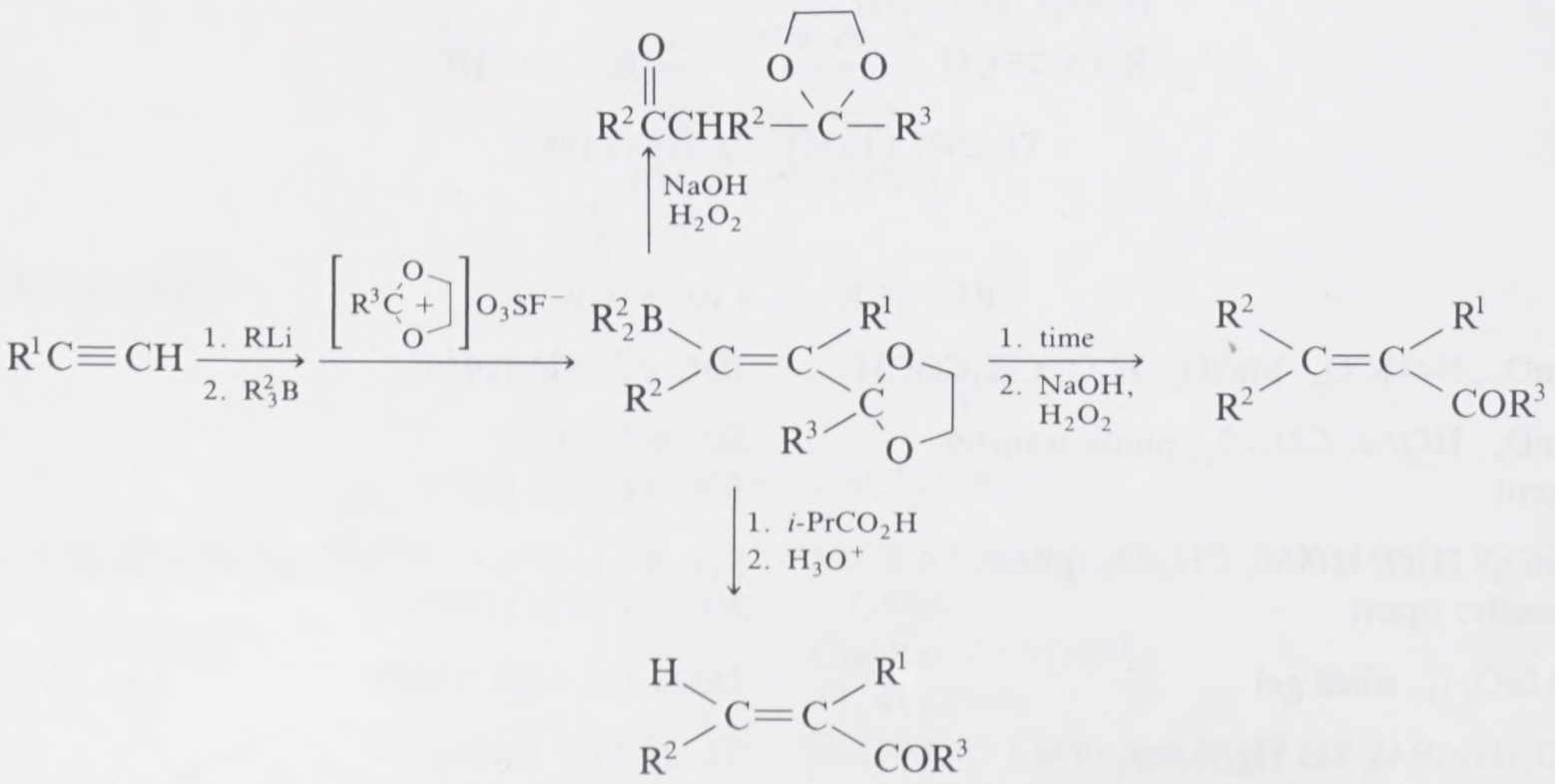
Org Prep Proc Int *14* 362 (1982)



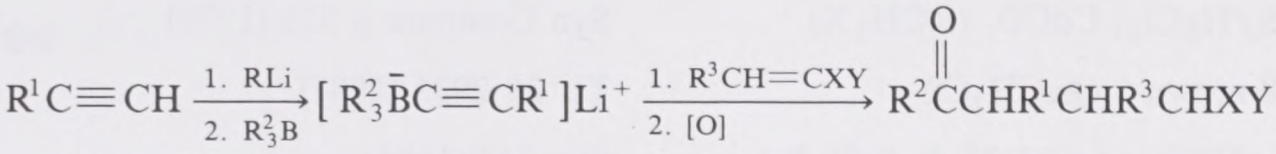
TL *28* 913 (1987)



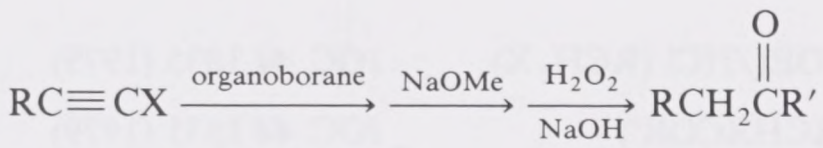
CC 544 (1973)
TL 2741 (1973); *28* 1003 (1987)



TL *27* 1935 (1986)



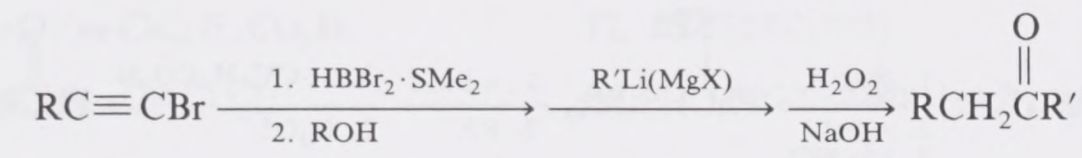
X	Y	
H, Me	NO_2	CC 913 (1977)
COMe, CO_2Et	CO_2Et	TL *22* 797 (1981)



X = Cl, Br, I

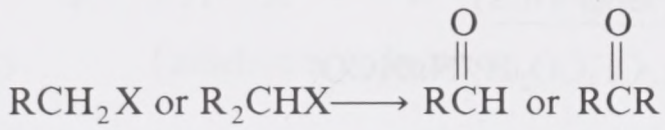
Organoborane

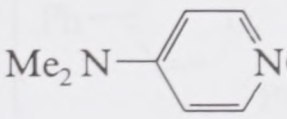
$R'BHBr \cdot SMe_2$	JOC *47* 3808 (1982); *51* 5270 (1986)
R'_2BH	JOC *47* 754 (1982); *51* 5270 (1986)
$(CH_3)_2CHC(CH_3)_2BHR'$	Syn 193 (1982) JOC *51* 5270 (1986)

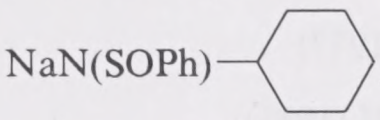
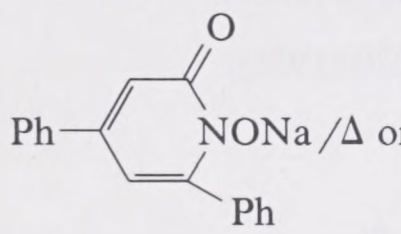


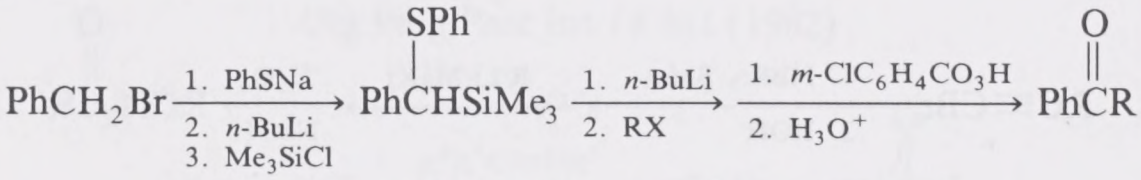
JOC *51* 5277 (1986)

4. Halides, Nitrates and Sulfonates

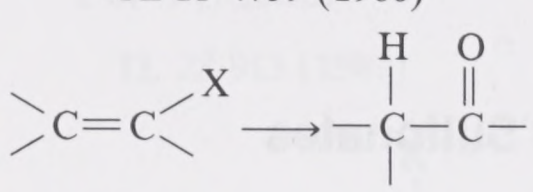


DMSO, base, (Ag^+) (RCH_2X, R_2CHX; X = halide, ONO_2, OTs, OSO_3^-)	JACS *79* 6562 (1957); *81* 4113 (1959); *88* 865 (1966); *89* 5505 (1967) JOC *24* 1792 (1959); *29* 3495, 3498 (1964); *35* 841 (1970); *40* 1990 (1975); *51* 1088, 1264 (1986) Chem Ind 88 (1959) TL 4445 (1960); 2743 (1972); 917 (1974) JCS 520 (1964) Chem Rev *67* 247 (1967) (review) CC 1338 (1970) Syn 608 (1984)
Me_3NO, Δ (RCH_2X)	Ber *94* 1360 (1961)
 (RCH_2X, R_2CHX)	BCSJ *54* 2221 (1981)
$(CH_2)_6N_4$, H_2O, H^+ ($ArCH_2X$)	Org Syn *30* 67 (1950) Org Rxs *8* 197 (1954) (review) Syn 161 (1979) (review) JACS *106* 3297 (1984)

$NaSPh/NCS/HgCl_2$, $CdCO_3$ (RCH_2X)	Syn Commun *6* 575 (1976)
KO_2SePh, 18-crown-6 ($ArCH_2Cl$)	TL *28* 2933 (1987)
KO_2SePh, K_2HPO_4 ($ArCH_2X$; X = Cl, Br)	Syn 747 (1984)
Me_2SeO, K_2HPO_4 [$ArCH_2X$ (X = Cl, Br)]	Syn 747 (1984)
 (1° allylic or benzylic)	JOC *46* 4617 (1981)
p-$AcOC_6H_4N(Tf)Na/NaOEt/HCl$ (RCH_2X)	JOC *44* 1835 (1979)
PhNHTf, K_2CO_3/HCl (RCHXCOR′)	JOC *44* 1835 (1979)
IF_5/H_2O (RCH_2I, R_2CHI)	Syn 419 (1977)
(n-$Bu_4N)_2Cr_2O_7$ (1° allylic RBr, 1° benzylic RCl and RBr, 2° alkyl RBr)	Chem Ind 213 (1979) JOC *51* 3347 (1986)
	JCS Perkin I 2493 (1979)

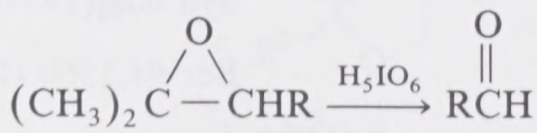


TL *21* 4759 (1980)

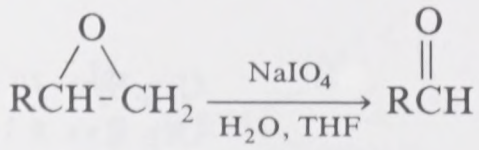


X	Reagent(s)	
F	$Hg(OAc)_2$, $CF_3CO_2H/NaHCO_3$	CL 651, 935 (1980)
Cl	H_2SO_4	Coll Czech Chem Commun *12* 93, 101, 129 (1947)
	$Hg(OAc)_2$, HCO_2H	BSCF 1941 (1976) TL 3489 (1979)
	$Hg(OAc)_2$, HOAc, $BF_3 \cdot OEt_2$	TL 1943 (1978)
	$Hg(OAc)_2$, CF_3CO_2H	TL 1943 (1978)
	$Hg(O_2CCF_3)_2$, CH_3NO_2	TL 3489 (1979); *22* 425 (1981) Helv *63* 1383 (1980)

5. Epoxides



JOC *51* 5447 (1986)



CC 1434 (1987)

6. Sulfides

$$RCH_2SPh \xrightarrow[2.\ CuO,\ CuCl_2,\ H_2O]{1.\ NCS} \underset{\displaystyle RCH}{\overset{\displaystyle O}{\overset{\|}{}}}$$

JOC *41* 3261 (1976)

7. Sulfones

$$(RCH_2SO_2Ar)\ R_2CHSO_2Ar \longrightarrow \underset{\displaystyle RCR}{\overset{\displaystyle O}{\overset{\|}{}}} \quad \underset{\displaystyle (RCH)}{\overset{\displaystyle O}{\overset{\|}{}}}$$

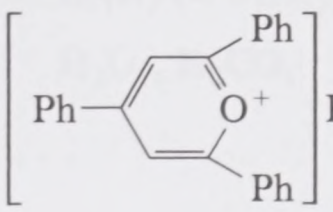
$LDA/MoO_5 \cdot py \cdot HMPA$	TL *21* 3339 (1980); *27* 5951 (1986) JACS *104* 6115 (1982); *107* 1034 (1985) (enal) JOC *51* 5311 (1986)
n-BuLi/$(Me_3SiO)_2$	JOC *48* 4432 (1983)
n-BuLi/$ClB(OMe)_2$/*m*-$ClC_6H_4CO_3H$	TL *26* 2333 (1985)
n-BuLi/$CCl_4/AgClO_4$, CF_3CO_2H	BCSJ *53* 3027 (1980) (aryl ketones only)

8. Amines

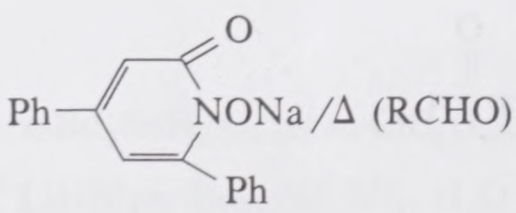
$$R^1-\underset{\displaystyle NH_2}{\underset{|}{CH}}-R^2 \longrightarrow R^1-\overset{\displaystyle O}{\overset{\|}{C}}-R^2$$

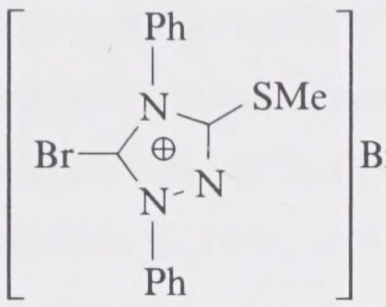
(aldehydes or ketones)

$KMnO_4$, aq *t*-BuOH ($R_2CO > RCHO$)	JOC *32* 3129 (1967)
$Ag(O_2CC_5H_4N)_2$ ($RCHO$, R_2CO)	JCS 4962 (1965)
$AgNO_3$, $Na_2S_2O_8$, NaOH ($RCHO$, R_2CO)	JCS C 1384, 1388 (1966)
IF_5/H_2O ($RCHO$, R_2CO)	Syn 419 (1977)
t-BuOCl, $NaHCO_3$/NaOEt/aq H_2SO_4 ($RCHO$, R_2CO)	JACS *76* 5554 (1954)
NCS/NaOMe/aq H_2SO_4 (R_2CO)	Coll Czech Chem Commun *24* 2975 (1959)
NBS/base/H_3O^+ (R_2CO)	JACS *90* 3245 (1968)



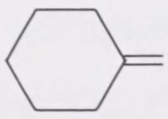
JCS Perkin I 2500 (1979)



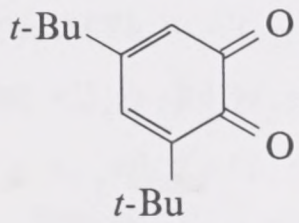


Br^-, Et_3N/ TL 2131 (1978)

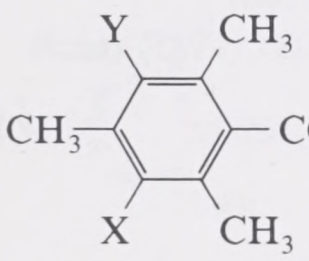
$Et_3N/EtO_2CN{=}NCO_2Et/H_3O^+$ (RCHO)



O /ArSOCl/Δ/H_2O (RCHO only) JOC *46* 4617 (1981)

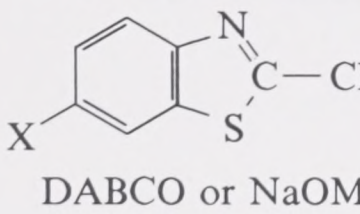


/H_3O^+ (R_2CO) JACS *91* 1429 (1969)



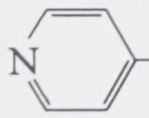
(X, Y = H, NO_2)/ JACS *91* 1429 (1969)

H_3O^+ (RCHO, R_2CO)



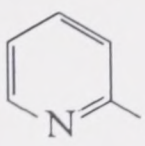
(X = H, NO_2)/ JCS Perkin I 1652 (1972)

DABCO or NaOMe/aq $(HO_2C)_2$
(RCHO, R_2CO)



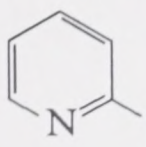
, DBU or NaOH/H_3O^+ Syn 756 (1982)

(RCHO, R_2CO)

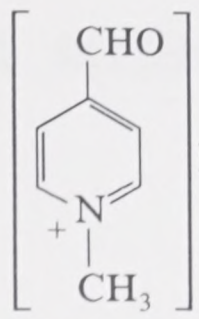


/*m*-$ClC_6H_4CO_3H$/KOH JACS *97* 6900 (1975)

(R_2CO, ArCHO)



/LDA/H^+ (RCHO) JOC *46* 1937 (1981)



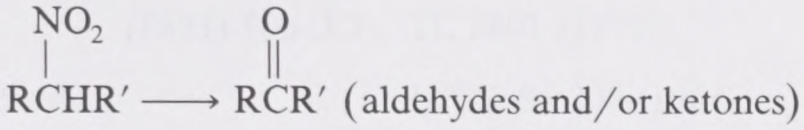
$PhSO_3^-$/DBU or Et_3N/H^+ JACS *104* 4446 (1982)

(RCHO, R_2CO)

$$R_2C{=}CRCH_2NR_2 \xrightarrow[2.\ Ac_2O]{1.\ H_2O_2} R_2C{=}CRC(=O)H$$

CL 1987 (1982)

9. Nitro Compounds



aldehydes only

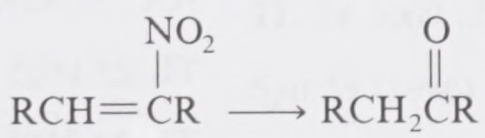
NaO-*t*-Bu/$KMnO_4$	JOC *46* 1037 (1981)

ketones only

$KMnO_4$, silica gel	CC 635 (1982)
$NaNO_2$, *n*-C_3H_7ONO	JOC *38* 1418 (1973)
VCl_2, HCl, H_2O	TL 2533 (1976)
$(NH_4)_2Ce(NO_3)_6$, Et_3N, H_2O	TL *23* 3521 (1982)
R_3SiCl, DBU/*m*-$ClC_6H_4CO_3H$	TL *28* 5361 (1987)
KO-*t*-Bu/*t*-BuO_2H, $VO(acac)_2$ or $Mo(CO)_6$	TL 331 (1977)
LDA/MoO_5·py·HMPA	TL *22* 5235 (1981)
Triton B/O_3	TL *28* 2883 (1987)

aldehydes and ketones

$TiCl_3$, NH_4OAc	JACS *93* 5309 (1971) JOC *38* 4367 (1973)
$CrCl_2$, CH_3OH, HCl	Syn 792 (1977)
OH^-/H^+ (Nef reaction)	Chem Rev *55* 137 (1955) (review) TL 1331 (1972); 3215 (1974) JACS *99* 3862 (1977); *108* 1039 (1986)
KOH or NaH-*t*-BuOH/$KMnO_4$	Ber *69* 1789 (1936) JOC *27* 3699 (1962); *47* 4534 (1982)
KOH/$KMnO_4$, H_2O, $MgSO_4$	JOC *50* 4971 (1985)
$NaOCH_3/O_3$	JOC *39* 259 (1974)
$NaOCH_3/{}^1O_2$	JOC *43* 1271 (1978)
$NaOCH_3/TiCl_3$	JOC *51* 4368 (1986)
$NaOCH_3$/silica gel	JACS *99* 3861 (1977)
$Et_3N/(NH_4)_2Ce(NO_3)_6$	Syn 44 (1980)
$Et_3N/(n\text{-}C_{16}H_{33}NMe_3)MnO_4$	Syn Commun *17* 195 (1987)
H_2O_2, K_2CO_3	Syn 662 (1980)



n-Bu_3SnH/O_3 or *m*-$ClC_6H_4CO_3H$	TL *28* 5365 (1987)
LiHB(*sec*-Bu)$_3$/H_2SO_4, H_2O	Syn 654 (1985)

$CrCl_2$, HCl, H_2O	TL *26* 3777 (1985)
Raney Ni, $NaH_2PO_2 \cdot H_2O$	TL *24* 417 (1983)
electrolysis	CL 607 (1983)

10. Ethers

$$ArCH_2OR \longrightarrow ArCH{=}O$$

$$R_2CHOCH_3 \longrightarrow R_2C{=}O$$

IF_5/H_2O	Syn 419 (1977)
UF_6/H_2O	JACS *98* 6717 (1976); *100* 5396 (1978)
$(NO)BF_4$ (silyl or stannyl ethers)	Syn 609 (1976)
$(NO_2)BF_4$	JOC *42* 3097 (1977)
$(NH_4)_2Ce(NO_3)_6$, $NaBrO_3$, H_2O (Me, Et, $PhCH_2$ and silyl ethers)	Syn 897 (1980)

$$R_2CHOCH_2Ph \xrightarrow[H_2SO_4]{CrO_3} RCR$$

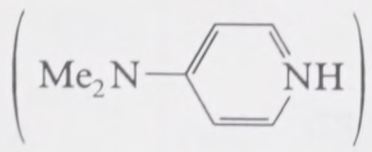
JOC *46* 1492 (1981)

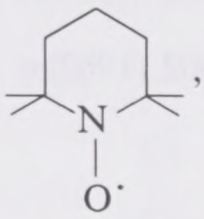
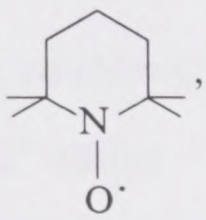
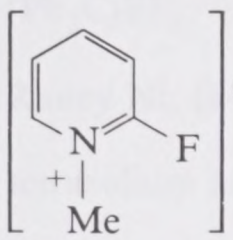
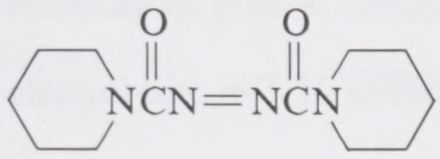
11. Alcohols

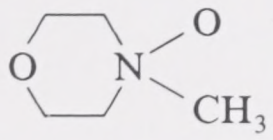
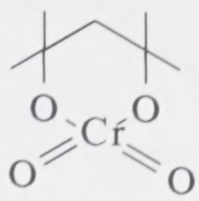
$$RCHR' \longrightarrow RCR' \text{ (aldehydes and/or ketones)}$$

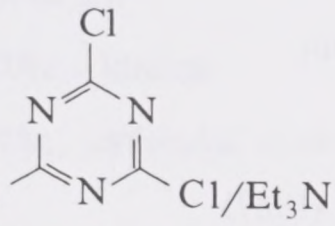
Reviews: "activated" DMSO reagents	Chem Rev *67* 247 (1967) Tetr *34* 1651 (1978) Syn 165 (1981)

Aldehydes only

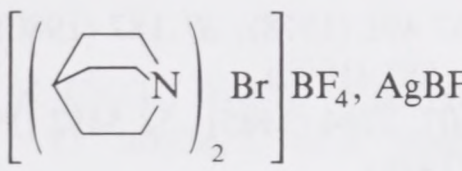
 CrO_3Cl (allylic, benzylic)	JOC *47* 1787 (1982)
CrO_3-graphite	Can J Chem *50* 3058 (1972)
cat $RuCl_3$, $NaIO_4$, H_2O, CH_3CN	JOC *52* 4592 (1987)
$RuCl_2(PPh_3)_3$	TL *22* 1605 (1981)
cat $RuCl_2(PPh_3)_3$, $(Me_3SiO)_2$	TL *24* 2185 (1983)
cat $RuCl_2(PPh_3)_3$, $PhI(OAc)_2$	TL *22* 2361 (1981)

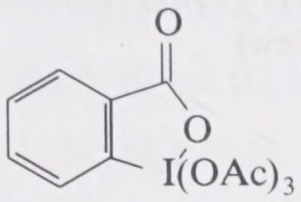
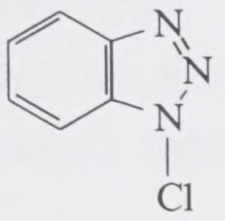
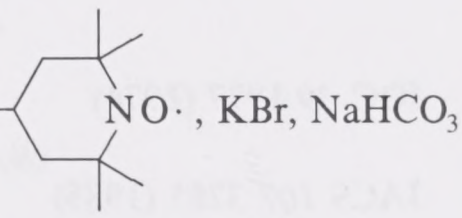
K_2FeO_4 (1° benzylic)	CL 1397 (1978)
$Pb(OAc)_4$, $Mn(OAc)_2$	TL *27* 2287 (1986)
t-BuO_2H, cat $(ArSe)_2$	TL 2801 (1979)
DMSO, air, Δ (allylic, benzylic)	JACS *86* 298 (1964)
DMSO, py·SO_3, *i*-Pr_2NEt	TL *28* 1603 (1987)
O_2, cat 	JACS *106* 3374 (1984)
cat CuCl (allylic, benzylic)	
O_2, cat 	JACS *106* 3374 (1984)
$CuCl_2$ (alkyl, allylic, benzylic)	
	CL 369 (1978)
Et_3N/hexamine (benzylic)	
 , *t*-BuOMgBr	JACS *106* 7970 (1984) TL *28* 527 (1987)
n-PrMgBr/*t*-BuOMgBr, *m*-$ClC_6H_4CO_3H$	BCSJ *50* 2773 (1977)
n-PrMgBr/*t*-BuOMgBr, NCS	BCSJ *50* 2773 (1977)
Ketones only	
O_3	JOC *41* 889 (1976)
O_2, $PdCl_2$, NaOAc	CC 157 (1977)
cat $PdCl_2$, K_2CO_3, CCl_4, Δ	CL 1171 (1981)
cat $Pd(PPh_3)_4$, K_2CO_3, PhBr, DMF	TL 1401 (1979)
t-BuO_2H, $(t\text{-}BuO)_3Al$ or Me_3Al	TL *21* 1657 (1980)
t-BuO_2H, cat SeO_2 (allylic)	TL *28* 3831 (1987)
t-BuO_2H, cat $VO(acac)_2$	TL *24* 5009 (1983)
t-BuO_2H, cat $Mo(CO)_6$, cat $[C_5H_5N(CH_2)_{15}CH_3]Cl$, $MgSO_4$	Syn 59 (1986)
t-BuO_2H, cat $(PhCH_2NMe_3)OMoBr_4$	TL *25* 4417 (1984)

H_2O_2, cat $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$, n-Bu_4NCl, K_2CO_3	TL *25* 173 (1984)
t-BuO_2H, cat $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$	Syn Commun *16* 537 (1986)
m-$ClC_6H_4CO_3H$, 10% HCl	TL 4115 (1975)
$PhICl_2$, py	TL 3635 (1973)
NBS (on $ROSiMe_3$)	JOC *43* 371 (1978)
NaOCl, HOAc	JOC *45* 2030 (1980); *52* 2602 (1987) TL *23* 4647 (1982)
$Ca(OCl)_2$, HOAc, CH_3CN	TL *23* 35 (1982)
NaOCl, cat $RuCl_3$	CC 1420 (1970) JOC *48* 1366 (1983)
cat $RuCl_2(PPh_3)_3$, PhIO	TL *22* 2361 (1981)
$NaIO_4$, cat RuO_2	JOC *50* 2759 (1985)
$NaIO_4$, cat RuO_2, cat $(PhCH_2NEt_3)Cl$	JOC *52* 1149 (1987)
cat $RuO_2\cdot 2\ H_2O$, electrolysis	JOC *51* 151 (1986)
cat K_2RuO_4, K_2SO_5	CC 58 (1979)
cat $R_4N(RuO_4)$ (R = n-Pr, n-Bu), 	CC 1625 (1987)
cat $IrH_5(i\text{-}Pr_3P)_2$	TL *28* 3115 (1987)
CrO_3, HOAc	JACS *75* 422 (1953)
cat CrO_3, t-BuO_2H, H_2O (benzylic)	TL *28* 2133 (1987)
$Na_2Cr_2O_7\cdot 2\ H_2O$-H_2SO_4-silica gel	Tetr *35* 1789 (1979)
$K_2Cr_2O_7$, H_2SO_4, ether (Brown) (2° alkyl, allylic)	JACS *83* 2952 (1961) JCS C 1972 (1966) JOC *36* 387 (1971)
$(C_5H_5NH)_2Cr_2O_7$, HOAc, EtOAc (2° allylic only)	JOC *51* 5472 (1986)
$(C_5H_5NH)_2Cr_2O_7$, $(C_5H_5NH)O_2CCF_3$	JACS *109* 4690 (1987)
cat  , CH_3CO_3H	TL *26* 5855 (1985)
$Cu(MnO_4)_2\cdot 8\ H_2O$	JOC *47* 2790 (1982)
$KMnO_4$, $CuSO_4\cdot 5\ H_2O$	JOC *44* 3446 (1979)
$NaMnO_4\cdot H_2O$ (solid)	TL *22* 1655 (1981)
$(NH_4)_2Ce(NO_3)_6$ or $Ce(SO_4)_2\cdot 2\ H_2SO_4$, $NaBrO_3$	TL *23* 539 (1982) JOC *50* 2759 (1985)

DMSO, Ac_2O	JOC *30* 1107 (1965) JACS *89* 2416 (1967); *109* 7477 (1987) (acyloin) Chem Rev *67* 247 (1967) (review)
DMSO, $PhSO_2Cl/Et_3N$	JOC *39* 1977 (1974)
DMSO, $TsCl/Et_3N$	JOC *39* 1977 (1974)
DMSO, $(TsO)_2/Et_3N$	JOC *39* 1977 (1974)
DMSO, P_2O_5	JACS *87* 4651 (1965)
DMSO, 	JOC *39* 1977 (1974)
DMSO, *i*-PrN=C=N-*i*-Pr, cat Cl_2CHCO_2H	JACS *107* 3285 (1985)
DDQ (2° allylic)	JOC *50* 5897 (1985)
DDQ, HIO_4 (2° allylic)	Syn 848 (1978)
$(Ph_3C)BF_4$	TL 2771 (1978)
Raney Ni, (1-octene)	JOC *51* 5482 (1986)
tetrazolium salt, KOH, EtOH	TL *28* 4323 (1987) (on α-hydroxy ketone)
electrolysis, KI, H_2O	TL 165 (1979)
electrolysis, poly-4-vinylpyridine·HBr	JOC *45* 5269 (1980)
electrolysis, *n*-$C_8H_{17}SCH_3$, Et_4NBr	TL *21* 1867 (1980)
electrolysis, NiOOH	Tetr *38* 3299 (1982)

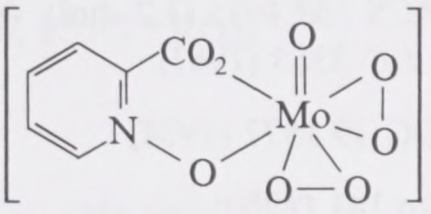
Aldehydes and ketones

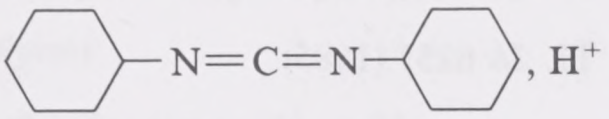
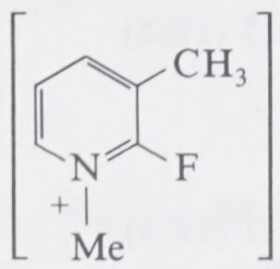
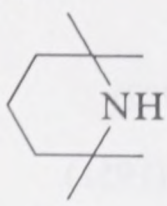
	JOC *51* 5454 (1986)
Cl_2, py	TL 3059 (1974)
Cl_2 or Br_2, HMPA (1° benzylic)	Syn 811 (1976)
$(n\text{-}Bu_3Sn)_2O/Br_2$ (1° benzylic)	TL 4597 (1976)
Et_3SnOMe/Et_3SnOMe, Br_2 (2° alkyl, 1° allylic, 1° or 2° benzylic)	CL 145 (1975)
NBS (on $ROSnR'_3$) (1° allylic or benzylic)	JACS *98* 1629 (1976)
NBA, NBS, or NCS (1° benzylic)	Chem Rev *63* 21 (1963)

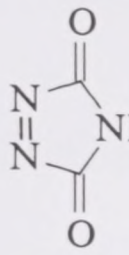
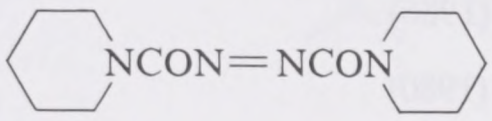
NIS, n-Bu_4NI	Syn 394 (1981)
	JOC *48* 4155 (1983) TL *28* 2921, 4259 (trifluoromethyl ketones) (1987)
 (1° benzylic)	JCS C 1474 (1969)
NaOCl (phase transfer) (1° benzylic)	TL 1641 (1976)
NaOCl, cat  , KBr, $NaHCO_3$	JOC *52* 2559 (1987)
$Ca(OCl)_2$ (1° benzylic)	TL 35 (1982)
CrO_3, HMPA (2° benzylic)	Syn 394 (1976)
CrO_3, Celite, Et_2O, CH_2Cl_2	Syn 815 (1979)
CrO_3-polymer	JACS *98* 6737 (1976)
CrO_3, cat n-Bu_4NX	TL *21* 4653 (1980)
CrO_3-H_2O-SiO_2	Syn 534 (1978)
$CrO_3 \cdot 2$ py (Collins)	JOC *26* 4814 (1961); *35* 4000 (1970) TL 3363 (1968); 399 (1979) Org Syn *52* 5 (1972); *55* 84 (1975) Syn 567 (1981) (β-hydroxy ketones)
$CrO_3 \cdot 2$ py, Celite	JOC *52* 5419 (1987)
$CrO_3 \cdot 3,5$-dimethylpyrazole	TL 4499 (1973)
CrO_3-py-HCl (PCC)	TL 2647 (1975) Carbohydr Res *67* 491 (1978); *81* 187 (1980) Syn 245 (review), 881 (1982) JOC *50* 2095, 2607, 2764 (1985); *52* 5452 (1987) JACS *108* 4603 (1986)
PCC-polymer	JOC *43* 2618 (1978)
PCC, molecular sieves (1° benzylic, 2° alkyl or benzylic)	CC 561 (1980) JCS Perkin I 1967 (1982) TL *26* 3731 (1985); *28* 675 (1987)
PCC, molecular sieves, py	TL *28* 703 (1987)
PCC, py	Chem Phys Lipids *27* 281 (1980)
PCC, alumina	Syn 223 (1980) JOC *47* 564 (1982) TL *28* 703 (1987)

PCC, Celite	JOC *50* 2626 (1985); *52* 3662 (1987) TL *28* 1791 (1987)
PCC, Celite, molecular sieves	TL *28* 171 (1987)
PCC, NaOAc	TL 2647 (1975) JCS Perkin I 599 (1981) Syn 245 (1982) (review) JACS *108* 4603 (1986); *109* 5167 (1987) JOC *50* 2707 (1985); *52* 5452 (1987)
PCC, NaOAc, py	Chem Phys Lipids *25* 381 (1979)
PCC, NaOAc, alumina	TL *28* 869, 6437 (1987)
PCC, NaOAc, molecular sieves	TL *28* 1073 (1987) JOC *52* 4885 (1987)
CrO_3-DMAP-HCl (1° allylic or benzylic, 2° allylic)	JOC *47* 1787 (1982)
CrO_3-bipy-HCl	Syn 691 (1980)
CrO_3-py-HF	Syn 588 (1982)
CrO_3, H_2SO_4, CH_3COCH_3 (Jones) (1° allylic or benzylic)	JCS 39 (1946); 2548 (1953) JOC *21* 1547 (1956); *25* 1434 (1960); *40* 1664 (1975) Org Syn *45* 28 (1965)
$(C_5H_5NH)HCrO_4$-silica gel	Tetr *35* 1789 (1979)
(n-Bu_4N)$HCrO_4$, $HCCl_3$ (1° allylic or benzylic)	Syn 356 (1979)
$Na_2Cr_2O_7$, H_2O (1° allylic, 1° or 2° benzylic)	JOC *35* 3589 (1970)
$Na_2Cr_2O_7$, H_2SO_4, DMSO	JOC *39* 3304 (1974)
$K_2Cr_2O_7$, H_2SO_4 (phase transfer)	TL 1601 (1978) JCS Perkin II 788 (1979) Syn 134 (1979)
$K_2Cr_2O_7$, DMSO or polyethylene glycol (1° allylic, 1° or 2° benzylic)	Syn 646 (1980)
$K_2Cr_2O_7$, benzene (phase transfer) (1° allylic or benzylic, 2° benzylic)	TL 4167 (1977)
(n-Bu_4N)$_2Cr_2O_7$, CH_2Cl_2 (1° allylic, 1° or 2° benzylic)	Syn Commun *10* 75 (1980)
($PhCH_2NEt_3$)$_2Cr_2O_7$, HMPA (1° allylic or benzylic; 2° benzylic)	Syn 1091 (1982)
$(C_5H_5NH)_2Cr_2O_7$ (PDC), CH_2Cl_2	TL 2647 (1975); 399 (1979) JOC *41* 380 (1976) Ind J Chem B *22* 69 (1983)
PDC, cat $(C_5H_5NH)O_2CCF_3$	JOC *50* 2981 (1987)

PDC, HOAc, molecular sieves	TL *26* 1699 (1985); *28* 5129 (1987) Syn Commun *16* 11 (1986)
cat PDC, $(Me_3SiO)_2$	TL *24* 2185 (1983)
PDC-polymer	JOC *46* 1728 (1981)
PDC, molecular sieves (1° or 2° benzylic, 1° allylic, 2° alkyl)	CC 561 (1980) JCS Perkin I 1967 (1982) JACS *109* 6389 (1987) TL *28* 2959 (1987)
$(Ph_3PCH_2PPh_3)Cr_2O_7$ (1° allylic, 1° or 2° benzylic)	TL *27* 1775 (1986)
CrO_2Cl_2, SiO_2-Al_2O_3	JOC *42* 2182 (1977)
$(Phen)CrOCl_3$	TL *21* 1583 (1980)
$(Phen)H_2CrOCl_5$	TL *21* 1583 (1980)
$(py)CrO_5$	TL 3749 (1977)
MnO_2 (particularly allylic, benzylic and propargylic)	JACS *77* 4399 (1955); *107* 1028, 1034 (1985); *108* 2691 (1986); *109* 4690, 6719 (1987) JCS 1430 (1952); 4685 (1956); 4983 (1963) Quart Rev *13* 61 (1959) JOC *24* 1051 (1959); *35* 3971 (1970); *51* 2863, 4158 (1986); *52* 398, 3662, 5067, 5700 (1987) Proc Chem Soc 110 (1964) Syn 65, 133 (1976) (reviews) CC 1237 (1986) TL *28* 5403 (1987)
$KMnO_4$ (on solid support) (1° allylic or benzylic)	JACS *99* 3837 (1977) TL *22* 4889 (1981)
$BaMnO_4$ (1° or 2° alkyl, 1° or 2° benzylic, 1° or 2° allylic, 2° propargylic)	TL 839 (1978); *23* 3283 (1982); *28* 5655, 5865 (1987) BCSJ *56* 914 (1983) JACS *106* 7861 (1984); *108* 4953 (1986) CC 1319 (1986) JOC *51* 4169 (1986)
$[n\text{-}C_{16}H_{33}N(CH_3)_3]MnO_4$ (benzylic)	CL 2131 (1984)
$AgMnO_4$ (1° alkyl, 1° or 2° benzylic)	TL *23* 1847 (1982)
$Pb(OAc)_4$, py	TL 3071 (1964); 4427 (1967)
Ag_2CO_3, Celite	Compt Rend C *267* 900 (1968) CC 1102, 1118 (1969) Tetr *29* 1011 (1973) Syn 401 (1979) TL *22* 3721, 3725 (1981)
$Ni(O_2CPh)_2$, Br_2	Syn Commun *10* 881 (1980)
$NiBr_2$, $(PhCO_2)_2$	JOC *44* 2955 (1979)

NiO_2 (1° or 2° allylic, benzylic, allenic)	JOC *27* 1597 (1964) Chem Rev *75* 491 (1975) TL 1595 (1979) JACS *104* 2642 (1982)
cat $Pd(OAc)_2$, PhI, *n*-Bu_4NCl, $NaHCO_3$, DMF (1° alkyl or benzylic, 2° alkyl)	TL *26* 6257 (1985)
RuO_4 (1° benzylic, 2° alkyl)	JACS *80* 6682 (1958) Rev Pure Appl Chem *22* 47 (1972) (review)
KIO_4, cat RuO_2, K_2CO_3 (2° alkyl)	Carbohydr Res *24* 192 (1972) Methods Carbohydr Chem *7* 3 (1976)
NaOCl, cat RuO_2	Methods Carbohydr Res *6* 337 (1972)
cat $H_2Ru(PPh_3)_4$, $H_2C{=}CHCH_2OCO_2Me$ (1° allylic, 2° alkyl or allylic)	TL *27* 1805 (1986)
O_2, CuCl, phenanthroline, K_2CO_3 (1° allylic or benzylic, 2° benzylic)	TL 1215 (1977)
O_2, cat *n*-Bu_4N 	JOC *52* 5467 (1987)
H_2O_2, cat WO_4^{2-} or MoO_4^{2-}, phase transfer catalyst (1° benzylic, 2° alkyl)	JOC *51* 2661 (1986)
H_2O_2, $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$	JOC *52* 1868 (1987)
$Fe(NO_3)_3$ on clay	Syn 849 (1980)
$FeCl_3$, hν	JOC *42* 171 (1977)
K_2FeO_4, Al_2O_3, $CuSO_4 \cdot 5\ H_2O$ (1° or 2° benzylic and allylic, 2° alkyl)	TL *27* 2875 (1986)
Ag_2FeO_4 (1° or 2° benzylic and allylic)	Syn Commun *16* 211 (1986)
$(NH_4)_2Ce(NO_3)_6$, $NaBrO_3$ (1° benzylic)	Syn 936 (1978) TL 539 (1982)
$[Ce(NO_3)_3]_2CrO_4$ (1° or 2° benzylic)	Syn Commun *14* 631 (1984) JOC *50* 5902 (1985)
$(Ph_3BiCl)_2O$	CC 1099 (1978)
Me_2SeO, molecular sieves	Syn 747 (1984)
$(PhSeO)_2O$ (1° allylic or benzylic)	CC 952 (1978)
$(ArSe)_2$, *t*-BuO_2H	JOC *47* 837 (1982)
$Al(O\text{-}t\text{-}Bu)_3$, CH_3COCH_3 (Oppenauer)	Org Rxs *6* 207 (1951)
EtMgBr/PhCHO (1° or 2° allylic, 2° alkyl)	TL *28* 769 (1987)

cat $Cp_2Zr(O\text{-}i\text{-}Pr)_2$, PhCHO or PhCOPh	JOC *52* 4855 (1987)
cat Cp_2ZrH_2, RCOR (1° or 2° alkyl, allylic, benzylic)	JOC *51* 240 (1986); *52* 4855 (1987)
DMSO,  , H^+ (Pfitzner-Moffatt)	JACS *85* 3027 (1963); *87* 5661, 5670 (1965); *88* 1762 (1966) Org Syn *47* 25 (1967) Chem Rev *67* 247 (1967)
DMSO, Ac_2O	JACS *87* 4214 (1965)
DMSO, P_2O_5	JACS *87* 4214, 4651 (1965)
DMSO, $SOCl_2/Et_3N$	Tetr *34* 1651 (1978)
DMSO, $(COCl)_2/Et_3N$ (Swern)	JOC *43* 2480 (1978); *44* 4148 (1979); *50* 2198 (1985); *51* 5282 (1986); *52* 5700 (1987) Tetr *34* 1651 (1978) Syn 165 (review), 567 (β-hydroxy ketones) (1981) Org Syn *64* 164 (1985) JACS *108* 1035 (1,2-diol), 4603 (1986); *109* 3353 (1987)
DMSO, $(MeSO_2)_2O/Et_3N$	JOC *39* 1977 (1974)
DMSO, $ClSO_2NCO/Et_3N$ (1° allylic or benzylic)	Syn 141 (1980)
DMSO, $(CF_3CO)_2O/Et_3N$	JOC *41* 957, 3329 (1976); *52* 4851 (1987) (α-dicarbonyl compounds) Syn 297 (1978)
DMSO, $py\cdot SO_3$, Et_3N	Chem Pharm Bull *30* 1921 (1982) JOC *52* 1252 (1987)
DMSO, $py\cdot SO_3/Et_3N$	JACS *89* 5505 (1967)
$DMSO/COCl_2/Et_3N$	JCS 1855 (1964)
DMSO, Cl_2/Et_3N	TL 919 (1973)
DMSO,  OTs^-, Et_3N	CL 369 (1978)
$PhSCH_3$ or $(CH_3)_2S$, Cl_2 or NCS/Et_3N or $i\text{-}Pr_2NEt$	JACS *94* 7586 (1972) JOC *38* 1233 (1973); *51* 5282 (1986); *52* 4505 (1987)
$CH_3COCOCl$, py/hν	JOC *41* 3030 (1976)
m-$ClC_6H_4CO_3H$,  (1° benzylic)	JOC *40* 1860 (1975)
DDQ (1° or 2° benzylic)	JOC *45* 1596 (1980)
5-deazaflavin, KOH (1° benzylic)	CC 825 (1977)

$EtO_2CN{=}NCO_2Et$, $EtO_2CCH_2NO_2$, PPh_3	TL 2295 (1981)
 (1° benzylic)	CC 744 (1966)
n-PrMgBr/*t*-BuOMgBr, 	BCSJ *50* 2773 (1977) JACS *106* 7970 (1984)
n-PrMgBr/*t*-BuOMgBr, $PhI(OAc)_2$	BCSJ *50* 2773 (1977)
$(NO)BF_4$ (1° or 2° benzylic)	Syn 609 (1976)
hν, platinised TiO_2 (1° alkyl or allylic, 2° benzylic)	TL *25* 3363 (1984)

Selective oxidation, 1° > 2° ROH

$RuCl_2(PPh_3)_3$	TL *22* 1605 (1981)
cat $RuCl_2(PPh_3)_3$, $(Me_3SiO)_2$	TL *24* 2185 (1983)
DMSO, ClCOCOCl/Et_3N	JACS *108* 1035 (1986)
DMSO, py·SO_3, *i*-Pr_2NEt	TL *28* 1603 (1987)

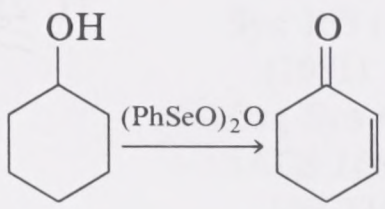
Selective oxidation, 2° > 1° ROH

$(Ph_3C)BF_4$	JACS *98* 7882 (1976) TL 2771 (1978)
RCHO (R = Ph, CCl_3), Al_2O_3	TL 3499 (1976)
NBA	JACS *74* 483 (1952); *76* 3682 (1954); *85* 1409 (1963)
NBS, H_2O	JACS *109* 3017 (1987)
Br_2, (*n*-$Bu_3Sn)_2O$	TL 4597 (1976)
Cl_2, py	TL 3059 (1974)
X_2, HMPA (X = Cl, Br)	Syn 811 (1976)
HOCl, HOAc	TL 4647 (1982)
NaOCl, HOAc	JOC *45* 2030 (1980) TL *23* 4647 (1982)
t-BuO_2H, cat $VO(acac)_2$	TL *24* 5009 (1983)
t-BuO_2H, cat $(PhCH_2NMe_3)OMoBr_4$	TL *25* 4417 (1984)
t-BuO_2H, cat $[C_5H_5N(CH_2)_{15}CH_3]PMo_{12}O_{40}$	Syn Commun *16* 537 (1986)

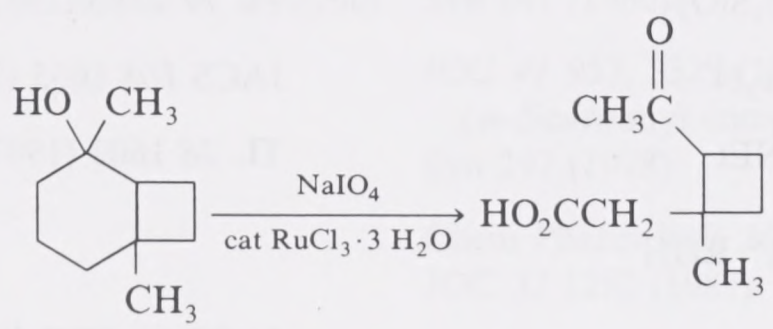
t-BuO_2H, cat $Mo(CO)_6$, cat $[C_5H_5N(CH_2)_{15}CH_3]Cl$, $MgSO_4$	Syn 59 (1986)
H_2O_2, cat $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$, n-Bu_4NCl, K_2CO_3	TL *25* 173 (1984)
H_2O_2, $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$	JOC *52* 1868 (1987)
$(NH_4)_2Ce(NO_3)_6$ or $Ce(SO_4)_2\cdot 2\ H_2SO_4$, $NaBrO_3$	TL *23* 539 (1982) JOC *50* 2759 (1987)
Raney Ni	JOC *51* 5482 (1986)
electrolysis, poly-4-vinylpyridine·HBr	JOC *45* 5269 (1980)

Selective oxidation, allylic or benzylic > alkyl ROH

See earlier sections

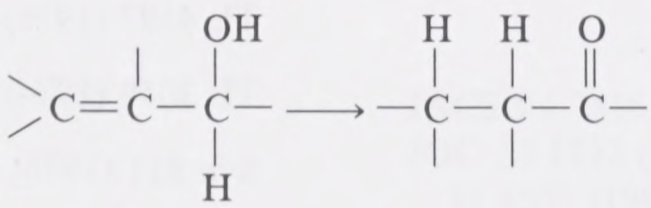


CC 952 (1978)

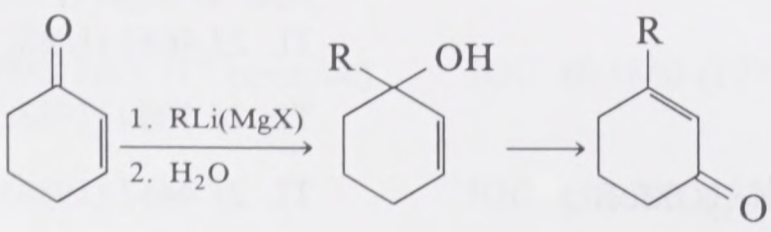


JOC *52* 689 (1987)

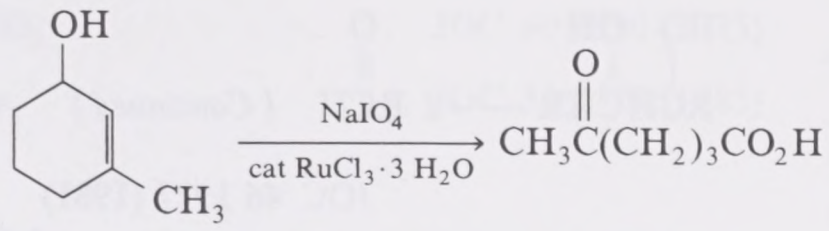
12. Allylic Alcohols

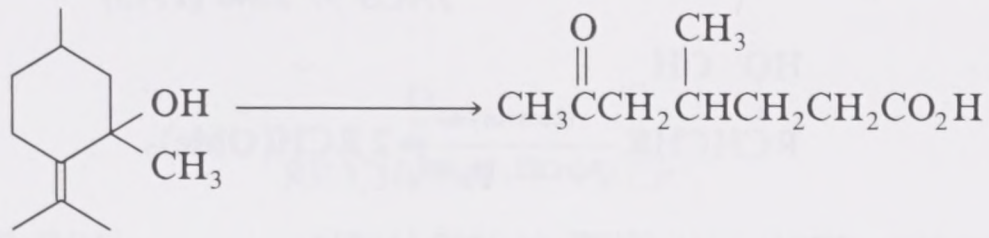


See page 627, Section 1.

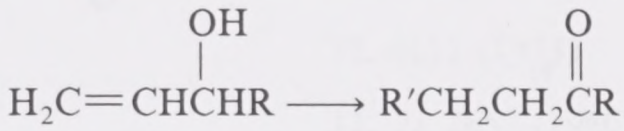


See page 587, Section 1.



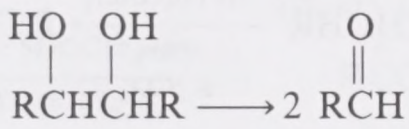


JOC *52* 689 (1987)

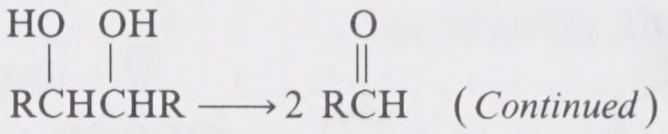


See page 817, Section 16.

13. Diols



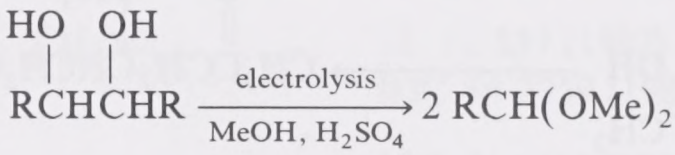
$Ca(OCl)_2$, H_2O, CH_3CN, HOAc	TL *23* 3135 (1982)
$(NH_4)_4[Ce(SO_4)_4]\cdot 2\ H_2O$, H_2SO_4	JACS *81* 1494 (1959)
$NaBiO_3$, H_3PO_4, H_2O	JCS 1907 (1950)
$I(OAc)_3$	JCS Perkin I 1483 (1978)
HIO_4	Org Rxs *2* 341 (1944)
$NaIO_4$, H_2O	TL *24* 1377 (1983); *28* 3035 (1987) JACS *109* 3353 (1987)
$NaIO_4$, NaOH	JOC *50* 2095 (1985)
Amberlite 904-$NaIO_4$	JCS Perkin I 509 (1982)
$Pb(OAc)_4$	Ann *599* 81 (1956) Newer Methods Prep Org Chem *2* 367 (1963) TL *27* 5853 (1986); *28* 2999 (1987)
HgO, I_2	JOC *51* 5446 (1986)
MnO_2	Angew *85* 401 (1973)
H_2CrO_4	JACS *82* 1401 (1960); *84* 1252, 2241 (1962)
PCC	Syn Commun *12* 833 (1982)



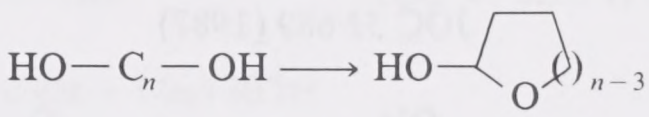
(*Continued*)

NIS — JOC *46* 1927 (1981)

electrolysis — JACS *97* 2546 (1975)

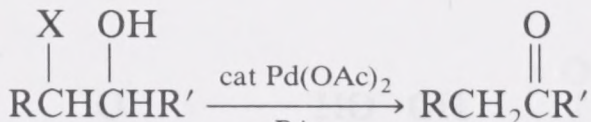


JOC *46* 3312 (1981)



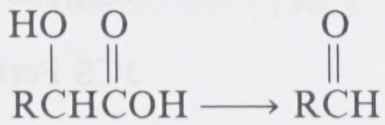
Reagent	n	
$RuCl_2(PPh_3)_3$	4	JACS *106* 1148 (1981)
	5	TL *28* 3123 (1987)
$BaMnO_4$	4	JCS Perkin I 1579 (1983)

14. Halohydrins



TL *23* 3085 (1982)

15. α-Hydroxyacids



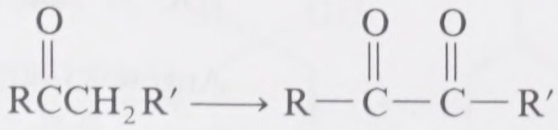
NIS — JOC *47* 3006 (1982)

$NaIO_4$, H_2O, HOAc, CH_3COCH_3 — TL 1725 (1968)

16. α-Thioacids

See page 617, Section 18.

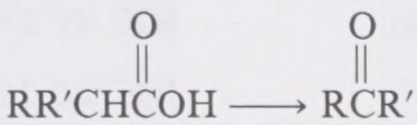
17. Ketones



SeO_2 — Org Rxs *5* 331 (1949); *24* 261 (1976) (reviews)
JOC *52* 2602 (1987)

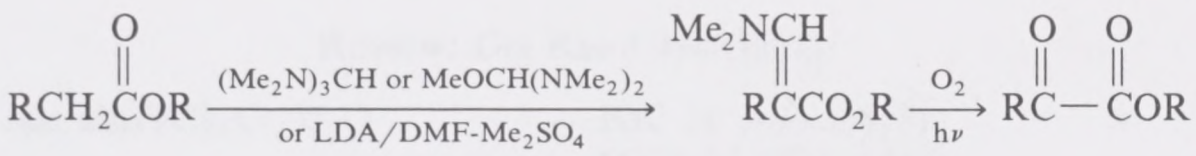
$CuBr_2$/KI, DMSO, Na_2CO_3	JOC *40* 1990 (1975)
t-BuOCH$(NMe_2)_2$/O_2, hν	JOC *50* 3573 (1985)

18. Carboxylic Acids

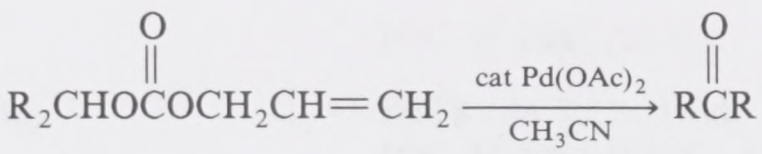


2 LDA/$(MeS)_2$/NCS, ROH	JACS *99* 3101 (1977); *107* 8066 (1985); *109* 4626 (1987)
2 LDA/$(PhS)_2$/electrolysis	TL 1045 (1979)
2 LDA/O_2/$Me_2NCH(OMe)_2$	TL 4611 (1975)
(*n*-Bu_4N)IO_4 (R = Ar)	TL *21* 2655 (1980)
(*n*-Bu_4N)IO_4 (R = OH in acid, product is R′CHO)	Syn 563 (1980)

19. Esters



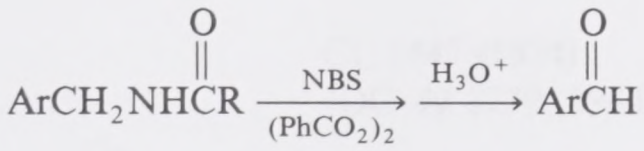
JOC *50* 3573 (1985)



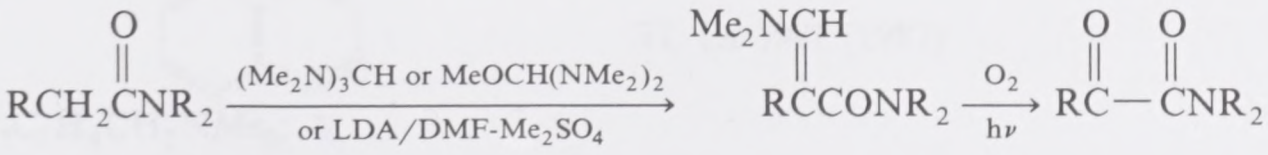
R_2CH = 1° allylic or benzylic, 2° alkyl

TL *25* 2791 (1984)

20. Amides



TL 3875 (1979)



JOC *50* 3573 (1985)

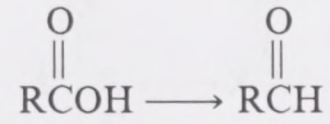
21. Nitriles

$$RR'CHCN \longrightarrow RC(=O)R'$$

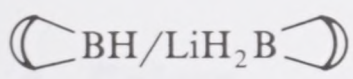
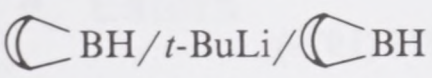
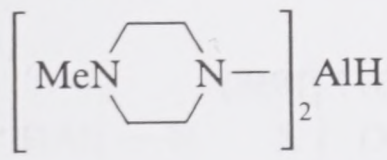
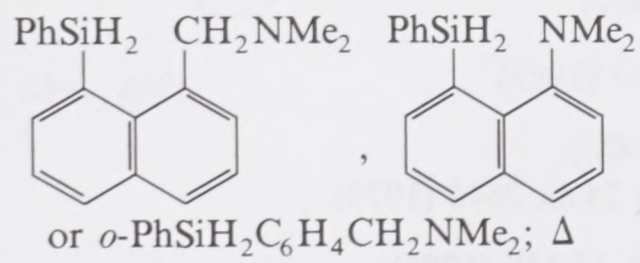
NaOH, O_2, $(Et_3NCH_2Ph)Cl$	Syn 1009 (1980)
LDA/*t*-$BuMe_2SiCl/I_2/Ag_2O$ (R = Ar)	JOC *39* 2799 (1974)
LDA/O_2/$SnCl_2$/NaOH	JOC *40* 267 (1975)
LDA/O_2/Na_2SO_3, buffer	TL *28* 2087 (1987)
base, O_2 (R = Ar)	Tetr *3* 97 (1958) TL 657 (1964)
K_2CO_3, air, DMSO (R = R′ = Ar)	Org Prep Proc Int *2* 137 (1970) JOC *48* 4097 (1983)
LiN(*i*-Pr)–⬡, air, DMSO	JOC *48* 4097 (1983)
LDA/PhSCl/NBS, H_2O	TL 3029 (1974)
PCl_5/NaOH	TL 437 (1967); 2301 (1973) JOC *33* 2211 (1968) JACS *109* 7270 (1987)

3. REDUCTION OF CARBOXYLIC ACIDS, ACID DERIVATIVES AND NITRILES TO ALDEHYDES

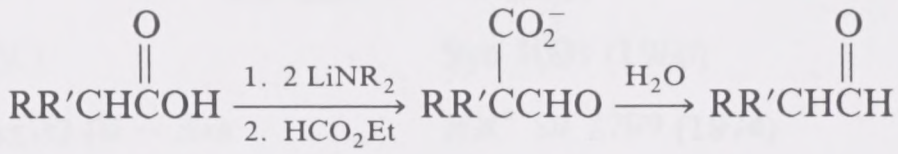
1. Carboxylic Acids



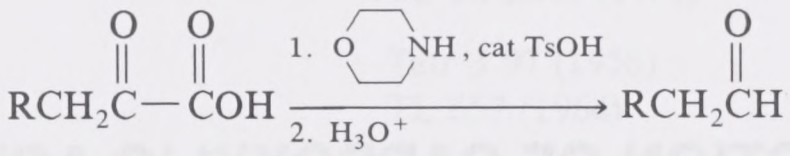
Review: Org Rxs *8* 218 (1954)

Li, RNH_2 (R = Me, Et)/NH_4Cl/H_3O^+	JOC *28* 2918 (1963) JACS *92* 5774 (1970)
$BH_3 \cdot SMe_2$/PCC	Syn 704 (1979)
$(CH_3)_2CHC(CH_3)_2BH_2$	JOC *37* 2942 (1972)
$(CH_3)_2CHC(CH_3)_2BHCl \cdot SMe_2$	JACS *106* 8001 (1984) JOC *51* 5264 (1986); *52* 5400 (1987)
$(CH_3)_2CHC(CH_3)_2BHBr \cdot SMe_2$	JOC *52* 5030 (1987) TL *28* 2389 (1987)
	TL *28* 4575 (1987)
	TL *28* 6231 (1987)
i-Bu_2AlH	J Gen Chem USSR *34* 1021 (1964)
	CL 1447 (1974) JOC *49* 2279 (1984)
 or *o*-$PhSiH_2C_6H_4CH_2NMe_2$; Δ	TL *28* 3941 (1987)
i-BuMgBr, Cp_2TiCl_2	Syn 871 (1981)
$(Me_2N{=}CHCl)Cl$/$LiHAl(O\text{-}t\text{-}Bu)_3$, cat CuI	TL *24* 1543 (1983)

o-HSC_6H_4OH, $POCl_3$, $HClO_4/LiAlH_4/H_2O$, $HgCl_2$	J Heterocyclic Chem *11* 943 (1974)
o-$(NH_2)C_6H_4$, PPA/NaOEt/MeI/$NaBH_4$ or $LiAlH_4/H_3O^+$	Syn 303 (1981)

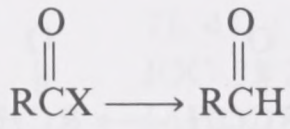


TL 699 (1970)

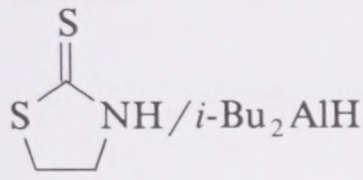
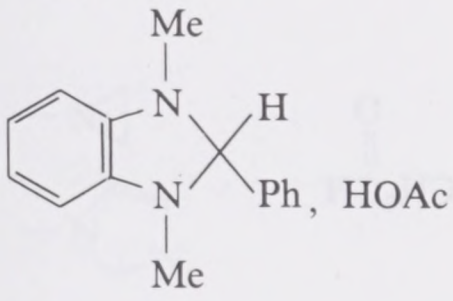


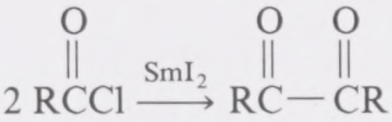
TL *23* 459 (1982)

2. Acid Halides



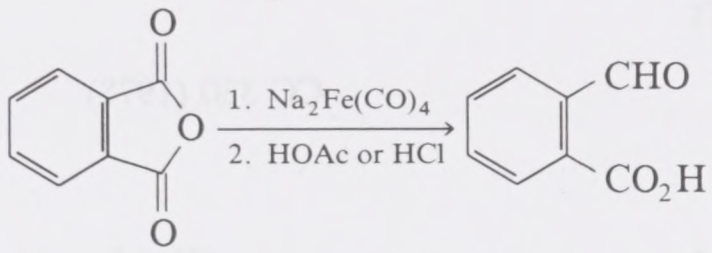
H_2, cat Pd, $BaSO_4$ (Rosenmund)	Ber *51* 585 (1918); *54* 425 (1921) Org Rxs *4* 362 (1948) Rec Trav Chim *90* 1323 (1971); *100* 21 (1981) JACS *108* 2608 (1986)
H_2, cat Pd-C, 2,6-lutidine	Syn 767 (1976) JACS *108* 2608 (1986)
H_2, cat $PdCl_2(PPh_3)_2$, R'_3N (R = aryl)	JACS *96* 7761 (1974)
$NaBH_4$, DMF, −70°C	TL *22* 11 (1981)
$NaBH_4$, py, DMF, O°C	Syn Commun *12* 839 (1982)
$NaBH_4$, $CdCl_2$	CC 354 (1978) JCS Perkin I 27 (1980)
$(Ph_3P)_2CuBH_4$	TL 1437, 2473 (1978); 975 (1979) JOC *45* 3449 (1980)
$[(Ph_3P)_2CuBH_3CN]_2$	TL *21* 813 (1980)
$LiHAl(O\text{-}t\text{-}Bu)_3$	JACS *79* 252 (1956); *80* 5377 (1958) J Lipid Res *8* 380 (1967) Syn 217 (1972)
Et_3SiH, cat Pd-C	JOC *34* 1977 (1969)
Et_3SiH, cat $PtCl_2(PPh_3)_2$ or $ClRh(CO)(EtPPh_2)_2$	CC 1703 (1970) JCS Dalton 2460, 2646 (1975)
polymethylhydrosiloxane, cat $RhCl_3$, cat $[(n\text{-}C_8H_{17})_3NCH_3]Cl$	J Mol Catal *37* 359 (1986)

n-Bu_3SnH	JOC *25* 284 (1960) JACS *88* 571 (1966)
n-Bu_3SnH, cat $Pd(PPh_3)_4$	CC 432 (1980) JOC *46* 4439 (1981)
$Na_2Fe(CO)_4$/HOAc	BCSJ *44* 2569 (1971)
$(Me_4N)HFe(CO)_4$	TL 781 (1977)
o-HOC_6H_4SH, $HBF_4/NaBH_4/H_2O$, $HgCl_2$	JCS Perkin I 323 (1976)
	JCS Perkin I 2470 (1980)
	JOC *51* 5400 (1986)



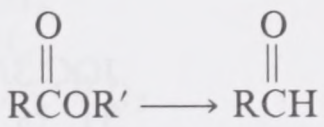
TL *22* 3959 (1981); *25* 2869 (1984)

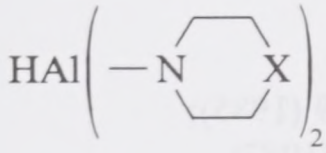
3. Anhydrides

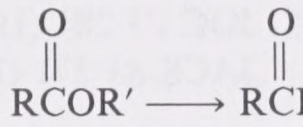


TL 3535 (1973)

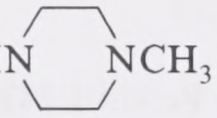
4. Esters

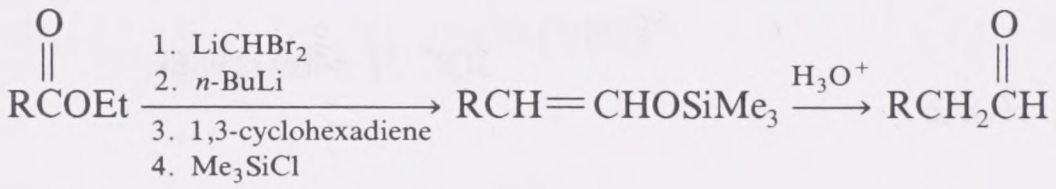


	CL 215 (1975)
i-Bu_2AlH	TL 619 (1962); 1779 (1969); *27* 2103 (1986) Bull Acad Sci USSR, Div Chem Sci 288 (1963) JOC *40* 3495 (1975); *48* 2775 (1983); *52* 2361 (1987) Syn 617 (1975) (review) JACS *107* 199 (1985)



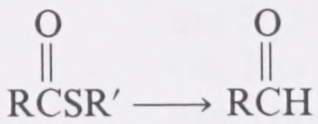
(*Continued*)

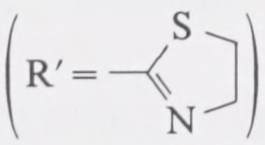
$LiAlH_4$, Et_2NH	JOC *52* 5486 (1987)
$NaAlH_4$	TL 2087 (1963)
$NaH_2Al(i\text{-}Bu)_2$	TL 619 (1962)
$NaH_2Al(OCH_2CH_2OCH_3)_2$	JACS *95* 7501 (1973)
$NaH_2Al(OCH_2CH_2OCH_3)_2$, 	Syn 526 (1976)
$LiHAl(O\text{-}t\text{-}Bu)_3$ ($R' = C_6H_5$)	JOC *31* 283 (1966)



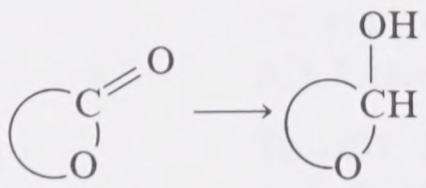
JACS *108* 1325 (1986)

5. Thioesters



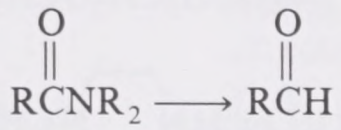
Raney Ni	Org Rxs *8* 229 (1954)
$i\text{-}Bu_2AlH$ 	CC 330 (1978)

6. Lactones

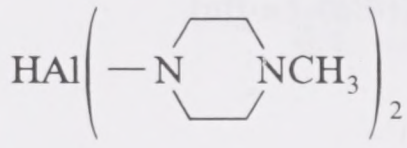
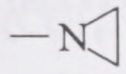
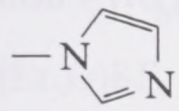
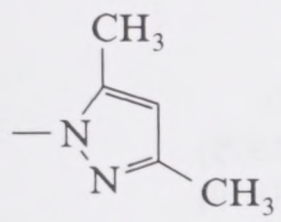
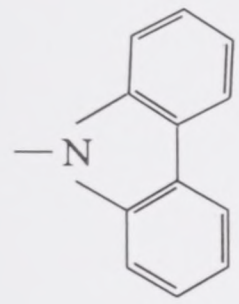
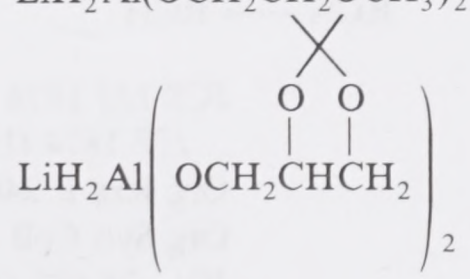


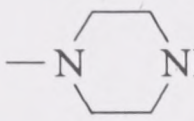
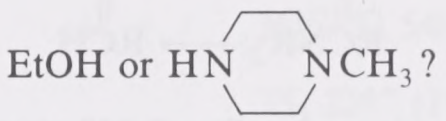
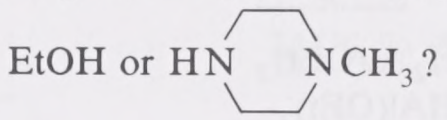
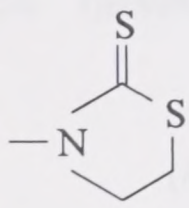
$(Me_2CHCHMe)_2BH$	JOC *51* 5032 (1986) TL *28* 1073 (1987)
$i\text{-}Bu_2AlH$	Helv *46* 2799 (1963) JOC *30* 3564 (1965); *50* 2489 (1985); *52* 4603, 4647, 4898, 5700 (1987) JACS *91* 5675 (1969); *97* 2287 (1975) Syn 617 (1975) (review) TL *27* 6341, 6345 (1986); *28* 221 (1987)
$NaH_2Al(OCH_2CH_2OCH_3)_2$, EtOH	Syn 526 (1976)

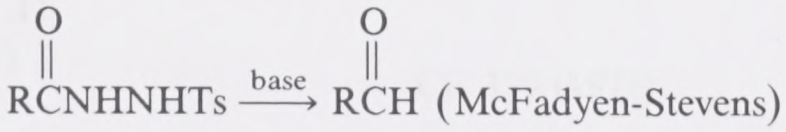
7. Amides



Review: Org Rxs *8* 252 (1954)

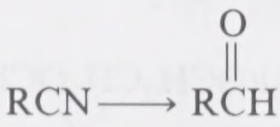
Amide	Reagent	
general	$LiH_2Al(OEt)_2$	JACS *86* 1089 (1964)
	$LiHAl(OEt)_3$	JACS *86* 1089 (1964)
		CL 875 (1975)
	$LiAlH_4$	JACS *83* 2016, 4549 (1961)
	$LiHAl(O\text{-}t\text{-}Bu)_3$	Ann *654* 119 (1962) JOC *35* 458 (1970)
	$LiAlH_4$	Org Rxs *8* 252 (1954) Angew *70* 165 (1958) Ann *654* 119 (1962) Angew Int *1* 351 (1962)
	$LiAlH_4$	Angew *70* 165 (1958) Ann *622* 37 (1959) J Med Chem *20* 510 (1977) TL *23* 525 (1982); *28* 3123 (1987)
	$LiAlH_4$	Ann *577* 11 (1952) JOC *18* 1190 (1953)
$-N(CH_3)_2$	$(Me_2CHCHMe)_2BH$	JACS *92* 7161 (1970)
	$NaAlH_4$	Tetr *25* 5555 (1969)
	$LiAlH_4$	Ber *84* 625 (1951)
	$LiH_2Al(OEt)_2$	JACS *81* 502 (1959); *86* 1089 (1964)
	$LiH_2Al(OCH_2CH_2OCH_3)_2$	JOC USSR *13* 1081 (1977)
		JOC USSR *13* 1081 (1977)
	$LiHAl(OEt)_3$	JACS *86* 1089 (1964)

Amide	Reagent	
— 	$NaH_2Al(OCH_2CH_2OCH_3)_2$, EtOH or  ?	JOC *51* 3566 (1986)
—$N(Me)CH_2CH_2NMe_2$	$NaH_2Al(OCH_2CH_2OCH_3)_2$, EtOH or  ?	JOC *51* 3566 (1986)
—NR_2 [R = Me, Et, $(CH_2)_5$]	$LiHAl(i\text{-}Bu)_2(n\text{-}Bu)$	JOC *49* 1717 (1984)
—NRPh	$LiAlH_4$	Angew *64* 458 (1952); *65* 525 (1953); *66* 174 (1954) Ber *88* 301 (1955)
	$i\text{-}Bu_2AlH$	Bull Acad Sci USSR, Div Chem Sci 2046 (1959)
—N(Me)OMe	$i\text{-}Bu_2AlH$	TL *22* 3815 (1981)
	$LiAlH_4$	TL *22* 3815 (1981); *28* 1857 (1987) JACS *107* 7790 (1985)
	$i\text{-}Bu_2AlH$	CL 1443 (1977) BCSJ *52* 555 (1979)
	$LiHAl(O\text{-}t\text{-}Bu)_3$	BCSJ *52* 555 (1979)

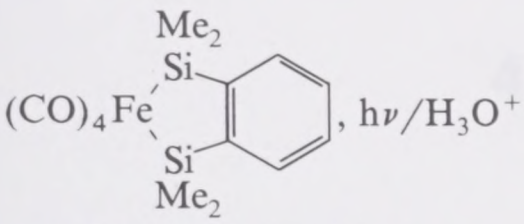


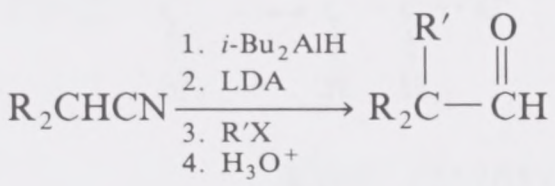
JCS 584 (1936)
Org Rxs *8* 232 (1954) (review)
JOC *26* 3664 (1961)
CC 793 (1978)

8. Nitriles



$SnCl_2$, HCl/H_2O (Stephen)	JCS *125* 1874 (1925); *127* 1874 (1925); *1686* (1956) Org Rxs *8* 246 (1954) (review) Org Syn Coll Vol *3* 626 (1955) JOC *28* 695 (1963)
$i\text{-}Pr_2AlH/H_2O$	Angew Int *12* 497 (1973)

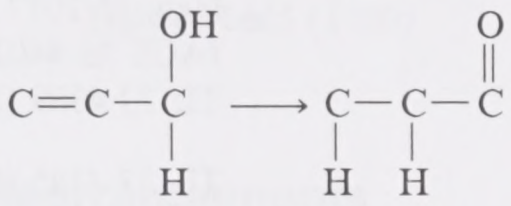
i-Bu_2AlH/H_2O	Proc Acad Sci USSR, Chem Sec *116* 879 (1958) JOC *24* 627 (1959); *29* 3046 (1964); *35* 186, 858 (1970); *37* 2138 (1972); *41* 3512 (1976); *46* 4600 (1981); *50* 2026, 2443 (1985); *52* 28, 4191 (1987) Rec Trav Chim *85* 343 (1966) Syn 617 (1975) (review) JACS *107* 7524 (1985); *108* 4614 (1986)
$LiHAl(OEt)_3/H_2O$	TL (3) 9 (1959) JACS *86* 1085 (1964)
$LiH_2Al(OEt)_2/H_2O$	JACS *86* 1085 (1964) JOC *44* 4603 (1979)
	JOC *46* 3372 (1981)
$(Et_3O)BF_4/Et_3SiH/H_2O$	CC 45 (1974) JOC *46* 602 (1981)
i-PrCl, $FeCl_3/Et_3SiH/H_2O$	JOC *46* 602 (1981)



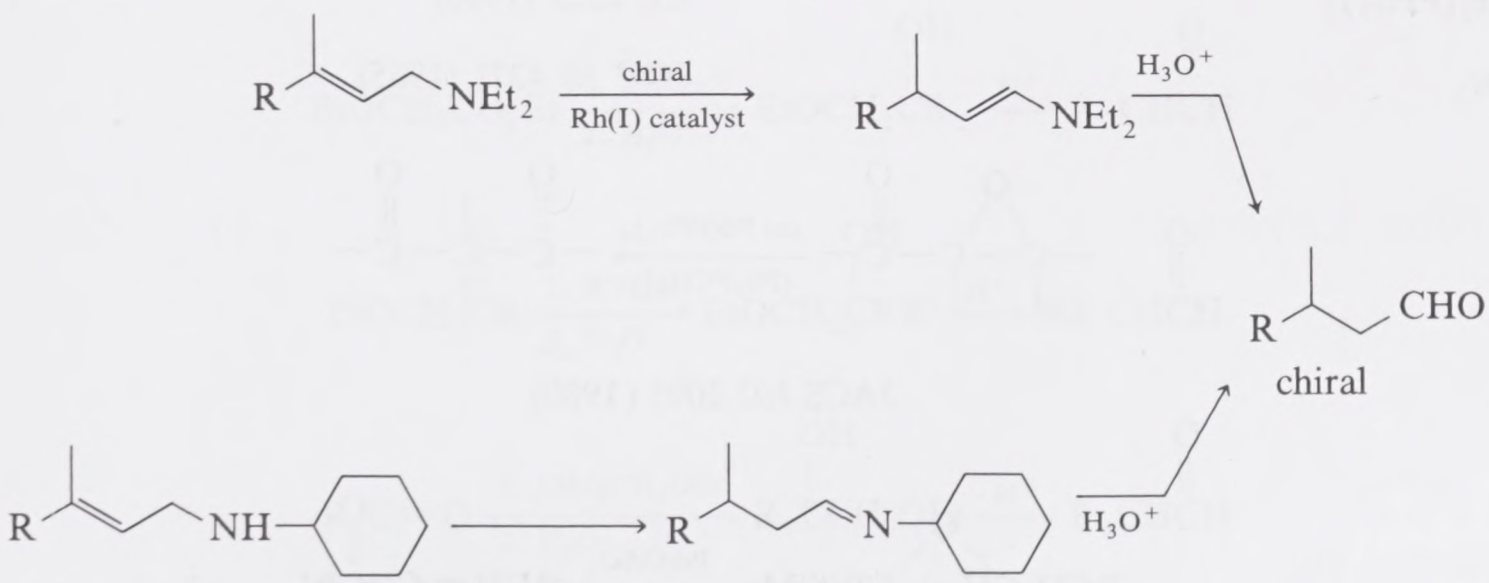
JOC *46* 5250 (1981)

4. REARRANGEMENTS

1. Isomerization

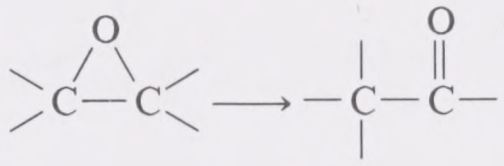


cat $Mo(N_2)_2(dppe)_2$	JOMC *252* 105 (1983)
cat $H_2Rh(PPh_3)_4$	JOMC *297* C37 (1985)
cat $RuHCl(PPh_3)_3$	TL 4133 (1974)
cat $[ClRh(CO)_2]_2$, NaOH (phase transfer)	JOC *45* 2269 (1980)
cat $Rh(ClO_4)(BINAP)(CH_3OH)_2$ (enantioselective)	TL *28* 4719 (1987)



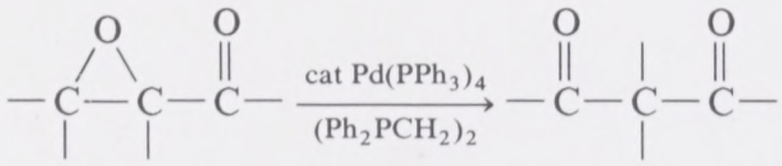
JACS *106* 5208 (1984)

2. Epoxides

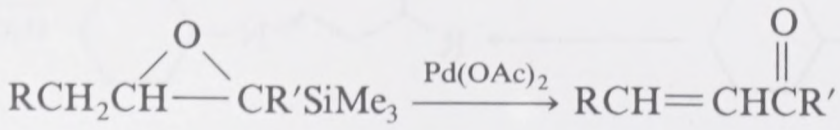


Review: Chem Rev *59* 737 (1959)

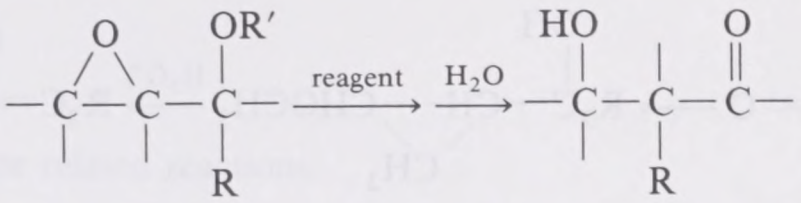
electrogenerated H^+	TL *24* 2857 (1983) JOC *50* 3160 (1985)
LiBr·HMPA, benzene	JACS *93* 1693 (1971)
LiBr or $LiClO_4$, *n*-Bu_3PO	JACS *90* 4193 (1968)
LiI	CC 1200 (1982)
NaI, CH_3I, DMF	Acta Chem Scand *18* 1551 (1964)
NaI, *n*-PrI, DMSO	CC 227 (1968)
$MgBr_2$	Helv *31* 1077 (1948) JACS *76* 4402 (1954); *79* 6283 (1957) TL *23* 4389 (1982)
$BeCl_2/AgBF_4$	TL *23* 4385 (1982)
$BF_3 \cdot OEt_2$	JACS *76* 1235 (1954); *84* 867 (1962); *105* 7352 (1983); *108* 3443, 4586 (1986) Org Syn Coll Vol *4* 375 (1963) TL *23* 4389 (1982)
$AlCl_3$	JACS *80* 1744 (1958)
cat $Co_2(CO)_8$	JOC *27* 2706 (1962)
cat $ClRh(PPh_3)_3$	JOC *42* 2299 (1977)
$NiBr_2(PPh_3)_2$	CL 1323 (1986)
$ZnBr_2$	JOC *30* 4271 (1965)



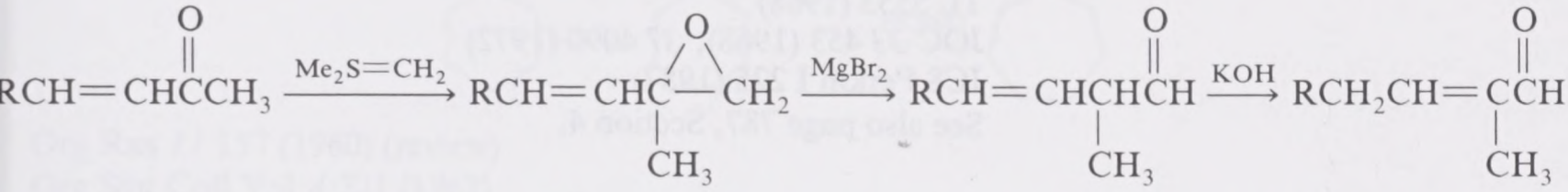
JACS *102* 2095 (1980)



CL 1997 (1982)

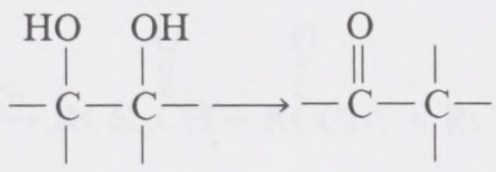


R′	Reagent	
H	$BF_3 \cdot OEt_2$	JACS *108* 3827 (1986) TL *27* 6233, 6237 (1986); *28* 5891 (1987) CL 113 (1987)
$SiMe_3$	$TiCl_4$ $(i\text{-PrO})_2TiCl_2$ cat Me_3SiX (X = I, OTf)	JACS *108* 3827 (1986) TL *27* 6233, 6237 (1986) TL *28* 3515 (1987)



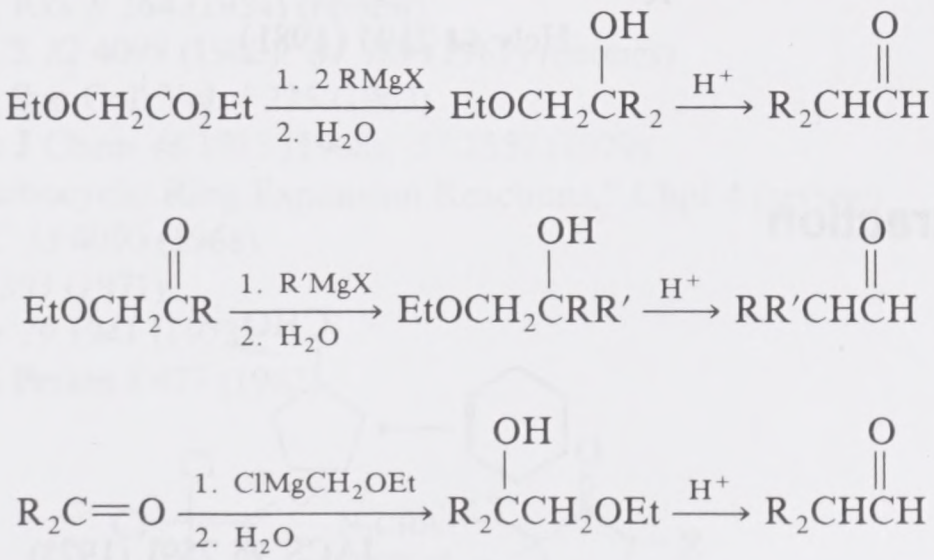
Helv *63* 1665 (1980)

3. Pinacol and Related Rearrangements

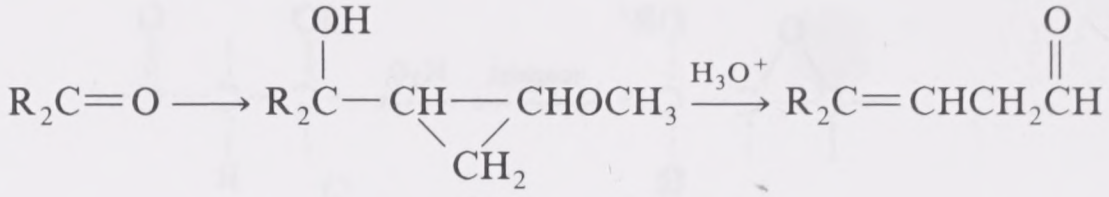


Reviews:

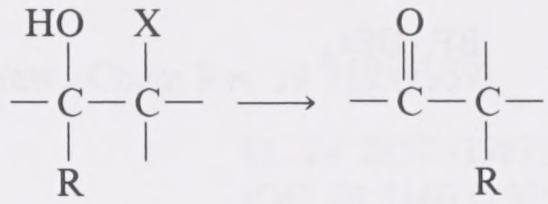
Org Syn Coll Vol *1* 462 (1941)
Quart Rev *14* 357 (1960)
"Molecular Rearrangements," Interscience, New York (1963), Vol 1, Chpt 1



JACS *61* 2134 (1939); *68* 2339 (1946)
BSCF 459 (1959)

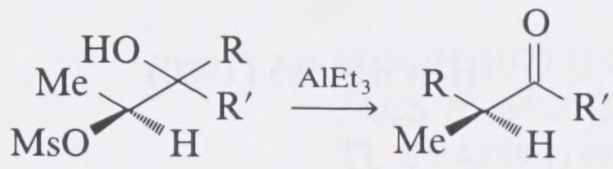


TL 3685 (1975)



X = Cl, OTs

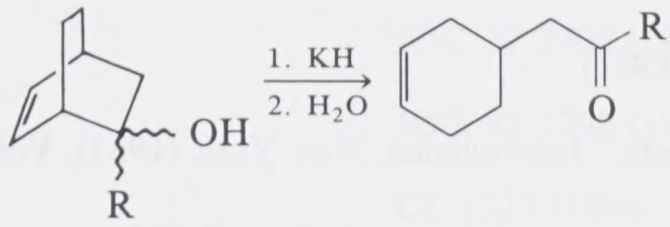
JACS *83* 1251 (1961)
CC 565 (1968)
TL 5553 (1968)
JOC *33* 453 (1968); *37* 4090 (1972)
JCS Perkin I 225 (1987)
See also page 787, Section 4.



R = aryl, vinylic

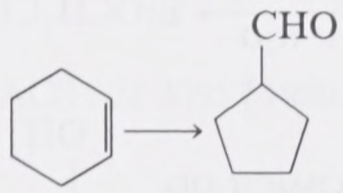
TL *24* 4997 (1983); *25* 1817 (1984)

4. Ring Opening



Helv *64* 2193 (1981)

5. Ring Contraction

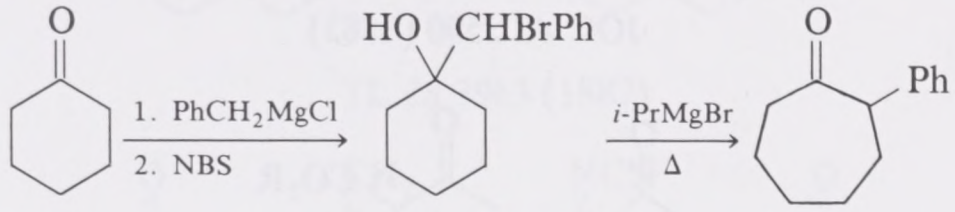


$Hg(ClO_4)_2$, H_2O	JACS *95* 2591 (1973)
$Tl(ClO_4)_3$, H_2O	JACS *95* 2591 (1973)
$Tl(NO_3)_3$, CH_3OH/H_3O^+	TL 5275 (1970); 4753 (1971)

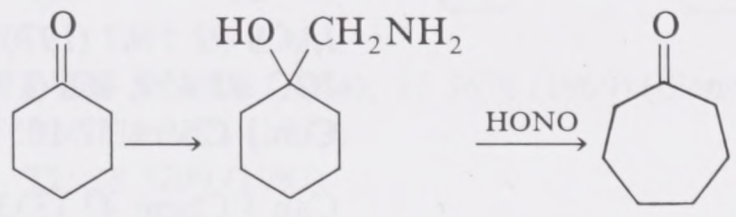
6. Ring Expansion

See page 733, Section 12 for related reactions.

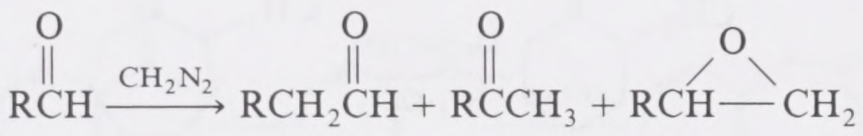
Review: "Carbocyclic Ring Expansion Reactions," Academic Press, New York (1968)

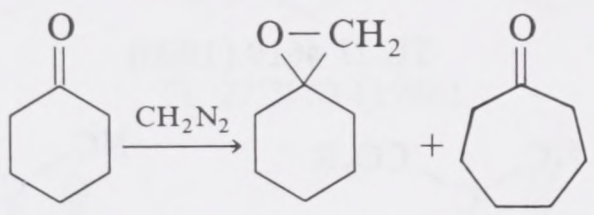


TL 5327 (1967)
JOC *33* 453 (1968)

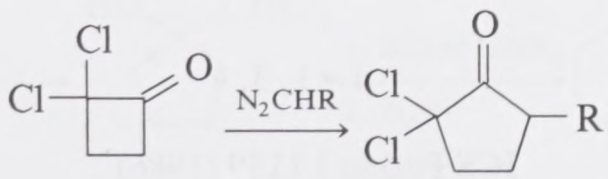


Org Rxs *11* 157 (1960) (review)
Org Syn Coll Vol *4* 221 (1963)
JCS 2513 (1965)
"Carbocyclic Ring Expansion Reactions," p 74 (review)
JOC *33* 2069 (1968); *39* 914 (1974); *43* 1050 (1978); *45* 185 (1980); *47* 2685 (1982); *52* 2602 (1987)
Angew Int *10* 491 (1971)
Tetr *29* 1941 (1973)
TL 4929 (1973)
Can J Chem *57* 1557 (1979)

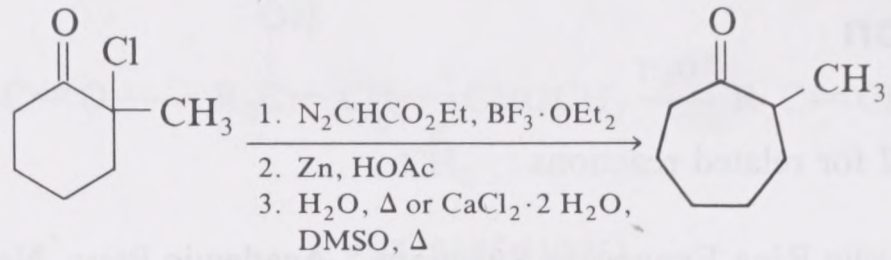




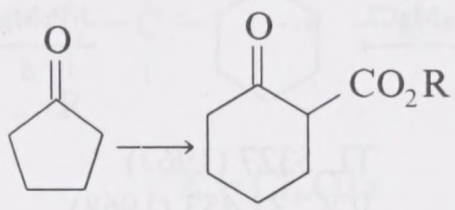
Newer Methods Prep Org Chem *1* 513 (1948) (review)
Org Rxs *8* 364 (1954) (review)
JACS *82* 4099 (1960); *84* 989 (1962) (enones)
Org Syn Coll Vol *4* 225 (1963)
Can J Chem *46* 1913 (1968); *57* 1557 (1979)
"Carbocyclic Ring Expansion Reactions," Chpt 4 (review)
JOC *33* 4090 (1968)
TL 393 (1971)
Tetr *29* 1941 (1973)
JCS Perkin I 477 (1982)



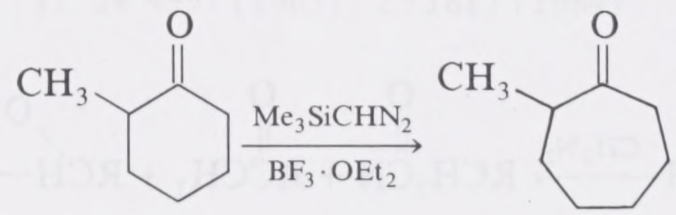
JACS *101* 4003 (1979); *105* 2435 (1983)
JOC *45* 2036 (1980); *48* 4763 (1983); *50* 3957 (1985)



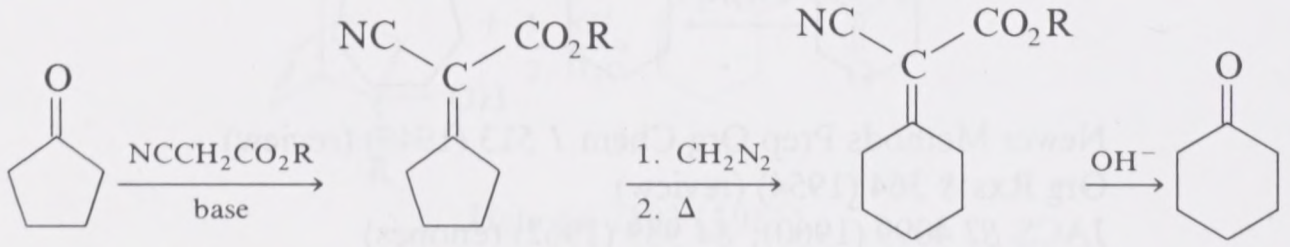
JOC *48* 2590 (1983)



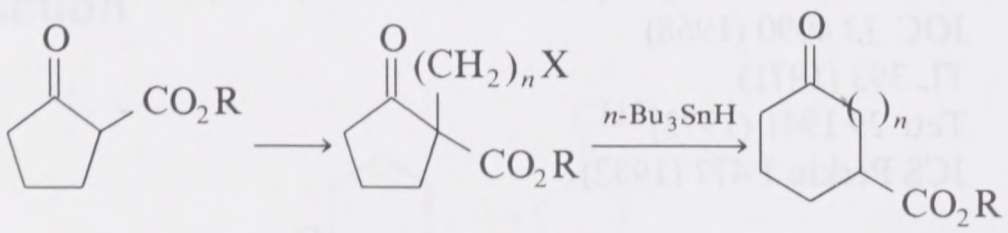
N_2CHCO_2Et, $(Et_3O)BF_4$	JACS *92* 5767 (1970) JOC *42* 459, 466 (1977) Can J Chem *57* 1557 (1979)
N_2CHCO_2R, $BF_3 \cdot OEt_2$	Can J Chem *42* 1333 (1964) TL 4937 (1973) Syn Commun *5* 125 (1975); *8* 413 (1978) JOC *52* 3455 (1987)
N_2CHCO_2R, $SbCl_5$	JOC *42* 459 (1977); *50* 3957 (1985)
N_2CHCO_2R, base/Δ, hν, H^+ or transition metal catalyst	See page 642, Section 7.16.



TL *21* 4619 (1980)

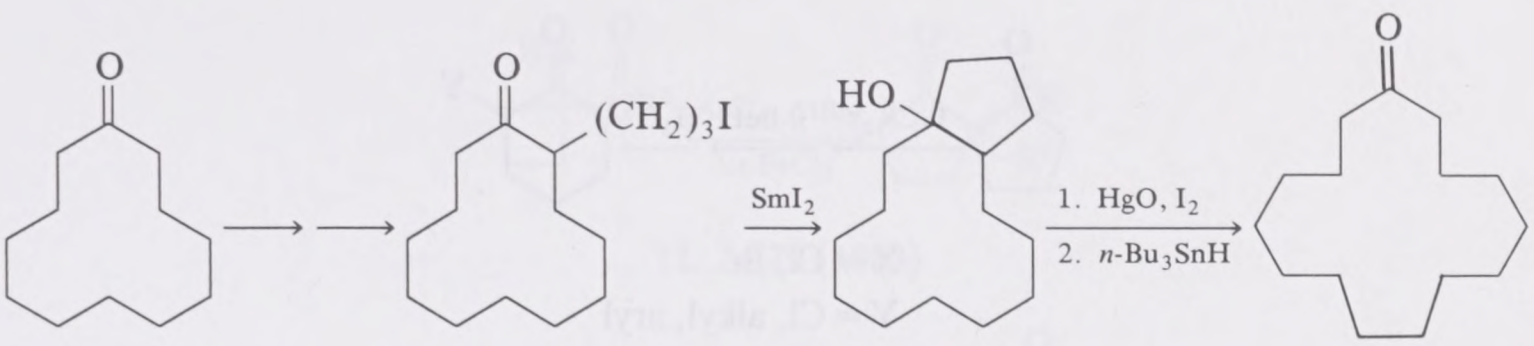


J Chem Res (S) 436 (1978)

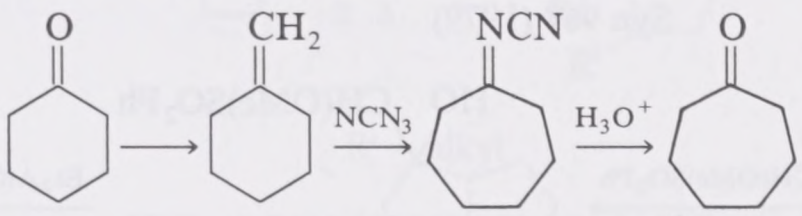


$n = 1, 3, 4$

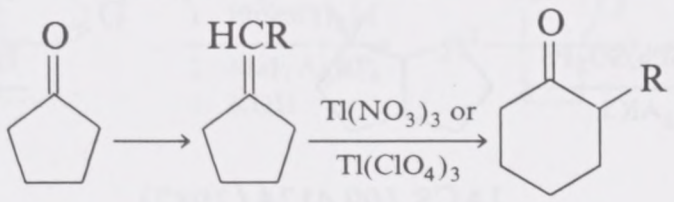
JCS Perkin I 1139 (1986)
JACS *109* 3493, 6548 (1987)
CC 666 (1987)



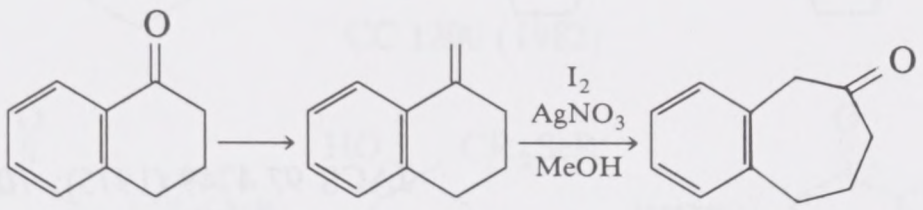
TL *28* 3963 (1987)



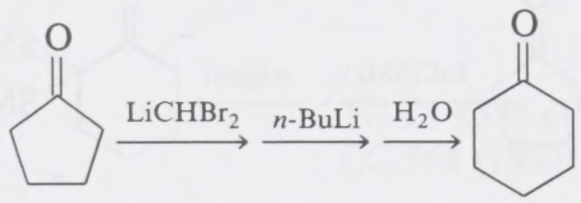
JACS *86* 4506 (1964); *91* 3676 (1969) (diene)
JOC *38* 2821 (1973)
TL *28* 3209 (1987)



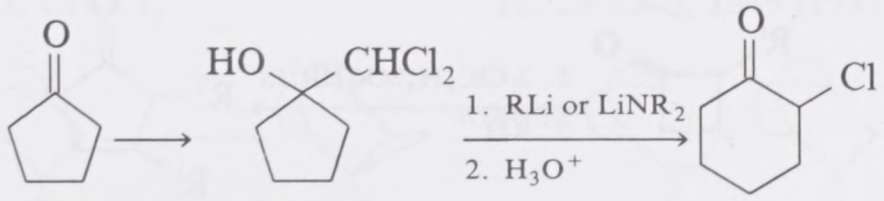
JACS *95* 2591 (1973)
JOC *38* 3455 (1973)
TL 1827 (1977)



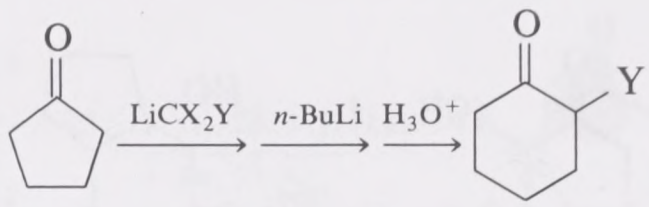
TL *27* 3783 (1986)



JOMC *40* Cl (1972); *97* 325 (1975)
Compt Rend *276* 433 (1973)
JACS *96* 6510 (1974); *106* 3030 (1984)
TL 2617 (1976); *28* 585 (1987)
BCSJ *50* 1592 (1977)



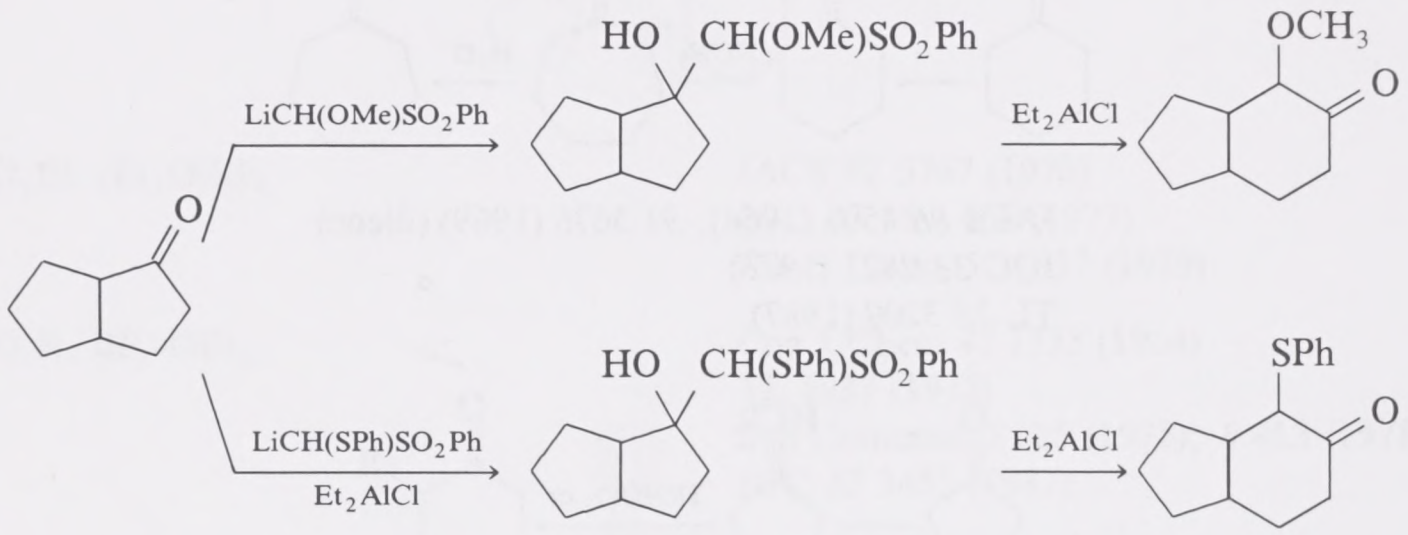
Ber *106* 2626 (1973)
BCSJ *50* 1592 (1977)



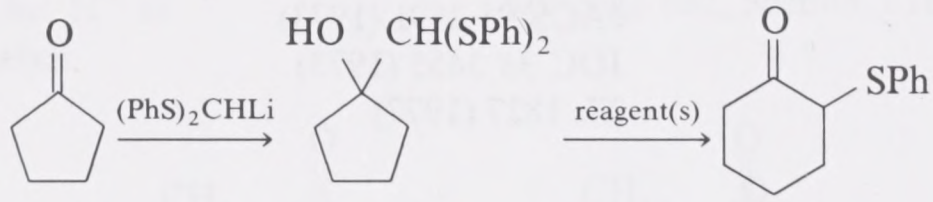
X = Cl, Br

Y = Cl, alkyl, aryl

JOMC *40* Cl (1972); *97* 325 (1975)
Compt Rend C *276* 433 (1973)
Syn 968 (1979)

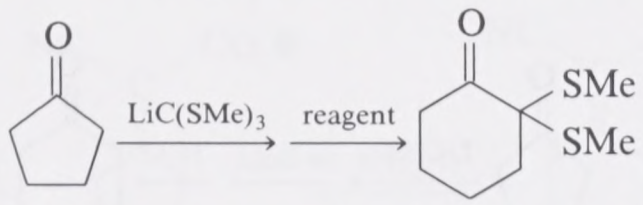


JACS *109* 4124 (1987)



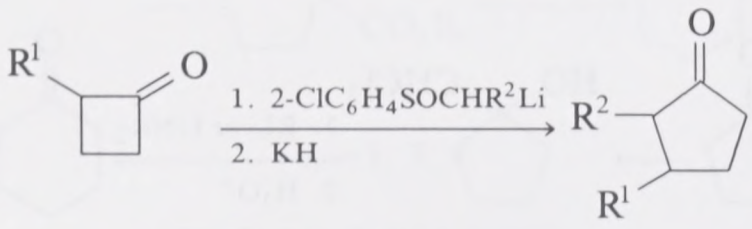
Reagent(s)

CuO_3SCF_3	JACS *97* 4749 (1975); *107* 4339 (1985)
2 RLi/H_2O	TL *28* 2203 (1987)



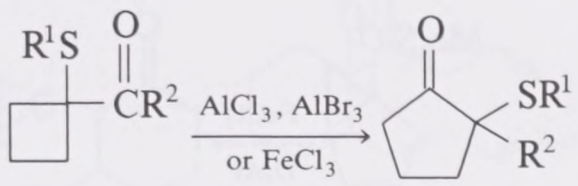
Reagent

$HgCl_2$	TL *21* 4301 (1980)
$CuBF_4 \cdot 4\ CH_3CN$	JOC *49* 608 (1984)
$CuClO_4 \cdot 4\ CH_3CN$	JOC *49* 608 (1984); *50* 1573 (1985)

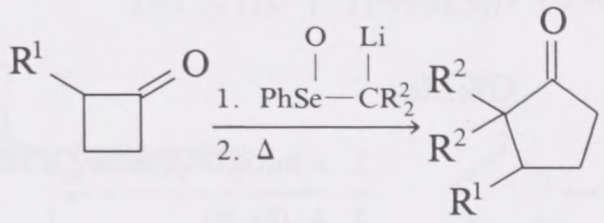


R^1 = aryl, vinylic

JOC *52* 774 (1987)

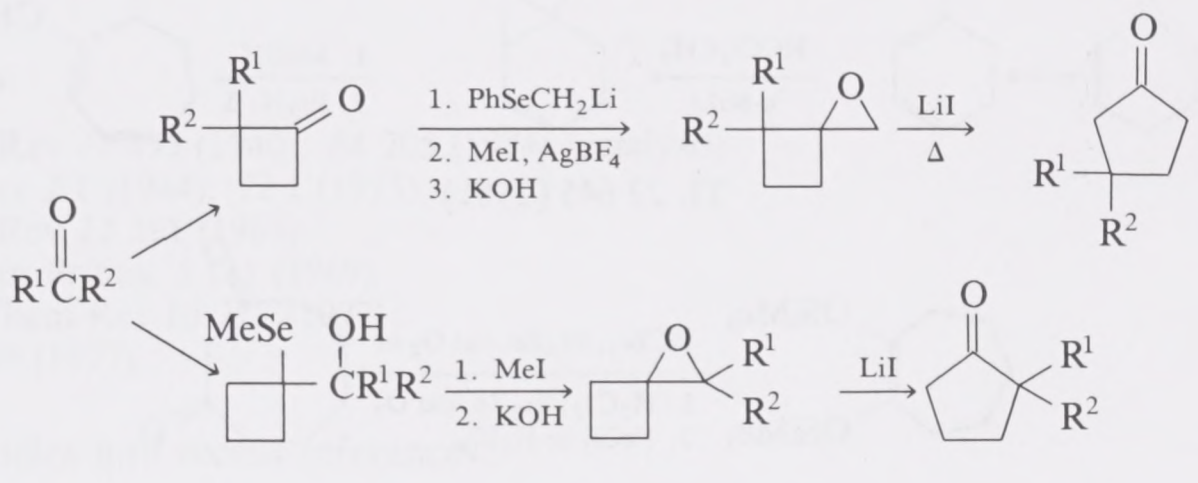


TL *24* 79 (1983)

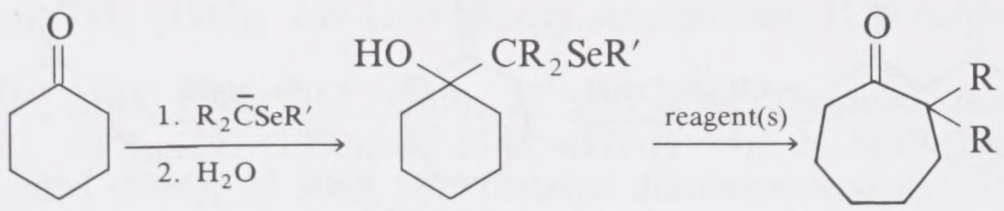


R^1 = alkyl

JOC *48* 2098 (1983); *52* 774 (1987)

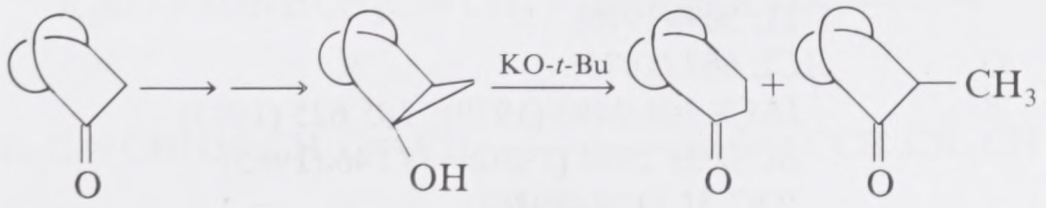


CC 1200 (1982)

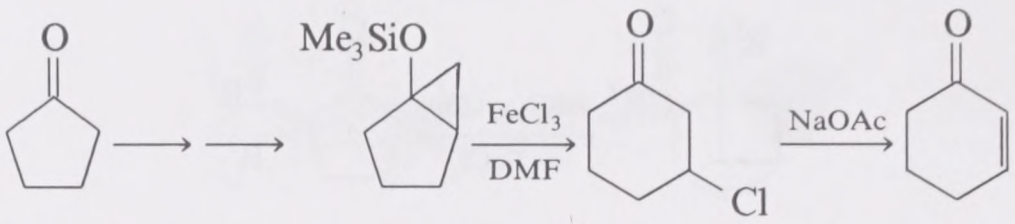


Reagent(s)

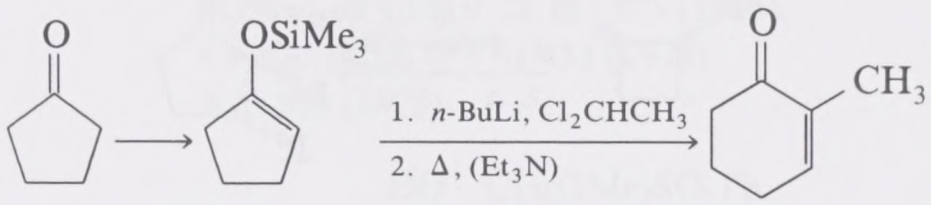
$MeOSO_3F$	TL *23* 4385 (1982) CC 564 (1982)
$AgBF_4$	TL *23* 983, 4385 (1982); *28* 1545 (1987)
$TlOEt, HCCl_3$	TL *23* 4385 (1982); *25* 2713, 5043 (1984); *28* 1545, 1549 (1987) JOC *50* 5200 (1985) (enones) CC 702 (1986)
$KOH, (PhCH_2NEt_3)Cl, CH_2Cl_2$	TL *28* 1545, 1549 (1987)



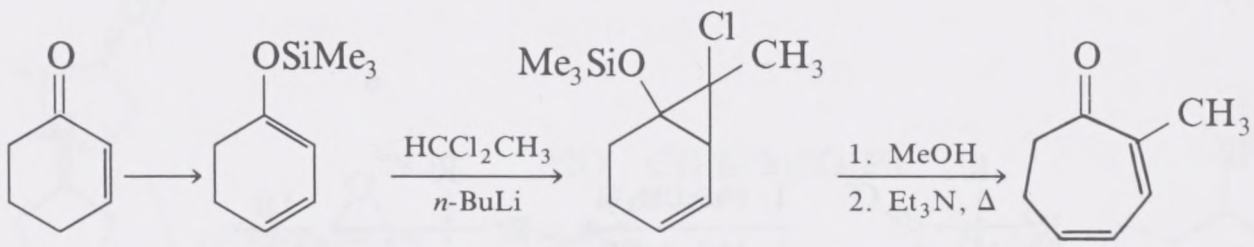
Can J Chem *58* 2730 (1980)



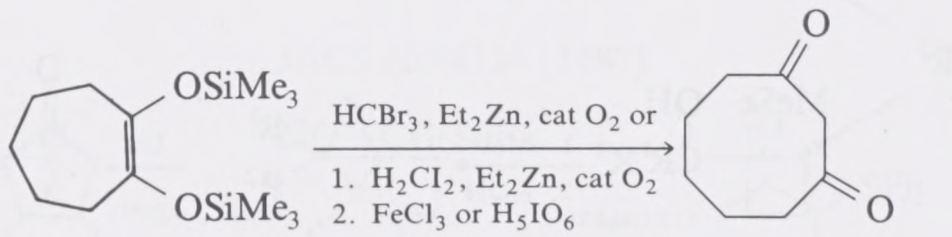
JOC *41* 2073 (1976); *44* 4481 (1979); *51* 3405 (1986)
Org Syn *59* 113 (1980)



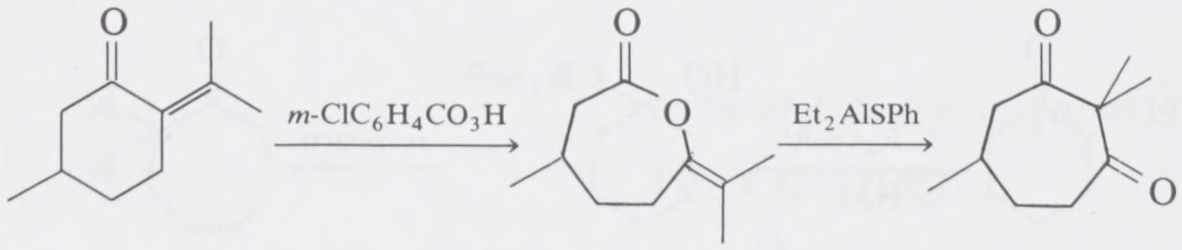
Syn 289, 291 (1981)
JACS *109* 3025 (1987)



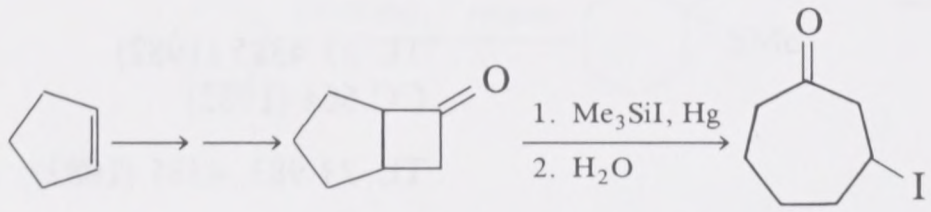
TL *22* 645 (1981)



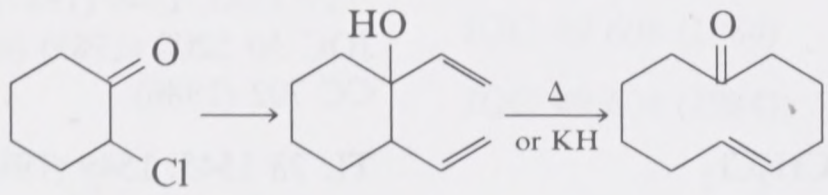
JOC *52* 3603 (1987)



TL *23* 99 (1982)

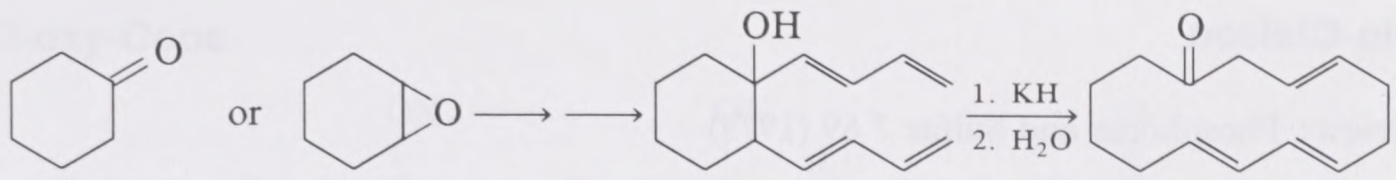


TL *21* 2639 (1980)



TL 509 (1970)
CL 667 (1973)
JACS *101* 2493 (1979); *105* 625 (1983)
BCSJ *53* 2958 (1980); *58* 146 (1985)
JOC *51* 1124 (1986)

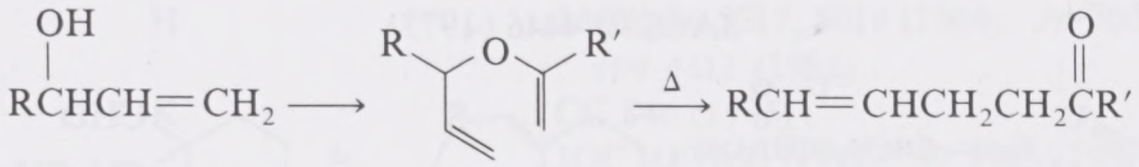
See page 639, Sections 7.7 and 7.8.



TL *22* 2471 (1981)
Tetr *37* 3967 (1981)
JACS *107* 7771 (1985)

7. Electrocyclic Rearrangements

7.1. Claisen



Reviews:

Chem Rev *27* 495 (1940); *84* 205 (1984) (catalysis)
Org Rxs *2* 1 (1944); *22* 1 (1975)
Quart Rev *22* 391 (1968)
Chem in Britain *5* 111 (1969)
Acct Chem Res *10* 227 (1977)
Syn 589 (1977)

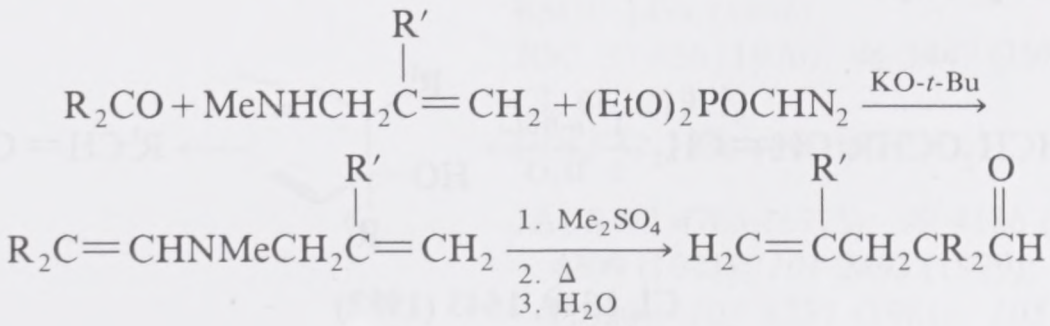
Key articles and recent references:

JACS *83* 198 (1961); *89* 4559 (1967); *92* 3126 (1970); *93* 5805, 5813 (1971); *103* 6983, 6984 (1981); *104* 4972 (1982) (carbanion acceleration); *106* 6868 (1984); *107* 2730, 5572 (anionic oxy-Claisen), 7352 (1985); *109* 1160 (alkoxy substitution), 1170 (substituent effects), 3987 (1987)
TL 493 (1961); 2145, 3243, 3253 (1969); *22* 3985 (1981) (organoaluminum promotion); *23* 3143 (1982); *24* 3, 4397 (1983); *25* 1543, 4579 (1984); *26* 3655 (1985); *27* 6267 ($PdCl_2$ catalyzed), 6311 (1986); *28* 3065, 5879 (catalyst diastereoselectivity) (1987)
Helv *50* 2091, 2095 (1967); *61* 3075 (1978)
CC 264 (1969)
Org Syn Coll Vol *5* 25 (1973)
JOC *48* 1829, 3876 (1983); *49* 2347 (1984); *52* 5190, 5742 (carbanion acceleration) (1987)

Heteroatom systems:

Fortschr Chem Forsch *16* 75 (1970)

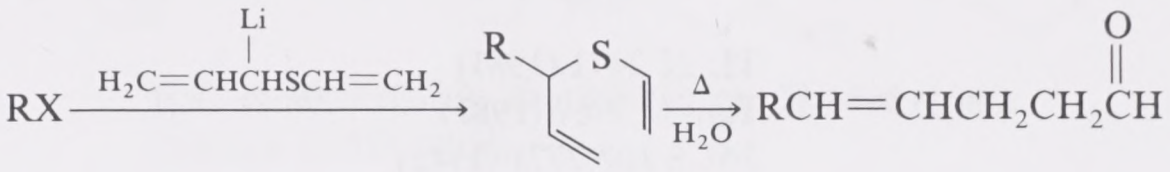
7.2. Amino-Claisen



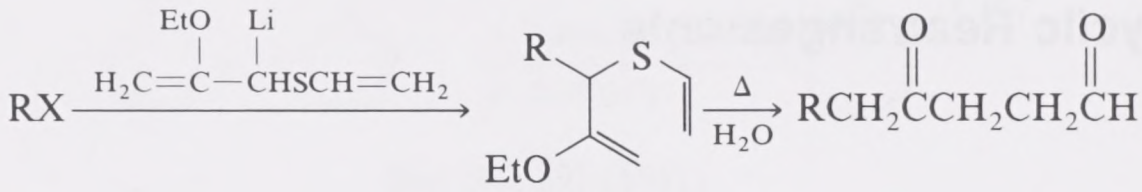
TL *25* 2303 (1984)

7.3. Thio-Claisen

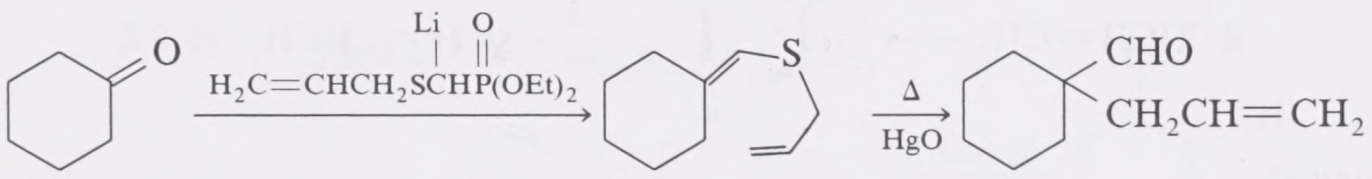
Review: Phosphorus and Sulfur *7* 69 (1979)



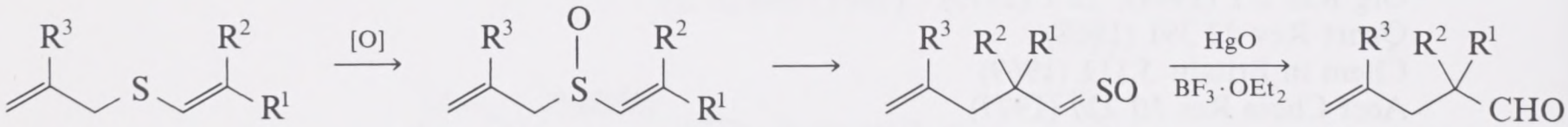
JACS *95* 2693 (1973)



JACS *95* 4446 (1973)



JACS *92* 5522 (1970)



JACS *107* 6731 (1985)

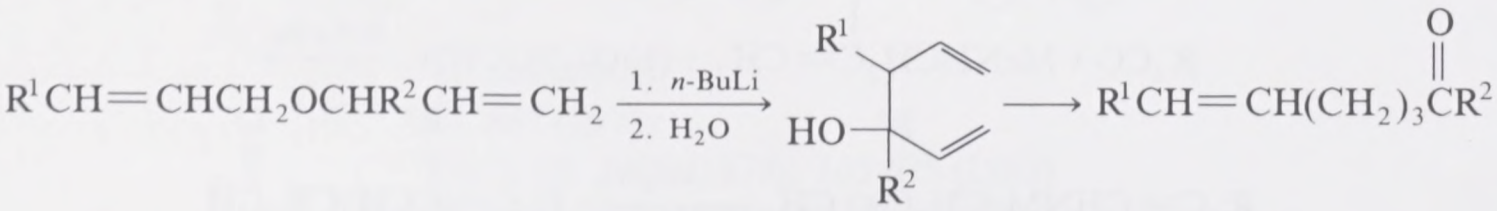
7.4. Claisen–Cope

CC 947 (1967); 1657 (1968); 248 (1972)
JACS *91* 3281 (1969)
Helv *53* 1145 (1970)
JCS C 220 (1970)
JCS Perkin I 2634, 2738, 2741 (1973)
Syn 532 (1978)
TL *23* 3839 (1982)

7.5. Cope–Claisen

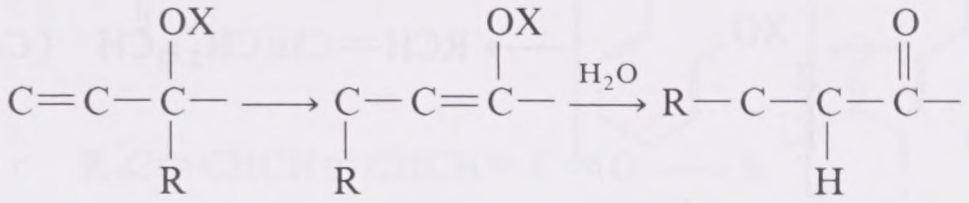
JACS *101* 1611 (1979); *102* 880, 6576 (1980); *103* 1853 (1981); *104* 7181 (1982)
JOC *47* 5229 (1982); *49* 3278 (1984)

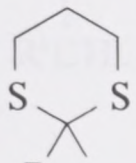
7.6. 2,3-Wittig-oxy-Cope



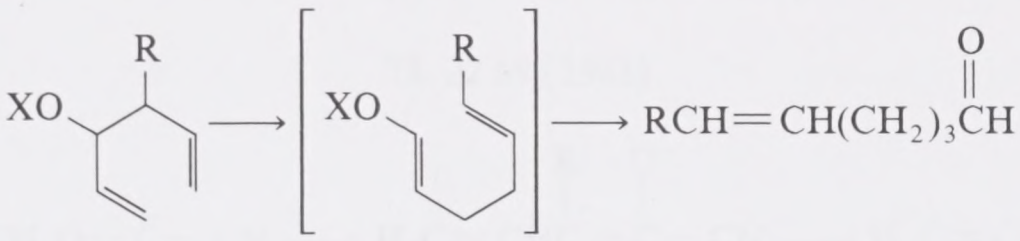
CL 1349, 1643 (1982)
TL *23* 3931 (1982)

7.7. 1,3-oxy-Cope

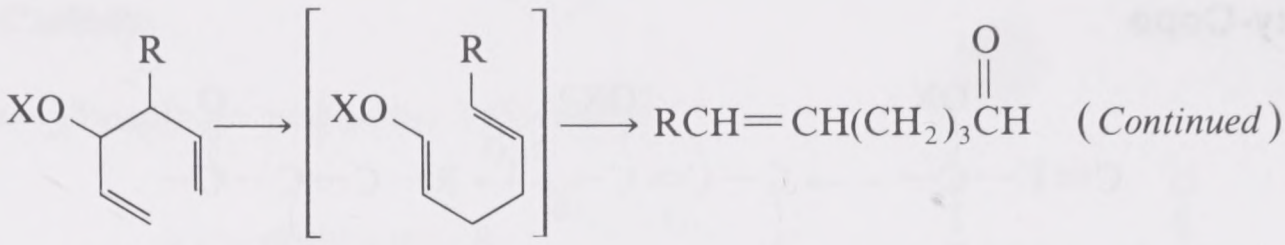


R	X	
benzylic	K	CC 846 (1976) JOC *43* 1050 (1978); *45* 185 (1980); *47* 798 (1982) JACS *103* 7661 (1981); *104* 4411 (1982)
	$SiMe_3$	CC 846 (1976) JOC *47* 798 (1982)
allylic	H	JACS *86* 5017, 5019 (1964); *94* 7074 (1972); *104* 4411 (1982)
	K	CC 846 (1976) JOC *43* 1050 (1978); *52* 3798 (1987) JACS *104* 891 (1982)
	$SiMe_3$	JACS *94* 7074 (1972); *96* 200 (1974) CC 846 (1976) JOC *41* 1233 (1976); *42* 280 (1977); *52* 3798 (1987)
	K	JOC *43* 4903 (1978)

7.8. 3,3-oxy-Cope



X	
H	JACS *86* 5017, 5019 (1964); *87* 1150 (1965); *89* 3462 (1967); *90* 4729, 4730, 4732, 6141 (enynol) (1968); *92* 2404 (1970) (enynol); *94* 4779, 7074 (1972); *95* 5281 (1973); *102* 3972 (1980); *106* 3869 (1984) (enynol); *108* 6343 (1986) TL 6115 (1966); 1337, 1341, 2681 (1969); 509 (1970); *23* 4263 (1982) [$Hg(O_2CCF_3)_2$ promoted] CC 143 (1968) (enynol); 491 (1974) BSCF 1491 (1968) JOC *35* 856 (1970); *46* 5447 (1981); *47* 4815 (1982) CL 667 (1973) BCSJ *53* 2958 (1980)
alkali metal	JACS *97* 4765 (1975); *99* 4186 (1977); *100* 2242, 4309 (1978); *101* 2493 (1979); *102* 774, 2463, 3972 (1980); *103* 6235 (1981); *105* 625 (1983); *106* 4038, 7614 (1984); *108* 7873 (1986)



(*Continued*)

X

Angew Int *15* 437 (1976)
Ber *112* 1420 (1979)
JOC *46* 9, 2199, 4272, 5447 (1981); *47* 2268, 3190 (1982); *50* 5747 (1985); *51* 1124 (1986); *52* 3798 (1987)
TL *22* 3167, 4651 (1981); *24* 2931 (1983); *25* 5103 (1984); *28* 31, 5351 (1987)
Tetr *38* 2195 (1982)
J Ind Chem Soc *61* 99 (1984) (review)
BCSJ *58* 146 (1985)

SiR_3

JACS *94* 7074 (1972); *95* 5281 (1973); *96* 200 (1974)
JOC *41* 1233 (1976); *46* 5447 (1981); *52* 622, 3798 (1987)

R

JOC *46* 5447 (1981)

7.9. oxy-Cope–Claisen

JOC *46* 5448 (1981)

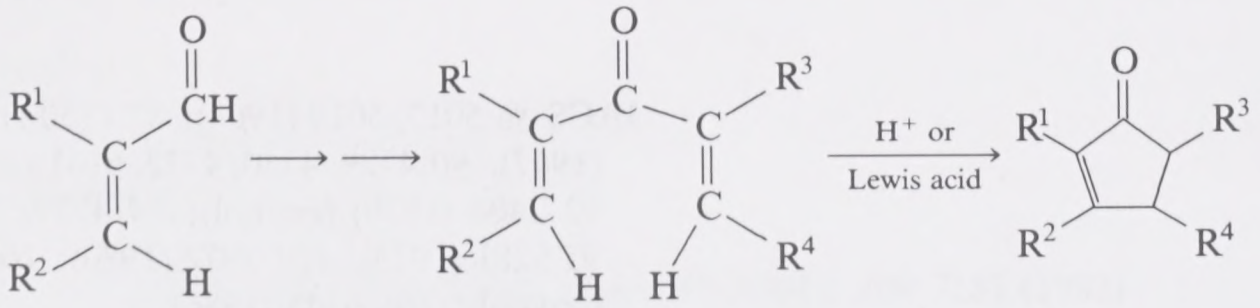
7.10. oxy-Cope–Cope

JOC *46* 5448 (1981)

7.11. Carroll

See page 775.

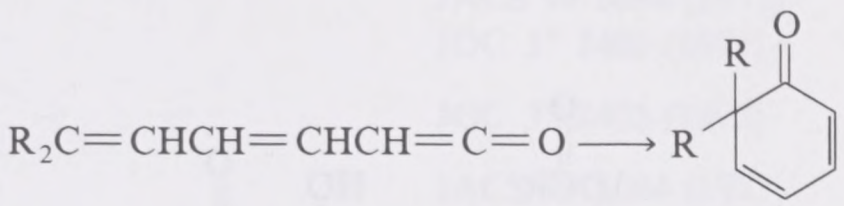
7.12. Nazarov



JCS 1430 (1952)
J Gen Chem USSR *27* 693 (1957); *30* 765 (1960)
Helv *54* 2913 (1971); *66* 2377, 2397 (1983) (both Si-directed)
JCS Perkin I 2271 (1972); 1026 (1973)
BCSJ *53* 169 (1980)
JOC *46* 3696 (1981)
JACS *104* 2642 (1982) (Si-directed)
Syn 429 (1983) (review)
TL *27* 2801, 5947 (Sn-directed) (1986)
Tetr *42* 2821 (1986) (Si-directed)

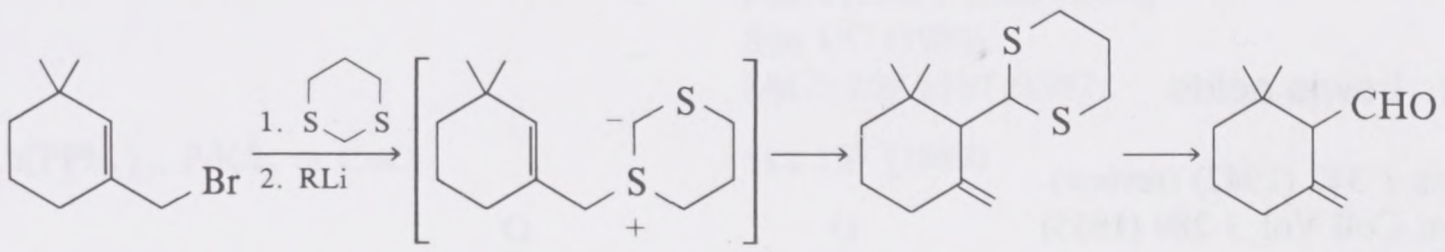
See page 658, Section 4; and page 661, Section 5 for related reactions.

7.13. Electrocyclization

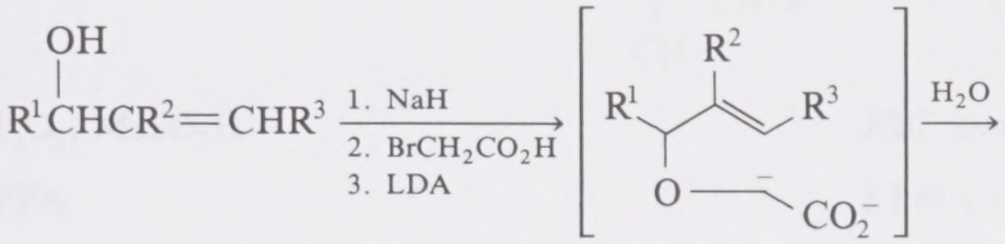


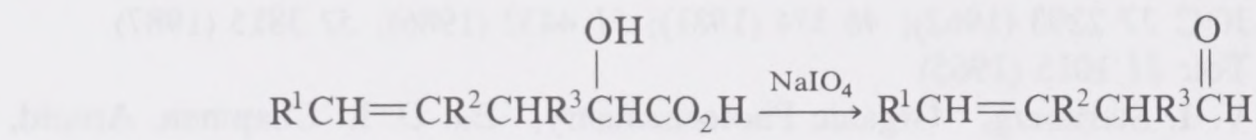
CC 1728 (1987)

7.14. 2,3-Sigmatropic Rearrangements

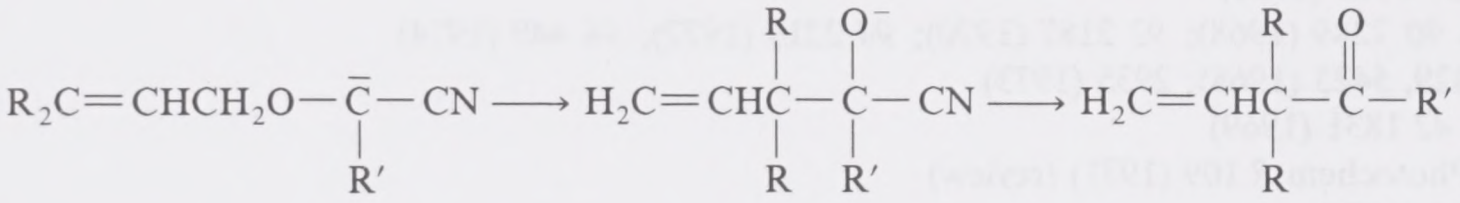


CC 757 (1972)

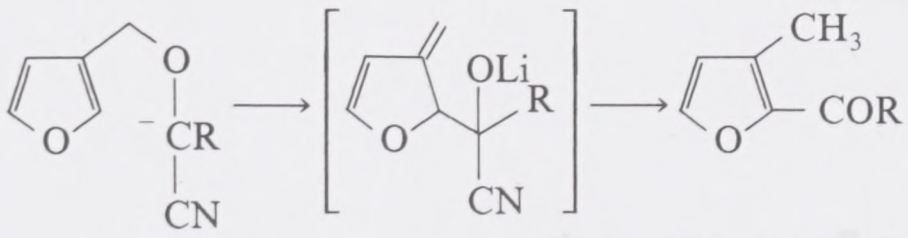




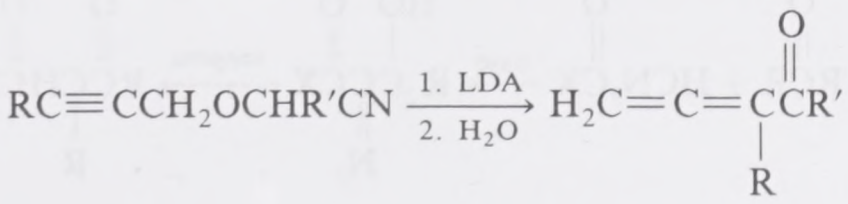
TL *22* 69 (1981)



TL *24* 2077 (1974)

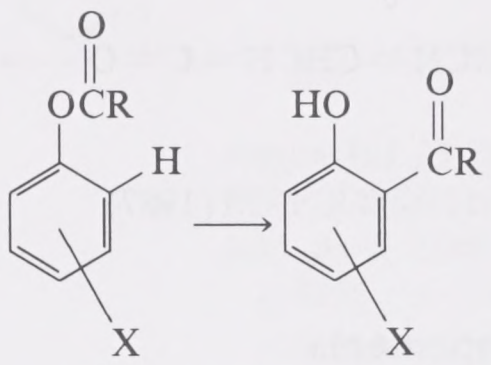


Syn Commun *7* 113 (1977)



Syn Commun *7* 273 (1977)

7.15. Fries Rearrangement



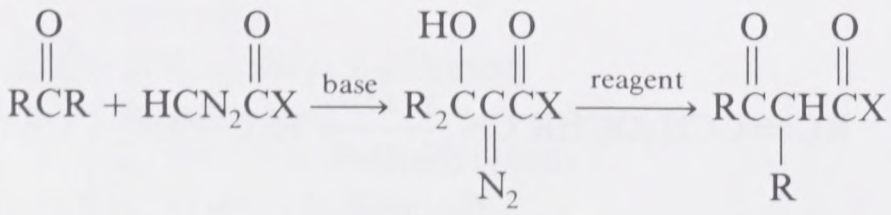
7.15.1. Lewis acids

Org Rxs *1* 342 (1942) (review)
Org Syn Coll Vol *3* 280 (1955)
"Friedel-Crafts and Related Reactions," Ed. G. A. Olah, Interscience, New York (1964), Vol 3, Chpt 33
TL *23* 3299 (1982) (meta-Fries)
Ber *115* 1089 (1982) (equilibrium)

7.15.2. Photochemical

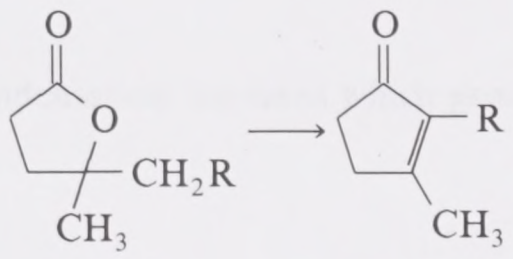
Proc Chem Soc 217 (1960)
JOC *27* 2293 (1962); *46* 374 (1981); *51* 4432 (1986); *52* 3815 (1987)
Tetr *21* 1015 (1965)
V. I. Sternberg, "Organic Photochemistry," Ed. O. L. Chapman, Arnold, New York (1967), Vol 1, Chpt 3 (review)
Chem Rev *67* 599 (1967) (review)
Helv *51* 1980 (1968)
JACS *90* 7249 (1968); *92* 2187 (1970); *94* 2219 (1972); *96* 449 (1974)
TL 3429, 5423 (1968); 2935 (1973)
BCSJ *42* 1831 (1969)
Adv Photochem *8* 109 (1971) (review)
CC 289 (1974)
BSCF 785 (1977)
Syn Commun *9* 877 (1979)
Ber *113* 261 (1980)
Syn 882 (1981)

7.16. Miscellaneous Rearrangements



X = R, OR

Reagent	
Δ	JACS *94* 8084 (1972) JOC *37* 2405 (1972)
hν	JOC *37* 2405 (1972)
H_2SO_4	JACS *94* 8084 (1972)
HCl	Ann 1767 (1974) J Chem Res (S) 76, 142 (1979) JCS Perkin I 1822 (1977)
cat $Rh_2(OAc)_4$	CC 959 (1979) JCS Perkin I 2566 (1981) Syn 197 (1983) JACS *109* 6187 (1987)
cat $ClRh(PPh_3)_3$, $PdCl_2$ or $CoCl_2$	Syn 197 (1983)



P_2O_5, $MeSO_3H$	JOC *38* 4071 (1973)
PPA	J Ind Chem Soc *34* 178 (1957)

5. CONDENSATION REACTIONS

See also page 167, Section 3 for condensation reactions which generate a carbon-carbon double bond.

1. Acetoacetic Ester

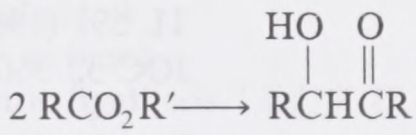
See also page 768, Section 20.

Org Rxs *1* 266 (1942) (review)
JOC *51* 268 (1986)

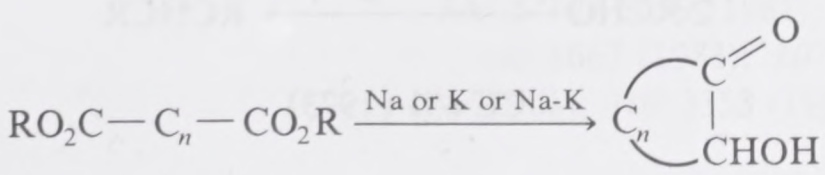
2. Acyloin

Reviews:

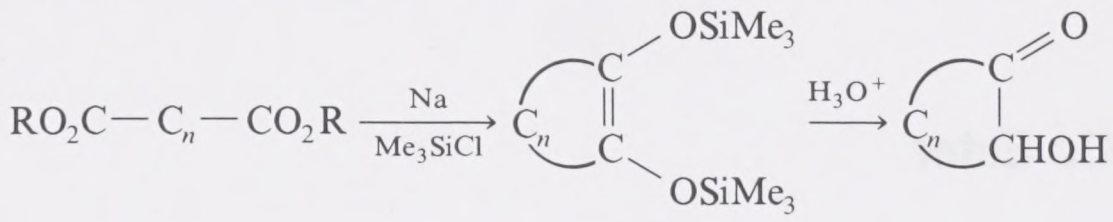
Org Rxs *4* 256 (1948); *23* 259 (1976)
Chem Rev *64* 573 (1964)
Syn 236 (1971) (Na, Me_3SiCl)
JOC *40* 393 (1975) (mechanism)



Na, ether	JACS *52* 3988 (1930); *53* 750 (1931)
Na, NH_3	JOC *5* 362 (1940)
Na, zylene	JACS *57* 2303 (1935) Org Syn Coll Vol *2* 114 (1943) JCS C 2617 (1968)

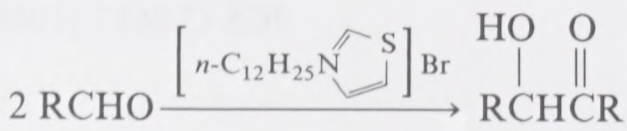


n	
2	JACS *72* 983 (1950) JOC *31* 2017 (1966) TL 1529 (1969)
3	JACS *72* 3376 (1950), *75* 3997, 6231 (1953)
4	JACS *72* 3376 (1950); *79* 6050 (1957)
7, 8, 10, 12, 14, 18	Helv *30* 1741 (1947)
7–12	JACS *88* 4267 (1966)
7–16	Helv *30* 1822 (1947)
8	JACS *74* 3626 (1952) Org Syn Coll Vol *4* 840 (1963)
8, 14, 16	Helv *30* 1815 (1947)



Review: Syn 236 (1971)

n	
2	Ber *100* 3820 (1967) TL 587, 3319 (1968); *28* 4669 (1987) Org Syn *57* 1 (1977)
3	Ber *97* 1383 (1964) JOC *35* 1272 (1970)
4	Ber *97* 1383 (1964) TL 591 (1968) JACS *107* 686 (1985)
5	Ber *100* 3820 (1967) TL 591 (1968) JOC *52* 3603 (1987)
8	Ber *97* 1383 (1964) JACS *106* 6006 (1984)
10	JACS *106* 6006 (1984)
22	JACS *109* 7477 (1987)



CC 891 (1973)

3. Dieckmann

Org Syn Coll Vol *2* 116 (1943)
Org Rxs *15* 1 (1967) (review)

4. Mannich

See page 429, Section 4.

5. Michael

See page 792, Section 2.

6. Thorpe–Ziegler

JACS *81* 4074 (1959); *106* 6006 (1984)
Org Rxs *15* 1 (1967) (review)

7. Aldol and Related Reactions

For aldol condensation followed by dehydration see page 167, Section 3.

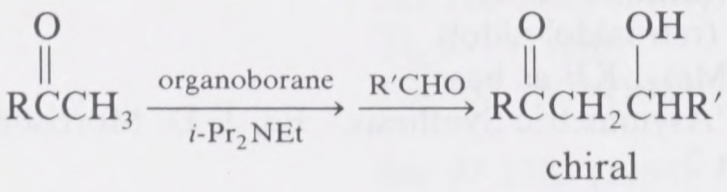
General references:

Org Rxs *16* 1 (1968) (aldol); *28* 203 (1982) (directed aldol)
BCSJ *53* 1417 (1980) (inter- and intramolecular aldol promoted by R_2AlOPh, pyridine)
Can J Chem *59* 3303 (1981) (thermal crossed aldol)
TL *22* 429 (1981) (intramolecular regioselectivity); *23* 4891 (1982) (transition state stereoselectivity)
Tetr *38* 2279 (retroaldol-aldol), 2939 (1982) (intramolecular)
JACS *104* 872 (1982) (intramolecular)
JOC *47* 1349 (1982) (intramolecular)
BCSJ *55* 3931 (1982) (retroaldol-aldol)
Syn 294 (1983) [$Si(OMe)_4$, KF as base]
C. H. Heathcock in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 2

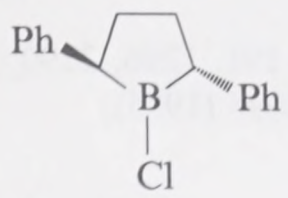
7.1. Metal Enolates

Li	JOC *45* 1066, 3846 (1980); *46* 191, 1296, 2290 (1981); *48* 4330 (1983); *50* 2095 (1985); *52* 4062, 4681 (1987) Angew Int *19* 557 (1980) JACS *103* 3099 (1981); *104* 5526, 5528 (1982); *105* 1667 (1983); *107* 5396 (1985); *108* 4603 (1986); *109* 3353 (1987)

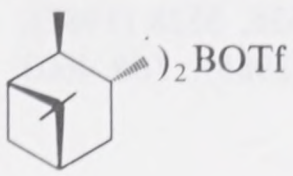
	TL *24* 5233 (1983); *27* 3511 (1986); *28* 985, 3835, 3839 (1987) JCS Perkin I 1809 (1983) Helv *68* 264 (1985) CC 1620 (1987) (enantioselective, chiral amide base)
B	CL 153 (1977); 153, 1193 (1981) JACS *101* 6120 (1979); *103* 1566, 1568, 3099 (1981); *104* 5521, 5523, 5528 (1982); *107* 5292 (1985) TL 1665, 2225, 2229, 3937 (1979); *21* 4291, 4675 (1980); *22* 3555 (1981); *23* 2387 (1982); *27* 4787 (1986) (enantioselective); *28* 1229 (1987) (enantioselective) BCSJ *53* 174 (1980) JCS Perkin I 1809 (1983) Pure Appl Chem *55* 1749 (1983) CC 147 (1983); 1102 (1987) JOC *52* 1347 (1987)
Al	CL 379 (1979) TL 2257 (1979); *23* 2387 (1982) Helv *68* 264 (1985)
Sn	CC 162 (1981) JCS Perkin I 1809 (1983) Pure Appl Chem *55* 1749 (1983) TL *24* 3347 (1983)
Ti	TL *22* 4691 (1981) Topics Curr Chem *106* 55 (1982) (review)
Zr	TL *21* 3975, 4607 (1980) JACS *104* 5528 (1982) JCS Perkin I 1809 (1983)
Zn	JOC *52* 3489 (1987)
Ce	TL *24* 5233 (1983); *28* 3817 (1987)
$(Et_2N)_3\overset{+}{S}$	JACS *103* 2106 (1981)



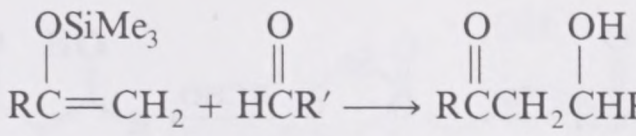
Organoborane



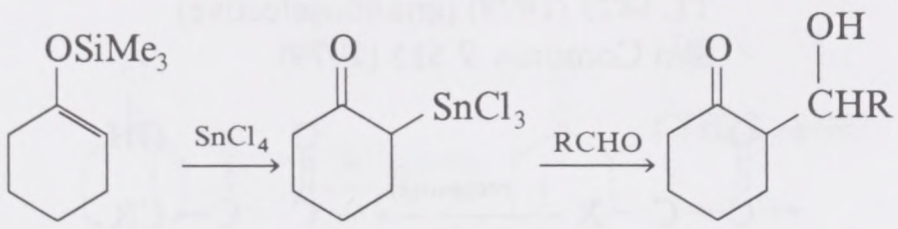
TL *27* 4721 (1986)



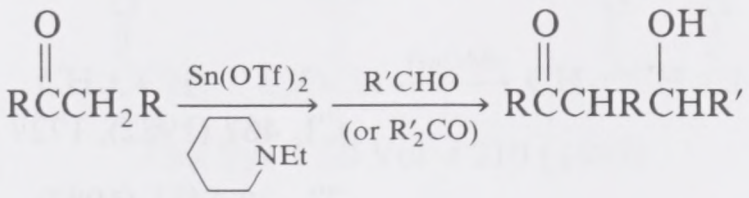
TL *27* 4787 (1986)



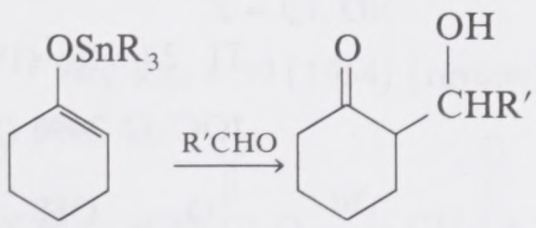
high pressure	JACS *105* 6963 (1983)
H_2O	JOC *51* 2142 (1986)
$BF_3 \cdot OEt_2$	JACS *105* 1667 (1983) TL *25* 5973 (1984)
$SnCl_4$	TL *24* 3347 (1983); *25* 5973 (1984)
$TiCl_4$	CL 1223 (1974) JACS *96* 7503 (1974); *107* 5292 (1985) Angew Int *16* 817 (1977); *22* 989 (1983) TL *24* 3341, 3343 (1983); *25* 5973 (1984); *27* 3369 (1986); *28* 985 (1987) JOC *50* 2375 (1985); *52* 120 (1987) Org Syn *65* 6 (1987)
cat *n*-Bu_4NF	JACS *99* 1265 (1977) JOC *48* 932 (1983)
$[(Et_2N)_3S]SiMe_3F_2$	JACS *103* 2106 (1981)
n-Bu_3SnF, cat $PdCl_2(PAr_3)_2$	TL *24* 5001 (1983)
cat $[(COD)Rh(Ph_2P(CH_2)_4PPh_2)]X$ ($X = PF_6$, ClO_4) or $Rh_4(CO)_{12}$	TL *27* 5517 (1986)
cat $[Rh(NBD)(dppe)]ClO_4$	TL *28* 793 (1987)



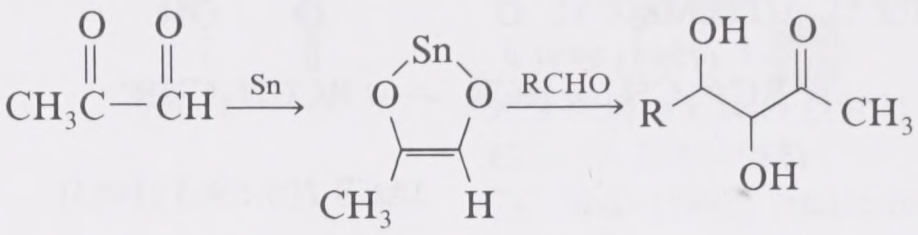
TL *24* 3347 (1983)



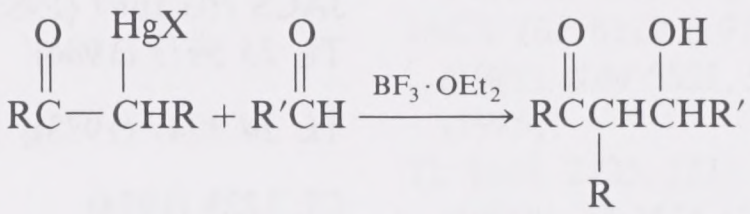
CL 353, 1441 (enantioselective with chiral diamine), 1459, 1601 (1982); 595 (1983)



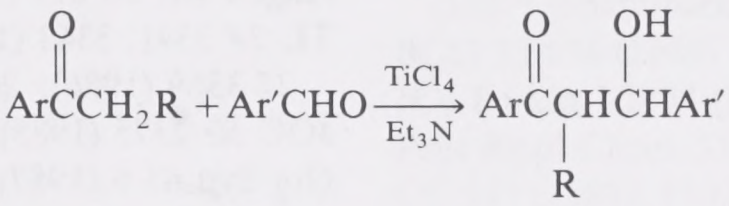
TL *23* 627 (1982)
CL 851 (1983)



CL 1825 (1983)

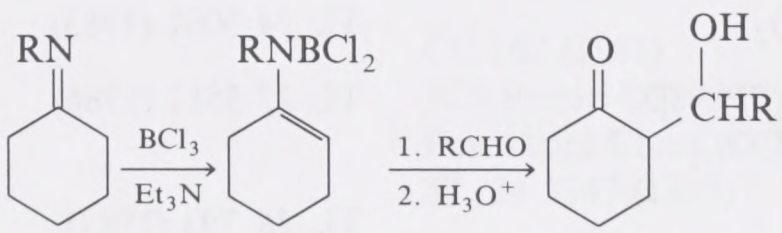


JACS *104* 2323 (1982)

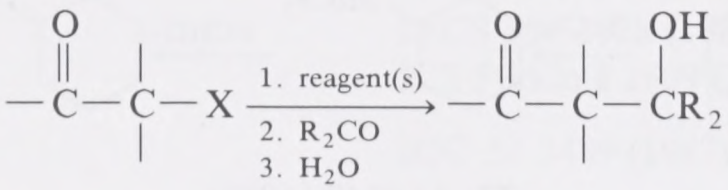


TL *28* 4135 (1987)

7.2. Related Reactions



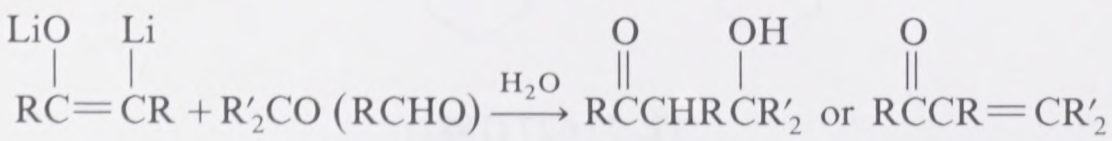
TL 1423 (1979) (enantioselective)
Syn Commun *9* 515 (1979)



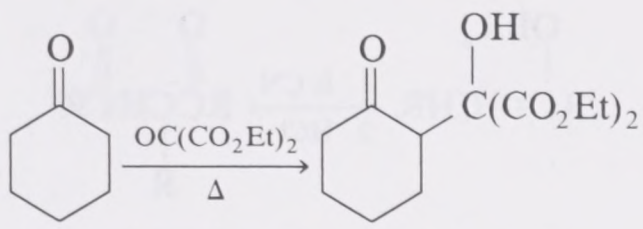
X = halogen

Reagent(s)

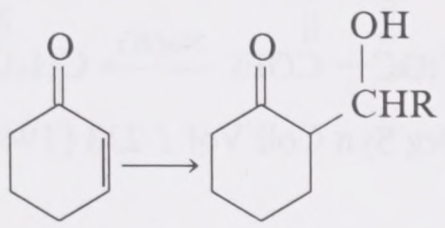
Sn	CL 467 (1982), 1727 (1983)
CuCl, Zn	TL *28* 6481 (1987)
CuBr, Zn, Et_2AlCl	BCSJ *53* 3301 (1980)
Zn	JACS *89* 5727 (1967)
Zn, Et_2AlCl, AgOAc	TL *28* 6481 (1987)
electrolysis, $LaBr_3$	JOC *52* 2496 (1987)



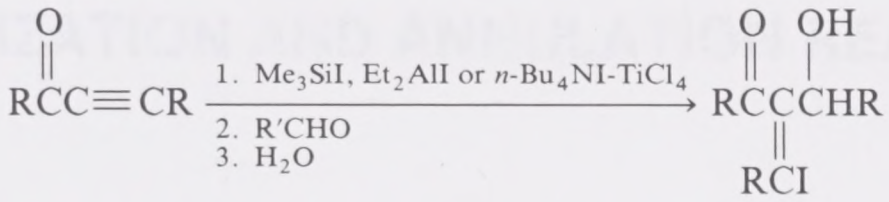
JACS *104* 1777 (1982)



TL *22* 4323 (1981)

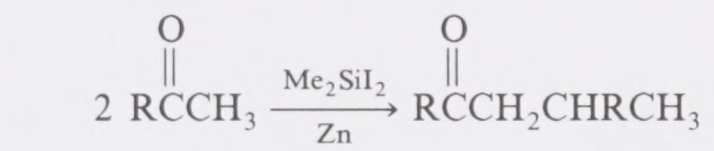


See page 776, Section 21.

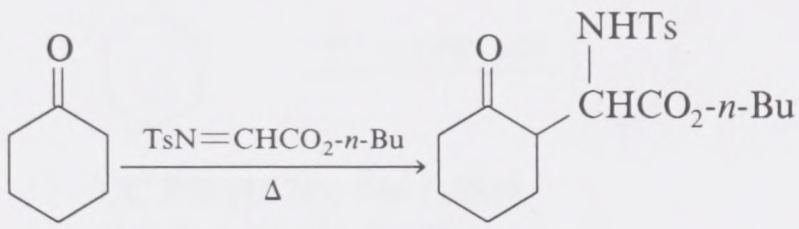


TL *27* 4767 (1986)

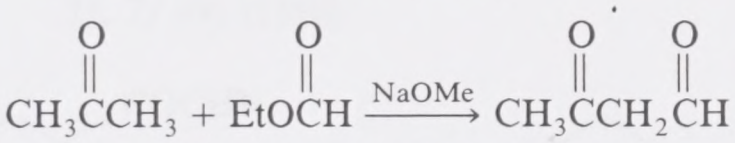
8. Other Condensation Reactions



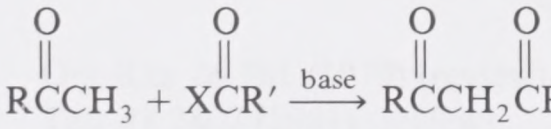
CL 1255 (1980)



TL *22* 4323 (1981)

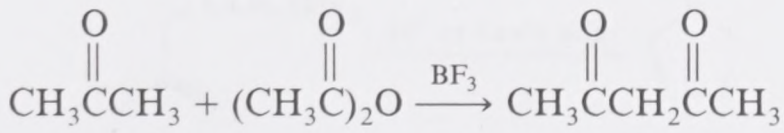


Org Syn Coll Vol *4* 210 (1963)

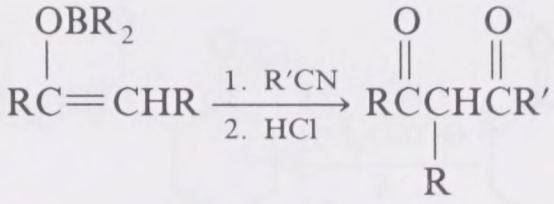


X = Cl, OR

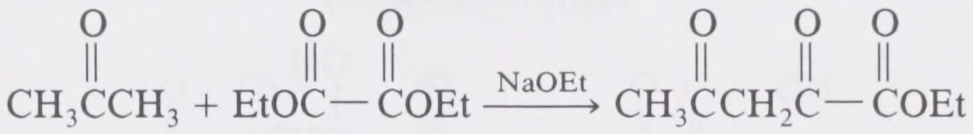
Org Rxs *8* 59 (1954) (review)



Org Rxs *8* 59 (1954) (review)
Org Syn Coll Vol *3* 16 (1955)



Syn Commun *12* 189 (1982)



Org Syn Coll Vol *1* 238 (1941)

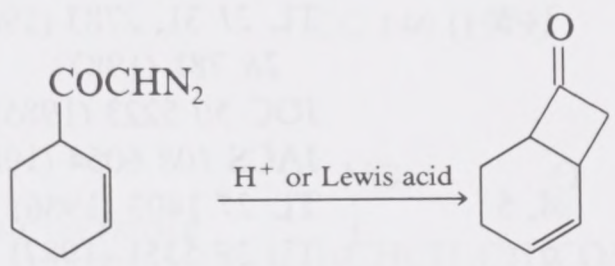
6. CYCLIZATION AND ANNULATION REACTIONS

Reviews:

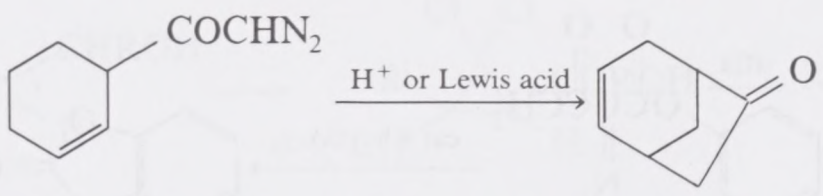
Tetr *32* 3 (1976)
Syn 177 (1976)

1. Cyclization

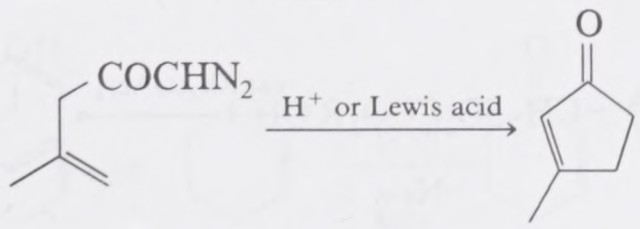
See also page 702, Section 3.



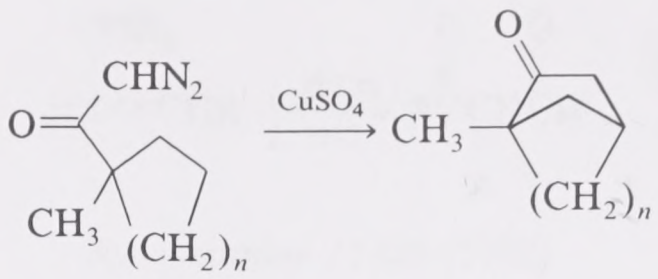
CC 876 (1974); 746 (1981)
Org Rxs *26* 361 (1979) (review)
JCS Perkin I 1924 (1980); 1203 (1981)
TL *21* 691 (1980)



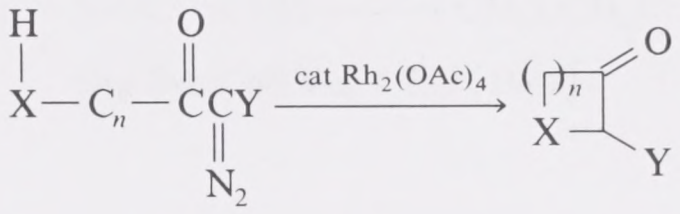
Org Rxs *26* 361 (1979) (review)
Tetr *37* 2407 (1981) (review)
J Chem Res (S) 5 (1981)



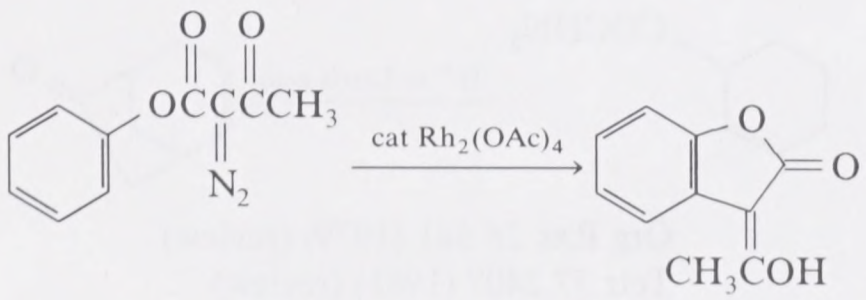
Org Rxs *26* 361 (1979) (review)
JACS *103* 1996, 2009, 2017 (1981)
Tetr *37* 2407 (1981) (review)



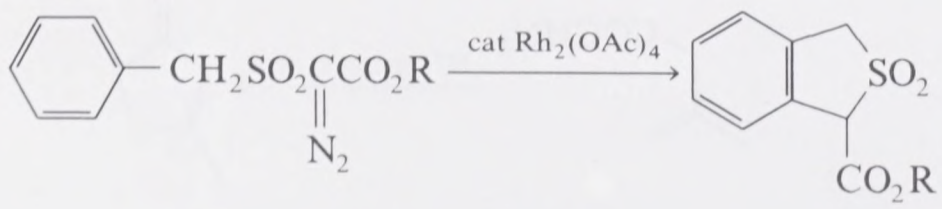
JOC *47* 3242 (1982)



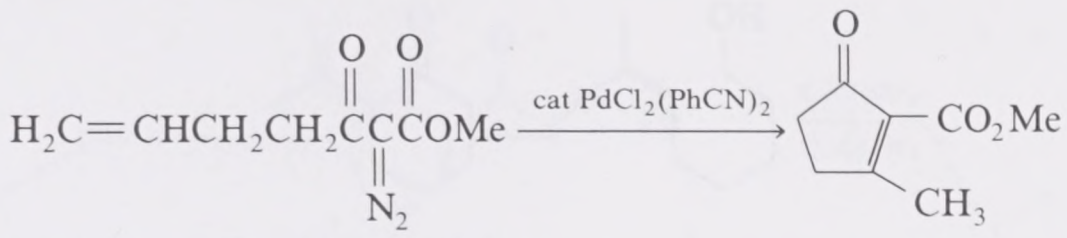
Y	X	n	
H	C	2	JACS *107* 5732 (1985); *109* 5432 (1987) TL *28* 165 (2-indanones); 4773 (1987)
		3	CC 129 (1984) (2-tetralones) TL *26* 6035 (1985)
CO_2R	C	1	JACS *106* 5295 (1984) TL *28* 637 (1987)
		2	JOC *47* 4808 (1982); *52* 28 (1987) JACS *105* 5935 (1983); *106* 5295 (1984); *107* 196, 5289 (1985); *108* 7686 (1986) TL *26* 3059 (1985); *28* 637, 5351 (1987)
		3	TL *24* 5453 (1983) (naphthols)
	N	1–3	TL *21* 31, 2783 (1980); *23* 3105 (1982); *28* 781 (1987) JOC *50* 5223 (1985) JACS *108* 6054 (1986)
	O	4, 5	TL *27* 1403 (1986)
		5	TL *28* 5351 (1987)
	O or S	2	JOC *50* 5223 (1985)
		3, 4	TL *28* 5351 (1987)
SO_2Ph	C	2	TL *28* 3459 (1987) JOC *52* 5742 (1987)



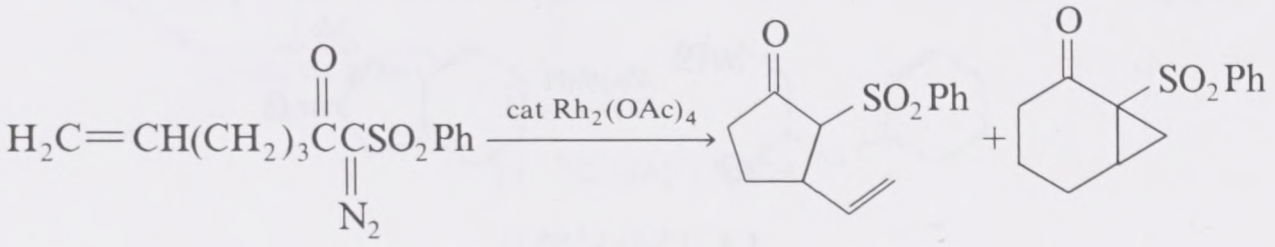
CC 1150 (1987)



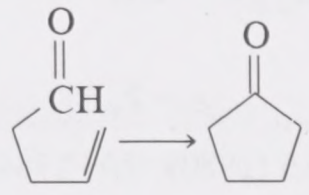
TL *27* 5679 (1986)



JOC *51* 3382 (1986)



TL *28* 3459 (1987)

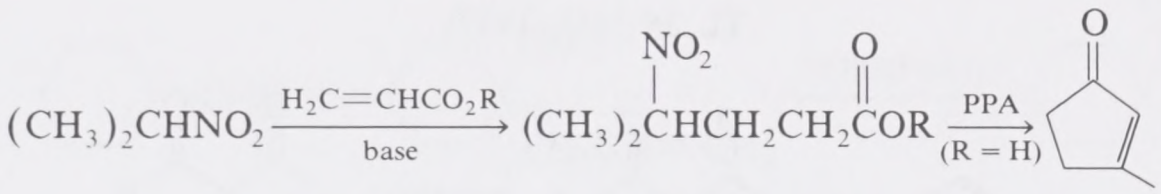


"$ClRh(PAr_3)_2$"

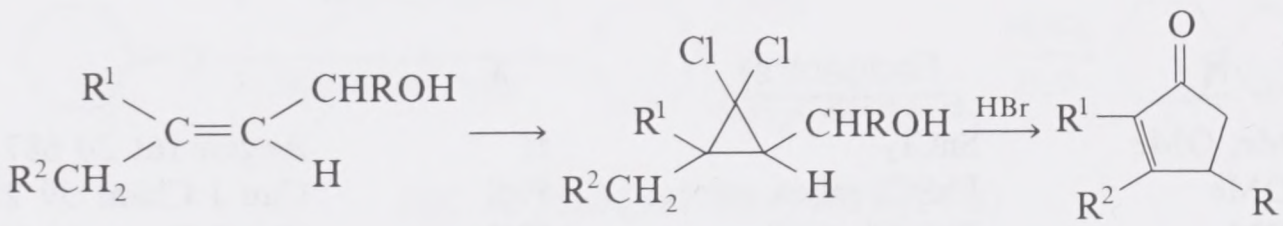
TL 1287 (1972)
JACS *98* 1281 (1976); *100* 640 (1978); *101* 489 (1979); *102* 190 (1980)

$SnCl_4$

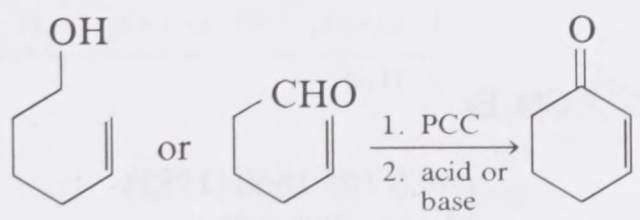
TL 1287 (1972)
CC 146 (1979)



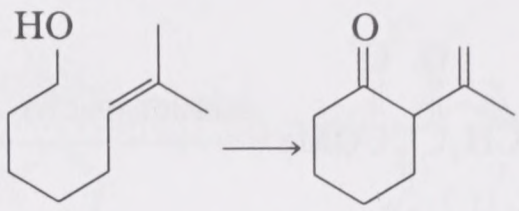
CC 1149 (1980)



JACS *96* 3713 (1974)
BCSJ *53* 1010 (1980)



TL 2461 (1978)

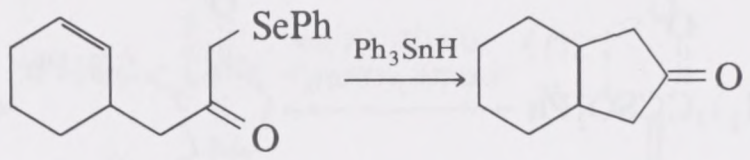


PCC

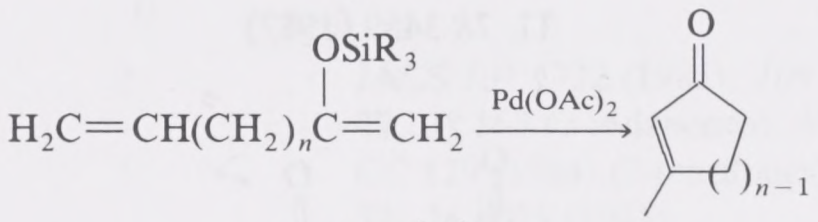
JOC *41* 380 (1976); *50* 2668 (1985)
TL 2461 (1978)

CrO_3, py, CF_3CO_2H

Can J Chem *55* 1039 (1977)

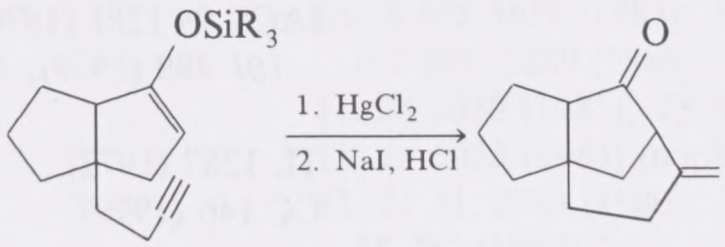


CC 1520 (1987)

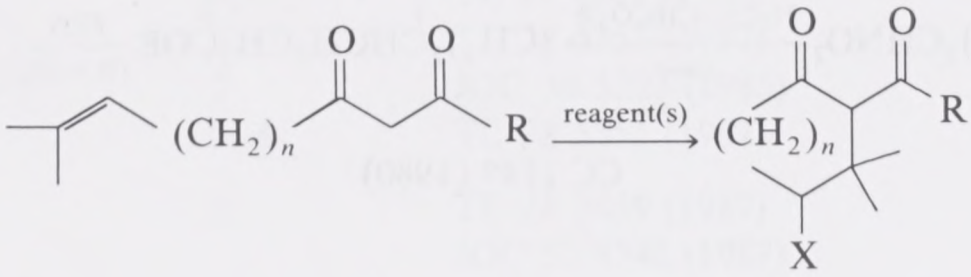


$n = 2, 3$

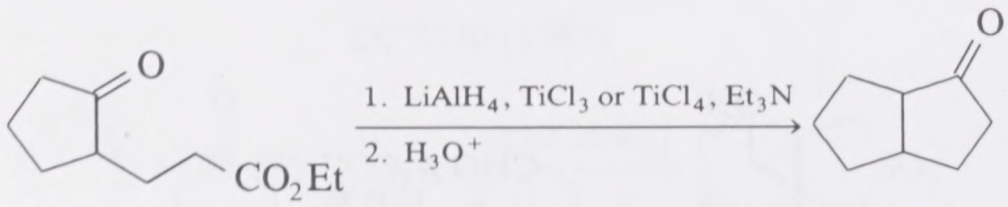
JACS *101* 494 (1979); *102* 4519 (1980); *104* 1784, 5808 (1982); *108* 2090 (1986)
TL *27* 2223 (1986)



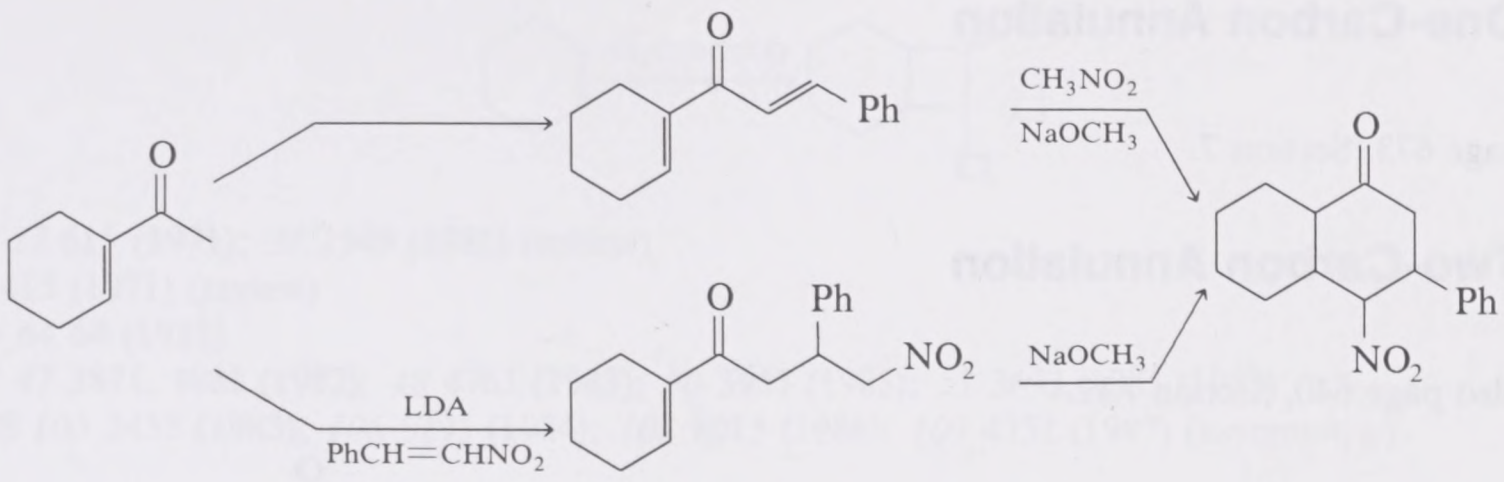
JACS *107* 1726 (1985)
TL *28* 3923 (1987)



n	R	Reagent(s)	X	
2	Me, OMe	$SnCl_4$	H	Angew Int *20* 687 (1981)
	OMe	PhSCl, silica gel	PhS	Can J Chem *59* 2239 (1981)
	OMe	PhSeCl, $AlCl_3$	PhSe	Can J Chem *59* 2239 (1981)
3	OMe	$SnCl_4$	H	Angew Int *20* 687 (1981)



JACS *105* 1660 (1983)
TL *24* 1885 (1983)
CC 1607 (1987)

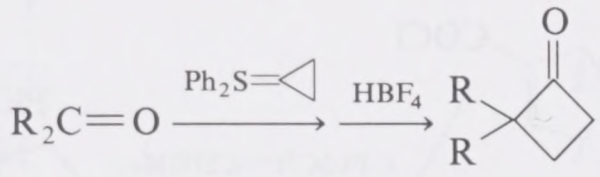


TL *28* 2945 (1987)

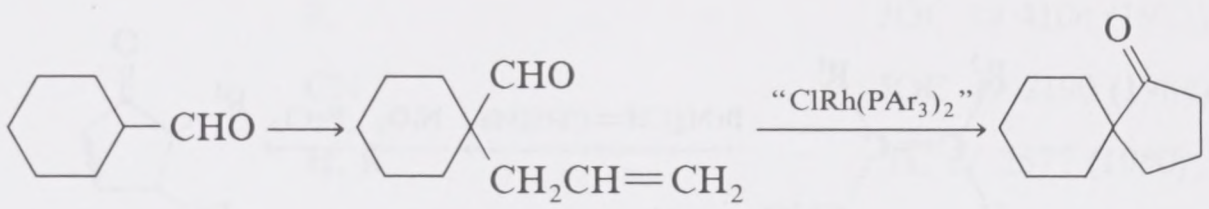
2. Spiroannulation

Review:

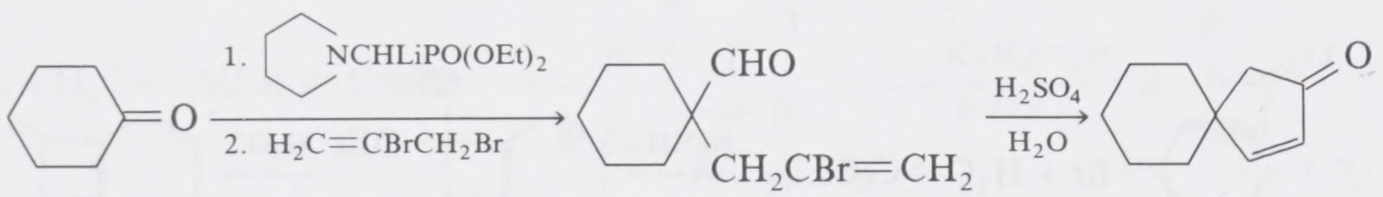
Syn 383 (1974) (Synthesis of Carbocyclic Spiro Compounds via Intramolecular Alkylation Routes)



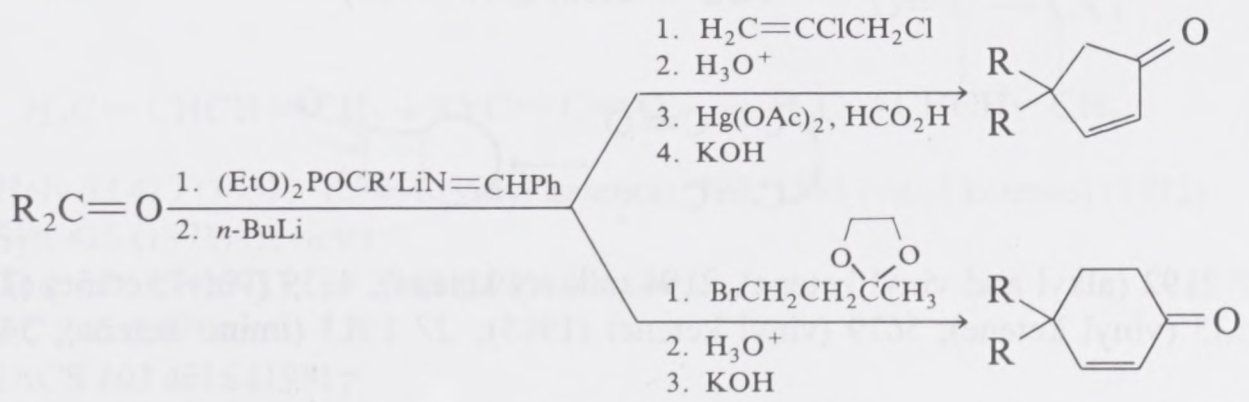
JACS *95* 5321 (1973)
Acct Chem Res *7* 85 (1974)



JACS *102* 190 (1980)



JOC *42* 2520 (1977); *43* 1027 (1978)



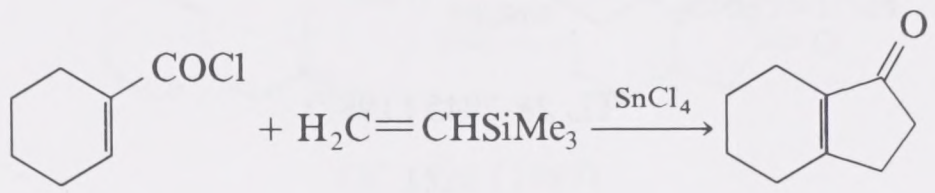
JACS *102* 5866 (1980)

3. One-Carbon Annulation

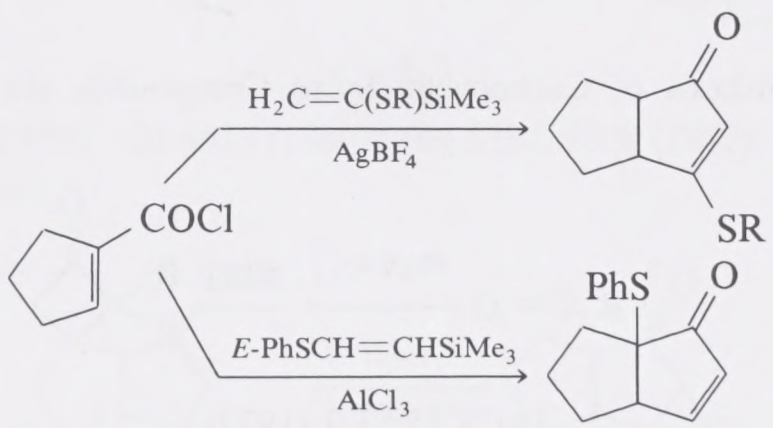
See page 673, Section 7.

4. Two-Carbon Annulation

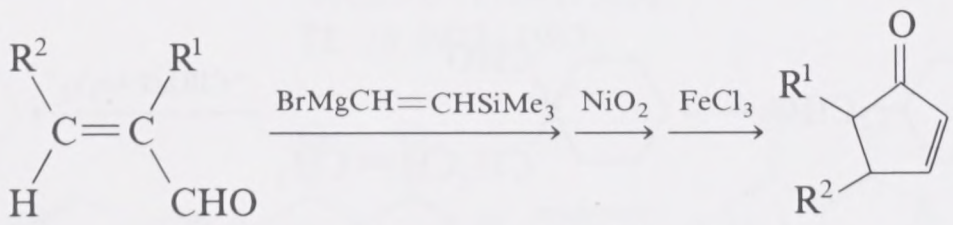
See also page 640, Section 7.12.



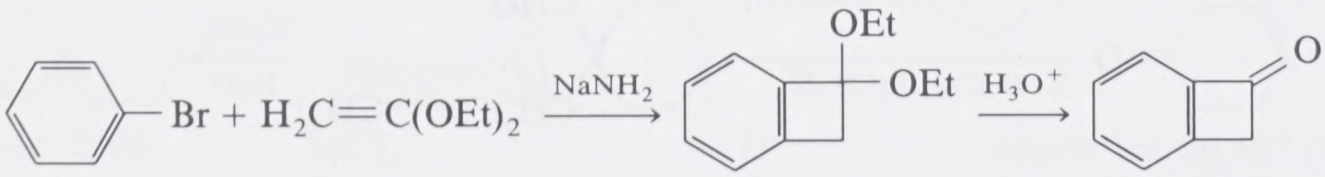
TL 1995, 1999 (1979)
JOC *45* 1046, 3017 (1980)



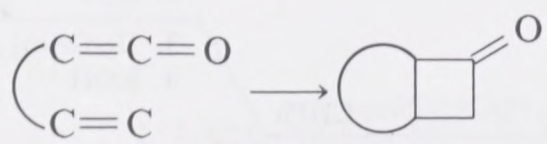
Organomet *1* 1240, 1243 (1982)



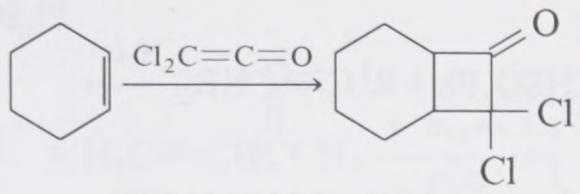
JACS *104* 2642 (1982)



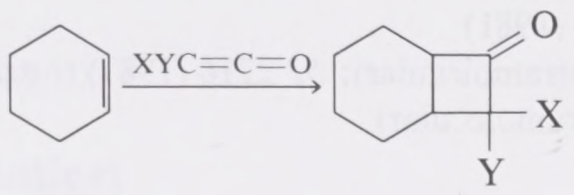
JOC *47* 2393, 2396 (1982)



JACS *107* 2192 (alkyl and vinyl ketene), 2194 (alkoxy ketene), 4339 (vinyl ketene) (1985)
TL *26* 3535 (vinyl ketene), 5619 (vinyl ketene) (1985); *27* 1913 (imino ketene), 5471 (vinyl ketene) (1986)
JOC *50* 2809 (vinyl ketenes), 5167 (alkoxy ketene), 5177 (phenoxy ketene) (1985); *52* 307 (chloro ketene), 1568 (vinyl ketene), 5413 (vinyl ketene) (1987)



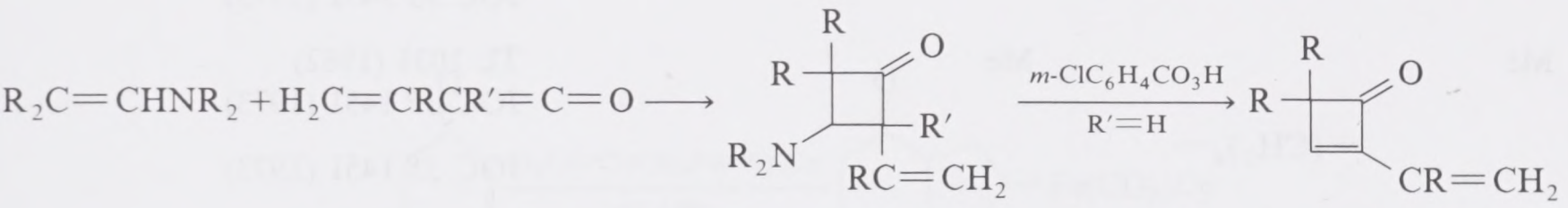
Tetr *27* 615 (1971); *37* 2949 (1981) (review)
Syn 415 (1971) (review)
Helv *64* 64 (1981)
JOC *47* 3871, 3881 (1982); *48* 4763 (1983); *50* 3957 (1985); *52* 3693, 4885 (1987)
JACS *105* 2435 (1983); *106* 5295 (1984); *108* 8015 (1986); *109* 4752 (1987) (asymmetric)



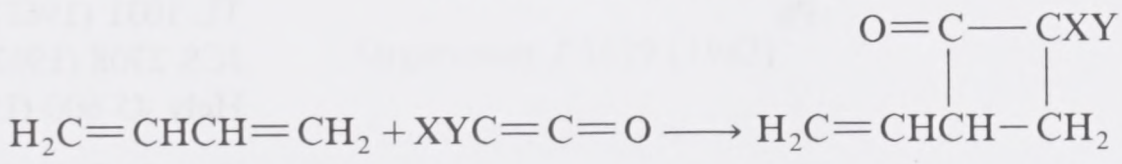
Reviews:

Org Rxs *3* 108 (1946) (preparation of ketenes); *12* 26 (1962)
J Chem Ed *53* 81 (1976)
Chem Soc Rev *10* 289 (1981) (cyano ketenes)
Chem Rev *86* 821 (1986) (conjugated ketenes)

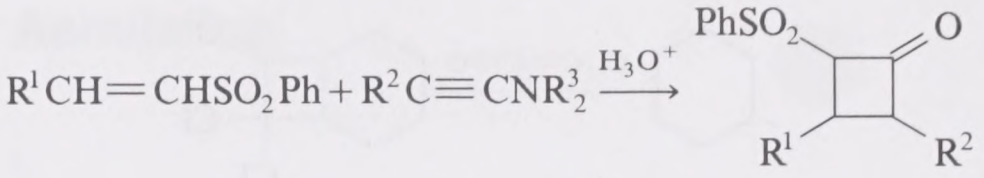
X	Y	
CF_3	CF_3	JACS *87* 4019 (1965)
$H_2C{=}CH$	H	JOC *41* 3303 (1976)
$H_2C{=}C(CH_3)$	H	JOC *31* 718 (1966)
vinylic	R	Helv *66* 2331 (1983)
Cl	R	JOC *38* 4106 (1973)
Cl	CN	JOC *49* 2190 (1984)
PhS	H, R	TL *21* 2577 (1980)
$-SCH_2CH_2S-$		TL *21* 2577 (1980)



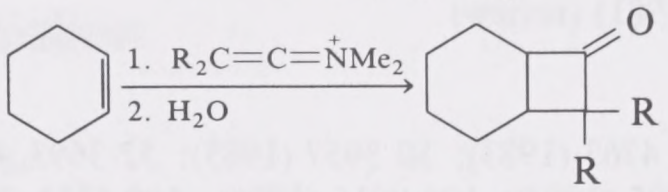
Helv *64* 2231 (1982)



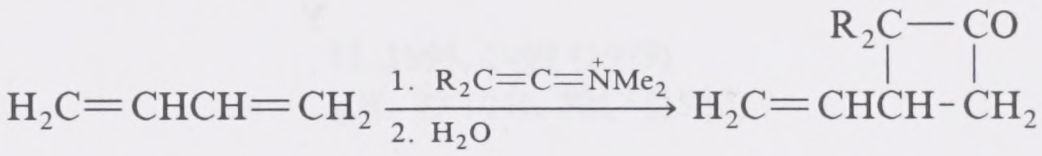
Helv *53* 417 (1953); *65* 451 (vinyl ketenes), 703, 1563 (vinyl ketenes) (1982)
Syn 415 (1971) (review)
Tetr *27* 615 (1971); *37* 2949 (1981) (review)
CC 245 (1978)
JACS *103* 4616 (1981)
JCS Perkin I 684 (1981)
JOC *52* 1284 (1987)



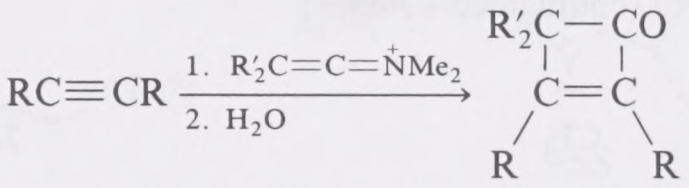
JOC *47* 1608 (1982)



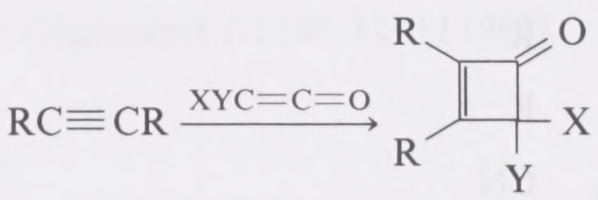
JACS *94* 2870 (1972); *104* 2920 (1982); *107* 2192, 2194 (1985) (both intramolecular)
Angew Int *20* 782, 879 (1981)
JOC *50* 5169 (1985) (intramolecular); *52* 2216 (1987) (intramolecular)
TL *27* 5211 (1986) (intramolecular)



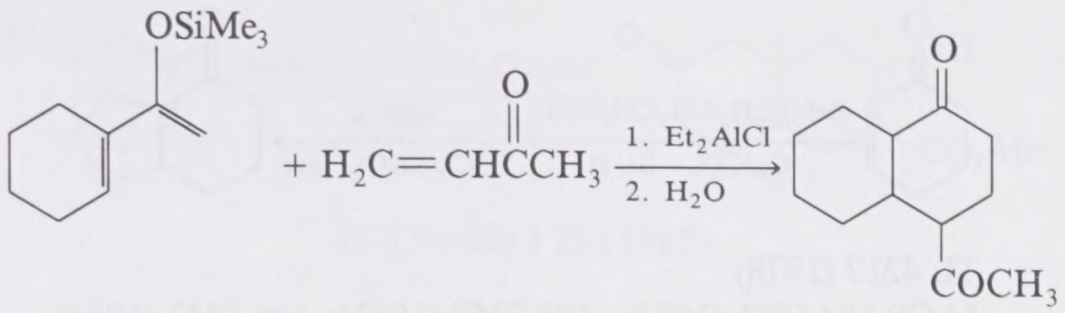
JACS *94* 2870 (1972)
Syn 706 (1981)



Angew Int *14* 569 (1975); *20* 879 (1981)
TL *25* 5043 (1984)



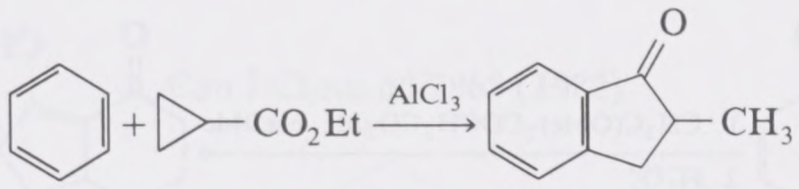
X	Y	
H	H	TL 1031 (1962) JOC *38* 1451 (1973)
Me	Me	TL 1031 (1962) JOC *38* 1451 (1973)
—$(CH_2)_4$—		JOC *38* 1451 (1973)
CF_3	CF_3	JOC *35* 3308 (1970)
Ph	Ph	TL 1031 (1962) JCS 2708 (1962) Helv *45* 600 (1962)
Ar	Ar	Tetr *36* 2291 (1980)
Cl	Cl	Ann *722* 232 (1969); 2074 (1974) JACS *96* 2267 (1974) TL 2715 (1976); *24* 23 (1983) Syn 689 (1979) JOC *48* 3382 (1983)
Cl	CN	JOC *50* 3226 (1985)



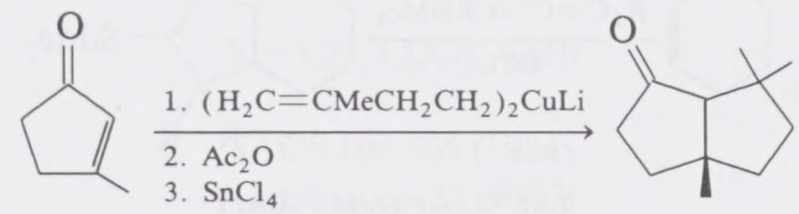
CC 1333 (1987)

5. Three-Carbon Annulation

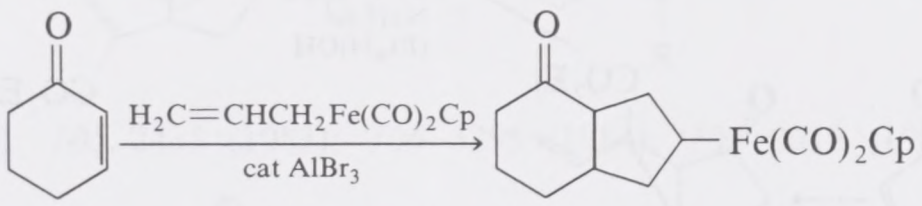
Review: Syn 529 (1984)



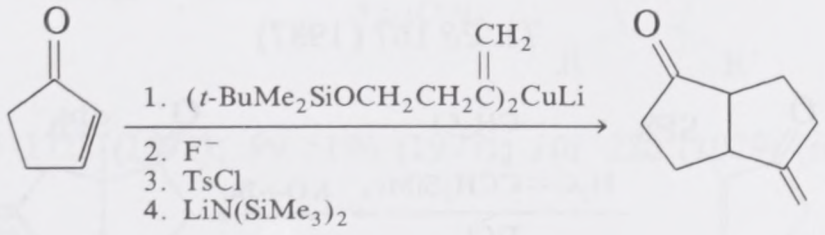
JOC *46* 3758 (1981)



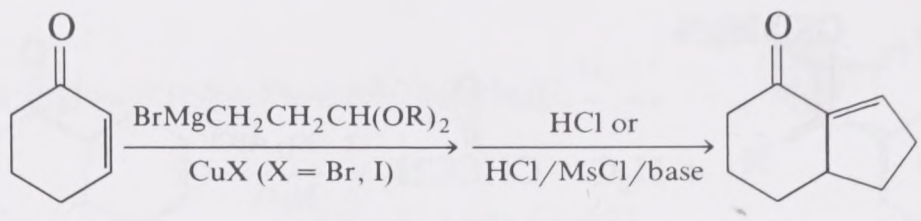
TL *23* 5471 (1982)



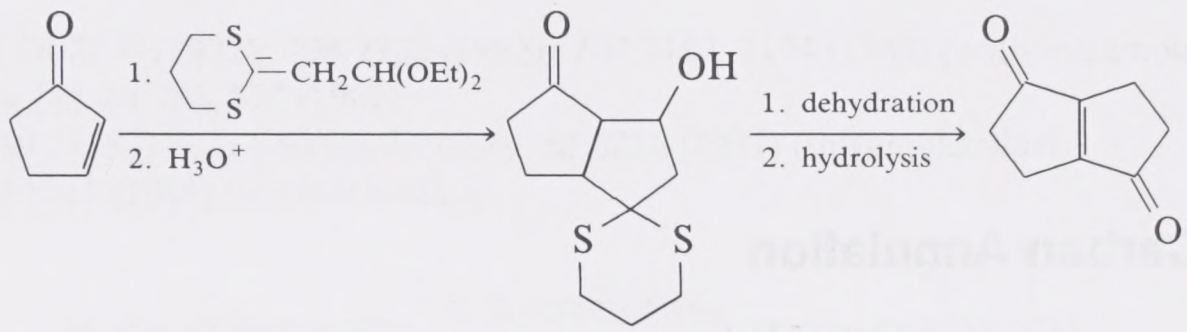
Organomet *1* 1679 (1982)



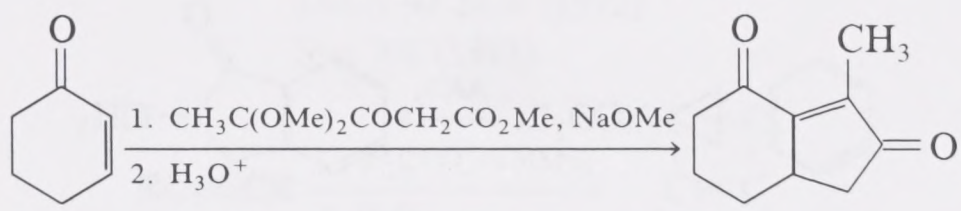
Organomet *1* 1243 (1982)



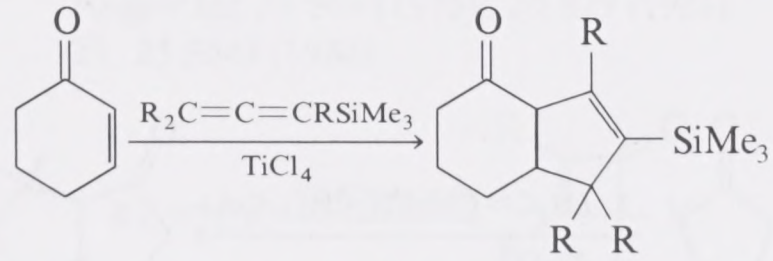
TL 4217 (1978)
JACS *104* 6081 (1982); *105* 7352 (1983); *106* 1442 (1984)
JOC *47* 5045 (1982)



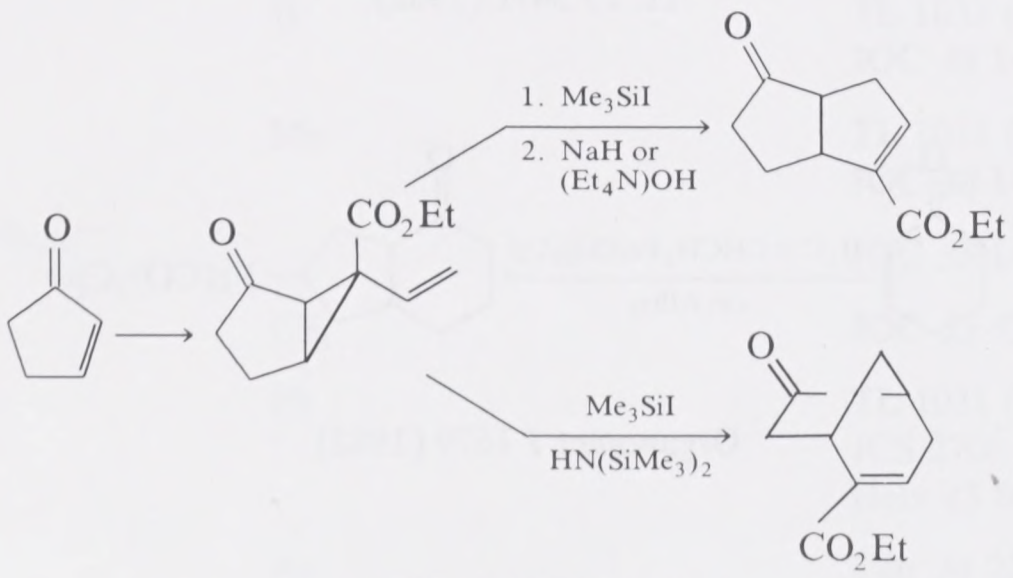
JOC *51* 3861 (1986)



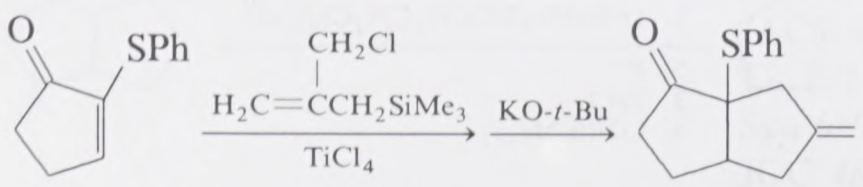
JOC *47* 4791 (1982)



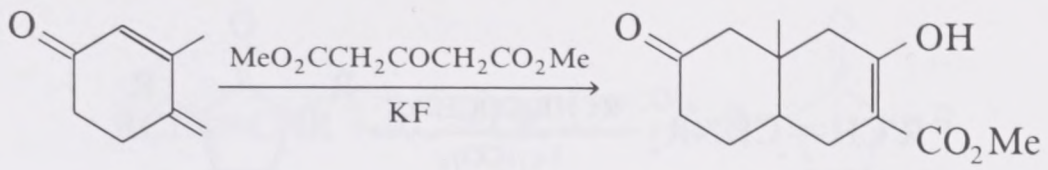
JACS *103* 1604 (1981)
Tetr *39* 935 (1983)



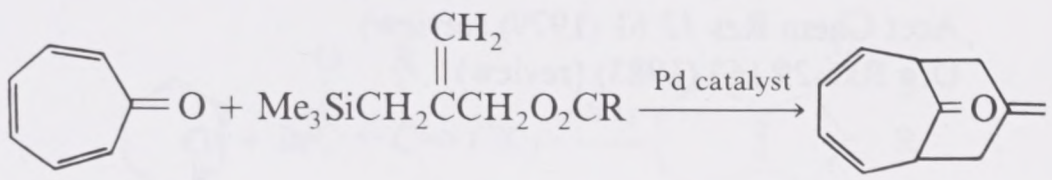
TL *28* 167 (1987)



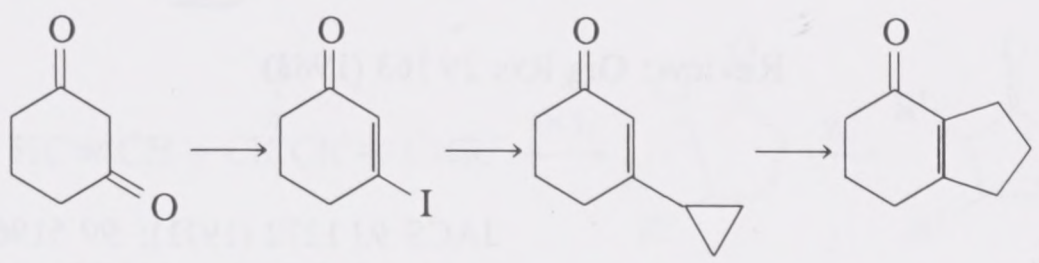
TL *21* 4557 (1980)



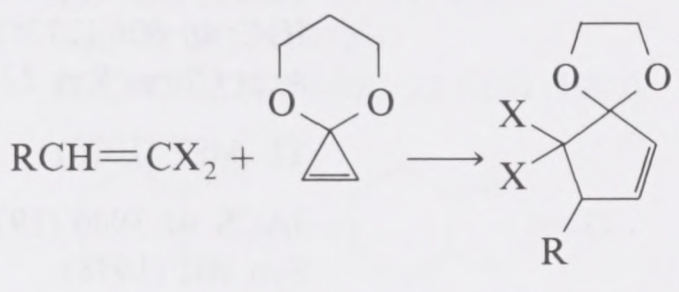
JCS Perkin I 25 (1982)



JACS *109* 615 (1987)

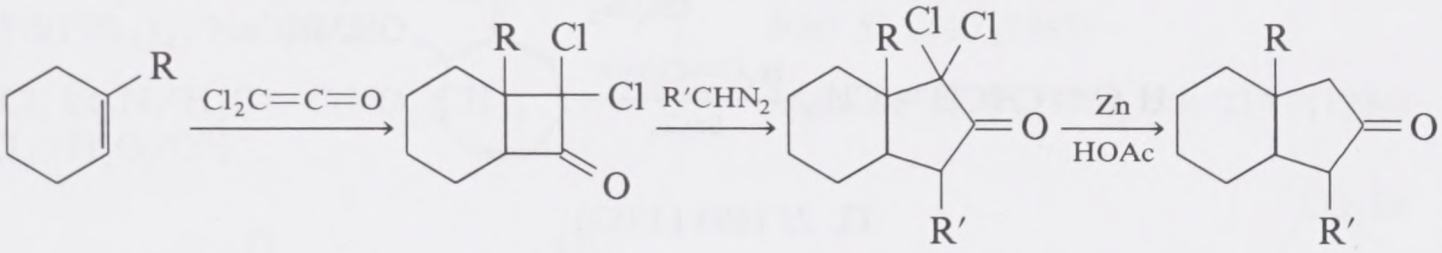


Can J Chem *60* 2965 (1982)

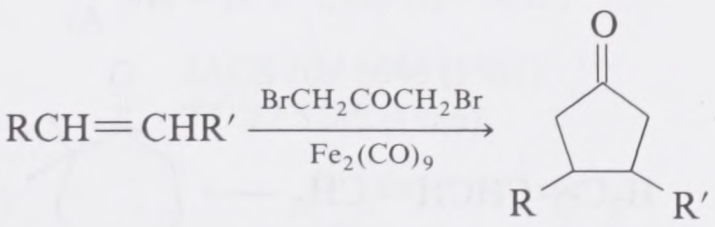


X = CN, CO_2R, COR

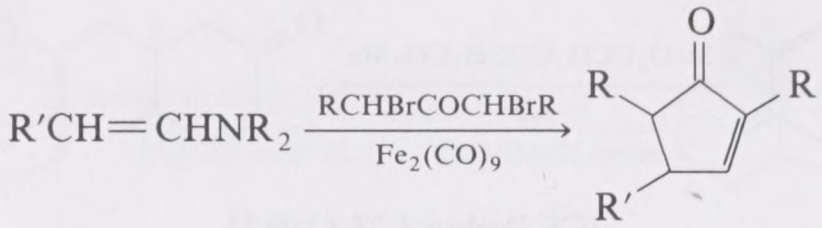
JACS *106* 805 (1984)
Org Syn *65* 22 (1987)



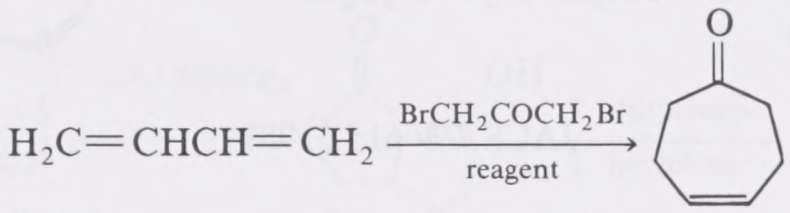
JACS *101* 4003 (1979); *105* 2435 (1983); *106* 5295 (1984); *108* 8015 (1986); *109* 4752 (1987) (asymmetric)
JOC *45* 2036 (1980); *48* 4763 (1983); *50* 3957 (1985)



JACS *94* 7202 (1972); *95* 2722 (1973); *99* 5196 (1977); *101* 220 (1979) (intramolecular); *105* 7358 (1983)
TL 4347 (1976); 993 (1978)
Acct Chem Res *12* 61 (1979) (review)
Org Rxs *29* 163 (1983) (review)



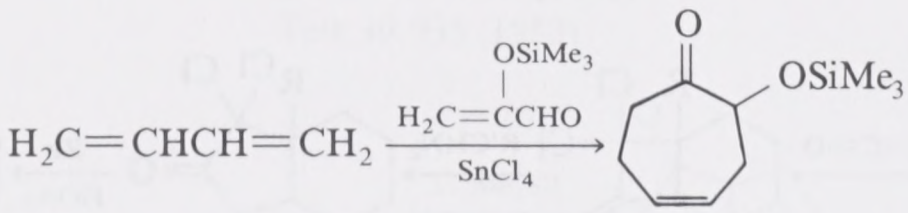
JACS *94* 1772 (1972); *99* 5196 (1977); *100* 1799 (1978)
Acct Chem Res *12* 61 (1979) (review)
Org Rxs *29* 163 (1983) (review)



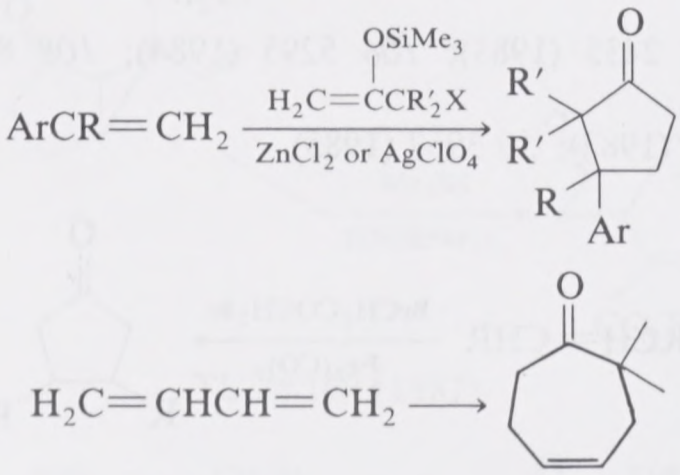
Review: Org Rxs *29* 163 (1983)

Reagent(s)

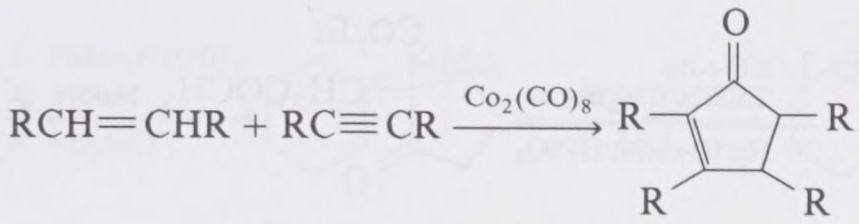
$Fe_2(CO)_9$	JACS *93* 1272 (1971); *99* 5196 (1977); *100* 1765 (1978); *101* 220 (1979) (intramolecular) TL 1741 (1973); 1049 (1974); *27* 2881 (1986) JOC *40* 806 (1975) Acct Chem Res *12* 61 (1979) (review)
Zn, $B(OEt)_3$	TL 4487 (1975)
Zn-Cu	JACS *94* 3940 (1972); *96* 5466 (1974) Syn 902 (1978)
Zn-Cu, ultrasound	TL *27* 687 (1986)
Zn-Cu, Me_3SiCl	Syn 902 (1978) Ber *117* 3325 (1984)



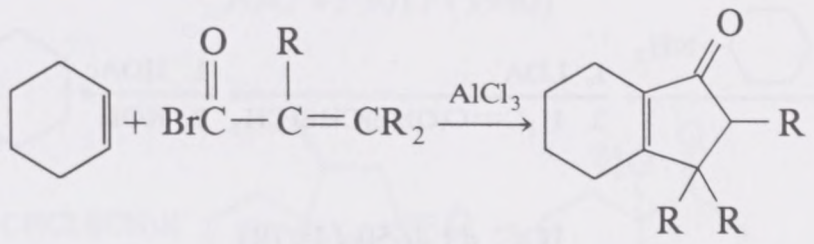
TL *23* 1693 (1982)



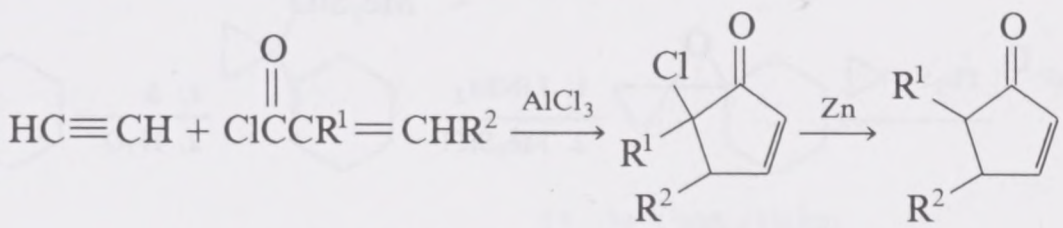
Angew Int *18* 163 (1979)
CL 103 (1979)
JACS *104* 1330 (1982)
TL *27* 2881 (1986)



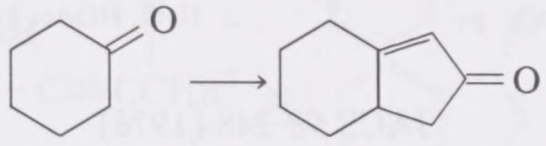
See page 677, Section 8.



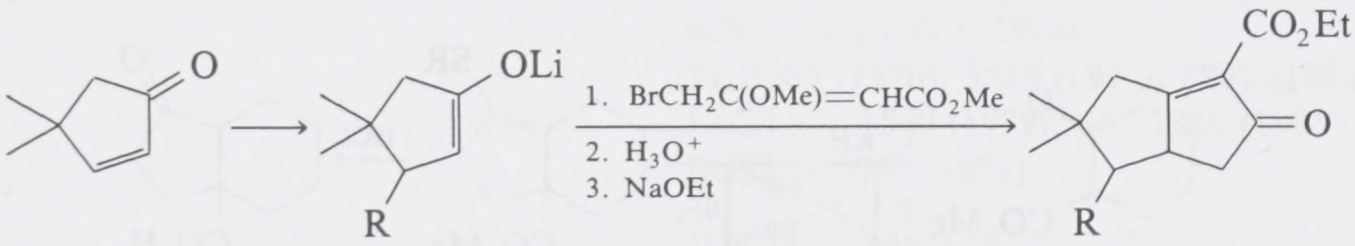
TL 4553 (1979)



Compt Rend C *266* 478 (1968)
BSCF 3098 (1970)
TL 3131 (1970); 4413 (1976)
Tetr *28* 4027 (1972)
JOC *45* 2224 (1980); *52* 5280 (1987)

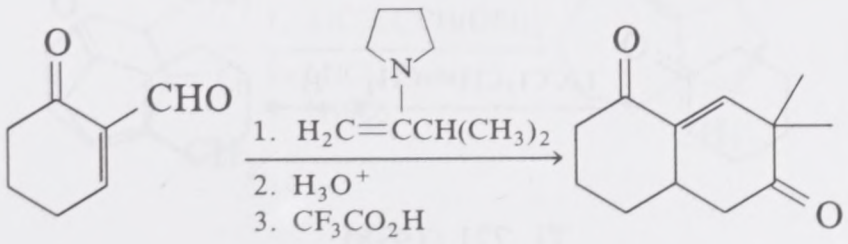


LDA/ $BrCH_2C(OEt)=CHPO(OMe)_2$ / H_3O^+/NaH	TL 3279 (1979) Can J Chem *60* 1114 (1982)
LDA/ $BrCH_2COCH=PPh_3$	Angew Int *18* 940 (1979)
LDA/ $ClCH_2C(=CH_2)O_2P(OEt)_2$, 5% $Pd(PPh_3)_4$/NaOH, Δ	TL *27* 1115 (1986) JOC *52* 1440 (1987)
Me_3SiCl, Et_3N/ $H_2C=C(NO_2)CH_3$, $SnCl_4/H_2O/OH^-$	JACS *98* 4679 (1976); *106* 2149 (1984)

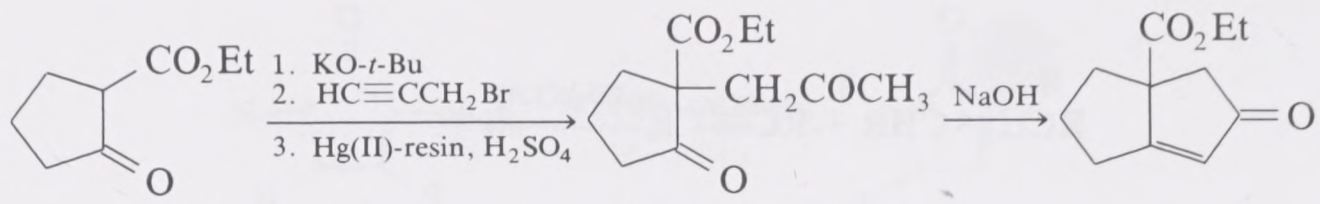


R = H or $CH_2CH=CH_2$

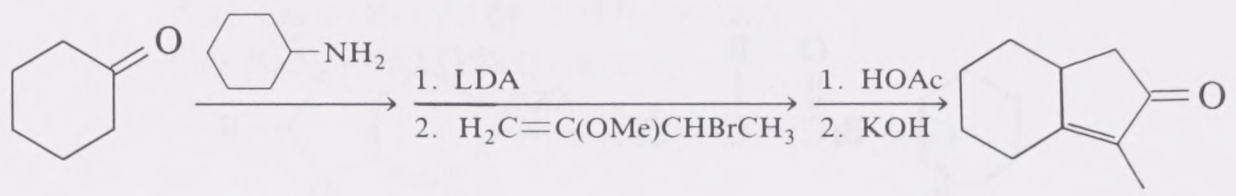
JACS *104* 6646 (1982)
TL *27* 5245 (1986)



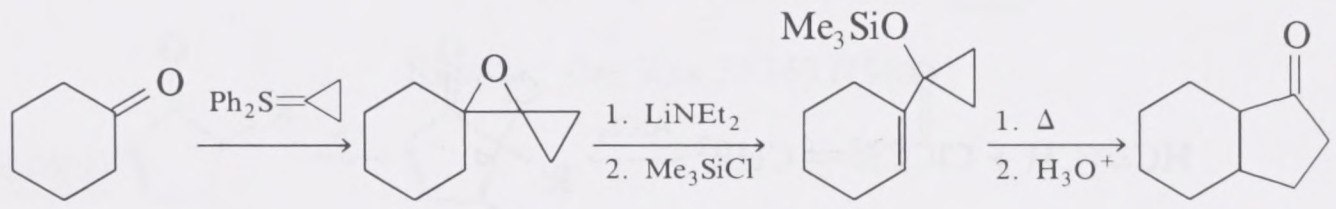
TL *27* 1449 (1986)



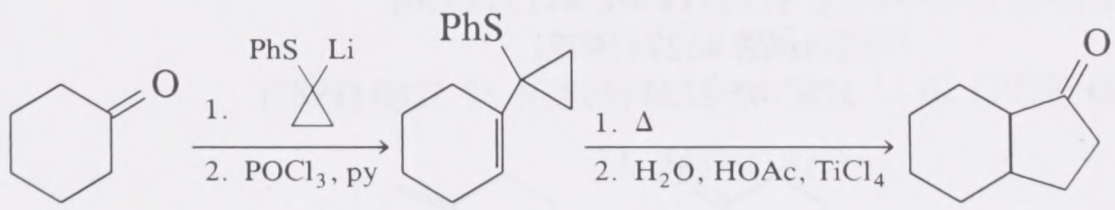
JOC *46* 2815 (1981)



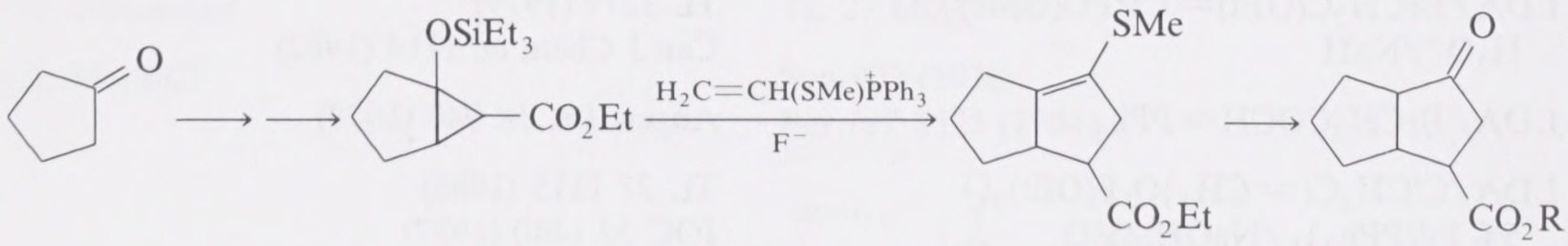
JOC *43* 4650 (1978)



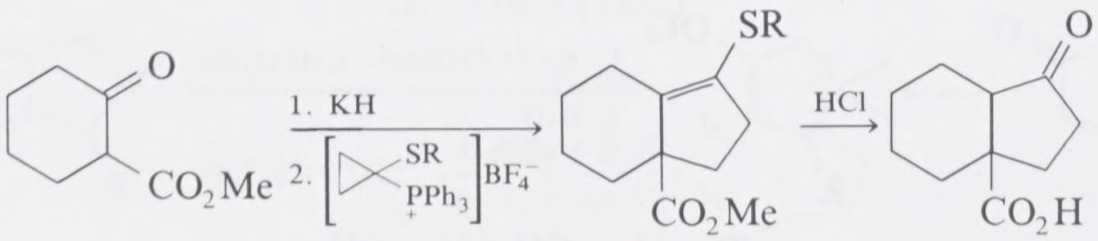
JACS *95* 5311 (1973)
Acct Chem Res *7* 85 (1974)



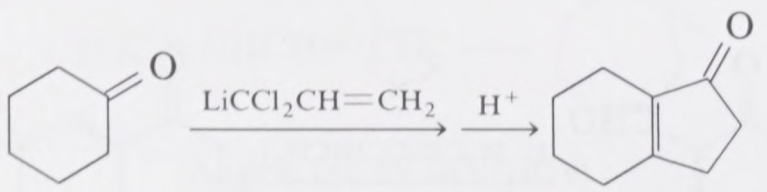
JACS *98* 248 (1976)



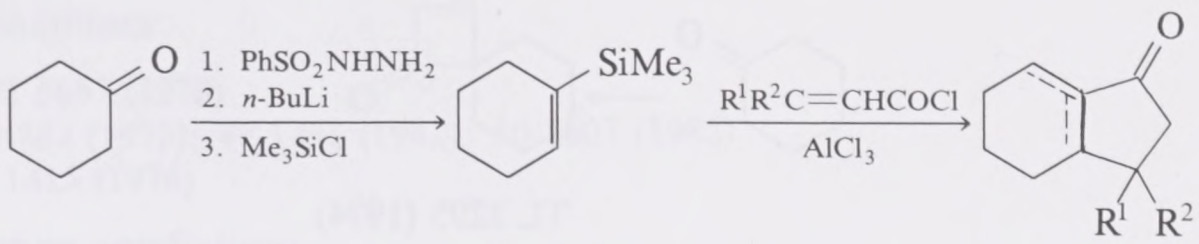
JACS *107* 734 (1985)
JOC *52* 1, 4139 (1987)



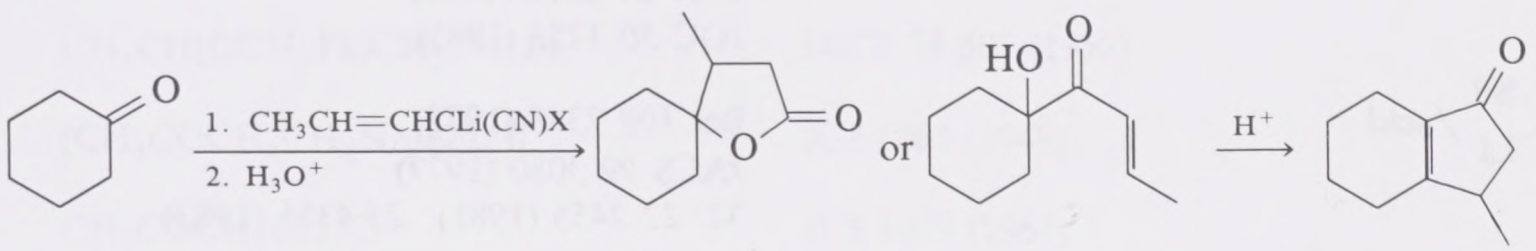
TL 4531 (1975)
JOC *46* 1828 (1981)



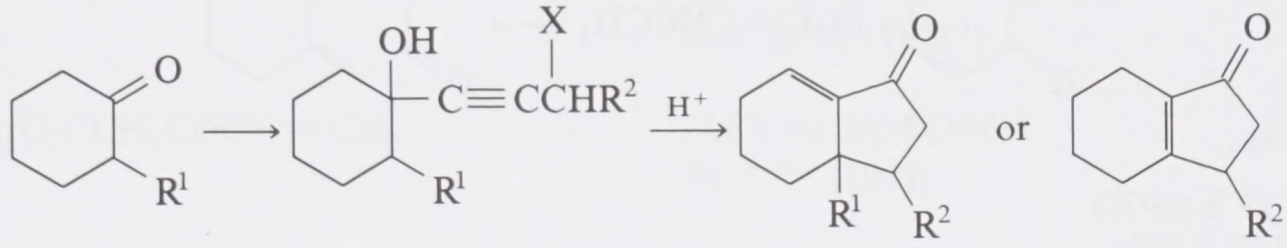
TL 771 (1978)
BCSJ *53* 1010 (1980)



JOC *45* 3017 (1980)

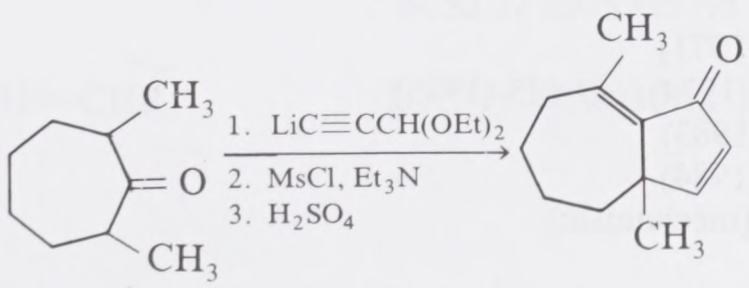


X	
NMe_2	TL *21* 1205 (1980)
$OCH(OEt)CH_3$	JOC *45* 395 (1980)
$OSiMe_3$	JOC *44* 462 (1979); *45* 395 (1980)

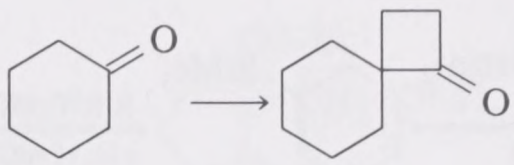


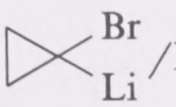
($R^1 = H$)

X	
OH	Helv *59* 1226 (1976) JCS Perkin I 410 (1976) TL 3585 (1976); 3529 (1979); 3897 (1980) JACS *101* 1599 (1979); *107* 1769 (1985) BCSJ *54* 2747 (1981)
NEt_2	JCS 2247 (1953)

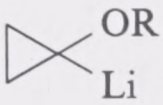


TL *22* 3565 (1981)

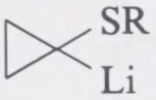


 /H^+

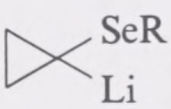
TL 3295 (1974)
Ber *108* 2368 (1975)

 /HBF_4 or $SnCl_4$

TL *22* 2455 (1981)
Helv *64* 2598 (1981)
JOC *50* 3255 (1985)

 /acid

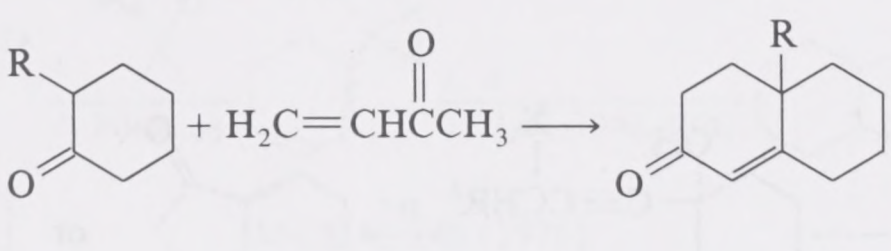
Ber *108* 2368 (1975)
JACS *99* 3080 (1977)
TL *22* 2455 (1981); *23* 4385 (1982)

 (R = Ph, Me)/TsOH

TL *23* 4385 (1982)

6. Four-Carbon Annulation

6.1. Robinson and Related Annulations



Reviews:

Tetr *32* 3 (1976)
Syn 177 (1976)

Stereochemistry:

JOC *29* 2501 (1964); *31* 2543 (1966); *33* 3913 (1968); *36* 178, 594 (1971)
TL 4807 (1965)
CC 753 (1967); 47, 1249 (1968)
Can J Chem *47* 4307 (1969)
JACS *93* 1539 (1971)

Acid promotion:

TL 4995 (1971)
JOC *45* 5399 (1980)
JACS *108* 4561 (1986)

Amino acid-catalyzed chiral annulation:

Angew Int *10* 496 (1971)
JOC *39* 1612, 1615 (1974); *40* 675 (1975)
JCS Perkin I 2349 (1983)
Org Syn *63* 26, 37 (1984)
TL *27* 1501 (1986) (mechanism)

Aprotic conditions:

JOC *48* 3349 (1983)

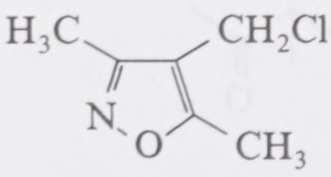
Use of enamines:

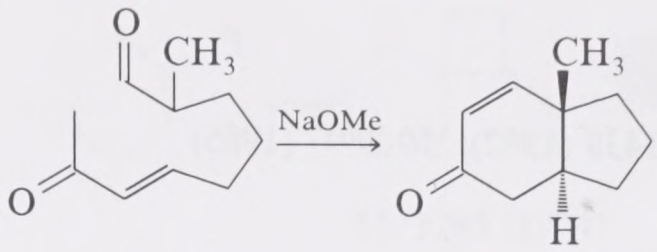
JACS *92* 5657 (1970)
JOC *40* 862 (1975); *47* 1438 (1982); *50* 2607 (1985)
Tetr *32* 1415 (1976)

Chiral imine annulation:

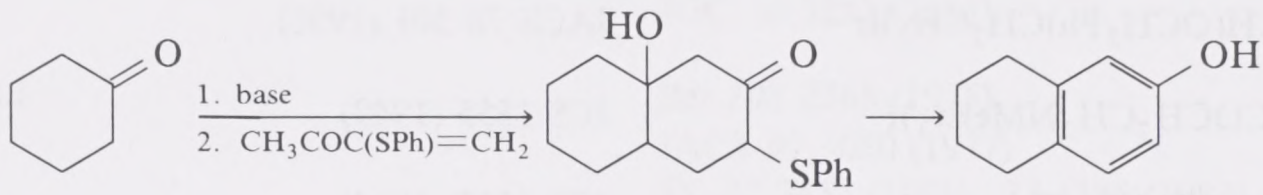
JACS *107* 273 (1985)

Modified Michael acceptors and their equivalents:

$CH_3CH(OCH_2Ph)CH_2CH_2Br$	JACS *78* 501 (1956)
$(CH_3COCH_2CH_2NMeEt_2)I$	JCS 1855 (1949)
$CH_3COCH_2CH_2Cl$	JCS 1029 (1964)
$ClCH_2COCH_2CH_2Cl$	CC 367 (1971)
$CH_3OCH_2COCH_2CH_2OCH_3$	JACS *100* 1263, 2140, 2150 (1978)
$RCH_2COC(SiMe_3)=CH_2$	JACS *95* 6152, 6867 (1973); *96* 6179 (1974); *107* 7184 (1985) Org Syn *58* 158 (1978) CC 174 (1982) Can J Chem *60* 509 (1982) Tetr *39* 925 (1983)
$CH_3O_2CCH_2COCH=CH_2$	JACS *86* 2034 (1964) TL 2755 (1972)
$CH_3CH(SePh)COCH=CH_2$	Syn Commun *8* 211 (1978)
$H_2C=CH(CH_2)_3COCH=CH_2$ (bis-annulation)	JACS *101* 5070 (1979)
$CH_3C(SiMe_3)=CHCH_2I$	JACS *96* 3682, 3684 (1974)
$CH_3CCl=CHCH_2Cl$	Coll Czech Chem Commun *13* 300 (1948) Helv *32* 1284, 2360 (1949) BSCF 780 (1954) JACS *82* 4245 (1960) JOC *30* 3642 (1965); *57* 4807 (1986) Tetr *25* 2159 (1969) Acct Chem Res *5* 311 (1972) BCSJ *52* 2978 (1979)
$Ph_3\overset{+}{P}CH=C(OEt)CH=CHR$ (R = H, Me)	JOC *43* 4673 (1978)
	JACS *89* 5459, 5463, 5464 (1967) JOC *37* 1652, 1659, 1664 (1972)

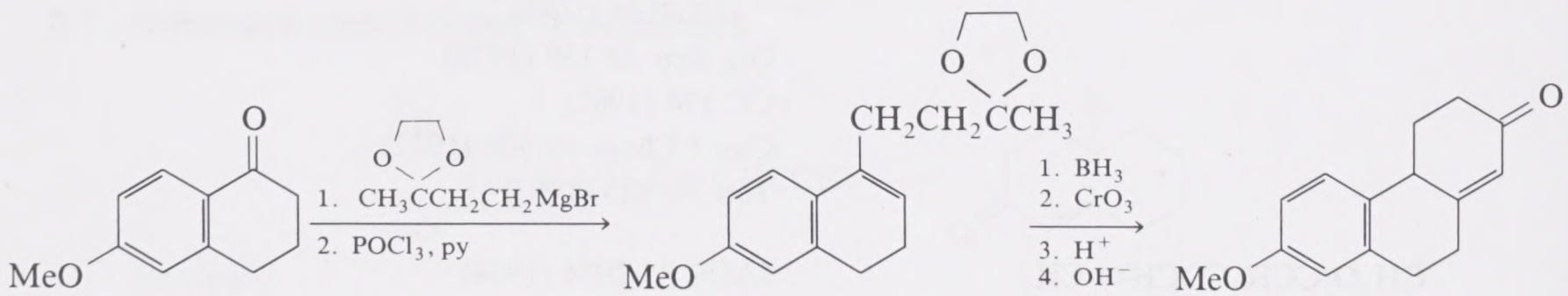


JACS *104* 310, 3767 (1982)



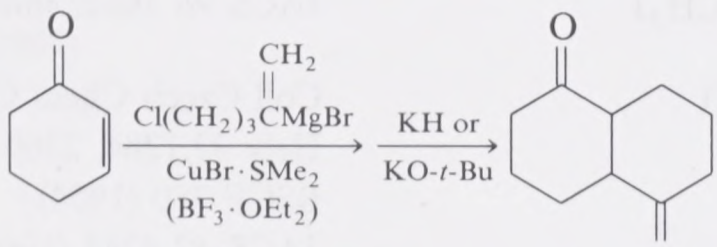
JOC *47* 1200 (1982)

6.2. Reversed Robinson Annulation

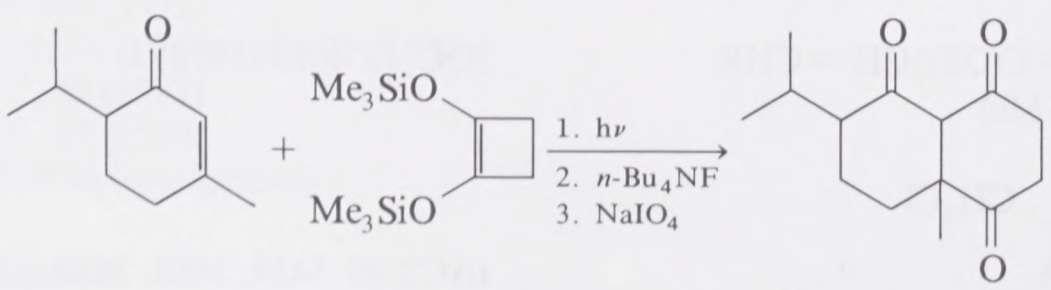


TL 3105 (1976)

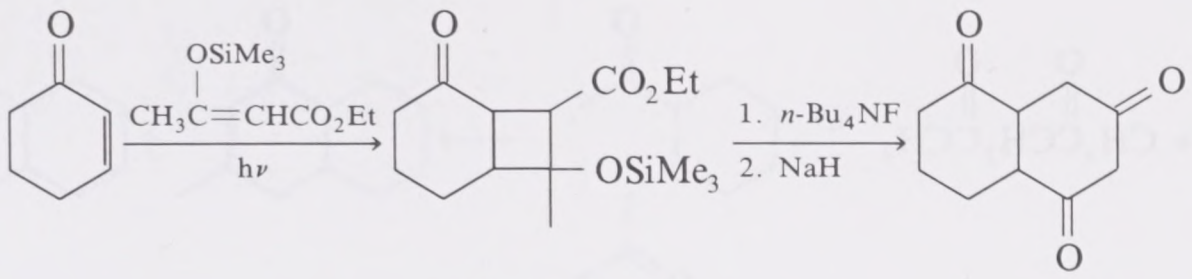
6.3. Other Four-Carbon Annulations



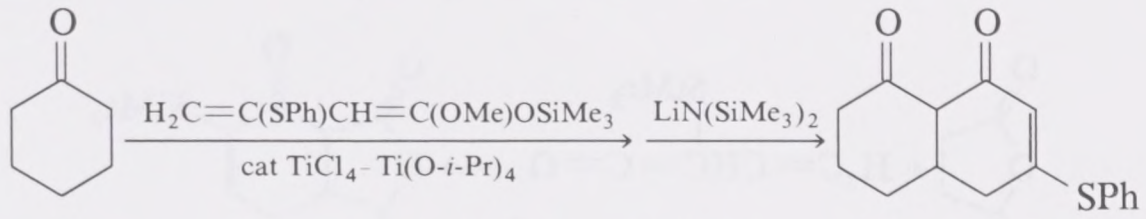
JOC *49* 4567 (1984)
CC 1342 (1987)



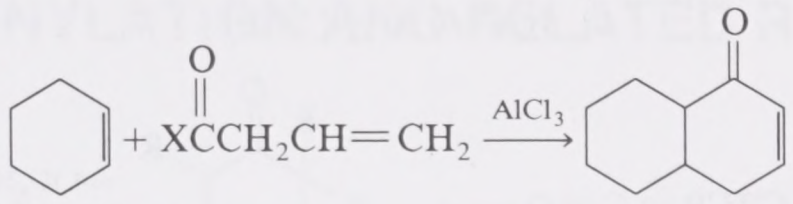
Syn 1024 (1980)



TL *23* 295 (1982)

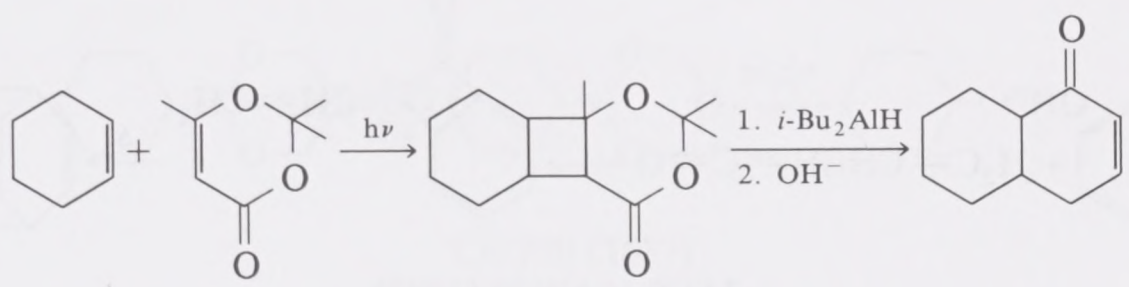


JOC *52* 110 (1987)

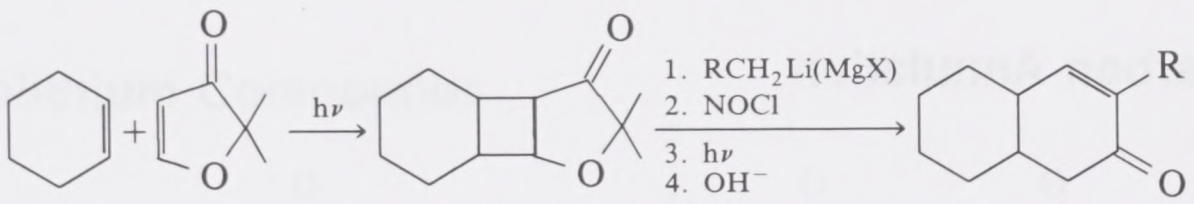


X = Cl, Br

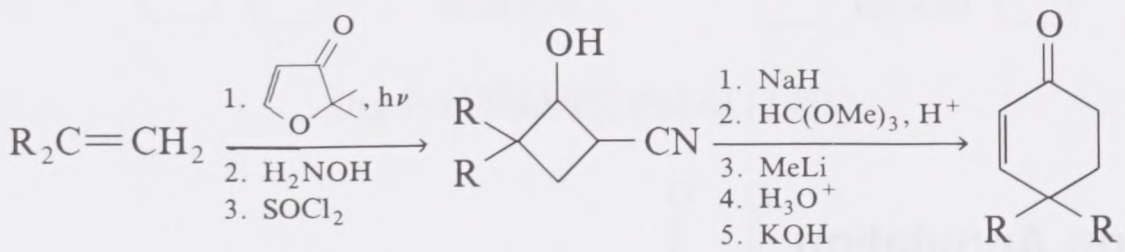
CC 263 (1979)
JOC *44* 4042 (1979)



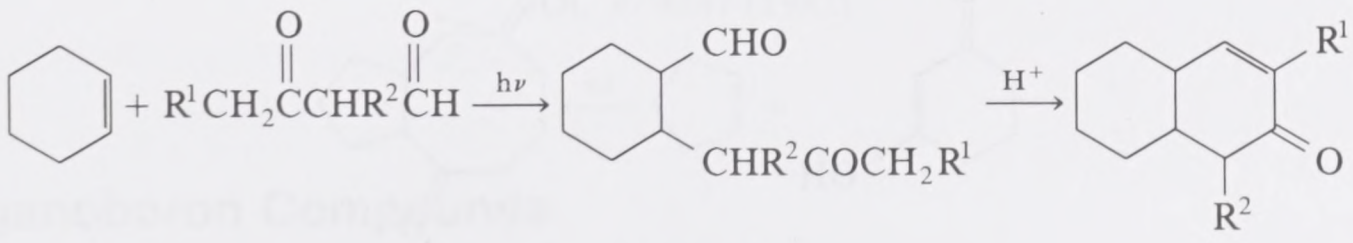
JACS *102* 3634 (1980)



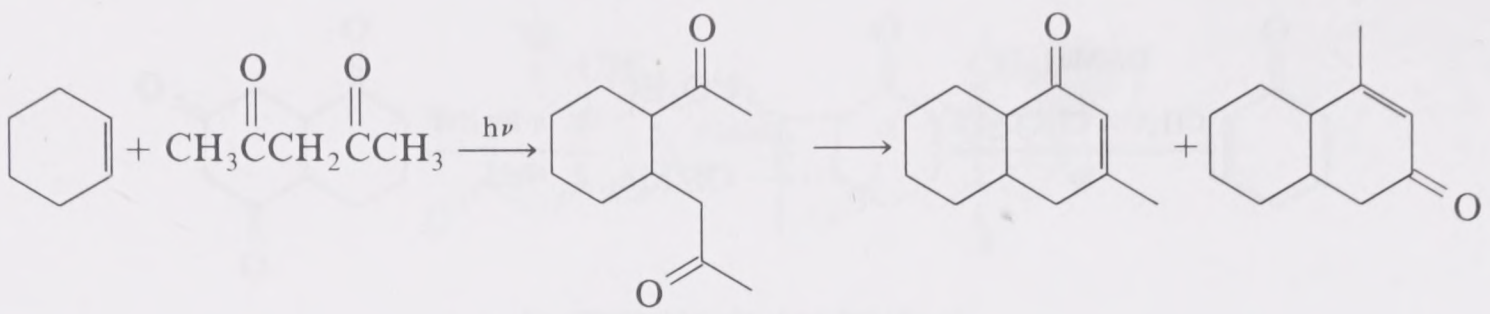
JACS *104* 4990 (1982)



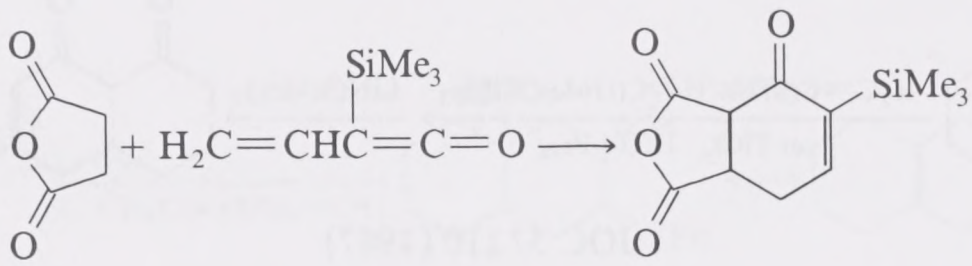
TL 2657 (1979); *23* 1235 (1982)



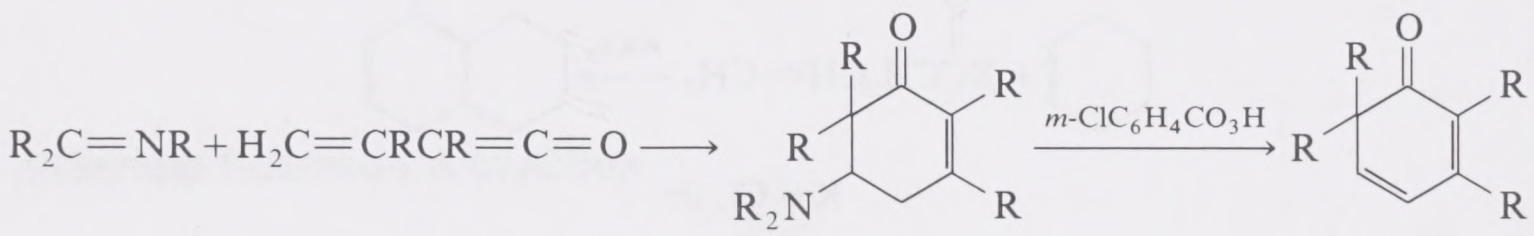
TL 3969 (1975)
JOC *40* 1865 (1975)



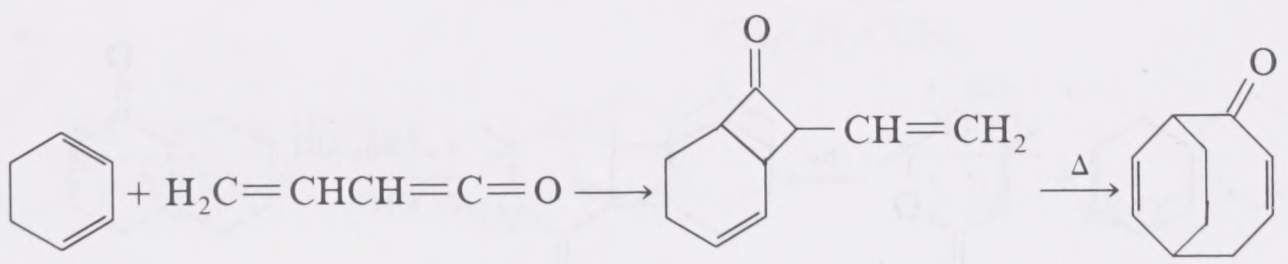
Can J Chem *41* 440 (1963)



JOC *45* 4810 (1980)

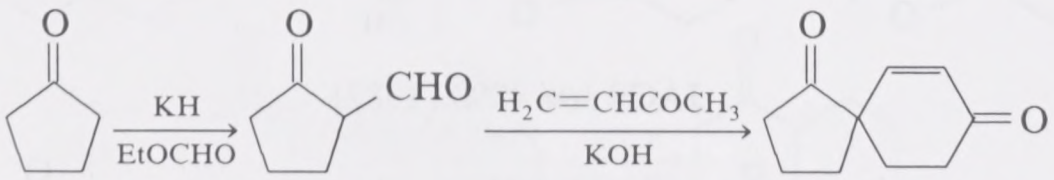


Helv *65* 2230 (1982)



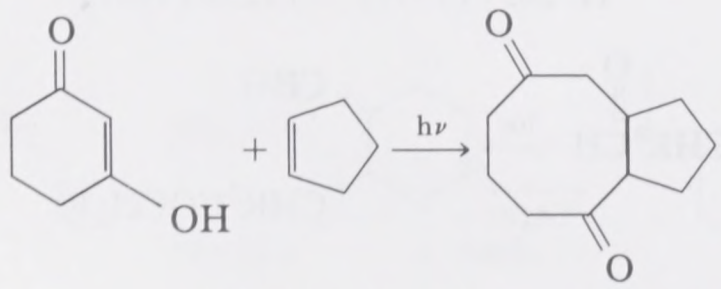
JACS *104* 7670 (1982)

7. Five-Carbon Annulation



Syn 796 (1983)

8. Six-Carbon Annulation

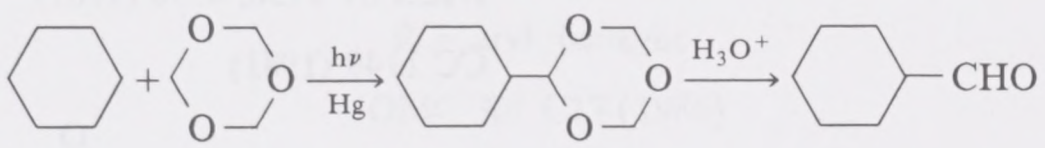


TL *23* 5485 (1982)
JOC *52* 2905 (1987)

7. CARBONYLATION AND RELATED REACTIONS

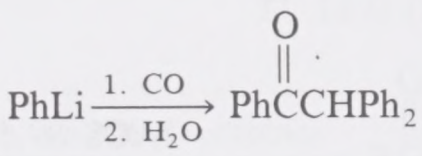
See also page 681, Section 8.

1. Alkanes

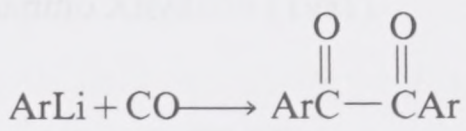


CC 970 (1987)

2. Organolithium Compounds



Org Prep Proc Int *13* 144 (1981)

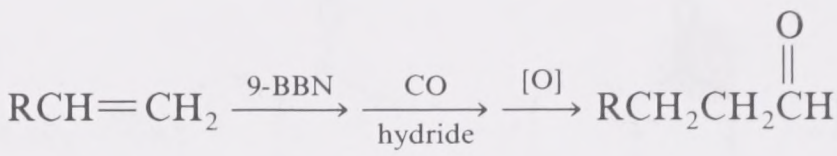


JOC *47* 4347 (1982)

3. Organoboron Compounds

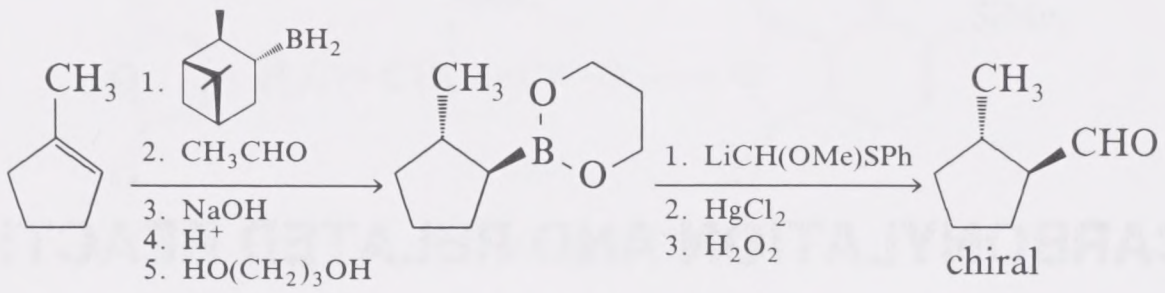
Review:

Acct Chem Res *2* 65 (1969)

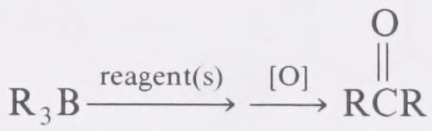


Hydride

$LiHAl(O\text{-}t\text{-}Bu)_3$	JACS *90* 499 (1968); *91* 2144, 4606 (1969)
$KHB(O\text{-}i\text{-}Pr)_3$	CC 607 (1979); 1273 (1982) Syn 701 (1979)

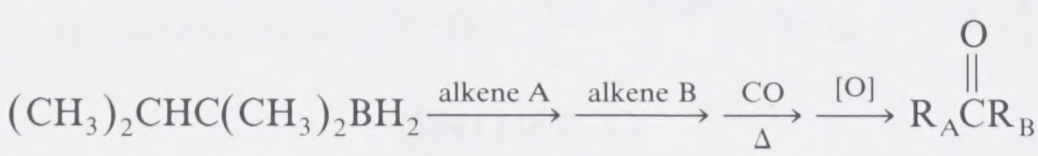


JACS *107* 4980 (1985); *109* 7553 (1987)

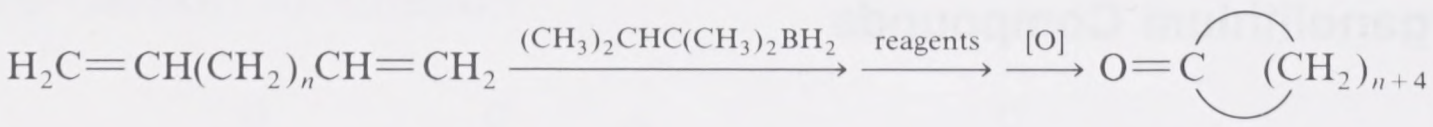


Reagent(s)

CO, H_2O, Δ	JACS *89* 2738, 4530 (1967)
$LiC(SPh)_3$	CC 1149 (1981)

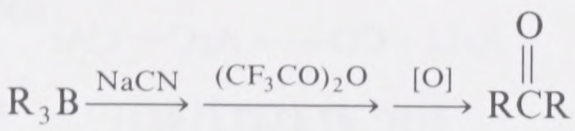


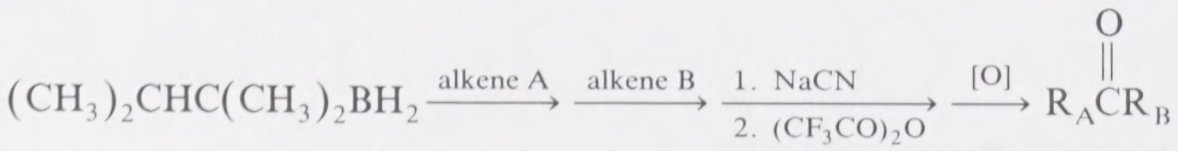
JACS *89* 5285 (1967)
Syn 196 (1972)



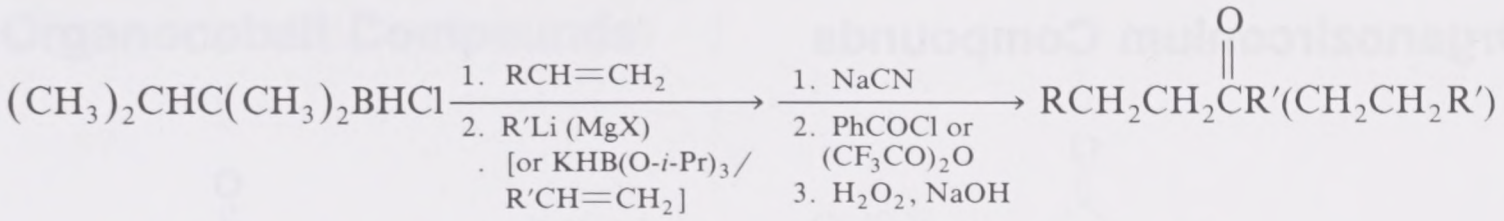
Reagents

CO, Δ	JACS *89* 5477 (1967) CC 594 (1968); 607 (1979)
KCN, $(CF_3CO)_2O$	TL *21* 2381 (1980); *22* 2075 (1981) Syn Commun *10* 93 (1980)

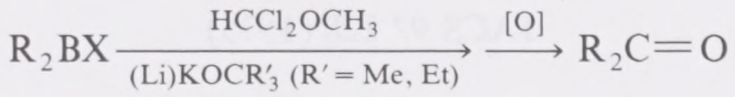




CC 1529 (1970); 1048 (1971); 186 (1973)
JCS Perkin I 129 (1975)
Syn Commun *10* 675 (1980)

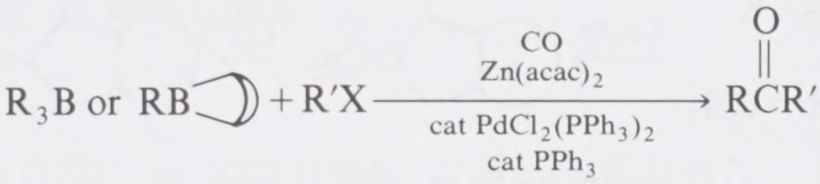


JACS *102* 5919 (1980)
JOC *45* 4542 (1980)



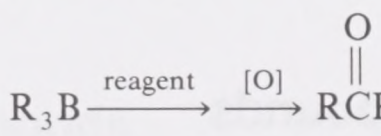
X = Cl, Br, OR

JACS *95* 6876 (1973); *104* 6844 (1982); *109* 5420 (1987) (chiral)
JOC *44* 2417 (1979); *47* 863 (1982)
Organomet *1* 212 (1982)
Tetr *40* 1325 (1984) (chiral)
TL *28* 3771 (1987)



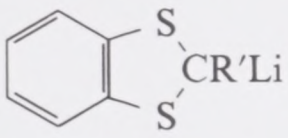
R′ = aryl, benzylic

JOMC *301* C17 (1986)

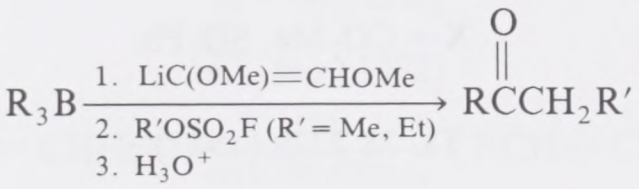


Reagent

$LiCH(SPh)_2R'$ CL 961 (1973)

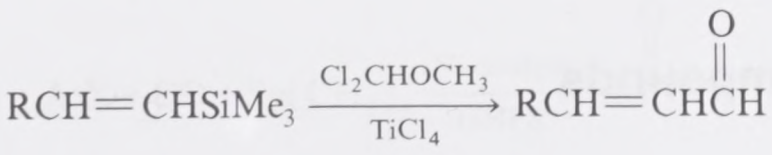


TL 1893 (1979)



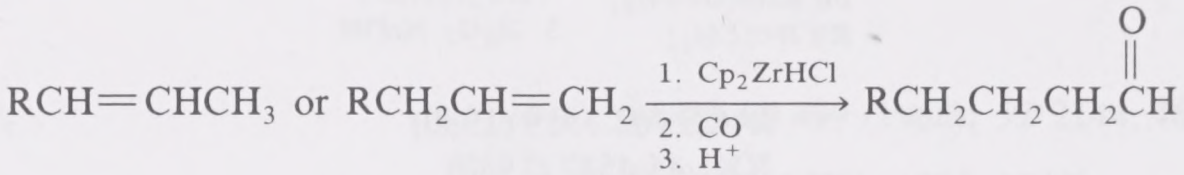
CL 1059 (1981)

4. Organosilicon Compounds

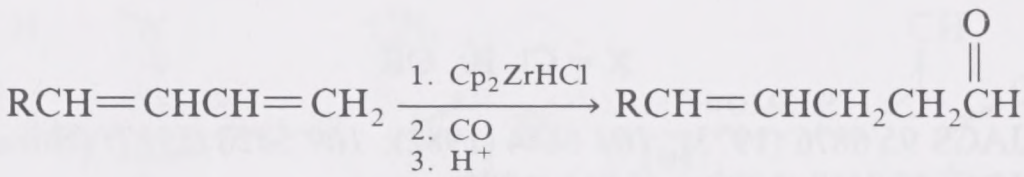


CL 859 (1978)

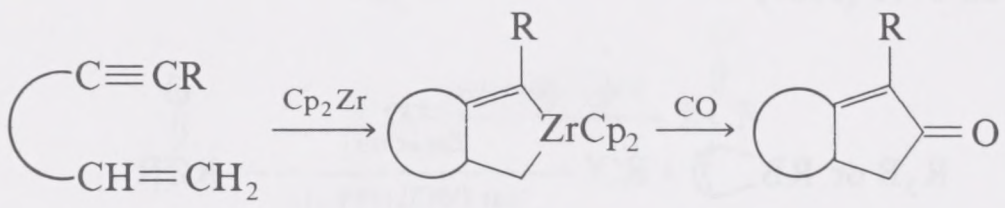
5. Organozirconium Compounds



JACS *97* 228 (1975)

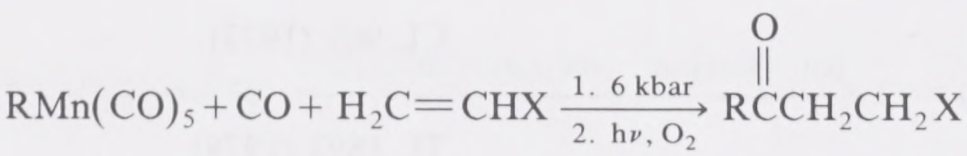


JACS *98* 262 (1976)



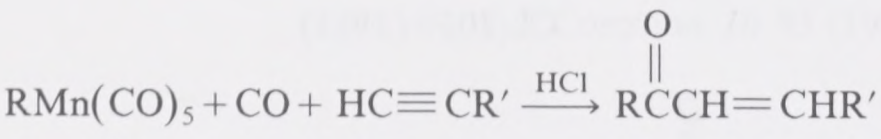
JACS *107* 2568 (1985)
TL *27* 2829 (1986); *28* 917 (1987)

6. Organomanganese Compounds



$X = CO_2Me, SO_2Ph$

TL *28* 2229 (1987)

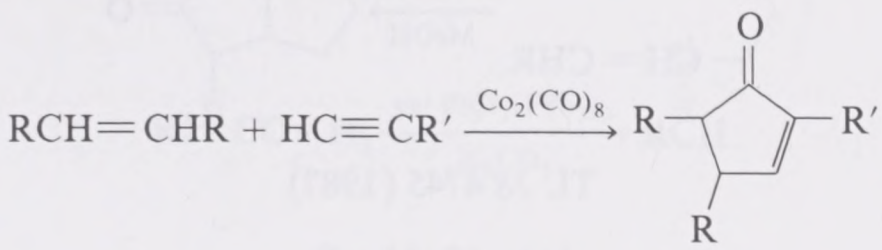


TL *28* 2233 (1987)

7. Organoiron Compounds

See page 712, Section 3.

8. Organocobalt Compounds



Reviews:

Tetr *41* 5855 (1985)
Ann NY Acad Sci *295* 2 (1977)

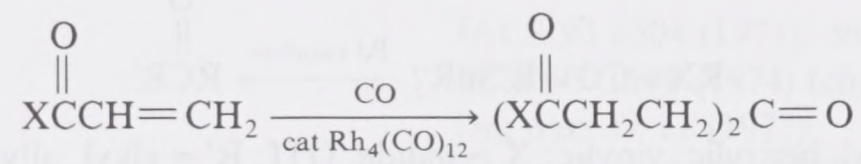
Intermolecular:

JCS Perkin I 977 (1973); 30 (1976)
J Chem Res (S) 8 (1977); 244 (1983); 344, 3131 (1984)
Organomet *1* 1560 (1982)
TL *24* 2905 (1983)
Tetr *41* 5995 (1985)
JOC *50* 5215 (1985); *52* 3595 (1987)

Intramolecular:

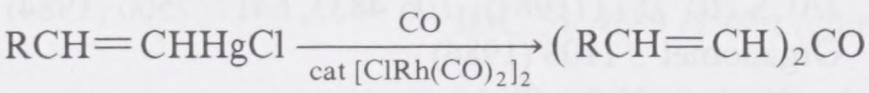
JOC *46* 5357, 5436 (1981); *49* 5025 (1984); *52* 569, 5296 (1987)
JACS *105* 2477 (1983); *108* 3128, 3835 (1986); *109* 7495 (1987)
TL *25* 4041 (1984); *26* 2475, 4851 (1985); *27* 1241, 1245 (1986); *28* 5465 (1987)
Bull Acad Sci USSR, Div Chem Sci 2434 (1984); 2455 (1985); 211, 213 (1987)
Tetr *41* 5861 (1985)

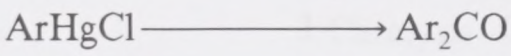
9. Organorhodium Compounds



$X = OR, NR_2$

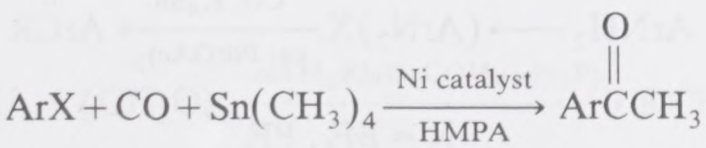
CL 361 (1982)



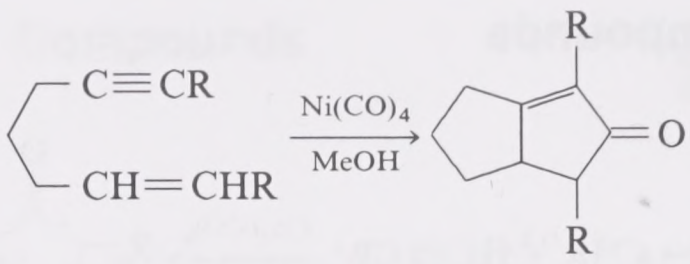


JOC *45* 3840 (1980)

10. Organonickel Compounds

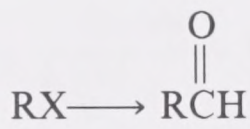


Syn 47 (1981)



TL *28* 4745 (1987)

11. Organopalladium Compounds

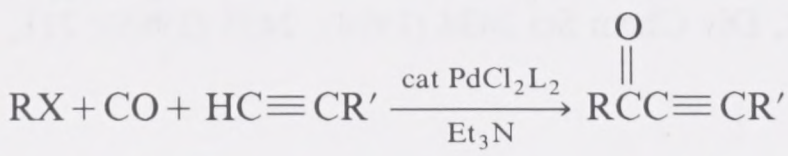


CO, cat $PdCl_2$, H_2, py (R = aryl) — BCSJ *49* 1681 (1976)

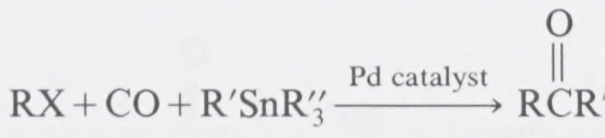
CO, cat $PdX_2(PPh_3)_2$ (X = Br, I), H_2, R_3N (R = aryl, heterocyclic, vinylic) — JACS *96* 7761 (1974)

CO, cat $Pd(PPh_3)_4$, NaO_2CH or $[-SiMeHO-]_x$ (R = aryl) — JOC *49* 4009 (1984)

CO, cat $Pd(PPh_3)_4$, *n*-Bu_3SnH (R = aryl, allylic, benzylic, vinylic; X = halide, OTf) — JACS *105* 7175 (1983); *108* 452 (1986)

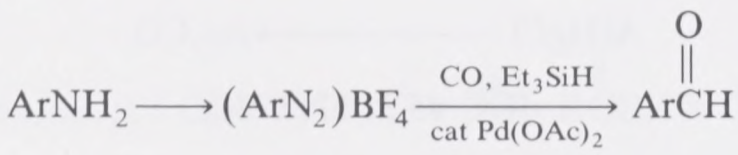


CC 333 (1981)

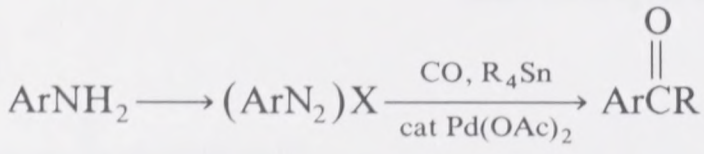


R = allylic, aryl, benzylic, vinylic; X = halide, OTf; R′ = alkyl, allylic, aryl, vinylic

TL 2601 (1979)
JOMC *205* C27 (1981)
JACS *105* 7173 (1983); *106* 4833, 6417, 7500 (1984)
Organomet *3* 1108 (1984)



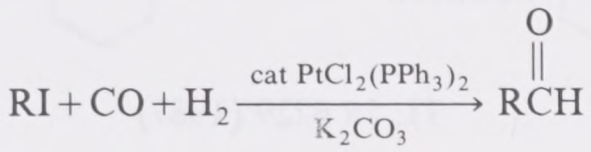
JOMC *270* 283 (1984)



X = BF_4, PF_6

CL 35 (1982)

12. Organoplatinum Compounds

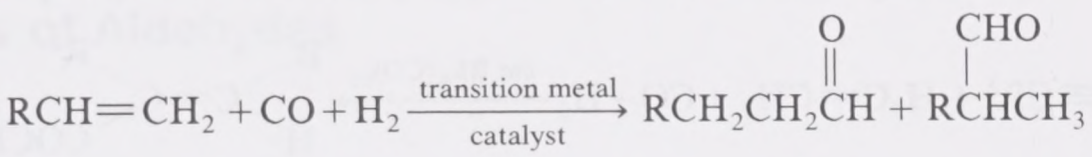


$$RI + CO + H_2 \xrightarrow[K_2CO_3]{\text{cat } PtCl_2(PPh_3)_2} RCH$$

R = 1°, 2° alkyl

CC 351 (1986)

13. Hydroformylation and Hydroacylation

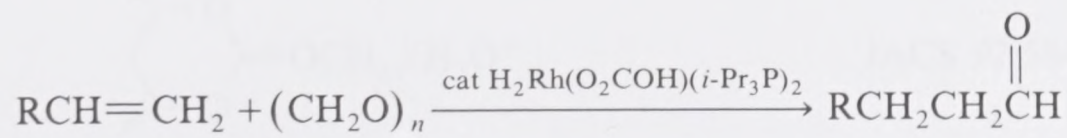


$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{catalyst}]{\text{transition metal}} RCH_2CH_2CH + RCHCH_3$$

Reviews:

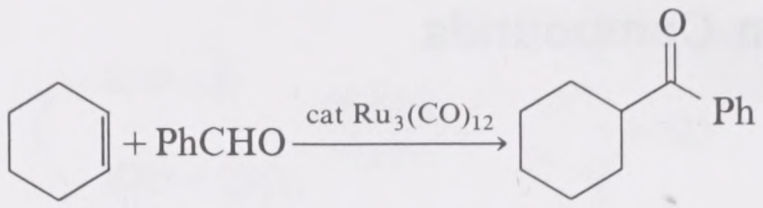
J. Falbe, "Carbon Monoxide in Organic Synthesis," Springer, New York (1970)
Catal Rev *6* 49 (1972)
"Organic Synthesis via Metal Carbonyls," Eds. I. Wender and P. Pino, Wiley, New York (1977)
J Mol Catal *4* 243 (1978)
Topics Curr Chem *105* 77 (1982) (chiral)
JACS *109* 7714 (1987) (fluoroalkenes)

Co	JACS *99* 1058 (1977); *103* 7590, 7594 (1981)
Rh	JACS *95* 6504 (1973); *99* 1058 (1977) BCSJ *47* 1698 (1974) (chiral) Org Syn *57* 11 (1977) Angew Int *19* 178 (1980) (review) JOC *46* 4422 (1981) (chiral) JOMC *279* 193 (1985) (chiral)
Pd	JOC *51* 4189 (1986) (chiral)
Pt	JACS *97* 3553 (1975); *109* 7122 (1987) (chiral) J Catalysis *45* 256 (1976) Helv *59* 642 (1976) (chiral) CL 361 (1978) (chiral) JOMC *213* 503 (1981); *279* 193 (1985) (chiral); *296* 281 (1985) (chiral) Helv *64* 1865 (1981)



$$RCH{=}CH_2 + (CH_2O)_n \xrightarrow{\text{cat } H_2Rh(O_2COH)(i\text{-}Pr_3P)_2} RCH_2CH_2CH$$

TL *23* 4967 (1982)



TL *28* 6229 (1987)

$$RCH{=}CH_2 + H\overset{\overset{\displaystyle O}{\|}}{C}R' \xrightarrow[(AcO)_2]{h\nu \text{ or}} RCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}R'$$

JOC *14* 250 (1949)

$$XCH{=}CH_2 + H\overset{\overset{\displaystyle O}{\|}}{C}R \longrightarrow XCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}R$$

X = COR, CO_2R, CN, etc.

See conjugate addition under the appropriate functional group.

$$R^1C{\equiv}CR^2 + H_2C{=}CH_2 + CO + H_2 \xrightarrow{\text{cat } Rh_4(CO)_{12}} \begin{matrix} R^1 \diagdown \\ H \diagup \end{matrix} C{=}C \begin{matrix} \diagup R^2 \\ \diagdown COCH_2CH_3 \end{matrix}$$

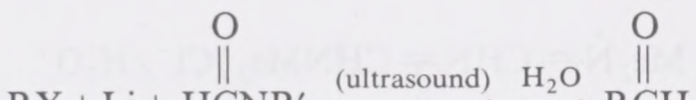
CL 401 (1982)

8. ELECTROPHILIC ACYLATION

1. Synthesis of Aldehydes

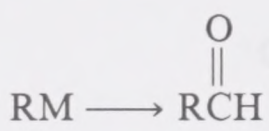
Reviews:

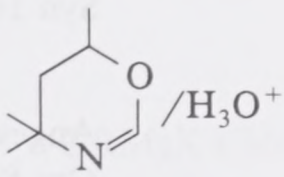
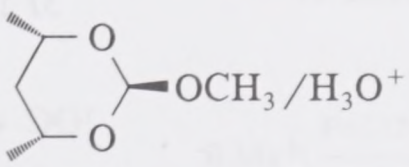
Quart Rev *20* 179 (1966)
Heterocycles *6* 731 (1977)



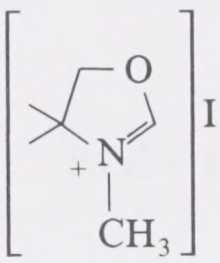
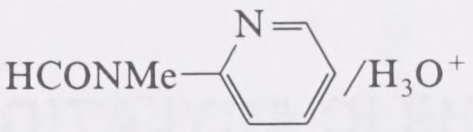
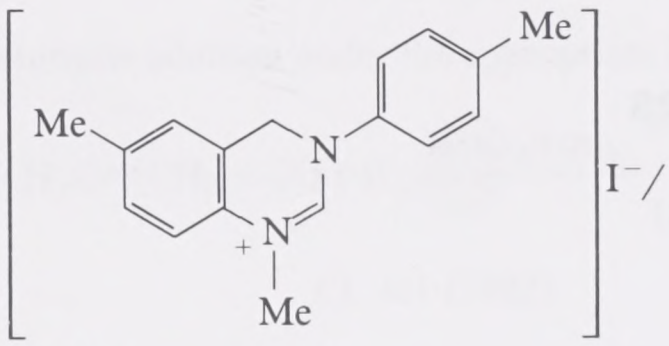
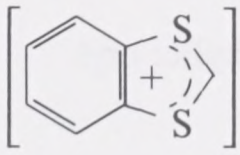
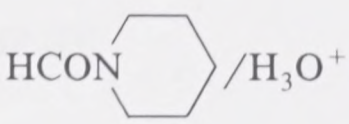
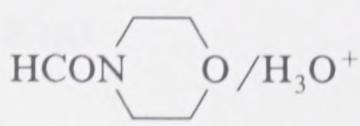
R = 1°, 2°, 3° alkyl; benzylic; aryl

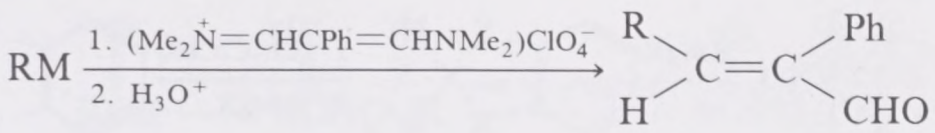
Syn 160 (1973)
TL *23* 3361 (1982); *27* 1791 (1986)



M	Reagents	
Li	$CNC(CH_3)_2C(CH_3)_3/H_3O^+$	JACS *91* 7778 (1969); *92* 6675 (1970)
	 $/H_3O^+$	TL 5151 (1969)
MgX	$Fe(CO)_5/H_3O^+$	BCSJ *55* 1663 (1982)
	 OCH_3/H_3O^+	JACS *92* 584 (1970)
	$EtOCH{=}NPh/H_3O^+$	JOC *6* 489 (1941)
	HCO_2MgBr/H_3O^+	TL *21* 2869 (1980)
	$HC(OEt)_3/H_3O^+$	JOC *6* 437 (1941)

$$RM \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}H \quad (\textit{Continued})$$

M	Reagents	
	 I^-, HMPA/H_3O^+	JACS *92* 6676 (1970) Angew Int *15* 270 (1976)
		Syn 403 (1978) TL 5179 (1978)
	 I^-/ H_3O^+	JACS *77* 5118 (1955)
	$(Me_2\overset{+}{N}{=}CHN{=}CHNMe_2)Cl^-/H_3O^+$	Syn Commun *11* 571 (1981)
	 ClO_4^-/hydrolysis	JCS Perkin I 1886 (1976) TL *22* 1821 (1981)
	$CH_3SOCH_2SCH_3/SO_2Cl_2$, SiO_2-H_2O	TL 3883 (1977)
Li or MgX	$HCONMe_2/H_3O^+$	JOC *6* 437 (1941); *51* 3762, 5106 (1986) JCS 3334 (1955); 4691 (1956); 1054 (1958) Chem Ind 1596 (1957) Compt Rend *275* 511 (1972) Syn 160 (1973)
		Angew Int *20* 878 (1981) Org Syn *64* 114 (1985) JOC *50* 2423, 2427 (1985); *51* 142 (1986); *52* 5560 (1987)
		JOC *49* 3856 (1984)
	$Cl_2CHB(O\text{-}i\text{-}Pr)_2/H_2O_2$	JOMC *122* 145 (1976)



R = 1° alkyl, benzylic, aryl

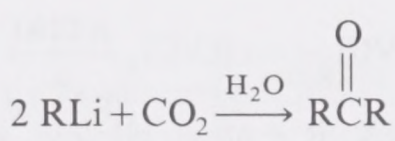
M = Li, MgX

Syn Commun *11* 561 (1981)

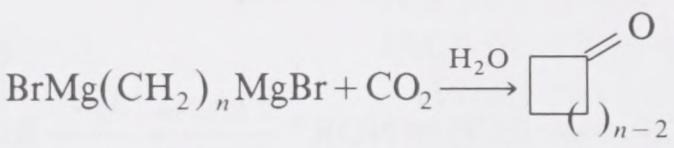
RM	
RMgX (R = 1°, 2° alkyl; aryl; alkynyl; propargylic; vinylic)	Ber *103* 643 (1970) Syn 379 (1975) J Chem Res (S) 343 (1981)
$RCH{=}CHCH_2M$ (M = MgX, ZnX, $Al_{2/3}Br$)	J Chem Res (S) 343 (1981)
$RCH{=}C{=}CHCH_2Al_{2/3}Br$	J Chem Res (S) 343 (1981)

2. Synthesis of Ketones

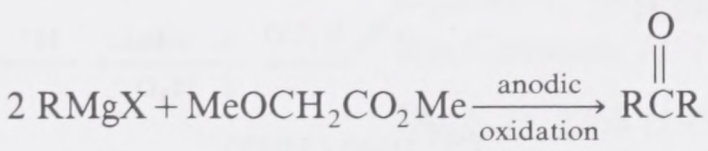
2.1. From Carbonyl Cation Equivalents



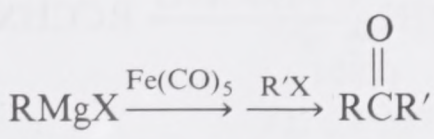
JACS *55* 1258 (1933); *75* 1771 (1953); *77* 2806 (1955)



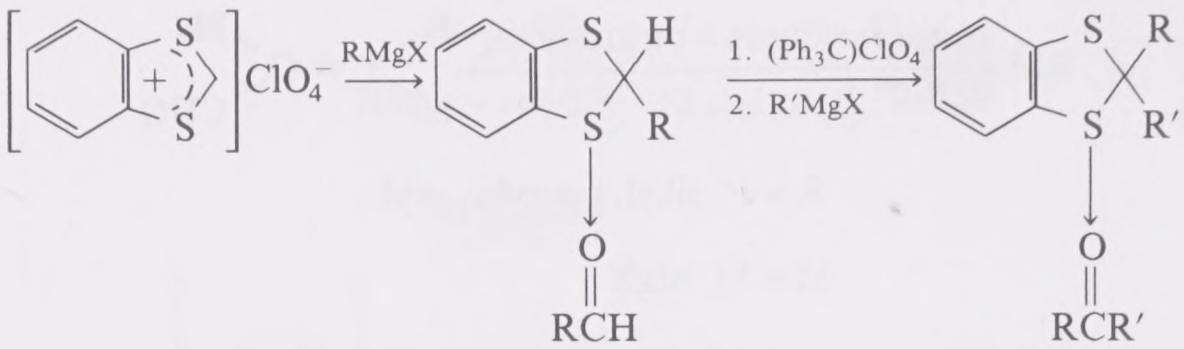
n	
3	Syn 721 (1983)
4	Ber *44* 1918 (1911)
5	Compt Rend *144* 1358 (1907)



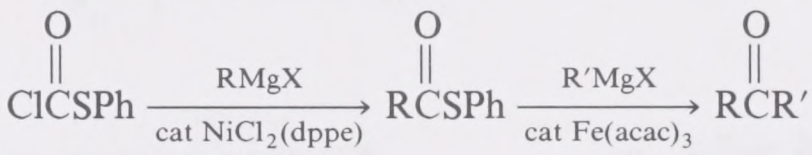
TL 3625 (1977)



TL 761 (1978)



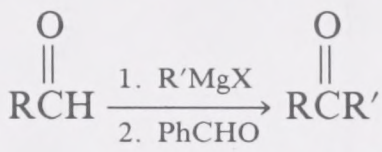
JCS Perkin I 1886 (1976)
TL *22* 1821 (1981)



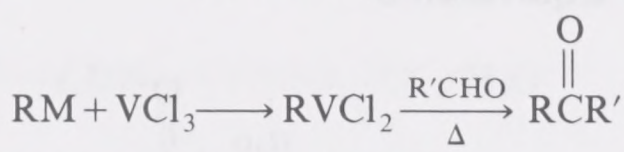
TL *26* 3595 (1985)

2.2. From Aldehydes

See page 709, Section 9, and page 721, Section 10, for related reactions.

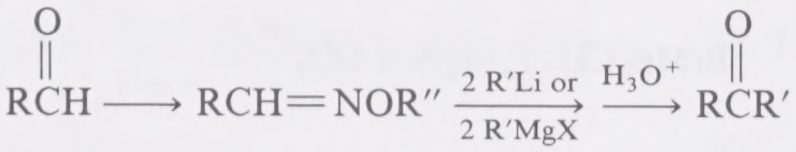


TL *28* 769 (1987)



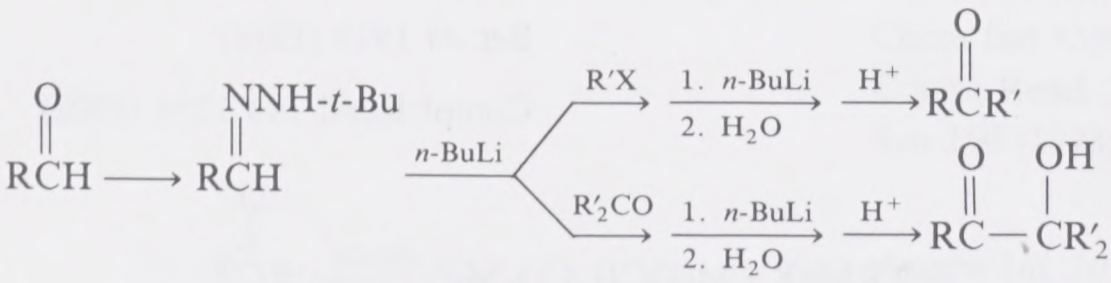
M = Li, MgX; R = alkyl, alkynyl, aryl, vinylic

JACS *107* 7179 (1985)
TL *27* 933 (1986)

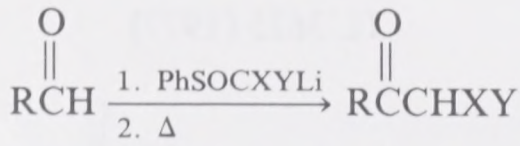


R = aryl > alkyl

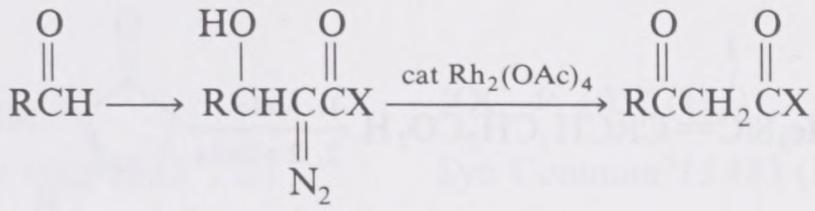
TL *27* 3033 (1986)



CC 1040 (1983)



X, Y	
H, F	TL *24* 725 (1983)
Cl, Cl	TL *24* 527 (1983)



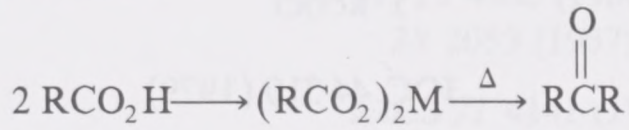
X = R, OR

CC 959 (1979)
JCS Perkin I 2566 (1981)
JACS *109* 6187 (1987)

See page 642, Section 7.16.

2.3. From Carboxylic Acids

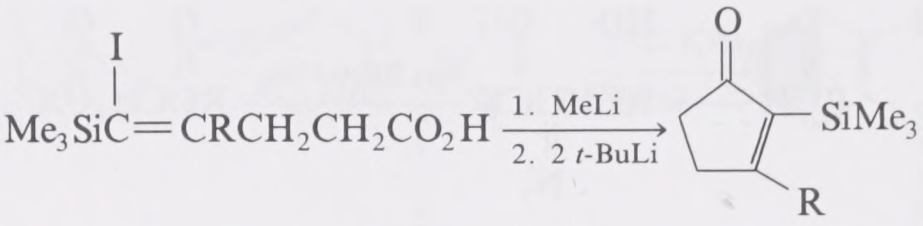
See also page 702, Section 3.



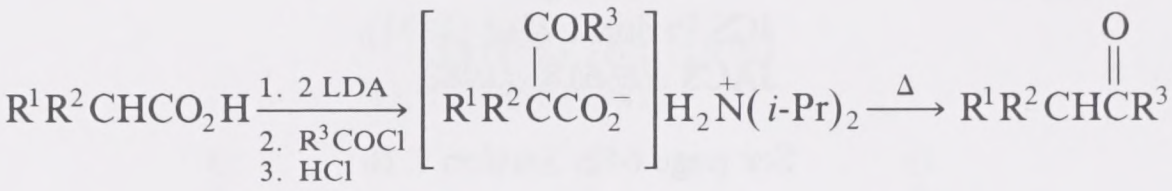
M	
Mg	Org Syn Coll Vol *4* 854 (1963)
Ba	Org Syn Coll Vol *1* 192 (1941)



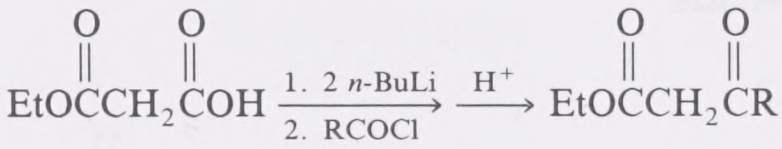
M	Reagent(s)	
Li	—	JCS 2012 (1950) JACS *91* 456 (1969); *92* 2590 (1970); *95* 4873 (1973); *103* 6157 (1981); *106* 1095, 2064, 6702 (1984); *107* 996, 5717, 7546 (1985); *108* 1617, 4484 (1986); *109* 3025 (1987) Org Rxs *18* 1 (1970) Org Syn Coll Vol *5* 775 (1973) TL 2877 (1974); *28* 2933 (intramolecular), 4965 (1987) JOC *40* 1768 (1975); *41* 1176 (1976); *48* 2260, 4789 (1983); *50* 325 (1985); *51* 2361 (1986); *52* 4171, 5501 (1987) Syn Commun *11* 7 (1981)
MgX	—	JACS *78* 2268 (1956) (perfluorinated acids); *106* 1095 (1984); *108* 7727 (1986) (LiO_2CCF_3) Austral J Chem *30* 427 (1977); *35* 1739 (1982) ($R'M = H_2C{=}CHMgBr$) JOC *48* 2260 (1983); *50* 325 (1985); *52* 3474 (1987)
	$NiCl_2$(dppe)	TL *24* 3677 (1983)
	[*p*-$MeOC_6H_4CCl{=}\overset{+}{N}Ph_2$]$Cl^-$	TL *23* 5059 (1982)
	Ph_2POCl, Et_3N	Syn Commun *8* 59 (1978) CC 412 (1986)



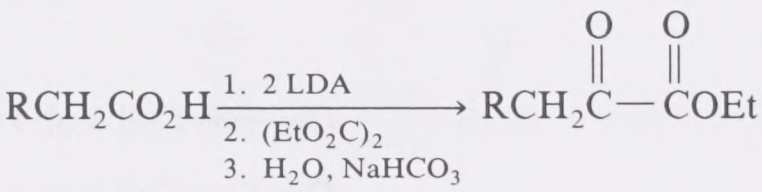
JACS *105* 6761 (1983)



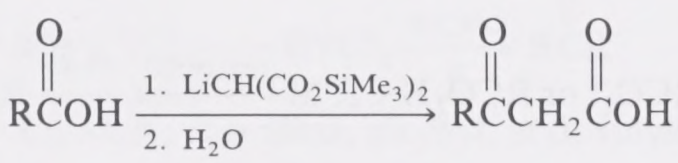
JOC *42* 1189 (1977)



JOC *44* 310 (1979)



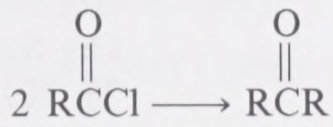
TL *22* 2439 (1981)



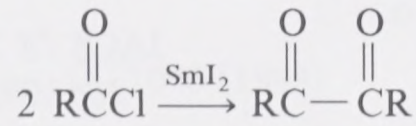
Syn 787 (1979)

2.4. From Acid Halides

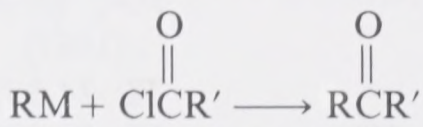
See also page 702, Section 3.



Et_3N/H_2O, Δ	JACS *69* 2444 (1947) Org Syn Coll Vol *4* 555, 560 (1963)
$Fe_2(CO)_9$	TL 3861 (1977)



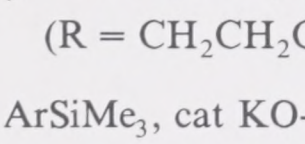
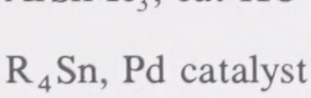
TL *22* 3959 (1981); *25* 2869 (1984)

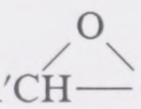


Reviews: Org Rxs *8* 28 (1954) (Mg, Zn, Cd); *22* 253 (1975) (Cu)

RM	
o-$LiC_6H_4CO_2Li$	JOC *46* 1057 (1981)
$LiCH_2CO_2SiMe_3$ (R = Me after H_3O^+, Δ)	Syn Commun *13* 183 (1983)
RLi, cat CuX (X = Cl, I) (R = 1°, 2°, 3° alkyl)	TL 829 (1971)
RMgX, THF, −78°C (R = 1°, 2°, 3° alkyl; aryl)	TL 4303 (1979); *21* 2303 (1980) Ber *114* 2479 (1981) CL 13 (1986)
RMgX, HMPA (R = 1°, 2° alkyl; aryl; alkynyl; vinylic)	Compt Rend C *275* 511 (1972)
RMgX, $FeCl_3$ (R = 1°, 3° alkyl)	JACS *75* 3731 (1953) JOC *26* 1768, 1772 (1961)
RMgX, cat $Fe(acac)_3$ (R = 1°, 2°, 3° alkyl; aryl)	TL *25* 4805 (1984); *26* 1285 (1985); *28* 2053 (1987)
RMgX, cat CuX (X = Cl, I) (R = 1°, 3° alkyl)	JACS *71* 4141 (1949); *75* 3731 (1953) TL 829 (1971); 467 (1972) Tetr *29* 3943 (1973); *37* 4189 (1981) J Chem Res (S) 46 (1978)
RMgX, cat Cu-CuCl (R = 1°, 3° alkyl)	TL 2523 (1970)
NaCo(I)Salen/MeMgI/H_3O^+	Tetr *37* 863 (1981)
R_4BLi (R = 1° alkyl, benzylic)	JOC *40* 1676 (1975)
$(R_3BMe)Li$, CuCl·COD (R = 1° alkyl)	TL 173 (1977)
$RAlCl_2$ (R = 1° alkyl)	JACS *108* 6036 (1986)
R_3Al, $Cu(acac)_2$, PPh_3 (R = 1° alkyl)	BCSJ *54* 1281 (1981)
$(R_4Al)Li$, cat CuCl (R = 1° alkyl)	CL 623 (1979)
R_4Si, $AlCl_3$ (R = 1° alkyl)	Syn 677 (1977)
$RSiR'_3$, $ZnCl_2$ (R = thienyl, furyl)	JOC *47* 3219 (1982)
$RSiR'_3$, $AlCl_3$ or $TiCl_4$ (R = vinylic)	CC 633 (1975) JCS Perkin I 2485 (1980); 2527 (1981) TL *22* 2985 (1981); *23* 263 (1982); *27* 4869 (1986) JOC *46* 2400 (1981) (intramolecular)
$R_2NC{\equiv}CSiR'_3$	Ann 1907 (1981)
$RSiR'_3$; $AlCl_3$, $ZnCl_2$ or $TiCl_4$ (R = alkynyl)	Ber *96* 3280 (1963) JOMC *37* 45 (1972) Syn 438 (1979); 29 (1981) Helv *62* 852 (1979); *64* 1123 (1981); *65* 13, 2413 (1982) CC 459 (1981) JOC *47* 3219 (1982); *52* 3662 (1987) TL *23* 3203 (1982); *28* 5543 (1987) Can J Chem *60* 379 (1982) JACS *106* 3548 (1984); *107* 6046 (1985)

RM (*continued*)

$RSiR'_3$; $AlCl_3$, $TiCl_4$ or $ZnCl_2$ (R = allylic)	JOMC *85* 149 (1975) TL 1871 (1976); 1385 (1977); 429 (1979); *21* 831, 3783, 4369 (1980); *23* 723 (1982) JOC *44* 3397 (1979); *47* 3219 (1982) Syn 446 (1979) CL 961 (1982) JACS *104* 4962 (1982)
$H_2C{=}CHC(CH_2){=}CH_2SiMe_3$, $TiCl_4$	Tetr *39* 883 (1983)
$H_2C{=}CH(OSiR_3)SiR_3$, $TiCl_4$ (product after hydrolysis is $R'COCH_2CH_2CHO$)	JOC *43* 2551 (1978)
$R^2CH{=}CR^1CH(SPh)SiMe_3$, $AlCl_3$	CC 377 (1981)
$R'C{\equiv}CCH_2SiMe_3$, $AlCl_3$ (R = $CR'{=}C{=}CH_2$)	TL *22* 3401 (1981)
 , $AlCl_3$ (R = $CH_2CH{=}CHCH_3$)	TL *22* 2883 (1981)
 CH_2SiMe_3, $AlCl_3$ (R = $CH_2CH_2CH{=}CH_2$)	Can J Chem *59* 802 (1981)
$ArSiMe_3$, cat KO-*t*-Bu (on R′COF)	Angew Int *20* 265 (1981)
R_4Sn, Pd catalyst (R = 1° alkyl, aryl, vinylic)	CL 1423 (1977) JOC *51* 2405 (1986)
$RSnR'_3$, Pd catalyst (R = 1° alkyl, allylic, alkynyl, benzylic, aryl, vinylic)	CL 1423 (1977) JACS *100* 3636 (1978); *105*, 6129 (1983) JOC *44* 1613 (1979); *47* 2549 (1982); *48* 4634 (1983) TL *24* 4283 (1983); *27* 2801 (1986); *28* 759 (1987)
$R_2NCH_2Sn(n\text{-}Bu)_3$	TL *27* 2361 (1986)
$RSnR'_3$ (R = alkynyl), Δ	Ann *716* 29 (1968)
$ROC{\equiv}CSnR'_3$	TL *22* 2637 (1981) Org Prep Proc Int *14* 189 (1982)
$R_2NC{\equiv}CSnR'_3$	Angew Int *18* 405 (1979) Ann 1907 (1981); 196 (1982)
$RSnR'_3$, $AlCl_3$ (R = vinylic)	BSCF 1251 (1977)
E-$(n\text{-}Bu)_3SnCH{=}CHSn(n\text{-}Bu)_3$, $AlCl_3$	TL *27* 5947 (1986) JOC *52* 1493 (1987)

$RSnR'_3$, cat $ClRh(PPh_3)_3$ (R = allylic)	JOMC *129* C36 (1977)
$R''COSnR'_3$, cat $PdCl_2(PPh_3)_2$ (R = R″CO)	TL *26* 6075 (1985)
R_4Pb, cat $Pd(PPh_3)_4$ (R = 1° alkyl)	CC 1302 (1987)
$RPbR'_3$ (R = alkynyl)	TL 2265 (1967) JCS C 317 (1968)
Cp_2ZrClR, $AlCl_3$ (R = 1°, 2° alkyl; vinyl)	JACS *96* 8115 (1974); *99* 638 (1977)
RMgBr, VCl_3 (R = 1° alkyl, aryl)	TL *27* 929 (1986)
RMnI (R = 1°, 2°, 3° alkyl; alkynyl; aryl; vinylic)	TL 3155 (1976); *22* 1239 (1981); *26* 1285 (1985); *27* 4869 (1986) Syn 130 (1977); 37 (1984); 50 (1985) Can J Chem *58* 287 (1980) Tetr *40* 683 (1984)
$Fe(CO)_4^{2-}$,  (R = R′CH=CH)	CL 1067 (1979)
$RRh(CO)L_2$ (R = 1° alkyl, aryl, allylic)	JACS *97* 5448 (1975) JOC *42* 1194 (1977)
RCu·COD (R = 1° alkyl)	CC 1030 (1982)
RCu·*n*-Bu_3P (R = 1° alkyl)	CC 1030 (1982)
RCu, LiI (R = 1° alkyl)	CC 1030 (1982)
$R_fCF{=}CFCu$	JACS *108* 4229 (1986)
$RC{\equiv}CCu$, (LiI or Et_3N)	JOC USSR *3* 1298 (1967) JACS *91* 6464 (1969) TL 2659 (1970) JOC *40* 131 (1975); *46* 4107 (1981)
R_2CuLi (R = 1° alkyl, aryl)	BSCF 797 (1970) TL 4647 (1970); 2113 (1971) JACS *94* 5106 (1972); *108* 3731, 4603 (1986) CC 1030 (1982) JOC *52* 4274 (1987)
$(Z\text{-}RCH{=}CH)_2CuLi$, [cat $Pd(PPh_3)_4$]	Tetr *42* 1369 (1986)
$R_2C{=}CHCu\cdot MgX_2$, cat $Pd(PPh_3)_4$	Tetr *42* 1369 (1986)
R_2CuMgX (R = 1°, 3° alkyl; allylic; aryl)	TL 2113 (1971); 3377 (1980) JOMC *188* 293 (1980)
(**R**CuMe)Li (R = 2°, 3° alkyl)	TL *21* 3151 (1980)
(**R**CuMe)MgX (R = 1°, 2°, 3° alkyl; aryl)	JOC *41* 2750 (1976)
$[RCuC{\equiv}CC(CH_3)_3]Li$ (R = 1° alkyl)	CC 1030 (1982)
(RCuCN)Li (R = 1° alkyl)	CC 1030 (1982)
$(Me_3SiCH{=}CHCH_2CuCN)Li$	TL *22* 2985 (1981)

RM (*continued*)

$(R_2CuCN)Li_2$ (R = 1° alkyl)	CC 1030 (1982)
$(R'SO_2CH_2CuR)Li$ (R′ = Me, Ph) (R = 1°, 2°, 3° alkyl; aryl)	CC 358, 1030 (1982)
$(CH_3SOCH_2CuR)Li$ (R = 1°, 2°, 3° alkyl; aryl)	JOC *52* 1885 (1987)
$[CH_3SOCH_2Cu(CN)R]Li_2$ (R = 2° alkyl)	JOC *52* 1885 (1987)
(PhSCuR)Li (R = 2°, 3° alkyl)	JACS *95* 7788 (1973) Syn 662 (1974) Org Syn *55* 122 (1976) CC 1030 (1982)
(*t*-BuOCuR)Li (R = 1°, 2°, 3° alkyl)	TL 1815 (1973) JACS *95* 7788 (1973)
$(RCuNR'_2)Li$ (R′ = Et, Ph; R = 1° alkyl)	CC 1030 (1982)
$(RCuNCy_2)Li$ (R = 1°, 3° alkyl)	JACS *104* 5824 (1982) CC 1030 (1982)
$(RCuPPh_2)Li$ (R = 1°, 3° alkyl)	JACS *104* 5824 (1982) CC 1030 (1982)
$(RCuPCy_2)Li$ (R = 1° alkyl)	CC 1030 (1982)
$RC{\equiv}CAg$	JACS *78* 1675 (1956) TL 1303 (1970)
RI, Zn-Cu (R = 1° alkyl)	Ber *80* 129 (1947)
RZnX or R_2Zn (R = 1°, 2° alkyl; aryl)	JACS *69* 2350 (1947); *71* 3804 (1949) Org Rxs *8* 28 (1954)
RZnX, cat $Pd(PPh_3)_4$ (R = 1°, 3° alkyl; benzyl; aryl; vinylic; alkynyl)	TL *24* 5181 (1983); *28* 1055 (1987)
EtO_2CCH_2ZnBr, cat Pd(O)	CL 1559 (1982)
$(EtO_2CCH_2CH_2)_2Zn$, Me_3SiCl, HMPA	JOC *50* 2802 (1985)
$(RO_2CCHRCH_2)_2Zn$, cat $PdCl_2(o\text{-}Tol_3P)_2$	TL *27* 83 (1986); *28* 337 (1987)
$(EtO_2CCH_2CH_2)_2Zn$, Me_3SiCl, CuI	JACS *106* 3368 (1984)
$(RO_2CCH_2CH_2)_2Zn$; HMPA or cat $PdCl_2(PPh_3)_2$ or cat $CuBr{\cdot}SMe_2$	JACS *109* 8056 (1987)
$ArCH_2Br$, cat Pd(O), Zn	CL 1135 (1981)
$RC{\equiv}CZnX$	JOC USSR *2* 1859 (1966)

RCdX or R_2Cd, MgX_2 or LiX (R = 1° > 2° > 3° alkyl; aryl)	JACS *67* 740 (1945); *72* 5333 (1950) Chem Rev *40* 15 (1947) Org Rxs *8* 28 (1954) Org Syn Coll Vol *3* 601 (1955) JCS A 453, 456 (1966) Can J Chem *58* 287 (1980) JOC *47* 2590 (1982)
RCdX or R_2Cd, $FeCl_3$ (R = 1° alkyl)	JOC *26* 1772 (1961)
$RC{\equiv}CCdX$	JOC USSR *3* 210 (1967); *4* 2032 (1968)
R_2Hg, cat $Pd(PPh_3)_4$ (R = 1° alkyl, aryl)	CL 951 (1975)
$RCH{=}CHHgCl$, $AlCl_3$	JOC *43* 710 (1978)

$$2\ RMnI + COCl_2 \longrightarrow RC(=O)R$$

R = 1° alkyl

BSCF 570 (1977)

$$ClC(=O)SPh \xrightarrow[\text{cat } NiCl_2(dppe)]{R^1MgX} \xrightarrow[\text{cat } Fe(acac)_3]{R^2MgX} R^1{-}C(=O){-}R^2$$

TL *26* 3595 (1985)

$$RCCl + 2\ R'CH{=}PPh_3 \xrightarrow{H_2O} RCCH_2R'$$

Ber *95* 1513 (1962)

$$ArCCl + RCH_2C(Ph){=}C{=}O \text{ or } RCH_2CHPhCOCl \xrightarrow[Et_3N]{\text{Pd catalyst}} ArCC(Ph){=}CHR$$

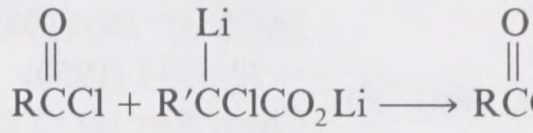
TL *26* 5143 (1985)
JOC *52* 3186 (1987)

$$RC{\equiv}CH + ClCR' \xrightarrow[\substack{\text{cat CuI}\\ Et_3N}]{\text{cat } PdCl_2(PPh_3)_2} RC{\equiv}CCR'$$

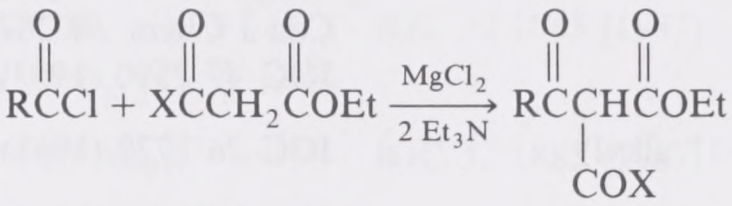
Syn 777 (1977)

$$RCCl + R_2\bar{C}CO_2^- \xrightarrow{H^+} RCCHR_2$$

Compt Rend *286* 401 (1978)

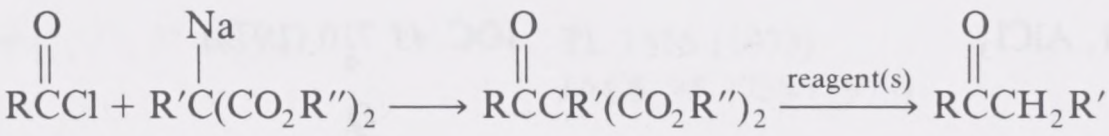


Syn 284 (1982)



X = Me, OEt

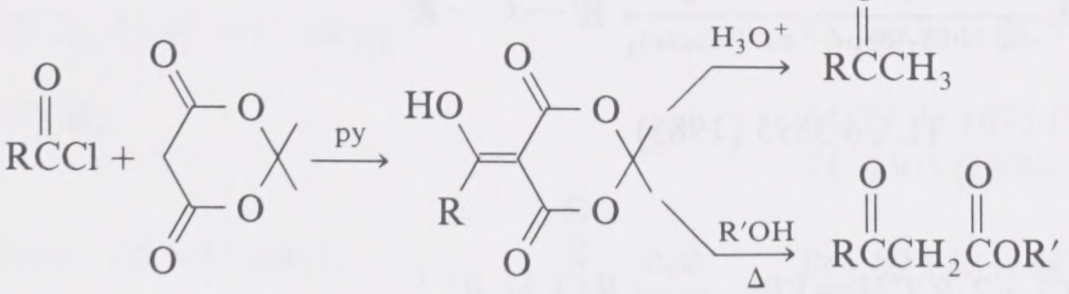
JOC *50* 2622 (1987)



Reagent(s)

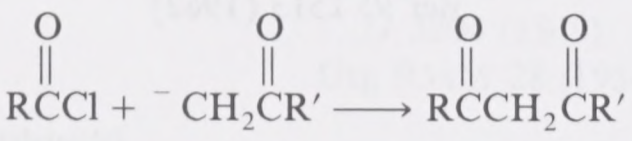
H_2, cat Pd-C ($R'' = PhCH_2$) — JCS 325 (1950)

H^+ — JCS 322 (1950); JACS *74* 831 (1952)

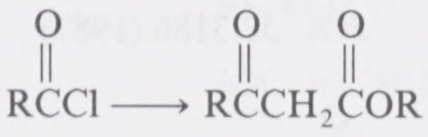


Syn Commun *10* 221 (1980)

JOC *43* 2087 (1978); *52* 1889 (1987); Syn 451 (1982); Org Syn *63* 198 (1984)



Org Rxs *8* 59 (1954) (review); JACS *107* 1280 (1985)



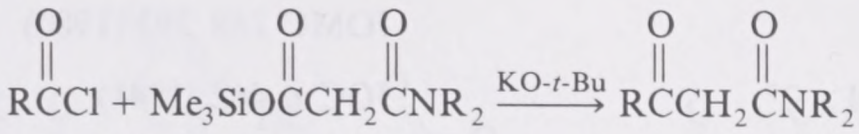
$LiCH_2CO_2R$ — See page 873, Section 2.

$NaCH(CO_2R)CO_2CH_2Ph/H_2$, cat Pd-C — JCS 2758 (1951)

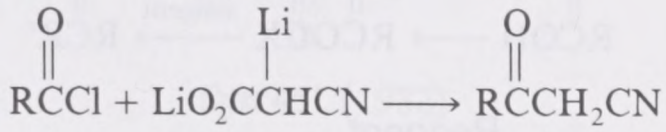
$LiO_2CCHLiCO_2R/H^+$ — JOC *44* 310 (1979); Org Syn *61* 5 (1983)

$ROMgCH(CO_2R)_2$, Δ — J Prakt Chem 322 (1980)

$BrMgO_2CCH(MgBr)CO_2R/H^+$ — BSCF 945 (1964); Syn 142 (1978)

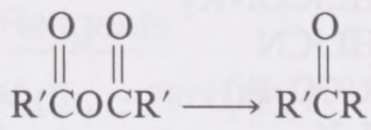


JACS *108* 5559 (1986)



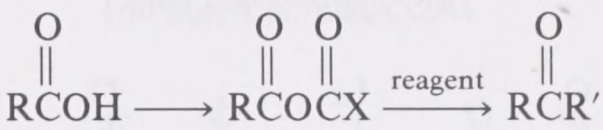
Syn 308 (1983)

2.5. From Acid Anhydrides

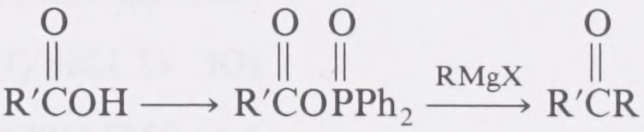


RX (R = allylic, benzylic), electrolysis	TL *27* 4175 (1986)
$RC\equiv CLi$	Ber *97* 1649 (1964) Monatsh *102* 214 (1971)
ArLi	JOC *41* 1268 (1976)
ArLi, TMEDA	Ann 2247 (1981)
RMgX (R = 1°, 2°, 3° alkyl; aryl)	JCS 1367, 1370 (1935) JACS *64* 2226 (1942); *67* 154 (1945); *80* 1225 (1958) JOC *13* 592 (1948); *25* 214 (1960); *51* 3502 (1986) CL 663, 687 (1974) Austral J Chem *30* 427 (1977) TL *27* 2001 (1986)
RMgX, HMPA, (5% $FeCl_3$) (R = 1°, 2° alkyl)	Compt Rend C *275* 511 (1972)
$RC\equiv CMgX$	JACS *58* 1861 (1936)
ArMgX, TMEDA	Angew *90* 1000 (1978) JOC *46* 2601 (1981) Ann 2247 (1981)
$LiAlR_4$, cat CuX or $CuCl_2$ (R = 1° alkyl)	CL 623 (1979)
$ArSiMe_3$, cat KO-*t*-Bu	Angew Int *20* 265 (1981)
$RC\equiv CSiMe_3$, $AlCl_3$	TL *28* 5543 (1987)
$RSnR'_3$, $AlCl_3$ (R = vinylic)	BSCF 1251 (1977)
RMnX (R = 1° alkyl, aryl, alkynyl, vinylic)	Syn Commun *9* 639 (1979) Tetr *40* 683 (1984) Syn 37 (1984); 50 (1985)
$RC\equiv CLi$, CuI	JACS *109* 6899 (1987)

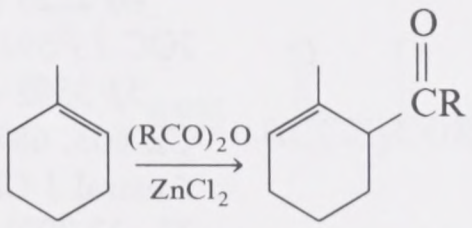
R_2CuMgX (R = aryl)	JOMC *188* 293 (1980)
R_2Cd (R = 1° alkyl, aryl > 2°, 3° alkyl)	JOC *6* 462 (1941)



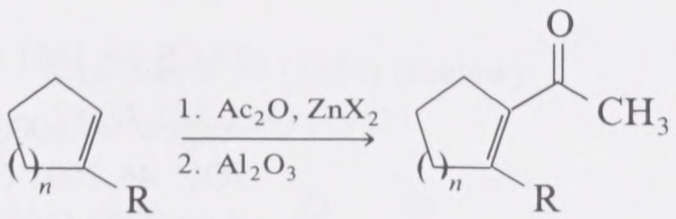
X	Reagent	
OR	RCHLiCOR	JOMC *127* C65 (1977)
	$RCHLiCO_2R$	JOMC *127* C65 (1977)
	$RCHLiCO_2SiMe_3$ (decarboxylation also)	TL 3713 (1978) Tetr *37* 307 (1981)
	$RCHLiCONR_2$	Syn 954 (1979)
	RCHLiCN	TL 1585 (1979)
	$^{-}CR(CO_2Et)_2$	JOC *22* 245 (1957)
	R′MgX	CL 687 (1974)
	RMnI	Syn 50 (1985)
	Et_2Cd	JOC *22* 245 (1957)
t-Bu, Ar	R′MgX	CL 663, 687 (1974)



Syn Commun *8* 59 (1978)
CC 412 (1986)



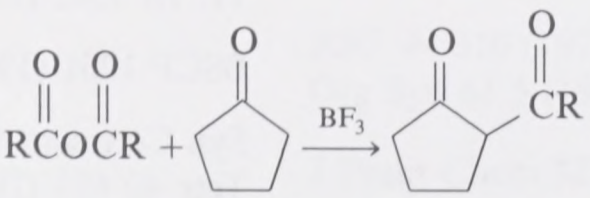
JACS *102* 3848 (1980)



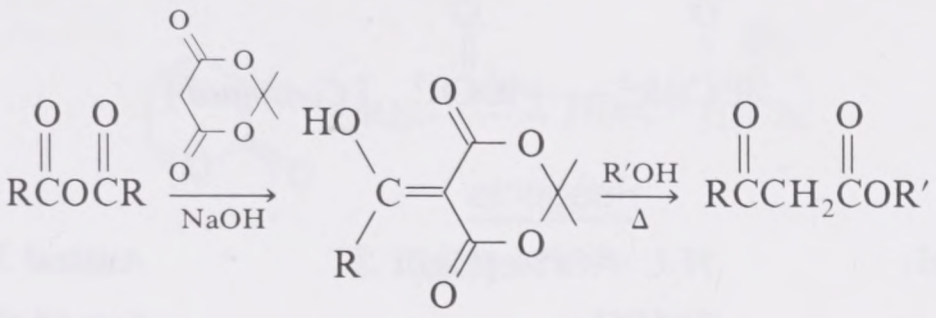
$n = 1, 2$

R = H, Me

TL *22* 3351 (1981)

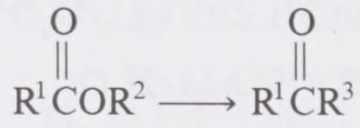


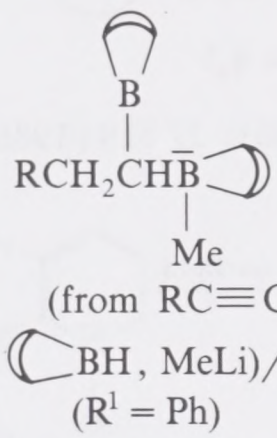
Org Rxs *8* 59 (1954) (review)
JOC *52* 3986 (1987)

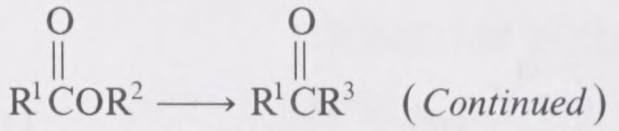


Syn 451 (1982)

2.6. From Esters and Lactones

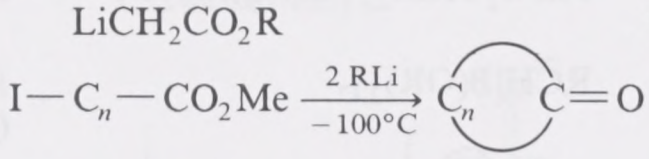


R^3	Reagents	
CH_3	CH_3MgBr, $-78°C/H_2O$ (R^2 = 2-pyridyl)	TL *28* 1603 (1987)
	$^-CH_2SOCH_3/Al(Hg)$, H_2O	JACS *87* 1345 (1965) JOC *31* 2355 (1966); *46* 4825 (1981)
	$^-CH_2SOCH_3/Zn$, NaOH	JOC *52* 4477 (1987)
	$^-CH_2SO_2CH_3/Al(Hg)$, H_2O	JOC *33* 61 (1968)
	$^-CH_2SO\bar{N}Ar/H_2O$	JACS *90* 5548 (1968)
	R_3SnCH_2Li (R = Me, Ph)/ H_2O	TL *27* 4339 (1986)
CH_2R	$PhSO_2CRLi_2/Al(Hg)$, H_2O	JOC *45* 4002 (1980); *47* 564 (1982)
	$R\bar{C}H[B(OR)_2]_2$	JACS *99* 3196 (1977) Organomet *1* 20 (1982)
CH_2CH_2R	 (from $RC\equiv CH$, BH, MeLi)/H_2O (R^1 = Ph)	CL 1193 (1981)
1° alkyl	1° RI, cat $NiCl_2$, Zn/H_3O^+	CL 531 (1981)
1° alkyl, aryl	RMgX ($R^1 = CO_2R$)	JOC *45* 2883 (1980) Syn Commun *11* 943 (1981)
1° alkyl, aryl	RMgX, Et_3N	Syn 877 (1980)
1° alkyl	RLi	JACS *109* 8071 (1987) ($R^1 = RCF_2$)
1°, 2°, 3° alkyl; 1° benzylic; aryl	RLi or RMgX/H_2O ($R^1 = CF_3$, CO_2Et)	JOC *52* 5026 (1987)
1°, 2° alkyl	RMgX, HMPA	Compt Rend C *273* 1543 (1971)
allylic	$RCH{=}CRCH_2MgCl/KH$	TL *23* 335 (1982)



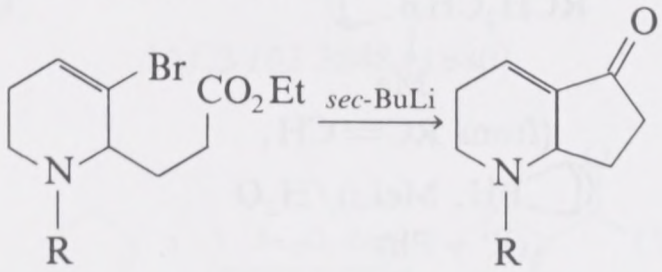
(*Continued*)

R^3	Reagents	
$CHMeCH_2CMe{=}CH_2$	$H_2C{=}C(Me)MgBr$	Austral J Chem *30* 427 (1977)
RCHX (X = Cl, Br)	RCHXLi	Syn 68 (1981) TL *25* 835 (1984)
CF_2CF_3	$LiCF_2CF_3$	JOC *52* 2481 (1987)
CH_2OH	$Me_3SiCHLiOCO_2Li/H_3O^+$	TL *28* 1847 (1987)
RCH(OH)	$RCHLiOCO_2Li/H_3O^+$	TL *28* 1847 (1987) (R = $SiMe_3$) Syn 415 (1987) (R = Ph)
$PhCHNH_2$	$PhCHLiNLiCO_2Li/H_3O^+$	Syn 415 (1987)
CH_2SPh	$LiCH(SPh)SiMe_3$	TL *22* 2803 (1981)
CHRSPh	$R\bar{C}(SPh)[B(OR)_2]_2$	Organomet *1* 280 (1982)
$CClRCH{=}CH_2$	$RCCl{=}CHCH_2Li/H_3O^+$	JOMC *215* 1 (1981)
$CCl{=}CHCH_3$	$ClCH{=}CHCH_2Li/H_3O^+$	JOMC *215* 1 (1981)
$C{\equiv}CR$	$LiC{\equiv}CR$	Syn 307 (1978) TL 937 (1978) (lactones); *28* 3651 (1987) (lactones)
CH_2COR	$^-CH_2COR$	JACS *67* 1510 (1945) Org Rxs *8* 59 (1954) (review)
CH_2CO_2R	$LiCH_2CO_2R$	See page 873, Section 2.

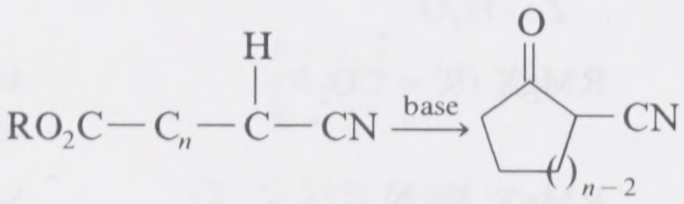


$n = 4,5$

TL *26* 4987 (1985); *27* 519 (1986)

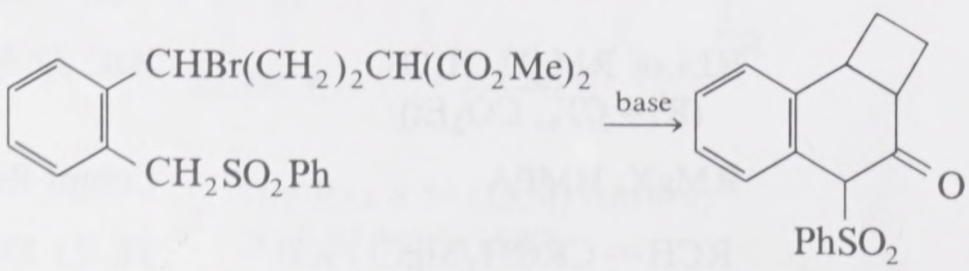


JACS *109* 6115 (1987)

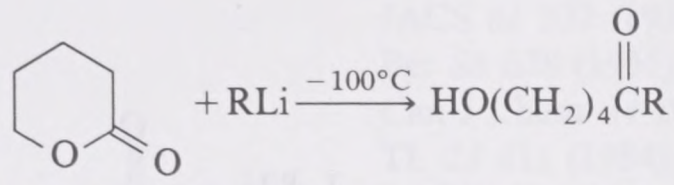


$n = 3, 4$

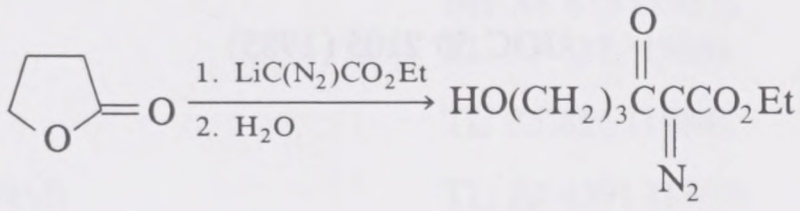
TL *28* 4641, 4645 (1987)



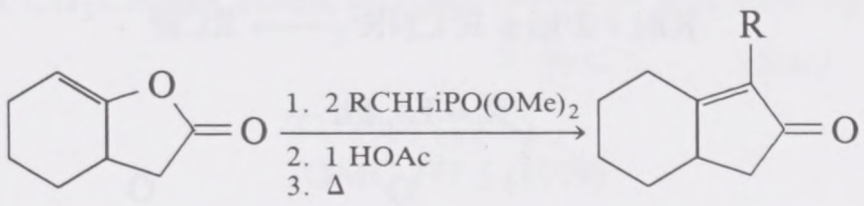
TL *28* 709 (1987)



TL *28* 651 (1987)

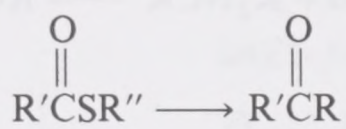


TL *28* 5351 (1987)



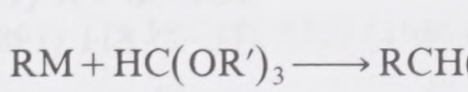
JACS *107* 7967 (1985)

2.7. From Thioesters



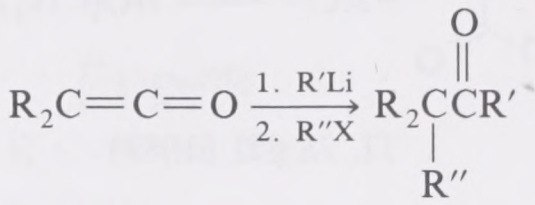
RMgX ($R'' = C_5H_4N$) ($R = 1°, 2°$ alkyl; aryl)	JACS *95* 4763 (1973) BCSJ *47* 1777 (1974) J Med Chem *23* 1392 (1980) JOC *46* 3760 (1981); *51* 938 (1986) TL *23* 2533 (1982)
RMgX, cat $Fe(acac)_3$ ($R'' = Ph$; $R = 1°, 2°$ alkyl; aryl)	TL *26* 3595 (1985)
R_2CuLi ($R = 1°, 2°, 3°$ alkyl; aryl)	JACS *96* 3654 (1974); *108* 4943 (1986) CC 1231 (1981)

2.8. From Ortho Esters



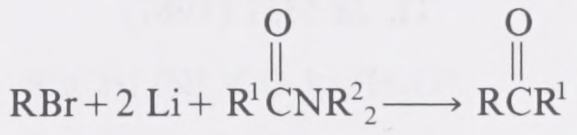
RM	
RMgX	TL *22* 545 (1981)
$RC{\equiv}CMgX$	JCS 4244 (1955)
$RCH{=}CR'CH_2MBr$ (M = Mg, Zn)	JOMC *222* 1 (1981)

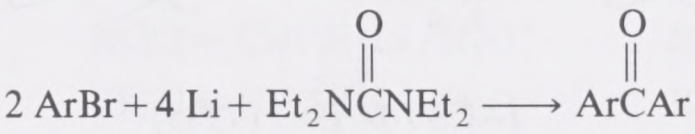
2.9. From Ketenes



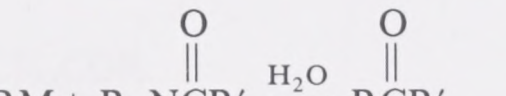
JOC *50* 2105 (1985)

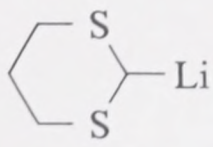
2.10. From Amides





Syn 160 (1973)



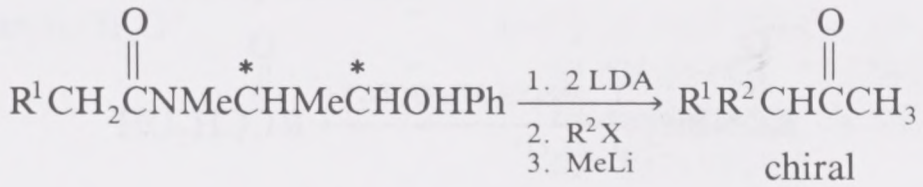
RM	
RLi (R = 1°, 2° alkyl)	Ber *88* 678 (1955) JCS 4691 (1956) JOC *24* 701 (1959); *51* 3290, 3566 (1986) Can J Chem *54* 1098 (1976) JOMC *177* 5 (1979) Angew Int *20* 795 (1981) TL *23* 109 (1982); *25* 811 (1984); *28* 651, 3573 (1987)
	TL *25* 811 (1984)
ArLi	Ber *88* 678 (1955) Chem Ind 1596 (1957) Bull Acad Sci USSR, Div Chem Sci 769 (1961) Tetr *27* 1221 (1971) JOC *38* 901 (1973) TL *25* 811 (1984)
RCH=CHLi	TL *27* 775 (1986) (intramolecular)
RC≡CLi	TL *25* 811 (1984) CL 13 (1986)
RC≡CLi, $BF_3 \cdot OEt_2$	CL 35 (1983) JOC *52* 1372 (1987)

RMgX (R = 1°, 2° alkyl) — JACS *61* 232 (1939); Ber *88* 678 (1955); Can J Chem *54* 1098 (1976); TL *25* 811 (1984); *28* 2999 (1987); JCS Perkin I 795 (1985); JOC *51* 3566 (1986)

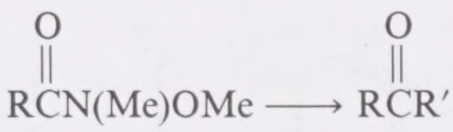
ArMgX — Ber *88* 678 (1955); TL *25* 811 (1984)

$RC{\equiv}CMgX$ — TL *25* 811 (1984)

$RLa(OTf)_2$ (R = 1°, 2° alkyl) — TL *28* 4391 (1987)



TL 3961 (1978); JOMC *177* 5 (1979)

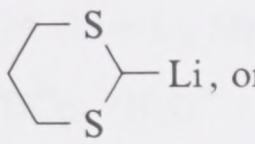


R′Li (R′ = 1° alkyl) — TL *22* 3815 (1981); *27* 5467 (1986)

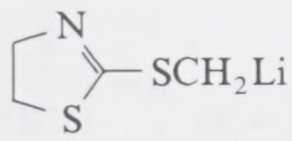
ArLi — TL *22* 3815 (1981); *28* 6331 (1987); JOC *51* 5106 (1986); *52* 2615 (1987)

$RCH{=}CR'Li$ — JACS *107* 8066 (1985)

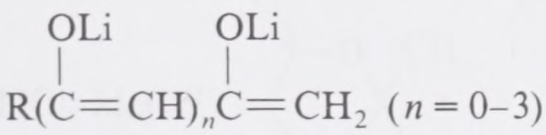
$RC{\equiv}CLi$ — TL *22* 3815 (1981); *28* 1857 (1987); JOC *50* 2309, 3972 (1985)

PhSCH(OMe)Li, 

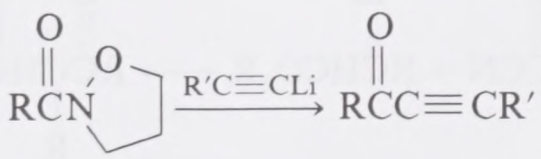
, or — TL *28* 1857 (1987)



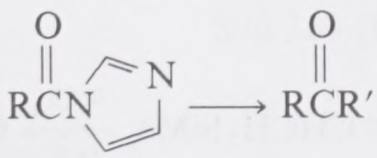
R′MgX (R′ = 1° alkyl, allyl, benzyl, alkynyl, aryl, vinyl) — TL *22* 3815 (1981); *28* 1857, 6331 (1987)



TL *24* 1851 (1983)

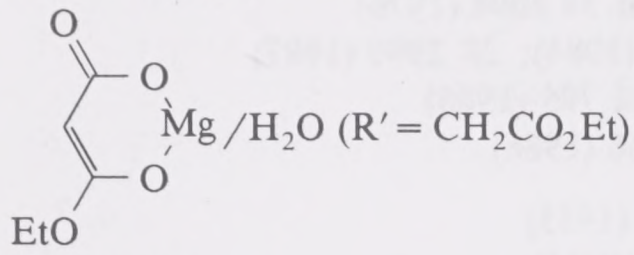


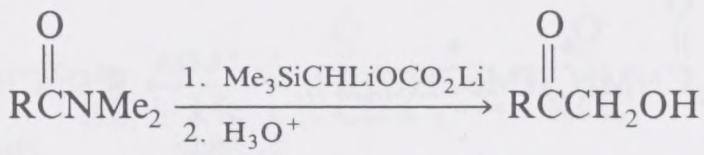
JOC *51* 5320 (1986)



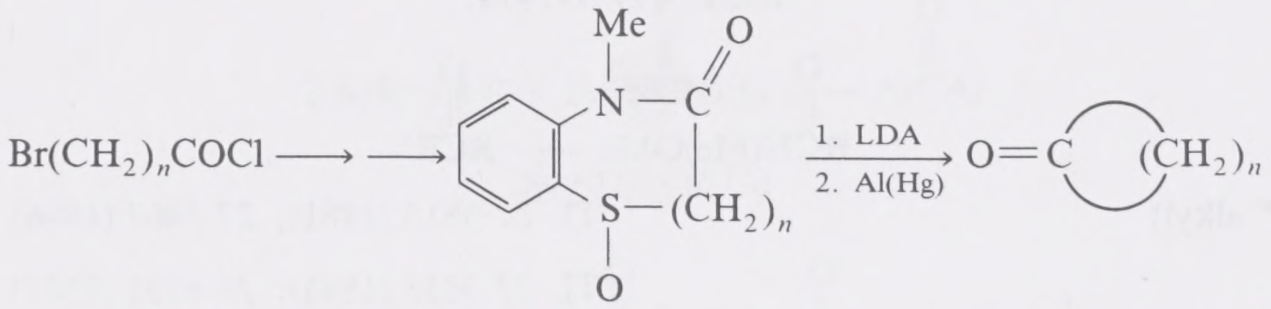
R′MgBr (R′ = Me, Et, Ph) — Ann *655* 90 (1962)

R′MgX (R′ = aryl > alkyl; R = CO_2R) — JOC *46* 211 (1981)

$Mg(O_2CCHRCOXR)_2$ (X = O, S; R′ = CHRCOXR)	Angew Int *18* 72 (1979) TL *28* 5249 (1987)
	BSCF 945 (1964)
$(Na)KCH_2NO_2$	Syn 478 (1978)
$LiCHRCO_2R$	TL *27* 5281 (1986); *28* 2837 (1987) JACS *109* 4717 (1987) CC 1228 (1987)



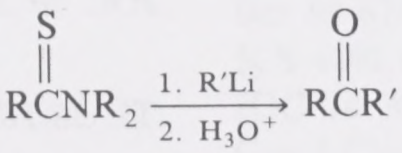
TL *28* 1847 (1987)



$n = 7,11$

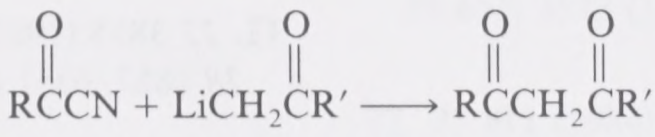
TL 4487 (1979)

2.11. From Thioamides

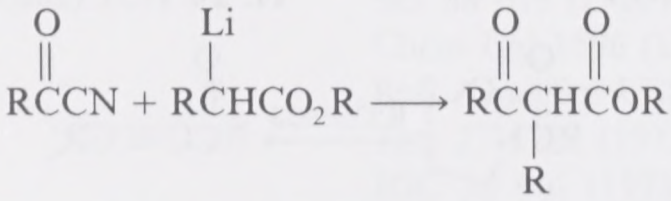


TL *28* 1529 (1987)

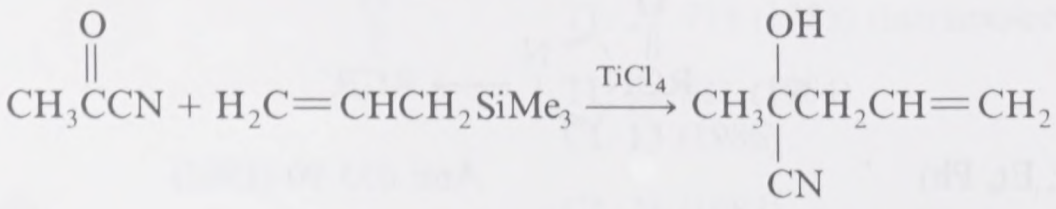
2.12. From Acid Nitriles



TL 1339 (1979)

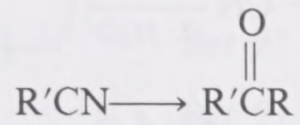


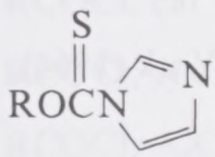
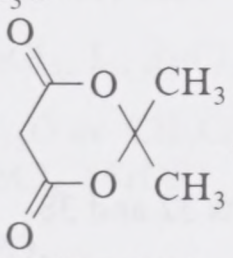
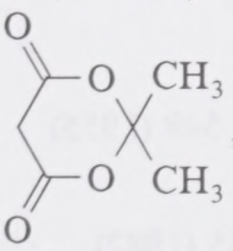
TL *28* 4011 (1987)

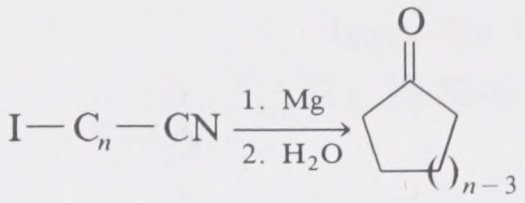


TL *22* 1171 (1981)

2.13. From Nitriles

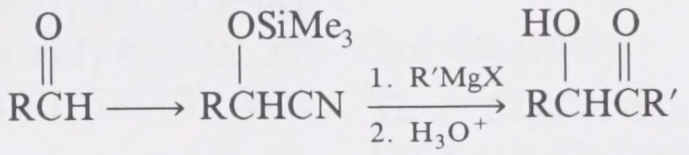


RLi ($R = 1°$, $2°$ alkyl; aryl)/H_3O^+	Helv 729 (1962) JACS *92* 336 (1970); *107* 1028 (1985) TL *22* 1509 (1981); *28* 4329 (1987) JOC *47* 4347 (1982)
$Me_3SiCHLiOCO_2Li/H_3O^+$ ($R = CH_2OH$)	TL *28* 1847 (1987)
$RMgX$ ($R = 1°$ alkyl, aryl)/H_3O^+	JACS *52* 1267 (1930); *67* 2059, 2197 (1945); *70* 426 (1948); *72* 876 (1950); *73* 3948 (1951); *74* 4607 (1952); *79* 881 (1957); *109* 3378 (1978) BSCF 867 (1935) Bull Soc Chim Belg *44* 523 (1935) JOC *15* 359 (1950); *45* 237 (1980) Org Syn Coll Vol *3* 26 (1955) JCS Perkin I 795 (1985)
$R_2C{=}CHCH_2MgX/H_3O^+$	Ann Chim 287 (1964) JACS *108* 1311 (1986)
$RMgX$ ($R = 2°$, $3°$ alkyl; aryl), cat $CuBr/H_3O^+$	JOC *52* 3901 (1987)
$R_3P{=}CHR''/H_3O^+$ ($R = CH_2R''$)	JACS *89* 7009 (1967)
$R''_2C{=}CHCH_2Br$ ($R'' = H$, Me), $Zn(Ag)/H_3O^+$	TL *22* 649 (1981)
$R'CH{=}CHCH_2M$ ($M = Li$, MgX, ZnX)/H_3O^+	JOMC *69* 1 (1974) (review)
$R'CH{=}CHCH_2TiCp_2/H_3O^+$	CC 342 (1981) JOMC *224* 327 (1982)
 ($R = 2°$ alkyl), Ph_3SnH, cat $AIBN/H_3O^+$	JOC *49* 1313 (1984) (intramolecular)
HCl, MeOH/  , Et_3N, Δ/HCl ($R = Me$)	Syn 130 (1981)
HCl, MeOH/  , Et_3N, $\Delta/NaOEt/H_3O^+$ ($R = CH_2CO_2Et$)	Syn 130 (1981)
$R'CHBrCO_2R'$, Zn/H_3O^+ ($R = R'CHCO_2R'$)	Org Syn Coll Vol *4* 120 (1963) JOC *48* 3833 (1983)

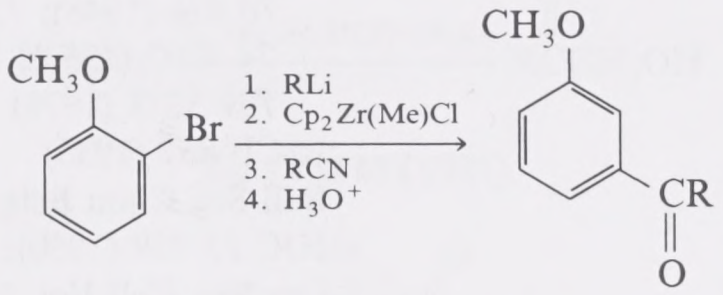


$n = 4, 5$

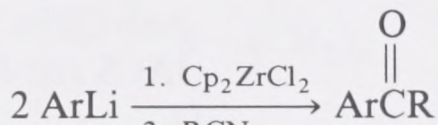
JOMC *87* 25 (1975)



TL *27* 1933 (1986)



JACS *109* 7137 (1987)

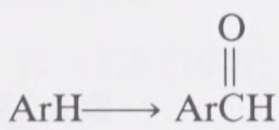


TL *28* 3245 (1987)

3. Friedel–Crafts and Related Reactions

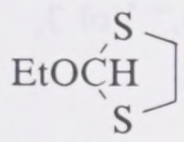
Reviews:

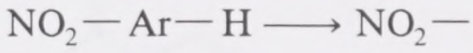
Chem Rev *55* 229 (1955)
"Friedel-Crafts and Related Reactions," Ed. G. A. Olah, J. Wiley and Sons, New York (1964), Vol 3, Pts 1 and 2
Syn 533 (1972)
G. A. Olah, "Friedel-Crafts Chemistry," Wiley Interscience, New York (1973)



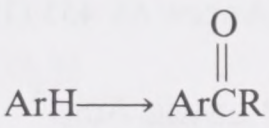
Review: "Friedel-Crafts and Related Reactions," Chpts 32 and 38

HCN, HCl, $ZnCl_2$ or $AlCl_3/H_2O$	Org Rxs *9* 37 (1957)
$Zn(CN)_2$, HCl/H_2O	TL *23* 4567 (1982)
$Zn(CN)_2$, $AlCl_3$, HCl/H_2O	Org Syn Coll Vol *3* 549 (1955) JOC *52* 336 (1987)
$(CH_3)_2C(OH)CN$, $AlCl_3$	Syn Commun *12* 485 (1982)
CO, HCl, $AlCl_3$	Org Rxs *5* 290 (1949)
CO, HCl, $CuCl/AlCl_3$	Org Syn Coll Vol *2* 583 (1943)

$FCHO, BF_3$	JACS *82* 2380 (1960)
$Cl_2CHOCH_3, AlCl_3$	Ber *93* 88 (1960)
Cl_2CHOR (R = Me, *n*-Bu), $SnCl_4$	Ber *93* 88 (1960)
$Cl_2CHOCH_3, TiCl_4$	Ber *93* 88 (1960); *96* 308 (1963) CC 214 (1972) JCS Perkin I 340 (1973) JOC *50* 3121 (1985); *52* 1972 (1987) TL *27* 6299 (1986)
Cl_2CHO-*n*-Bu, $TiCl_4$	Ber *93* 88 (1960)
$HC(OEt)_3, AlCl_3$	Ber *96* 308 (1963) (phenols)
	BCSJ *54* 2120 (1981)
DMF, $POCl_3$	Org Syn Coll Vol *4* 331 (1963) "Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1211
$HCCl_3$, NaOH (on ArOH)	Org Rxs *28* 1 (1982) (review)

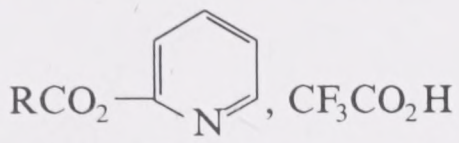
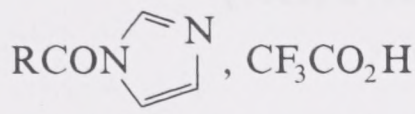


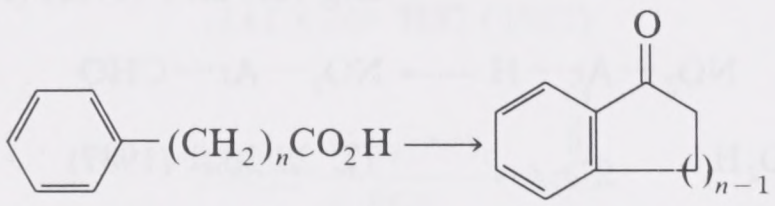
$HCCl_3$, KO-*t*-Bu/H_2O, HCO_2H	TL *28* 3021 (1987)
$HC(SPh)_3$, NaOH, DMSO/hydrolysis	CL 1623 (1984)



Review: "Friedel-Crafts and Related Reactions," Chpts 31 and 32

$RCO_2H, (CF_3CO)_2O, H_3PO_4$	Syn 303 (1979)
RCOCl, cat CF_3SO_3H	Angew Int *11* 300 (1972)
RCOCl, Nalfion-H	Syn 672 (1978)
$RCOCl, AlCl_3$	"Friedel-Crafts and Related Reactions," Vol 3, Pt 1, pp 1–382
RCOCl; cat $FeCl_3$, I_2, $ZnCl_2$ or Fe	Syn 533 (1972)
RCOCl, $(RCO)_2O$ or $CH_3C(=CH_2)O_2CR$; cat $(Ph_2B)SbCl_6$ (ArOR)	CL 165 (1986)
$(RCO)_2O, H_3PO_4$	Org Syn Coll Vol *3* 14 (1955)
$(RCO)_2O, AlCl_3$	Org Syn Coll Vol *1* 517 (1941) Ber *115* 3436 (1982) Tetr *38* 3555 (1982) JACS *109* 7122 (1987)
$(RCO)_2O, ZnCl_2$	Org Syn Coll Vol *2* 304 (1943)
$(RCO)SbF_6$	Syn 345 (1980)
$RCO_2SO_2CF_3$	Angew Int *11* 299 (1972)

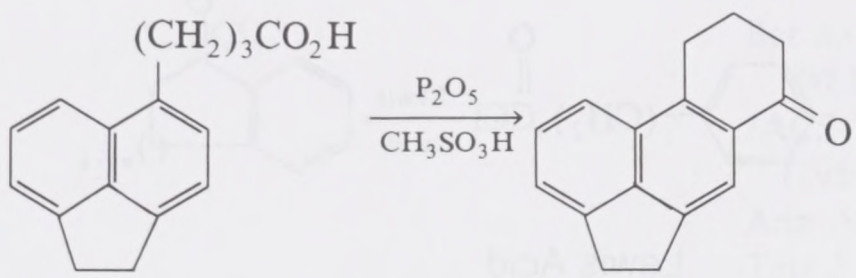
RCO_2POX_2 (X = F, Cl)	Ber *114* 926 (1981)
	Syn 139 (1980)
RCOSMe, CuOTf	JACS *102* 860 (1980)
$RCONMe_2$, $POCl_3$	Helv *42* 1659 (1959) JOC *25* 2049 (1960)
	BCSJ *53* 1638 (1980)
RCN, HCl, $ZnCl_2/H_2O$	Org Syn Coll Vol *2* 522 (1943) Org Rxs *5* 387 (1949) "Friedel-Crafts and Related Reactions," Vol 3, Pt 1, p 383 JOC *43* 4172 (1978) (intramolecular)
$(RC{\equiv}NH)OTf/H_2O$	JCS Perkin I 2894 (1980)
$(RC{\equiv}NMe)OTf/H_2O$	CC 1151 (1980)



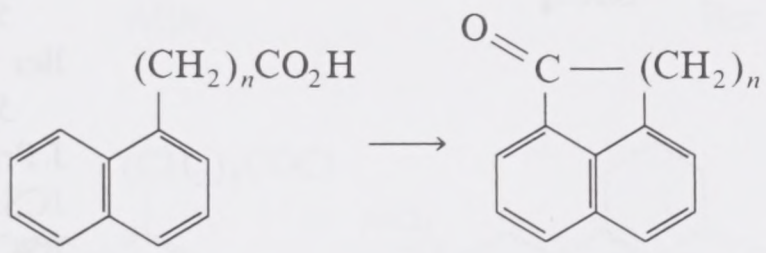
Reviews: Org Rxs *2* 114 (1944)
Angew *66* 435 (1954) (PPA)

n	Acid or Lewis Acid	
2	HF	JACS *61* 1272 (1939)
	CH_3SO_3H	JOC *46* 2974 (1981)
	CH_3SO_3H, P_2O_5	JOC *38* 4071 (1973)
	PPA	Helv *29* 859 (1946) JACS *72* 2965 (1950); *108* 1251 (1986) BSCF 810 (1957) Compt Rend *246* 779 (1958); *249* 2337, 2782 (1959) Syn Commun *11* 993 (1981) CC 185 (1982) JOC *51* 1402, 4250 (1986)
	$SnCl_4$	JCS 4306 (1954)
	$AlCl_3$, NaCl	JCS 2403 (1953)
3	HF	JACS *61* 1272 (1939) Can J Chem *49* 2712 (1971) JCS Perkin I 461 (1982) JOC *52* 1284 (1987)
	H_2SO_4	JCS 1125 (1932); 4306 (1954) Tetr *2* 271 (1958) JOC *28* 3571 (1963) TL *23* 2415 (1982)

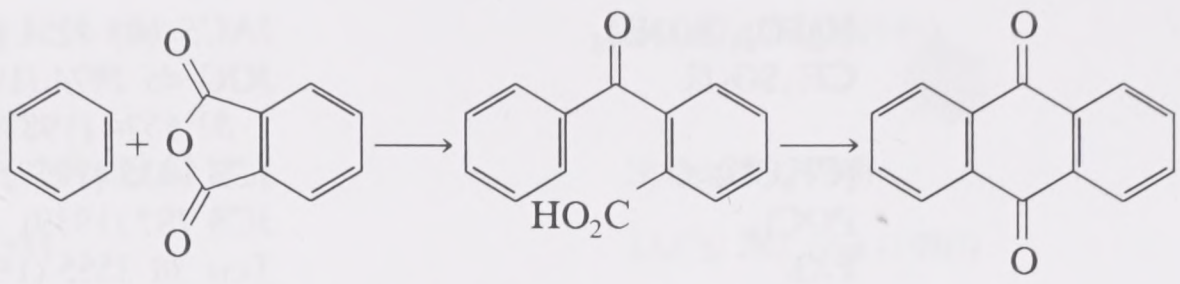
	H_2SO_4, $B(OH)_3$	JACS *103* 4251 (1981)
	CH_3SO_3H	JOC *46* 2974 (1981); *52* 5574 (1987)
	$(CF_3CO)_2O$	JCS 1435 (1957)
	$POCl_3$	JCS 787 (1939)
	P_2O_5	Tetr *38* 3555 (1982)
	PPA	JCS 1995 (1938)
		JACS *69* 58 (1947); *72* 2965 (1950); *73* 1411 (1951); *74* 5147 (1952); *78* 450 (1956); *103* 4251 (1981)
		Org Syn Coll Vol *3* 798 (1955)
		JOC *43* 4172 (1978); *46* 2547 (1981)
	$SnCl_4$	JCS 867 (1934); 790 (1939)
		JACS *69* 58 (1947)
	$AlCl_3$, NaCl	JCS 2403 (1953)
	$ZnCl_2$, HOAc, Ac_2O	JACS *69* 58 (1947)
4	PPA	JACS *73* 1411 (1951); *75* 720 (1953)
		BCSJ *35* 1380 (1962)
		Syn Commun *11* 993 (1981)
	$AlCl_3$, NaCl	JCS 2403 (1953)
5	PPA	JACS *77* 4596 (1955)



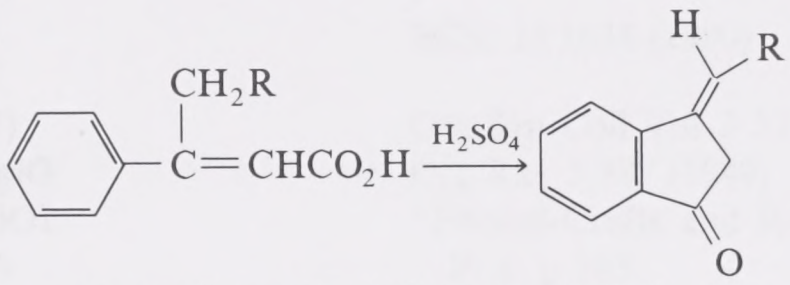
JOC *50* 5886 (1985)



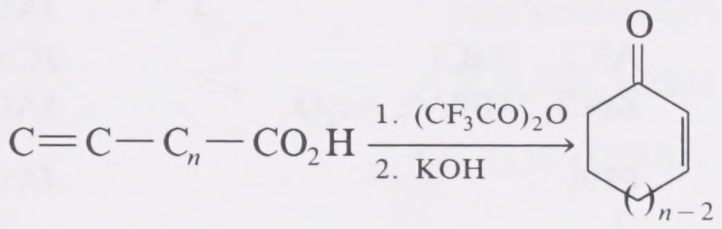
n	Reagent	
1	HF	JOC *44* 2158 (1979); *52* 1355 (1987)
	PPA	JCS 4306 (1954)
2	HF	JACS *62* 1855 (1940)
2 or 3	H_2SO_4 or PPA or $SnCl_4$	JCS 4306 (1954)
3	P_2O_5 or $SnCl_4$	JCS 787 (1939)



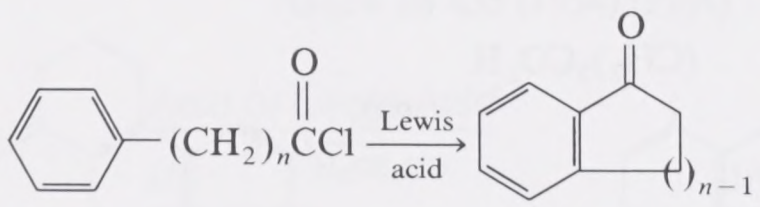
Houben-Weyl, Vol VII/3C, p 31 (review)
JOC *52* 3205 (1987)



Acta Chem Scand B *36* 371 (1982)

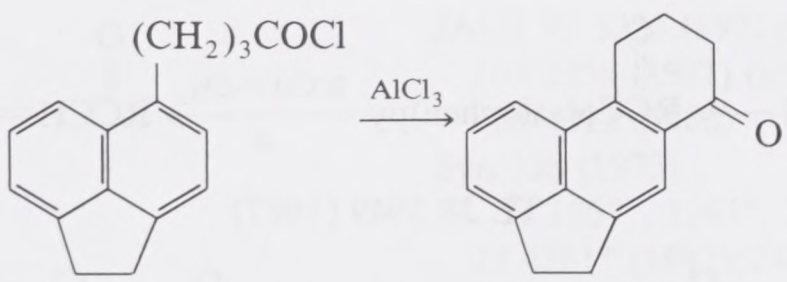


n		
3		JCS 1435 (1957) JCS C 217 (1968)
4		JOC *35* 858 (1970)

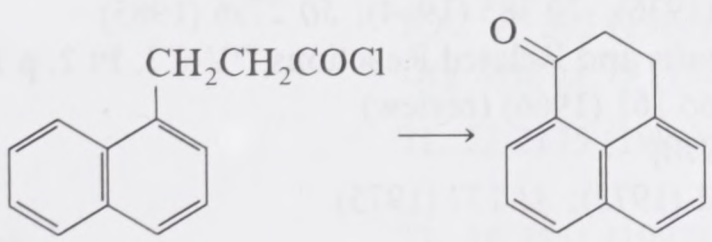


n	Lewis Acid	
2	$AlCl_3$	Ann *376* 269 (1910); *468* 277 (1929); *586* 52 (1954) Ber *46* 1700 (1913); *55* 1835 (1922) J Prakt Chem [2] *139* 95 (1934) JCS 1460, 3499 (1951) BSCF 810 (1957) Tetr *2* 271 (1958) JACS *80* 1243 (1958) Compt Rend *249* 2337, 2782 (1959); *252* 1971 (1961) BCSJ *35* 1380 (1962) JOC *46* 2431 (1981); *51* 5252 (1986)
	$SnCl_4$		
	$SnCl_4$	Compt Rend *246* 779 (1958); *249* 2782 (1959)
	$FeCl_3$	Ann *323* 246 (1902)
	$AgClO_4$	JCS 1718 (1957)

3	$AlCl_3$	JCS *75* 144 (1899); 187 (1936); 844, 3499 (1951) Ber *56* 1424 (1923); *61* 441 (1928) Ann *531* 129 (1937); *586* 52 (1954) Org Syn Coll Vol *2* 569 (1943) JOC *15* 950 (1950); *28* 357 (1963) Tetr *2* 271 (1958)
	$SnCl_4$	JACS *57* 782 (1935); *59* 475 (1937); *62* 2750 (1940); *63* 1682 (1941); *69* 58 (1947) JCS 4306 (1954) Ber *95* 1786 (1962) JOC *28* 3571 (1963) Org Syn Coll Vol *4* 900 (1963)
	$AgClO_4$	JCS 1718 (1957)
4	$AlCl_3$	JCS *79* 602 (1901) Helv *27* 801 (1944) BSCF 769 (1953) Ann *586* 52 (1954) Compt Rend *244* 2513 (1957) Tetr *2* 271 (1958) J Chem Res (S) 226 (1982)
	$AgClO_4$	JCS 1718 (1957)
5	$AlCl_3$	Ber *85* 826 (1952); *90* 1946 (1957) JACS *75* 3744 (1953); *76* 5462 (1954) Ann *586* 52 (1954) Tetr *2* 271 (1958) BCSJ *35* 1380 (1962) J Chem Res (S) 226 (1982)
6, 7	$AlBr_3$	Ber *90* 1946 (1957)

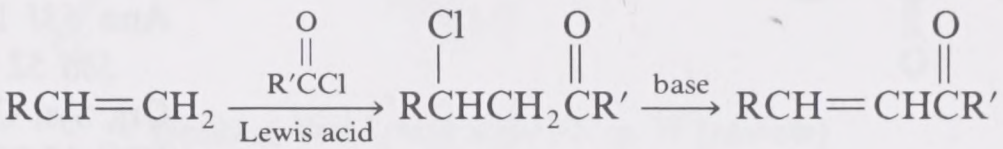


JACS *54* 4373 (1932)

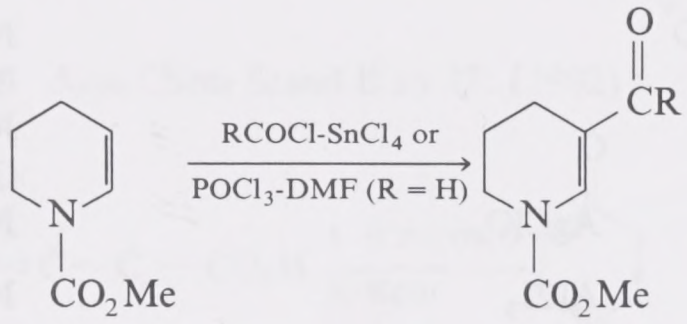


$AlCl_3$ Ber *55* 1835 (1922)
JCS 1991 (1938)

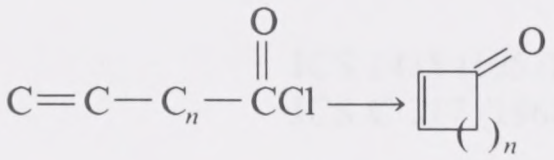
$SnCl_4$ JACS *72* 733 (1950)



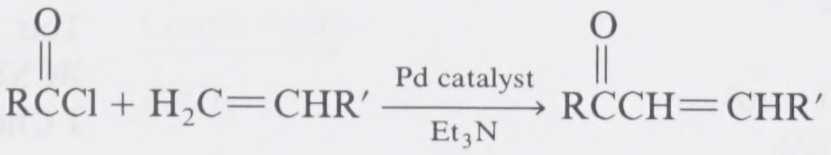
"Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1033 (review)
JOC *35* 858 (1970) (intramolecular)
CC 84 (1973) (intramolecular)
TL 2441 (1976); *27* 2341 (1986) (intramolecular)
JACS *108* 1265 (1986) (intramolecular)



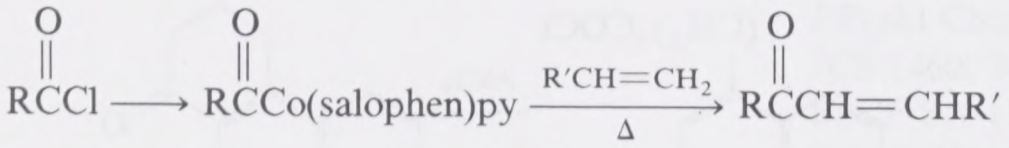
TL *23* 1201 (1982)



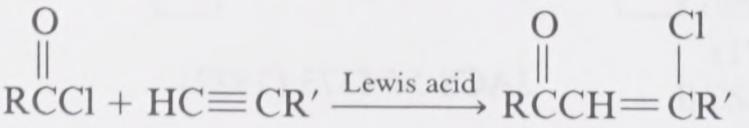
	n	
$AlCl_3$	2	BCSJ *52* 216 (1979)
$SnCl_4$	4	JOC *35* 858 (1970)
	2	JACS *109* 3025 (1987)



Transition Met Chem *4* 398 (1979)
TL *28* 4215, 5883 (1987)



TL *28* 5949 (1987)



JOC *1* 163 (1936); *29* 385 (1964); *50* 2796 (1985)
"Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1081 (review)
Chem Rev *66* 161 (1966) (review)
TL 1821 (1970)
Tetr *29* 4241 (1973); *31* 177 (1975)

9. NUCLEOPHILIC ACYLATION

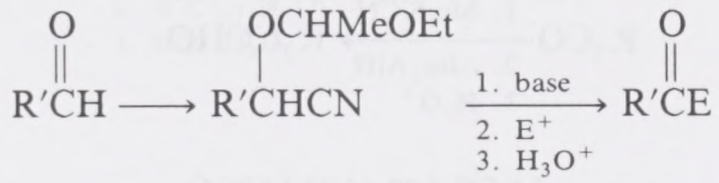
See also page 721, Section 10, and page 729, Section 11.

Reviews:

Angew Int *8* 639 (1969)
Chem Ind 687 (1974)
Tetr *32* 1943 (1976); *36* 2531 (1980)
Aldrichimica Acta *14* 73 (1981); *15* 35 (1982)

1. Cyanohydrin Derivatives

Review: Tetr *39* 3207 (1983)

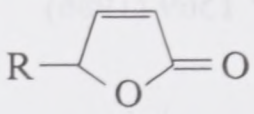


$\underline{E^+}$

RX — JACS *93* 5286 (1971); *96* 5272 (1974); *103* 5259 (1981) (intramolecular); *108* 4912 (1986)
Syn 358 (1973)
TL *22* 1359*, 1363*, 2651*, 3683 (1981); *23* 4361* (1982); *24* 4683 (1983) (*intramolecular)
JOC *51* 3393 (1986) (X = OTs, intramolecular)

RCHO, R_2CO — JOC *45* 395 (1980)
Org Syn *63* 79 (1984)

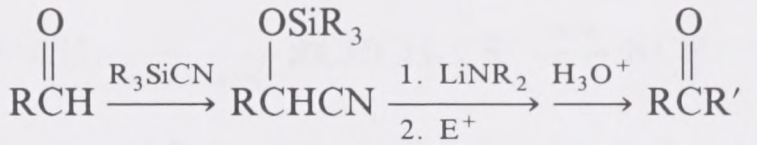
enone (1,4-addition) — TL *22* 2175 (1981)



(1,4-addition) — TL *28* 3551 (1987)

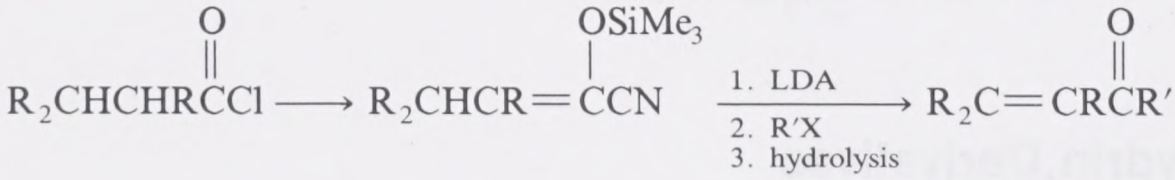
$PhCH{=}CHNO_2$ ($E = PhC(=CH_2)$) — Syn Commun *10* 717 (1980)

$H_2C{=}CMeCH{=}CHSO_nPh$ ($n = 1,2$; 1,6-addition) — Syn Commun *11* 709 (1981)

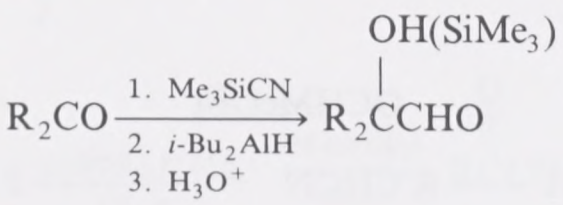


$E^+ = RX$; RCHO; R_2CO; RCOCl; enone; α,β-unsaturated esters; Michael acceptors

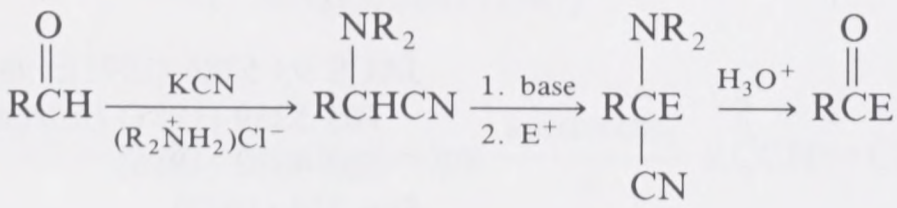
R	
aryl	Syn 777 (1973); 180, 391 (1975) Ber *112* 2045, 2062 (1979); *113* 302, 324 (1980) Tetr *39* 841 (1983) JOC *52* 564 (1987)
vinylic	Syn 777 (1973) JOC *44* 462 (1979); *45* 395 (1980); *52* 4135 (1987) Ber *113* 3783 (1980); *114* 959 (1981) Syn Commun *11* 709 (1981) JACS *106* 718 (1984) TL *27* 5359 (1986)



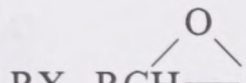
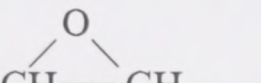
Ber *119* 722, 1772 (1986)

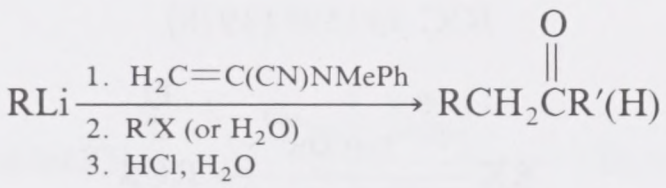


JACS *107* 4577 (1985)



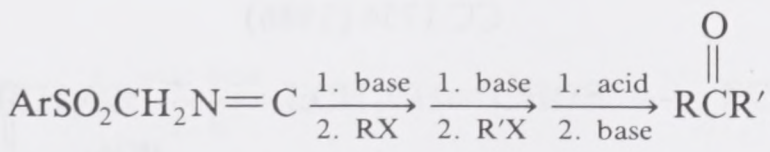
R	E^+	
H	RX	Heterocycles *19* 481 (1982)
	enone (1,4-addition)	Heterocycles *19* 1395 (1982)
alkyl	RX	BSCF 1653 (1961) Syn 127 (1979) JCS Perkin II 1645 (1982) TL *23* 3369 (1982); *24* 4683 (1983); *27* 1569 (1986)

	RX,  (1,4-addition)	TL 5175 (1978)
	$RCHO$, R_2CO	CL 71 (1980) TL *23* 639 (1982)
	$RCH{=}CRCO_2R$ (1,4-addition)	Z Chem *21* 68 (1981)
aryl	D_2O	CC 218 (1967) JCS C 2049 (1970)
	RX	JACS *82* 1786 (1960) JOC *26* 4740 (1961); *48* 1909 (1983) Tetr *31* 1219 (1975) Syn 127 (1979) TL *24* 4683 (1983)
	enone (1,4-addition)	TL *25* 4641 (1984); *27* 2985 (1986) (added Lewis acids) JOC *51* 1293 (1986)
	$H_2C{=}CHCN(CO_2R)$	JOC *37* 4465 (1972) JACS *98* 6321 (1976) J Heterocyclic Chem *15* 881 (1978) CL 399 (1979)
	RX, RCOCl,  , $H_2C{=}CHCN(CO_2R)$	JOC *44* 4597 (1979)
vinylic	RX R_2CO	CL 1263 (1982) TL *21* 1205 (1980)
hydrolysis	H_2O, $CuSO_4$	TL 2763 (1978)

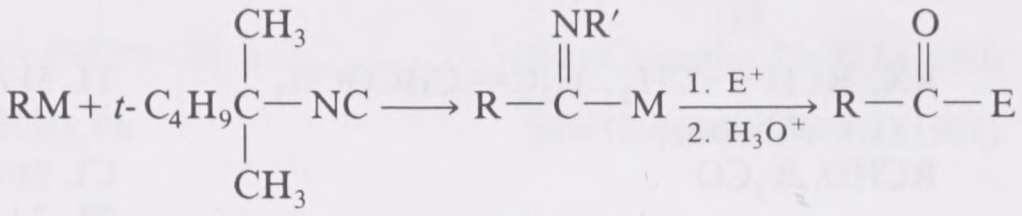


R	
alkyl	Syn 897 (1978)
enolate or imine anion	Syn 413 (1980)

2. Isonitriles



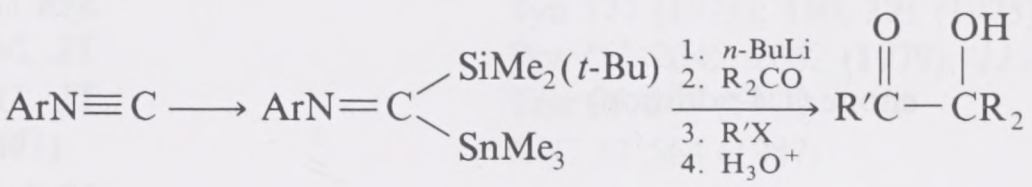
TL 4229 (1977); 5335 (1982) (cyclophanes); *28* 3825 (1987)
Syn 325 (1980)
JOC *46* 5159 (1981); *51* 1551 (1986)
Syn Commun *13* 331, 379, 1067 (1983)
JACS *107* 5238 (1985)



M = Li, MgX

E^+ = H_2O, D_2O, $ClSiMe_3$, RCHO, $H_2C\!-\!CHR$ (epoxide), CO_2, $ClCO_2Et$, RX (R = 1° alkyl, aryl, alkynyl, vinylic), $H_2C{=}CHCO_2Et$ (1,4-addition)

JACS *91* 7778 (1969); *92* 6675 (1970)
JOC *39* 600 (1974); *46* 5405 (1981); *47* 52 (1982)

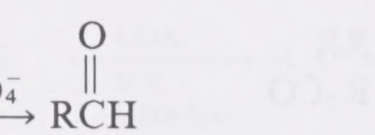


Ar = 2,6-xylyl

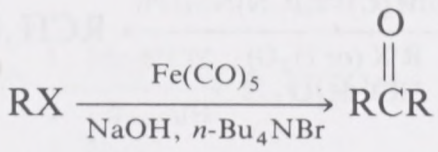
JACS *109* 7888 (1987)

3. Iron Carbonyl Reagents

Review: Acct Chem Res *8* 342 (1975)

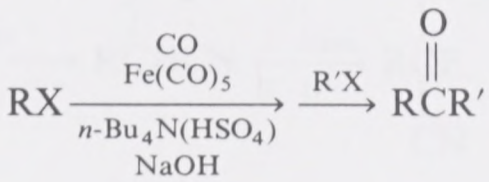


JOC *43* 1598 (1978)

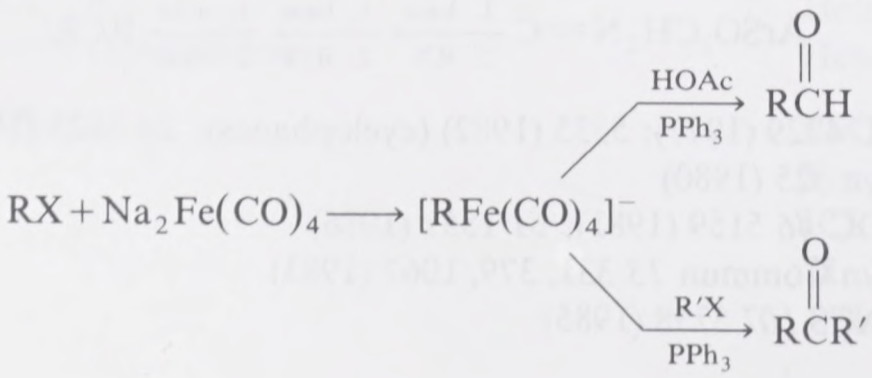


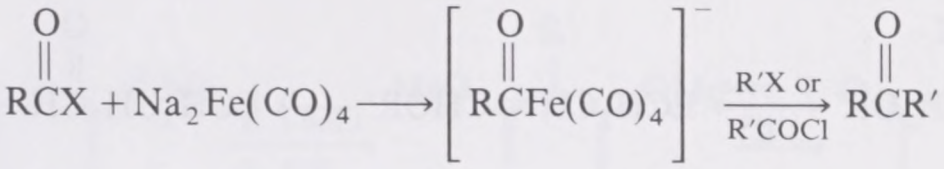
R = 1° alkyl, benzylic

CL 321 (1979)

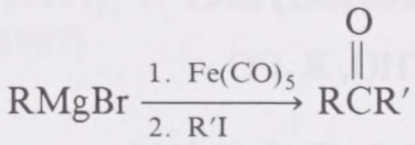


CC 1754 (1986)

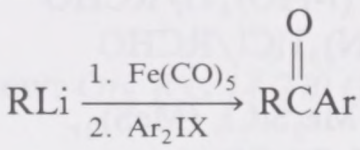




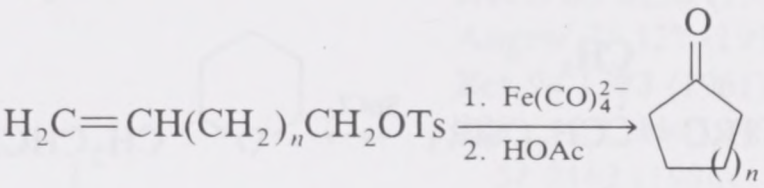
JOC *35* 4183 (1970)
JACS *92* 6080 (1970); *94* 1788, 5905 (1972); *95* 249, 2689 (1973); *99* 2515 (1977); *100* 4766 (1978)
Org Syn *59* 102 (1980)



TL 761 (1978)

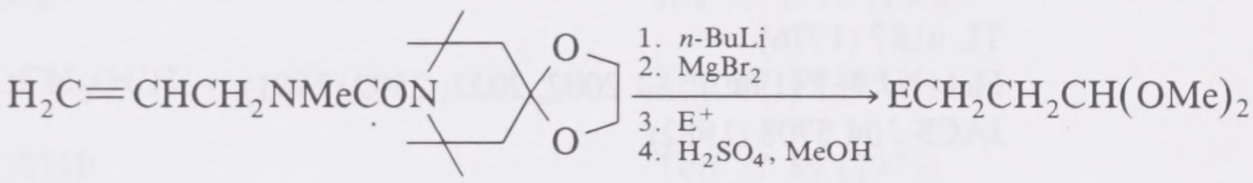


TL 1255 (1979)



TL *21* 4687 (1980)

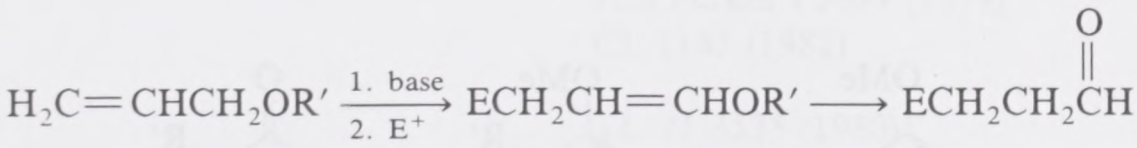
4. Allylic Amides



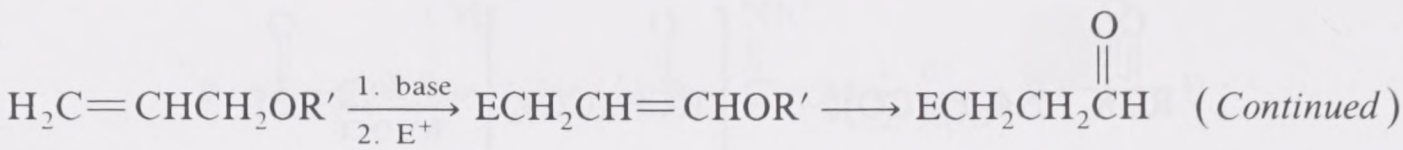
$E^+ = RX, RCHO, R_2CO$

Angew *18* 399 (1979)

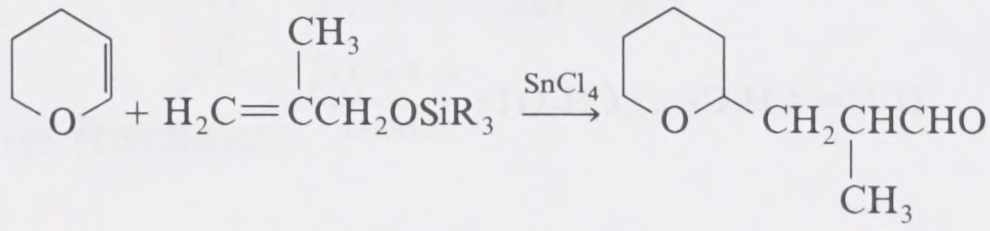
5. Allylic Ethers and Carbamates



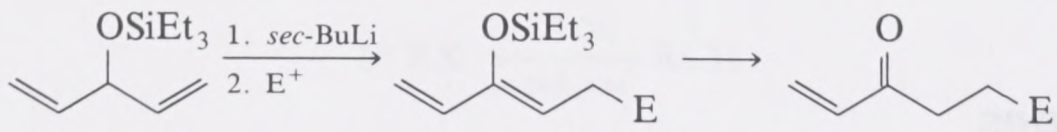
R′	E^+	
alkyl	RX	JACS *96* 5560 (1974) TL 833 (1979) CL 1637 (1982) (chiral)
	RX, epoxide (intramolecular)	TL 2115 (1976)



$SiEt_3$	RX	JACS *96* 5561 (1974)
$CONMe_2$	$(MeO)_2CO$, RX	Angew Int *19* 625 (1980)
$CON(i\text{-}Pr)_2$	RCHO, R_2CO	Angew Int *20* 1024 (1981); *21* 372 (1982); *25* 160 (1986)
	$(i\text{-}PrO)_3TiCl$/RCHO	TL *27* 4873 (1986)
	$(i\text{-}PrO)_3TiCl$, $(Et_2N)_3TiCl$ or $(i\text{-}PrO)_4Ti$/RCHO	TL *28* 5149 (1987)
	$(Et_2N)_3TiCl$/RCHO	Angew Int *25* 160 (1986)
CONHR′	RX, Me_3SiCl, $(MeS)_2$, $(MeO)_2CO$	Angew Int *20* 127 (1981)
$CONR_2$	review	Angew Int *23* 932 (1984)



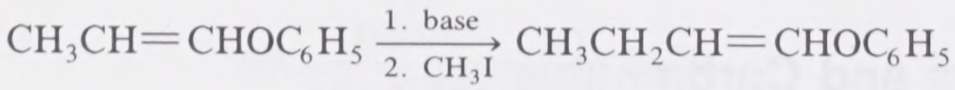
JOC *52* 5691 (1987)



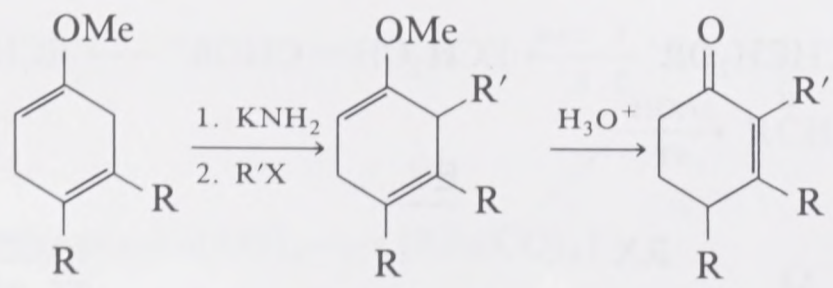
$E^+ = H_2O$, RX, RCHO, R_2CO, RCOCl, Me_3SiCl, $(MeS)_2$

TL 4187 (1976)
Helv *63* 967 (1980); *64* 2002, 2022, 2592 (1981)
JACS *104* 5708 (1982)

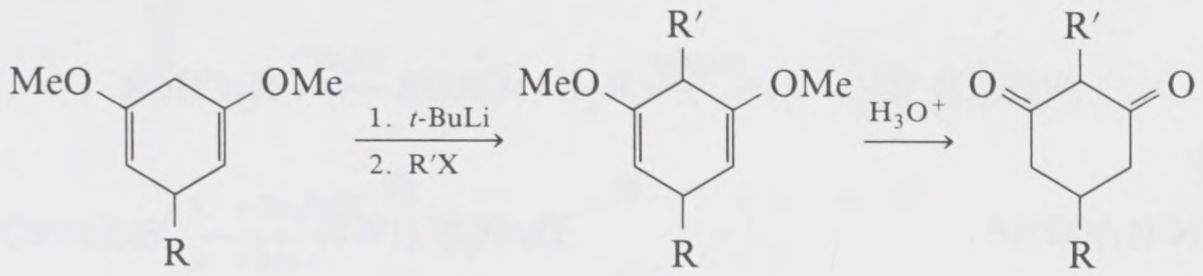
6. Vinylic Ethers



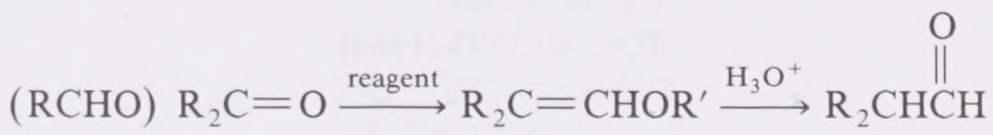
Helv *57* 2261 (1974)



JCS Perkin I 7 (1983)
TL *28* 4195 (1987)

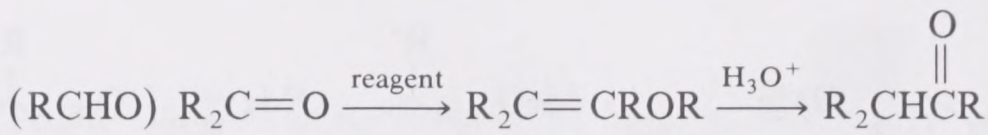


JOC *42* 3755 (1977); *47* 1576 (1982); *51* 1407 (1986)
TL *28* 4163 (1987)



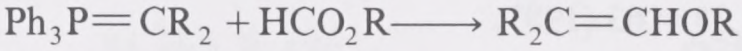
Review: Org Rxs *14* 270 (1965)

Reagent(s)	
$Ph_3P{=}CHOMe$	JACS *80* 6150 (1958) Angew *71* 127 (1959) Ber *94* 1373 (1961) JOC *35* 1385 (1970); *50* 2668, 2676 (1985); *51* 2162 (1986) Syn 604 (1973) TL 3979 (1973); *22* 1063 (1981) Tetr *31* 89 (1975)
$Ph_3P{=}CHO\text{-}n\text{-}Bu$	Ber *95* 2526 (1962)
$Ph_3P{=}CHOCH_2CH{=}CH_2$	JACS *92* 5522 (1970)
$Ph_3P{=}CHOAr$	Ber *95* 2514 (1962)
$Ph_3P{=}CHOCH_2OCH_3$	Tetr *31* 89 (1975)
$Ph_3P{=}CHOTHP$	Tetr *31* 89 (1975)
$(EtO)_2PO\overline{C}HOCH_2CH_2OCH_3$	TL 3629 (1978) JOC *44* 4847 (1979)
$(RO)_2PO\overline{C}HOTHP$ (R = Et, *n*-Bu)	TL 3629 (1978) JOC *44* 4847 (1979)
$Ph_2PO\overline{C}HOCH_3$	CC 314 (1977) JCS Perkin I 3099 (1979) CL 1143 (1982)
$Ph_2P\overline{C}HOCH_3$	TL *21* 3535 (1980)
$(MeO)_2POCHN_2$, R'OH, KO-*t*-Bu	TL *21* 2041, 5003 (1980)
m-$CF_3C_6H_4SeCHLiOCH_3$/MsCl, Et_3N	JACS *101* 6638 (1979)
$Me_3SiCH(Li)OCH_3$	CC 822 (1979) Organomet *1* 553 (1982)

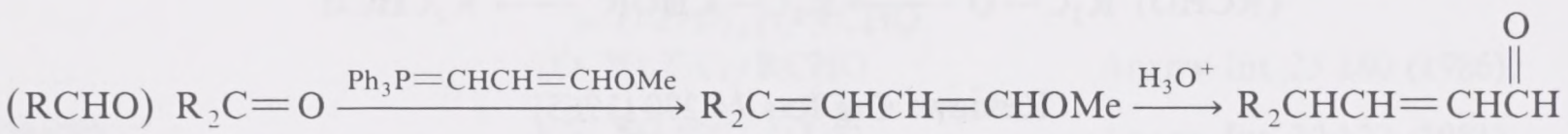


Reagent

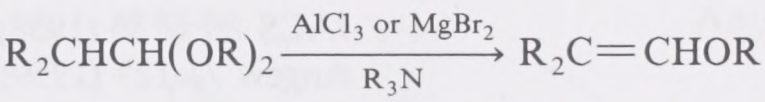
$(n\text{-BuO})_2PO\overline{C}(CH_3)OTHP$	TL 3629 (1978)
$Ph_2PO\overline{C}(CH_3)OCH_3$	CC 314 (1977) JCS Perkin I 3099 (1979)



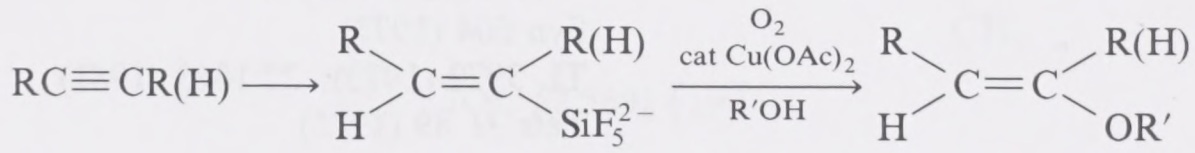
CL 967 (1981)
JOC *49* 3595 (1984)



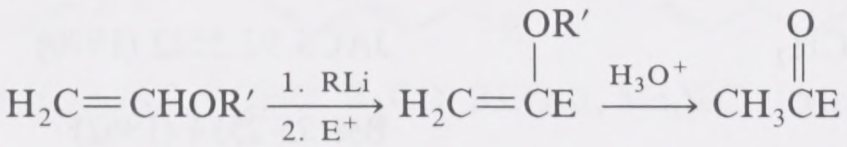
TL 3875 (1977)



Helv *62* 1451 (1979)

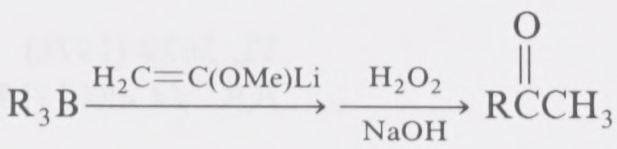


TL *21* 4105 (1980)

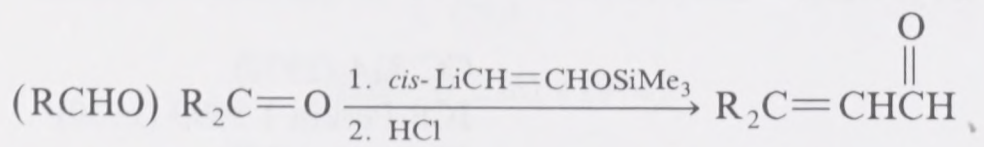


$R' = Me, Et, THP; E^+ = RX, RCHO, R_2CO, RCO_2Me, RCN$

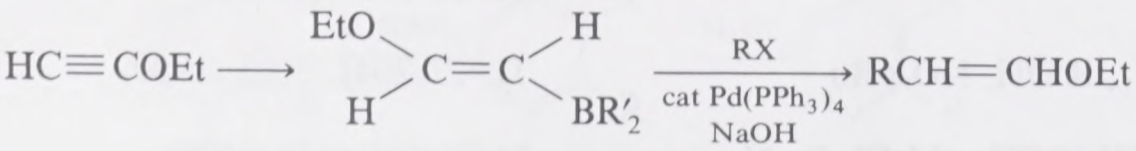
See page 185, Section 1.



JOMC *156* 123 (1978)

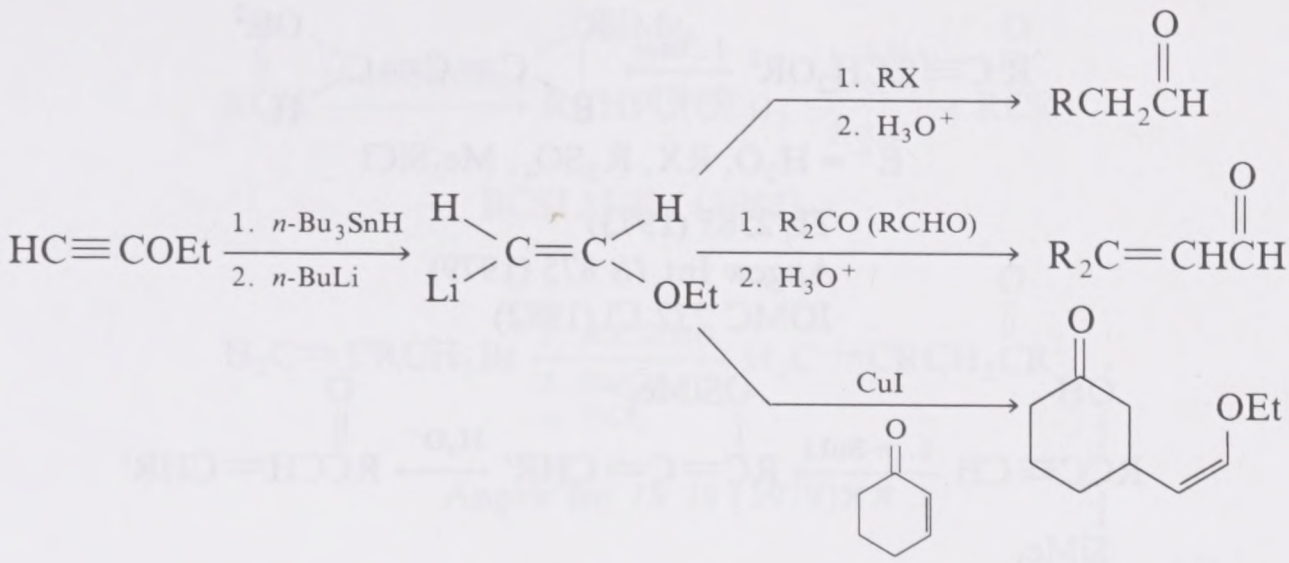


JOC *46* 3741 (1981)

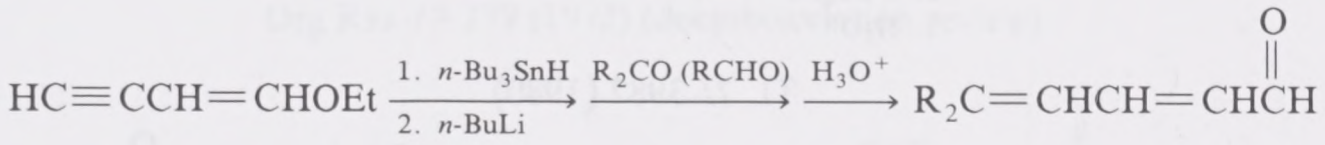


R = aryl, benzylic

JOC *47* 2117 (1982)

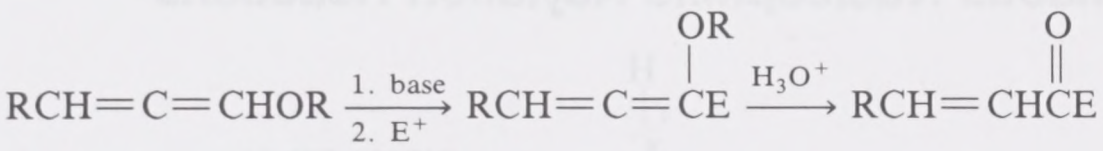


JACS *99* 7365 (1977)
TL 3589 (1977)
JOC *43* 1595 (1978)



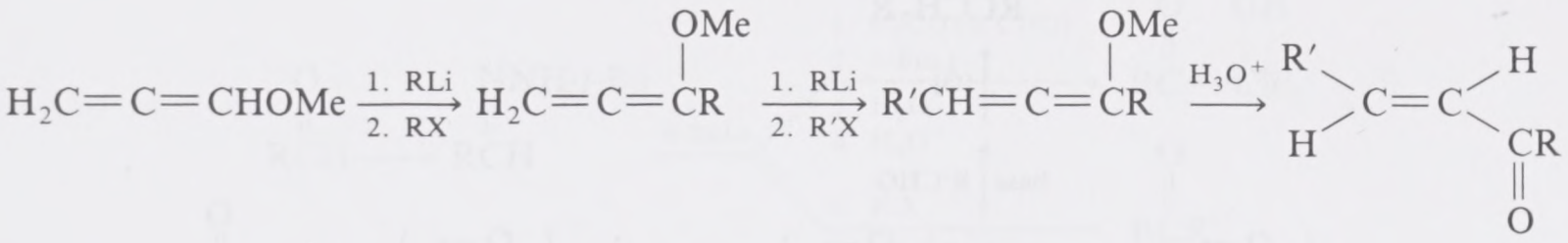
TL 717 (1978)

7. Allenic, Propargylic and Cyclopropyl Ethers

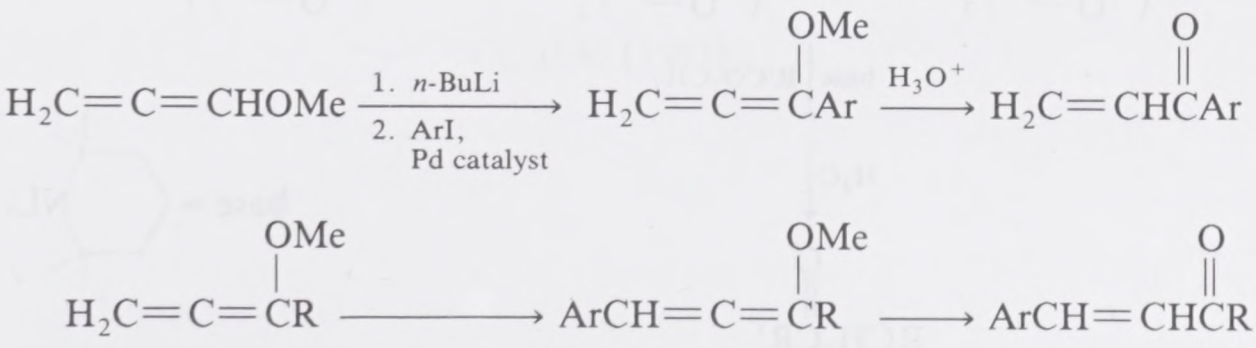


$E^+ = R'X, Me_2SO_4, RCHO, R_2CO, Me_3SiCl$

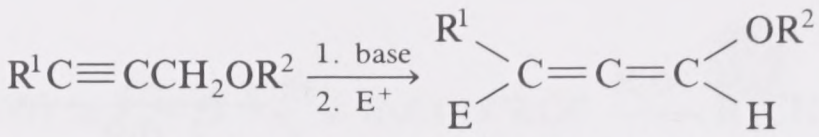
Rec Trav Chim *87* 916 (1968)
TL 2585 (1973)
Angew Int *18* 875 (1979)
JACS *104* 1119 (1982); *106* 5360 (1984)



TL 1137 (1978)

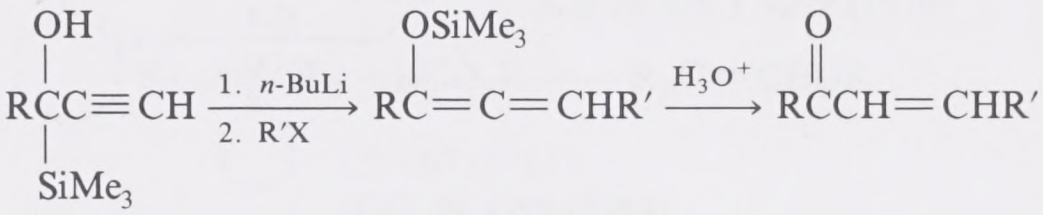


Syn 738 (1982)

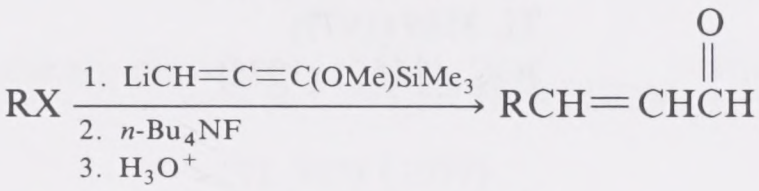


$E^+ = H_2O, RX, R_2SO_4, Me_3SiCl$

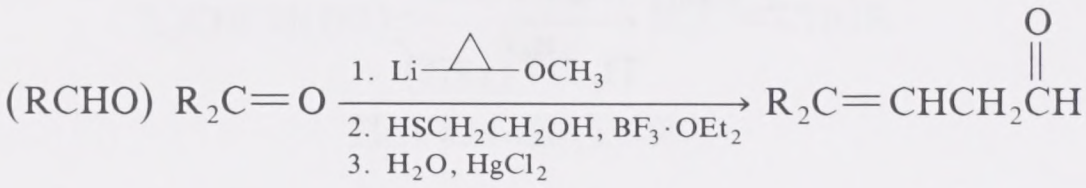
TL 2585 (1973)
Angew Int *18* 875 (1979)
JOMC *232* C1 (1982)



TL *28* 1299 (1987)

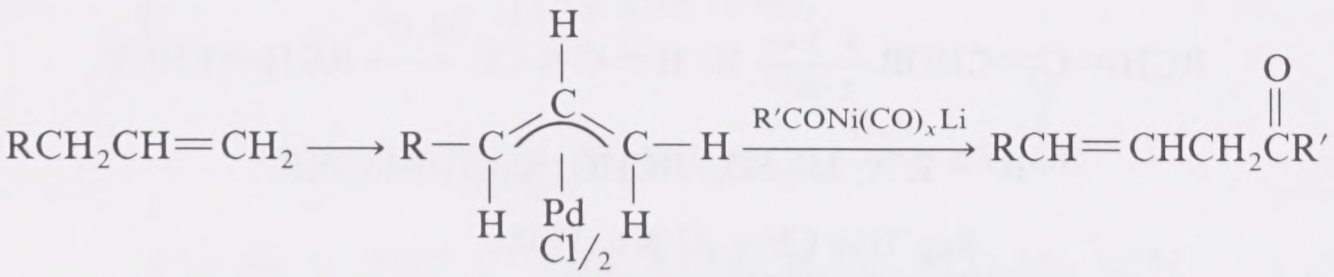


TL *21* 3987 (1980)

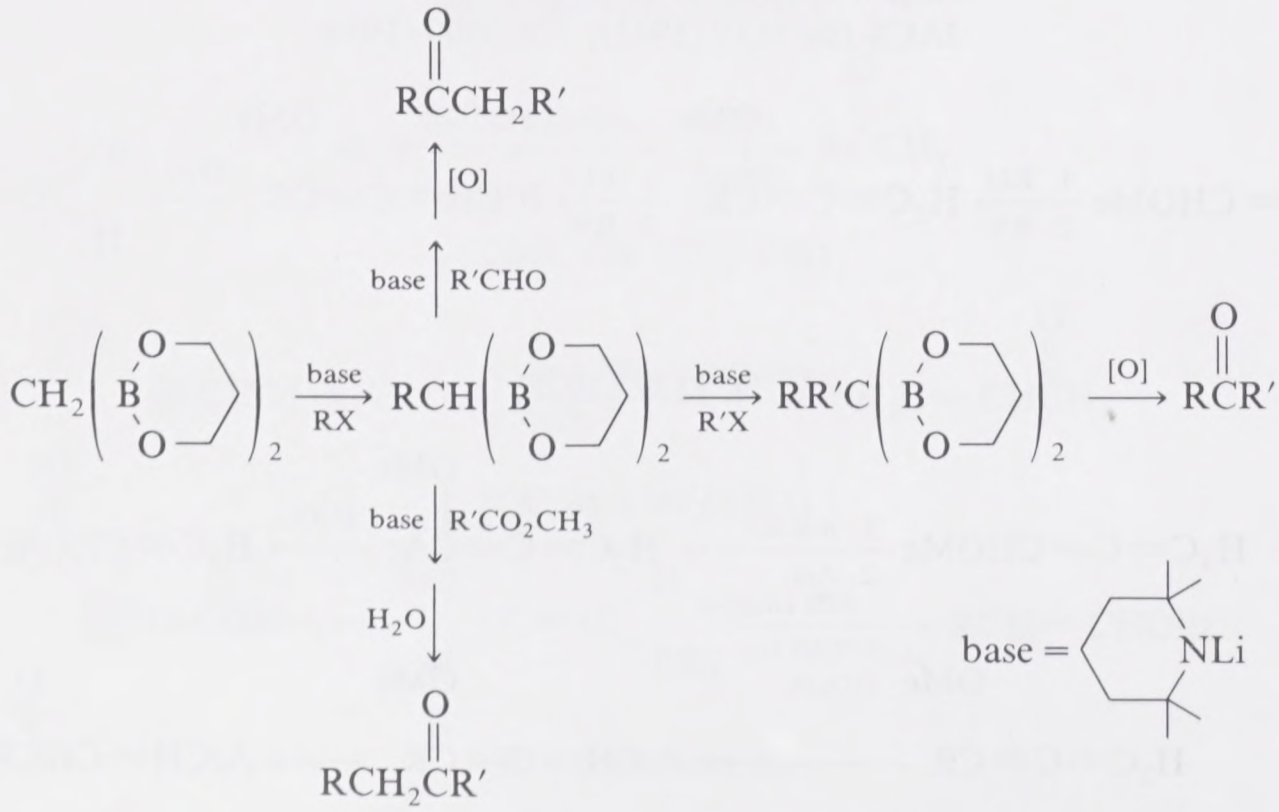


TL 3685 (1975)

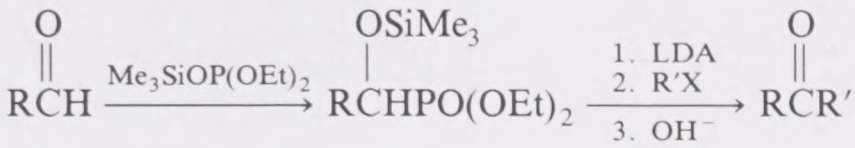
8. Miscellaneous Nucleophilic Acylation Reactions



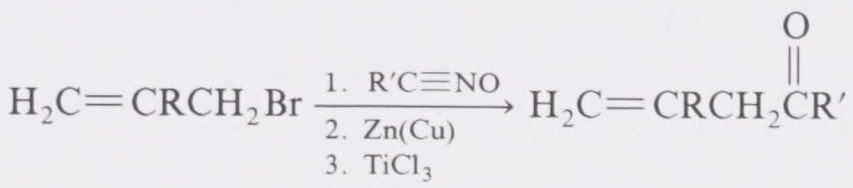
Organomet *1* 1188 (1982)



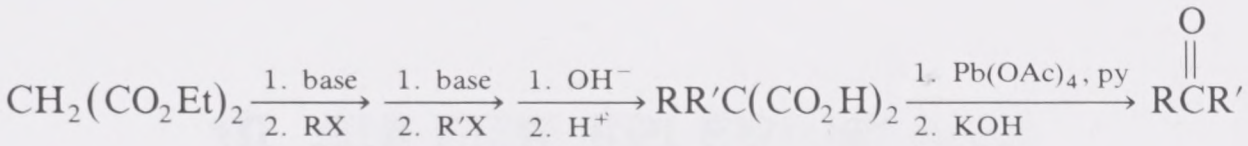
JACS *97* 5608 (1975); *99* 3196 (1977)
Organomet *1* 20, 280 (1982)



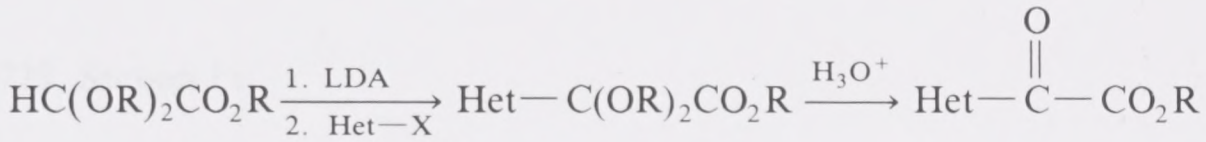
BCSJ *55* 224 (1982)



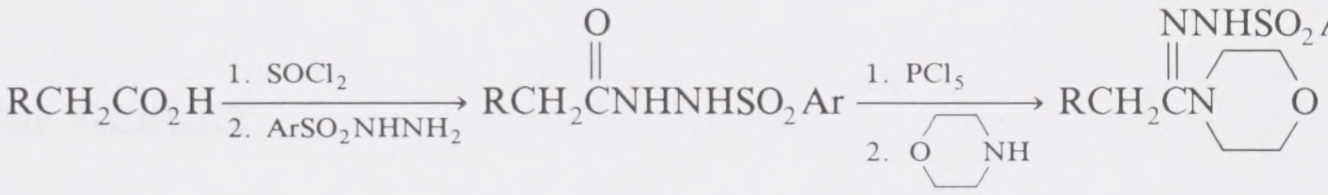
Angew Int *18* 78 (1979)

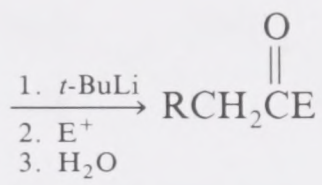


TL 6145 (1966)
Org Rxs *19* 279 (1972) (decarboxylation review)



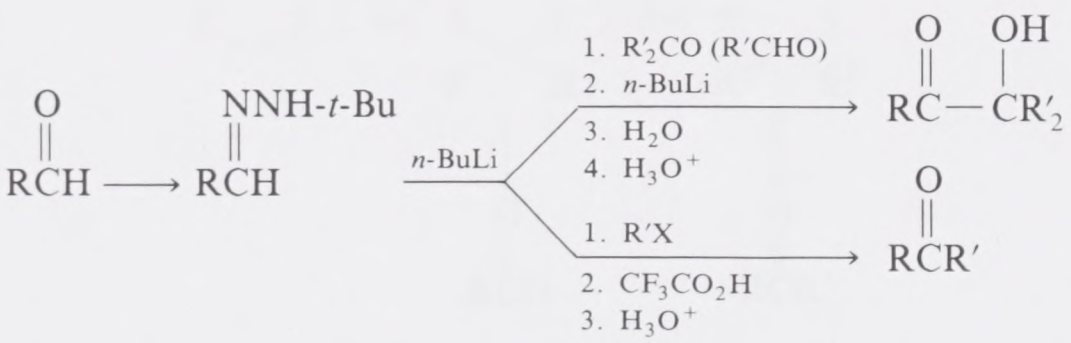
TL *27* 6059 (1986)





$E^+ = MeI, R_2CO$

CC 1121 (1981)



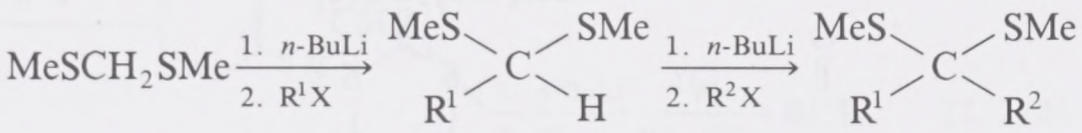
CC 1040 (1983)

10. SULFUR, SELENIUM AND TELLURIUM REAGENTS

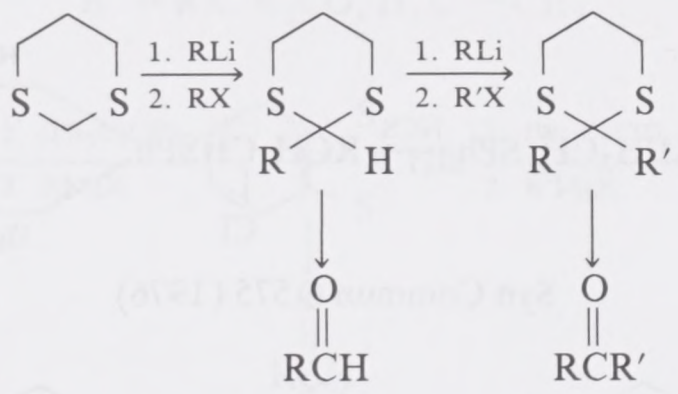
See also page 729, Section 11.

Review: Syn 357 (1977)

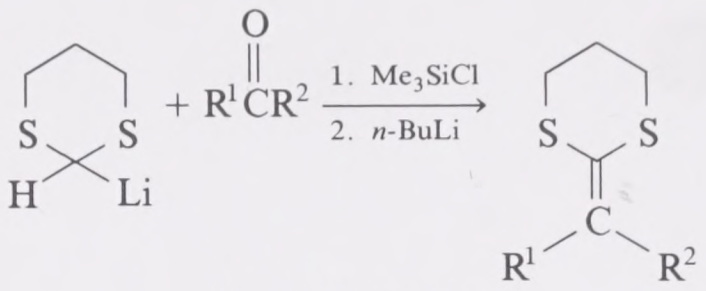
1. Sulfur Acetals



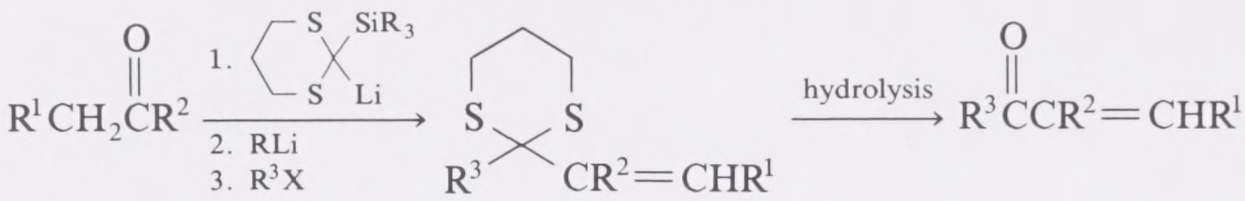
TL *23* 1047 (1982)



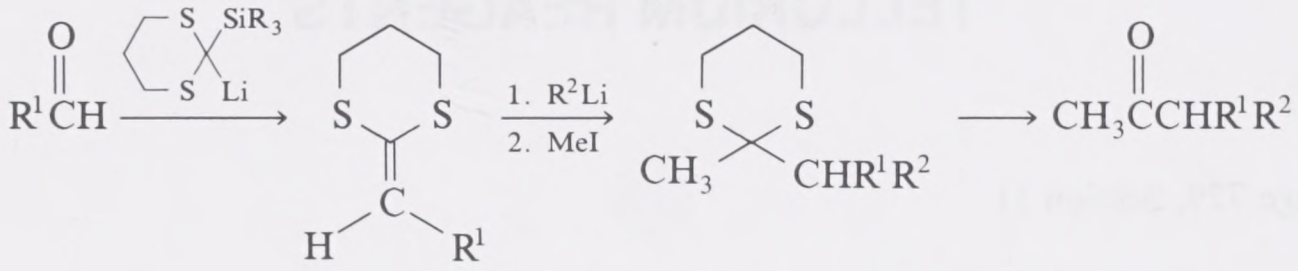
Syn *1* 17 (1969); 357 (1977); 561 (1980) (hydrolysis); 135 (1981) (hydrolysis); 580, 679 (1982) (both hydrolysis)
JOC *36* 366, 3553 (1971); *40* 231 (1975); *46* 1512 (1981); *47* 1145, 2212 (hydrolysis) (1982)
CC 529 (1972); 255 (1978) (hydrolysis)
Heterocycles *6* 731 (1977)
JCS Perkin I 1036 (1978)
Syn Commun *11* 343 (1981)
JACS *103* 3112 (1981)
Ann 1589 (1982)
TL *27* 2965 (hydrolysis), 6305 (alternate preparation) (1986)



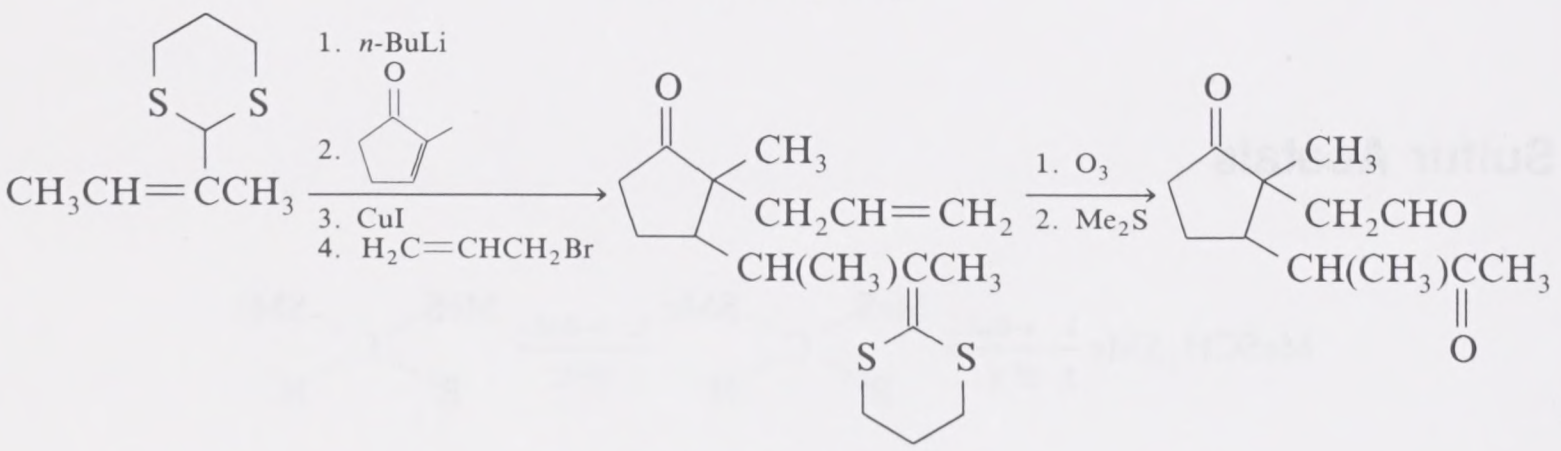
Syn 579 (1982)



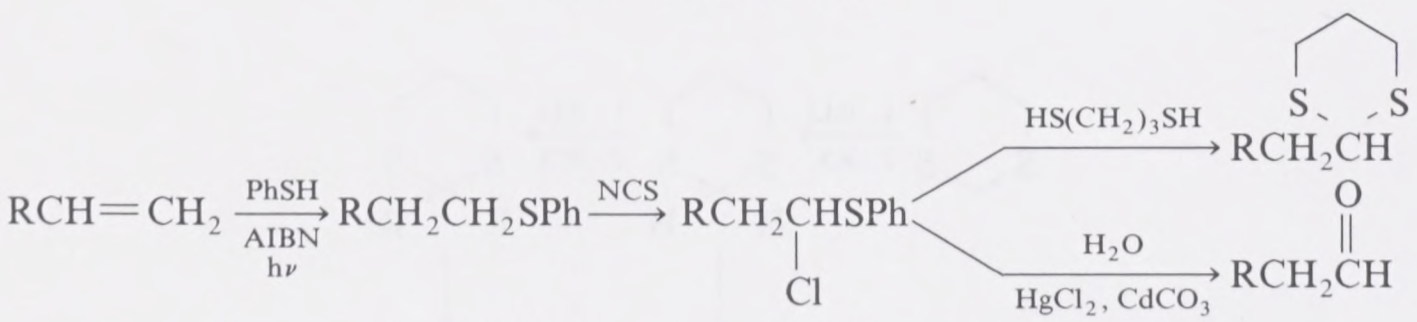
TL 3171 (1974)
Ann 811 (1977)
JCS Perkin I 2678 (1980)



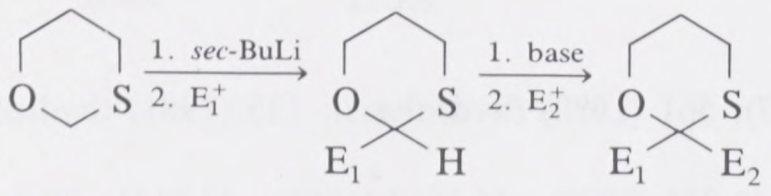
Ann 830 (1977)



JOC *46* 826 (1981)



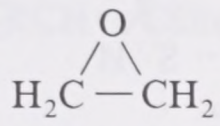
Syn Commun *6* 575 (1976)



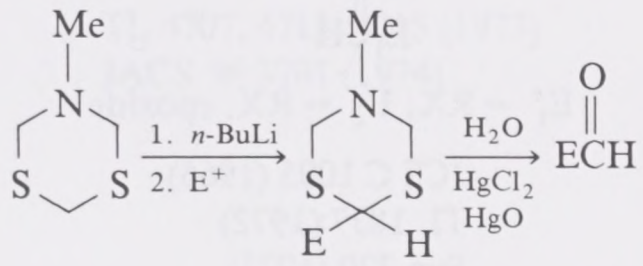
E_1^+	E_2^+	
RX	—	CC 814 (1977)
Me_3MCl (M = Si, Ge, Sn), Me_3PbOAc or $(MeX)_2$ (X = S, Se)	—	TL *22* 2005 (1981)

RCHO

JACS *106* 2937, 2943 (1984)

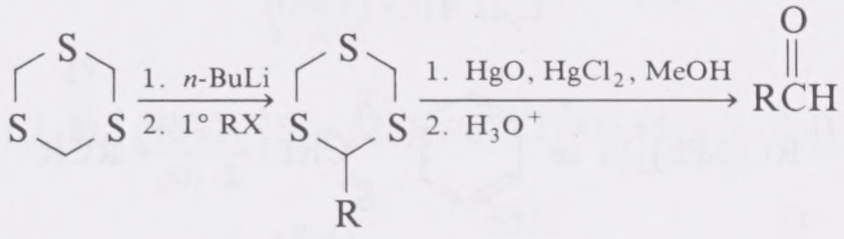


JACS *103* 3112 (1981)
(E_1 = 2-furyl)

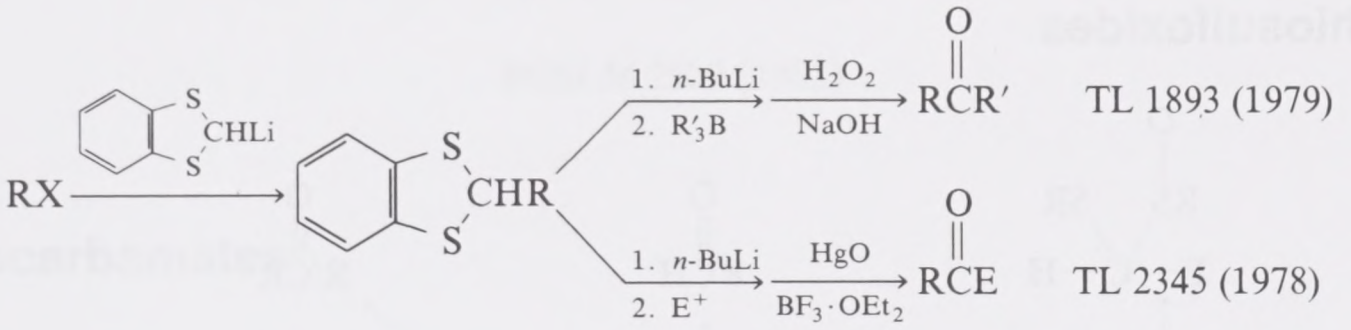


E^+ = RX, RCHO, R_2CO

JOC *42* 393 (1977)

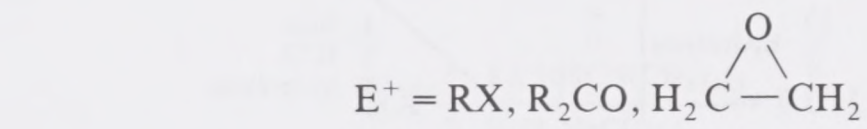


Org Syn *51* 39 (1971)

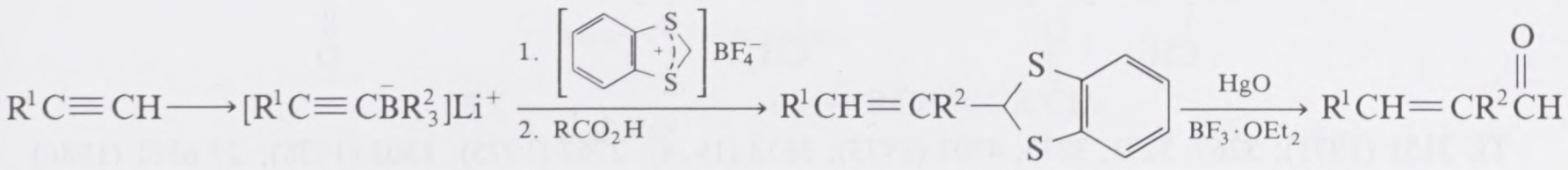


TL 1893 (1979)

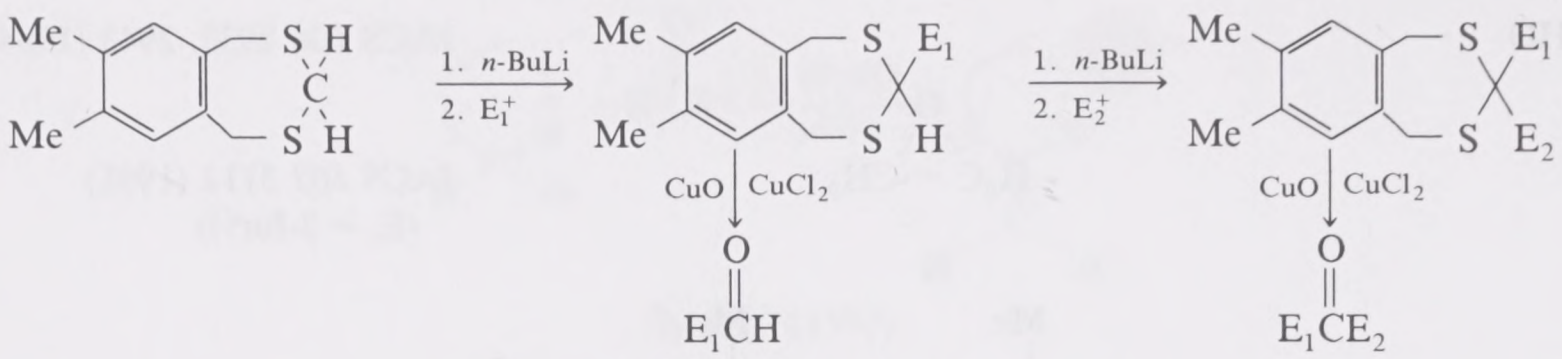
TL 2345 (1978)



JCS Perkin I 1886 (1976)
TL *22* 1821 (1981)

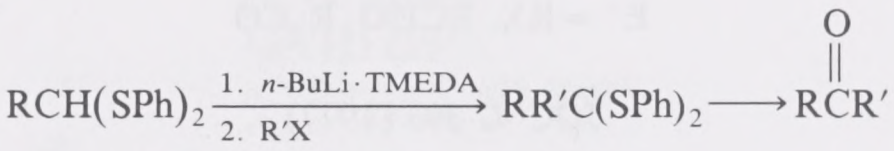


CC 164 (1981)

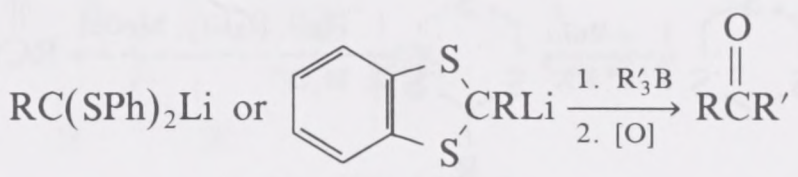


E_1^+ = RX; E_2^+ = RX, epoxide

JCS C 1005 (1966)
TL 1837 (1972)
Syn 720 (1975)

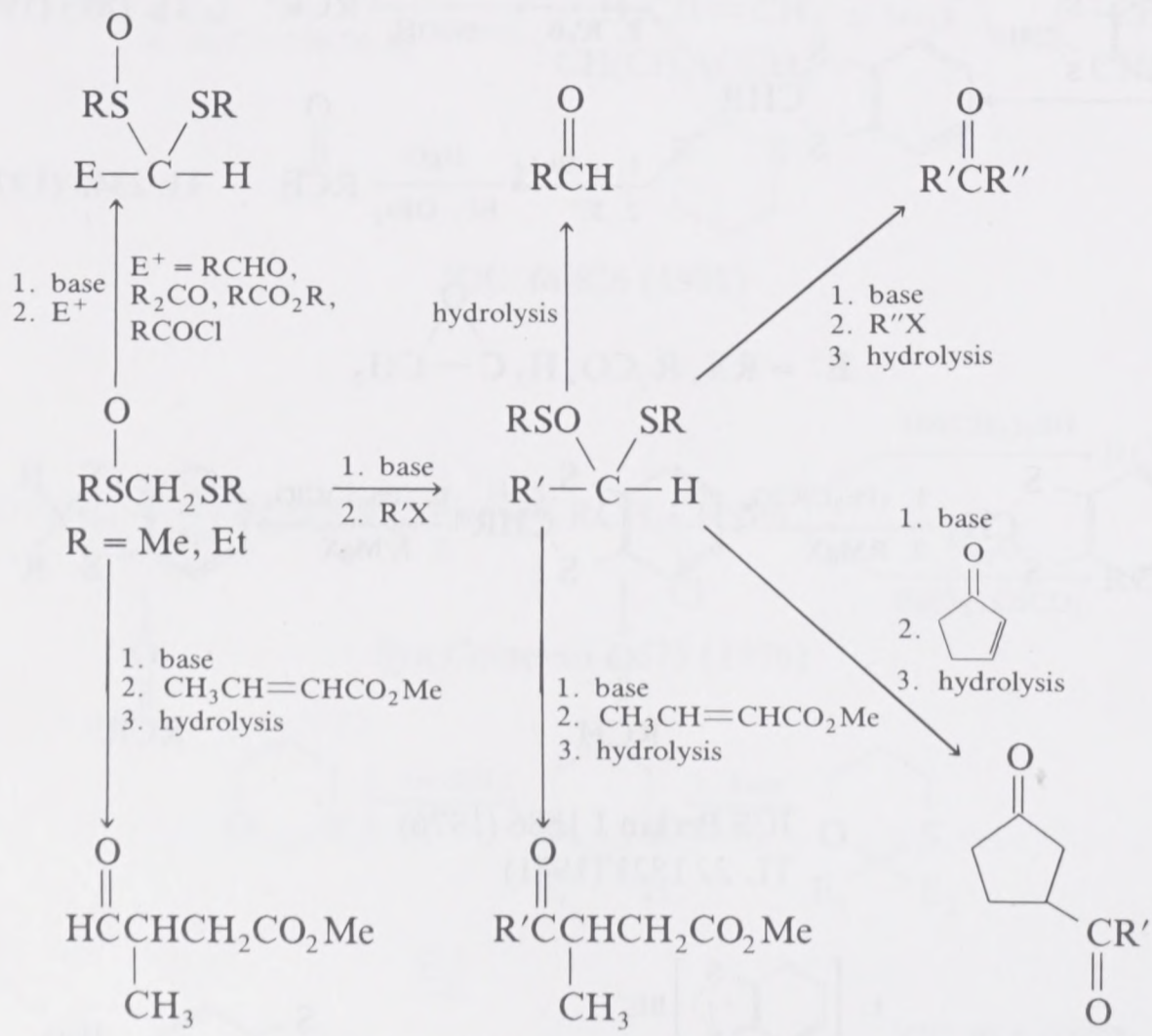


TL *21* 4763 (1980)

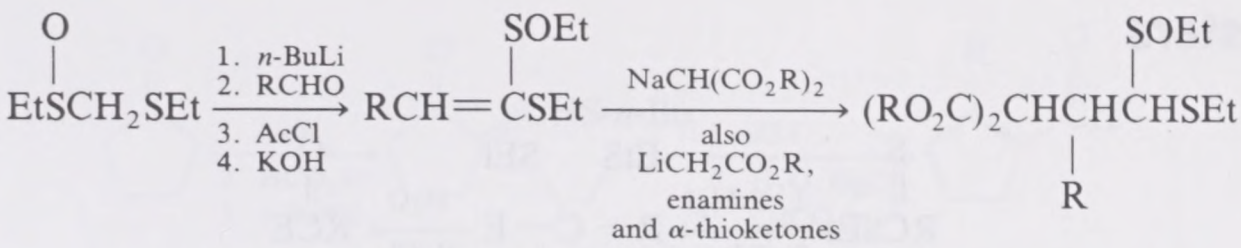


CL 961 (1973)
TL 1893 (1979)

2. α-Thiosulfoxides

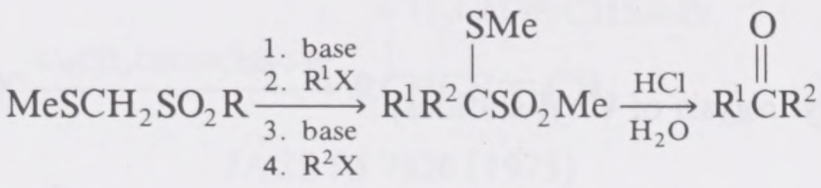


TL 3151 (1971); 3267, 3271, 3275, 4707 (1973); 3653 (1974); 2767 (1975); 1303 (1978); *27* 6381 (1986)
Syn 117 (1974)
JOC *52* 5466 (1987)

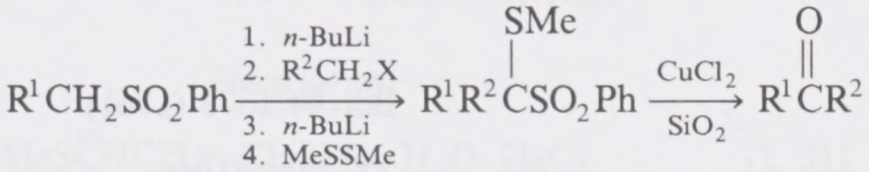


TL 4707, 4711, 4715 (1973)
JACS *96* 3701 (1974)

3. α-Thiosulfones

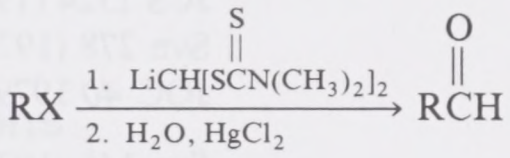


CL 813 (1982) (R = Me); 767 (1983) (R = *p*-Tol)

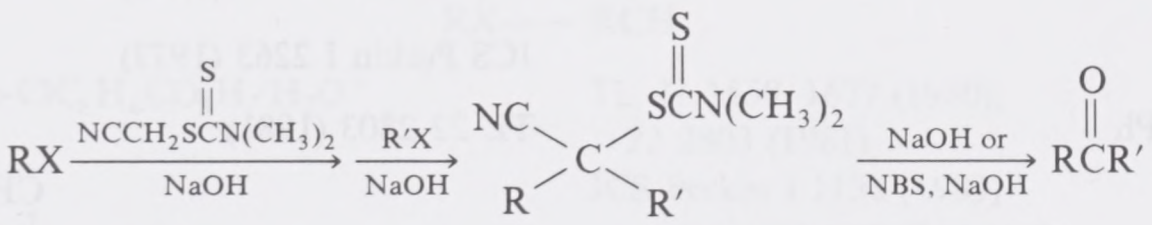


BCSJ *56* 2539 (1983)

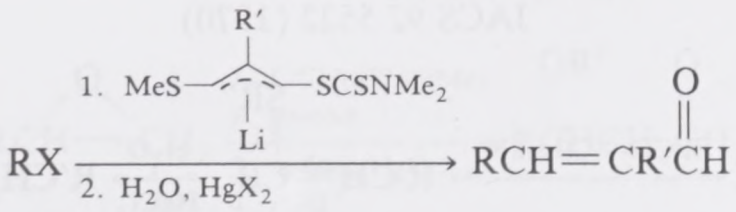
4. Thiocarbamates



CL 731 (1974)

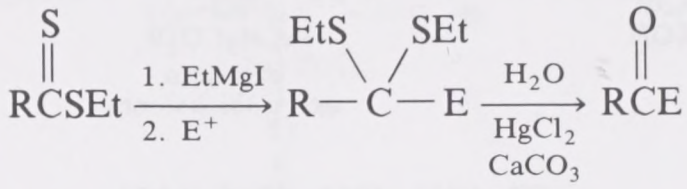


TL 2967 (1976)



TL 3625 (1974)

5. Thioesters



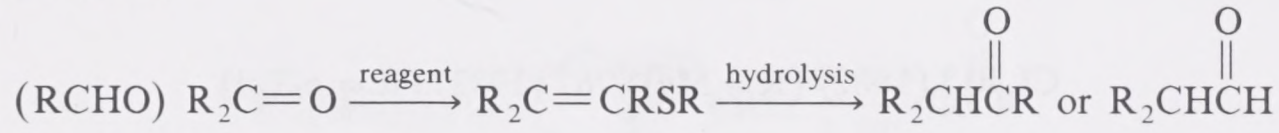
$E^+ = D_2O, CO_2, ClCO_2Et, RCHO, R_2CO$

TL 4657 (1978)

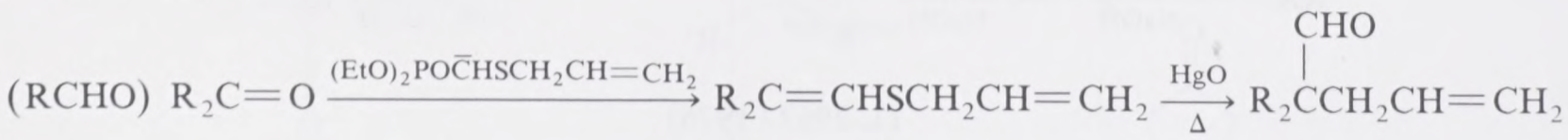
6. Vinylic and Allylic Sulfides and Selenides

Reviews:

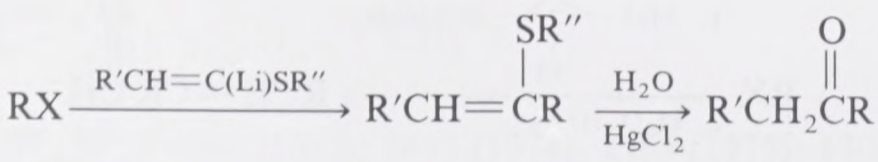
TL 4437 (1975) (hydrolysis of vinyl sulfides)
Syn 357 (1977)



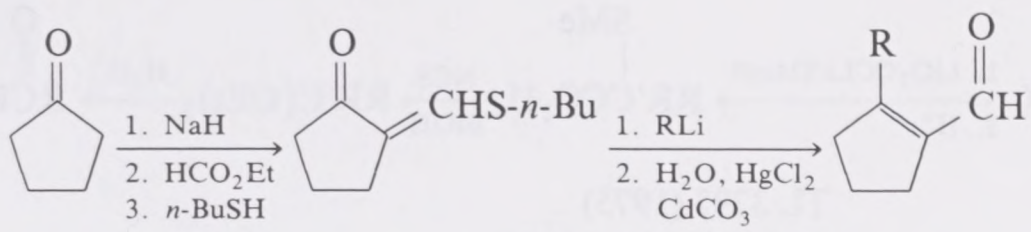
Reagent	
$Ph_3P{=}CHSMe$	Ber *94* 1373 (1961)
$Ph_3P{=}CHS\text{-}n\text{-}Bu$	TL 3787 (1968)
$Ph_3P{=}CHSPh$	TL 3665 (1969); 4451 (1974)
$Ph_3P{=}CHSR$ (R = Ph, $PhCH_2$, *n*-Pr)	Ann 2085 (1974)
$Ph_3P{=}C(CH_3)SPh$	TL 3787 (1968)
$(MeO)_2PO\overline{C}HSMe$	Syn 170 (1969)
$(EtO)_2PO\overline{C}HSMe$	JCS 1324 (1963) Syn 278 (1975) JOC *40* 1979 (1975)
$(EtO)_2PO\overline{C}HSAr$	Syn 145 (1970); 278 (1975)
$(EtO)_2PO\overline{C}RSMe$	JOC *35* 777 (1970); *44* 2967 (1979) JCS Perkin I 1879 (1974)
$Ph_2PO\overline{C}RSR$	JCS Perkin I 2263 (1977)
$Me_3SiCH(Li)SPh$	TL *22* 2803 (1981)



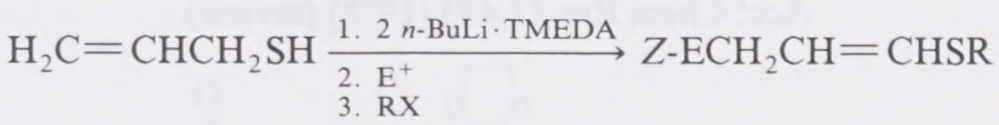
JACS *92* 5522 (1970)



JACS *95* 2694 (1973)

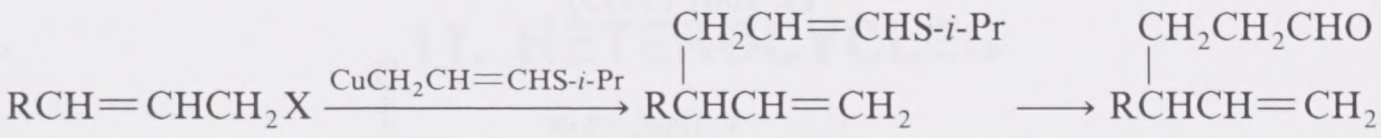


TL 1015 (1979)

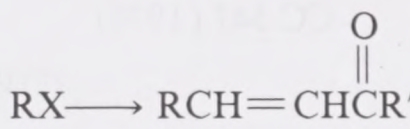


$E^+ = R'X, R_2CO, R_3SiCl$, epoxide

Ber *110* 1833 (1977)

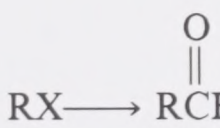


JACS *95* 7926 (1973)

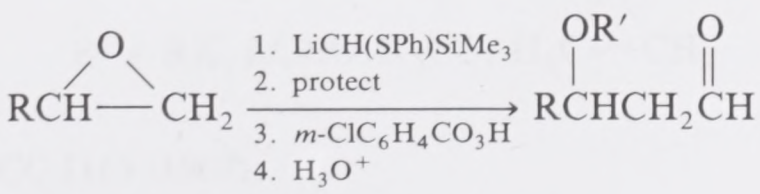


R′	Reagents	
H	$MeS\bar{C}HCH{=}CHSMe/H_2O, HgCl_2$	TL 311 (1970) JACS *93* 1724 (1971) BCSJ *48* 1567 (1975) JOC *41* 2506 (1976)
	$PhS\bar{C}HCH{=}CHOMe/H_2O$, HCl, $HgCl_2$	CL 345 (1977)
	$PhSe\bar{C}HCH{=}CHSePh/H_2O_2$	JOC *47* 1618 (1982)
Me	$PhSe\bar{C}HCH{=}CClCH_3/H_2O_2$, py	JOC *40* 2570 (1975)

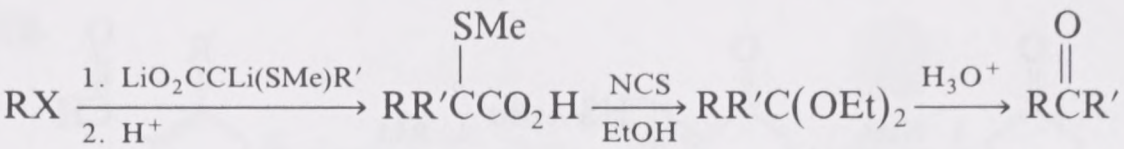
7. Miscellaneous Reactions



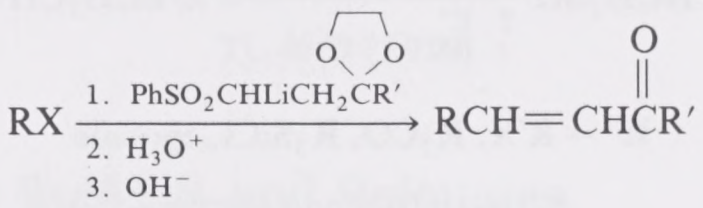
$Me_3Si\bar{C}HSPh/m\text{-}ClC_6H_4CO_3H/H_3O^+$	TL *21* 1559, 1677 (1980); *22* 2803 (1981) JCS Perkin I 1131 (1983)
$Me_3Si\bar{C}HSePh/H_2O_2$	TL 4223 (1976)
$LiCH(TePh)_2/NaI, I_2$	CL 1081 (1982)



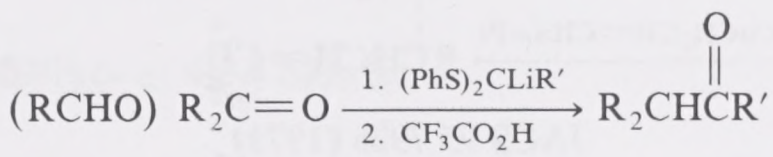
TL *21* 1559 (1980); *27* 4403 (1986)



TL 3797 (1975)
JACS *97* 3529 (1975)
Chem Rev *78* 363 (1978) (review)
Acct Chem Res *11* 453 (1978) (review)



TL 1007 (1975)



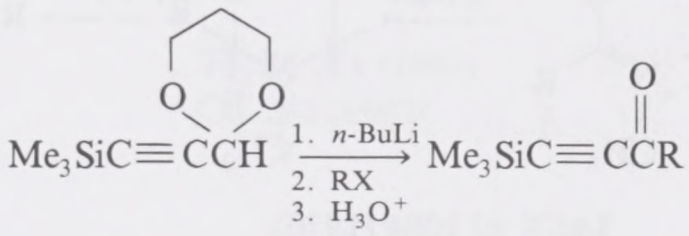
CC 547 (1976)

11. HETEROCYCLES

See also page 721, Section 10.

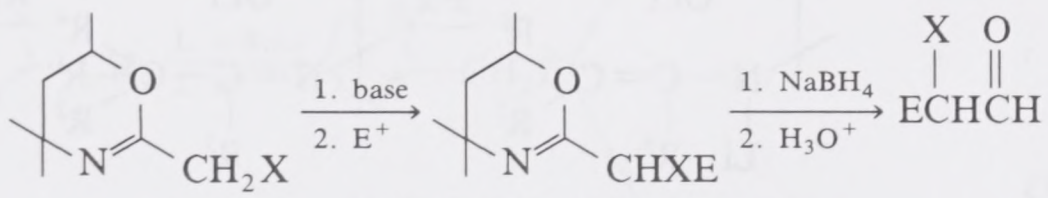
Review: Heterocycles *6* 731 (1977)

1. Dioxanes

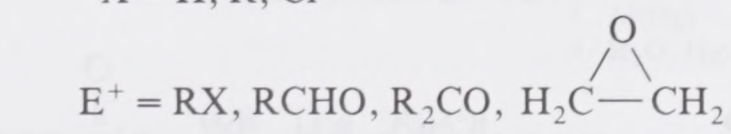


Tetr *39* 3073 (1983)

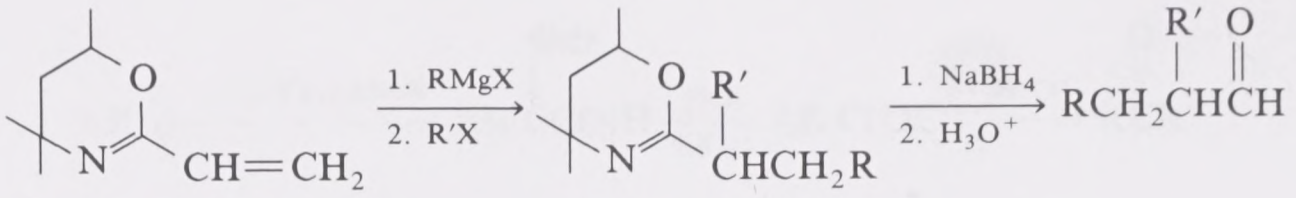
2. Dihydro-1,3-Oxazines



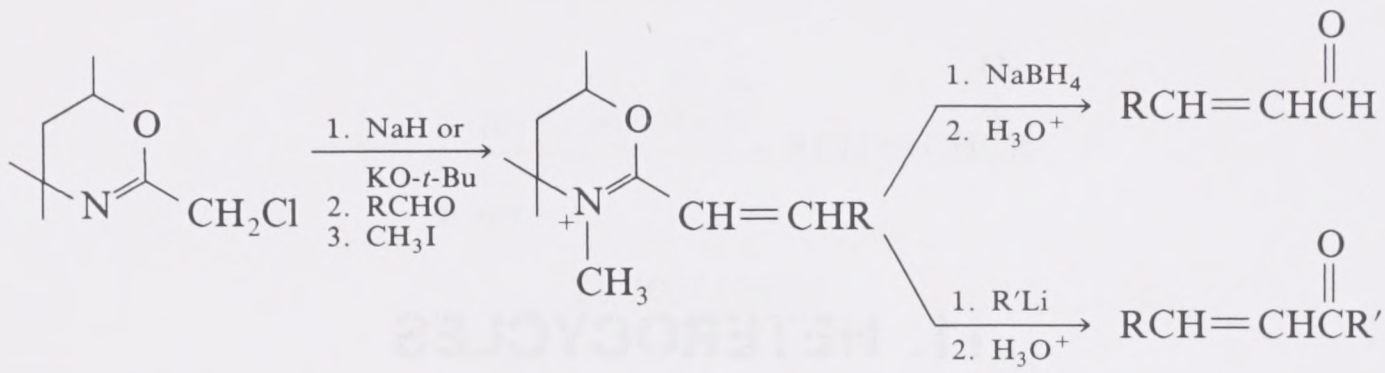
X = H, R, Cl



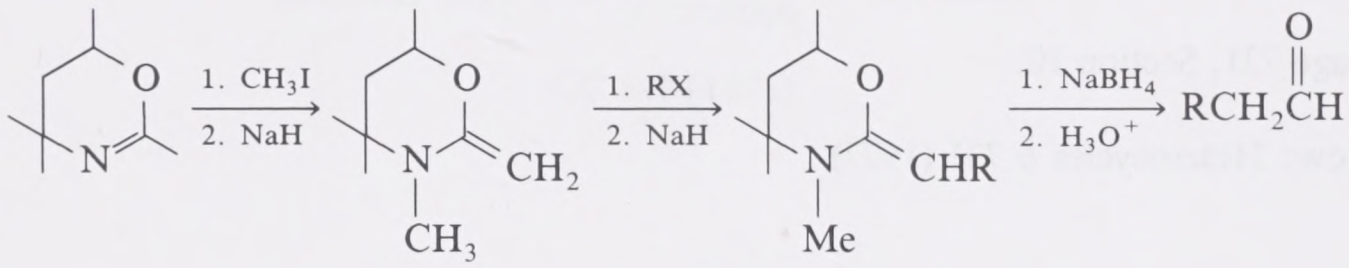
CC 1163 (1967)
JACS *91* 763, 764, 765, 2155 (1969)
Org Prep Proc Int *1* 193 (1969)
JOC *38* 36 (1973); *39* 618 (1974); *43* 2907 (1978)



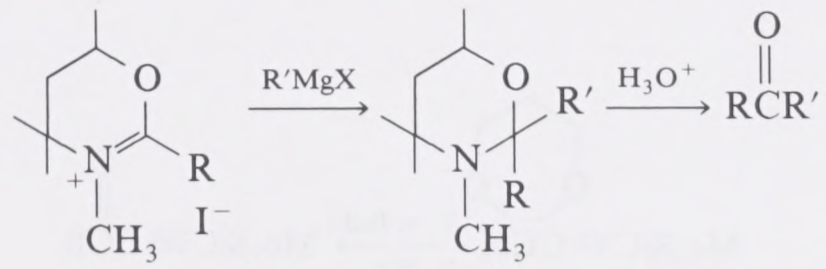
TL 1783, 4809 (1969)
Org Prep Proc Int *1* 213 (1969)
JOC *38* 36, 2136 (1973)



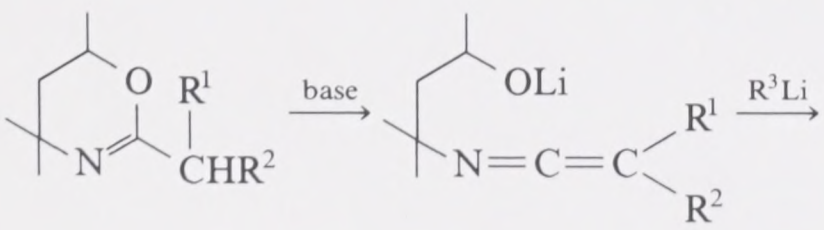
JOC *39* 623 (1974)

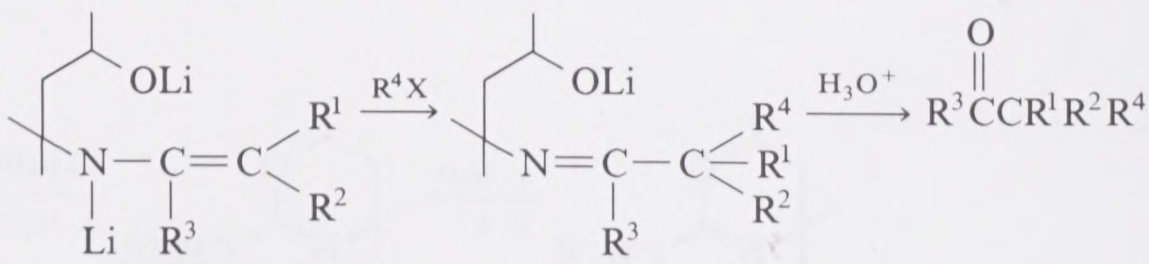


JACS *94* 3243 (1972)

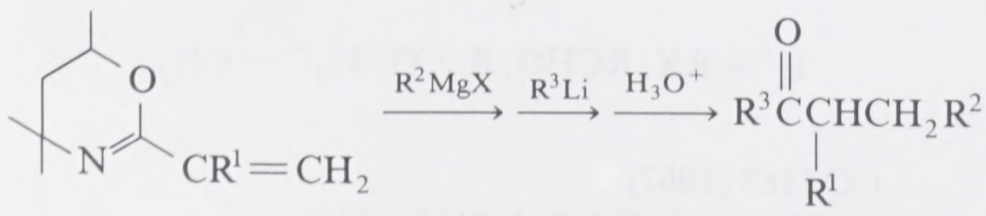


JACS *92* 1084 (1970)
JOC *37* 4289 (1972); *38* 175 (1973)



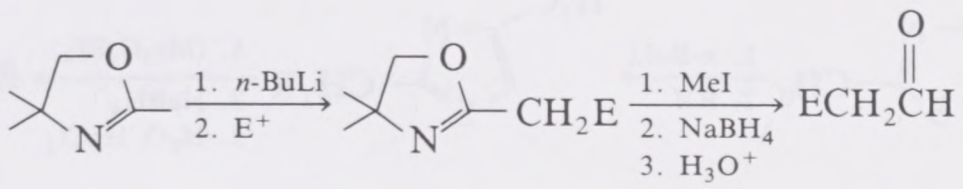


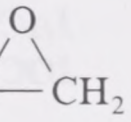
JACS *93* 2314 (1971)
JOC *38* 2129 (1973)



JOC *38* 2136 (1973)

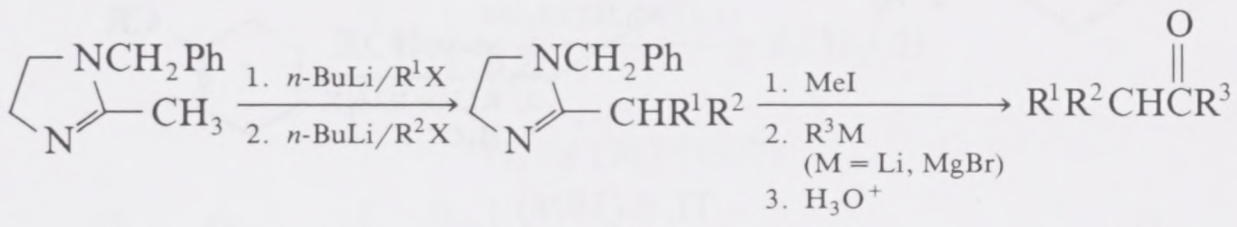
3. Oxazolines



$E^+ = RX, R_2CO,$ 

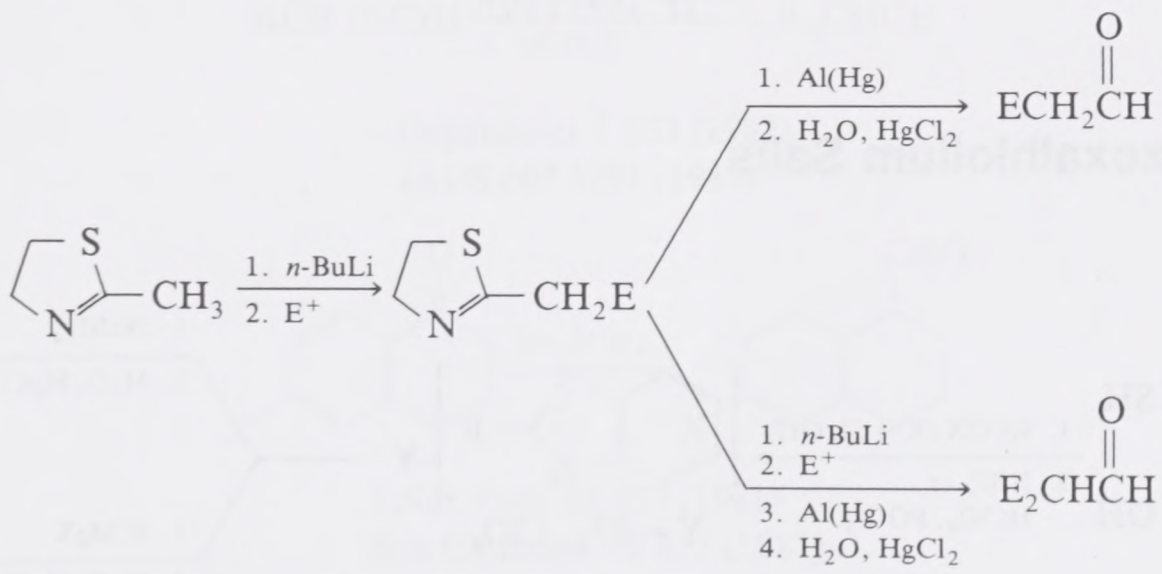
J Heterocyclic Chem *3* 531 (1966)
Tetr *29* 3417 (1973)
BSCF 2673 (1973)
Pure Appl Chem *51* 1255 (1979)

4. Imidazolines



TL *22* 261 (1981)
CC 282 (1982)

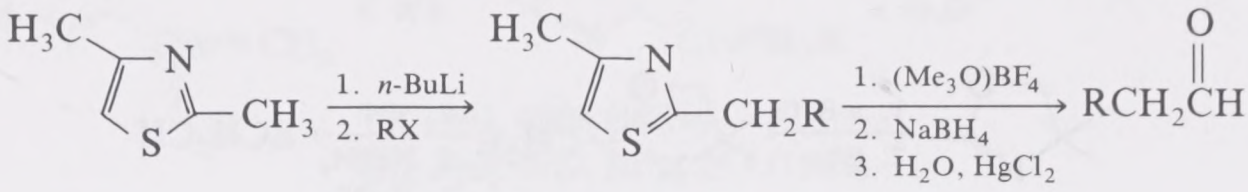
5. 2-Thiazolines



$E^+ = RX, RCHO, R_2CO$

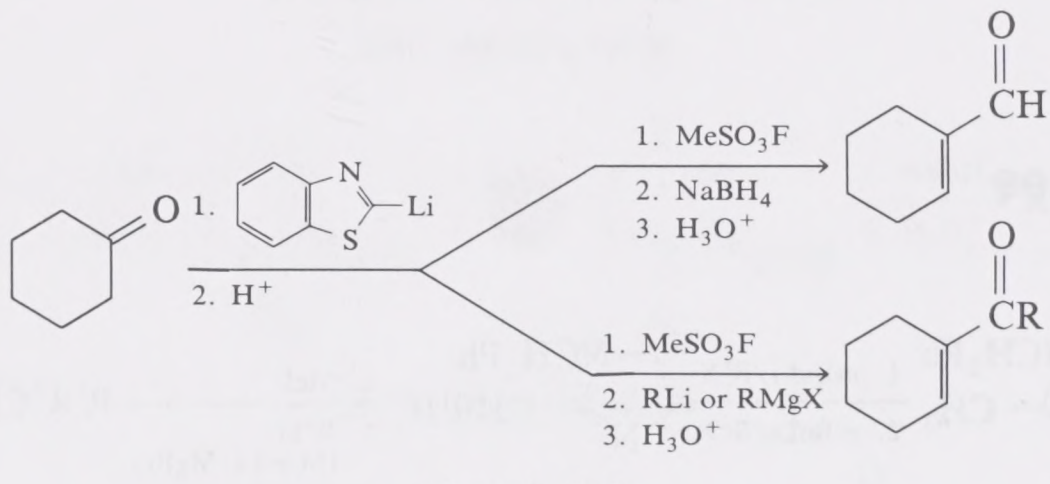
TL 3929 (1972)
JOC *40* 2021, 2025 (1975)

6. Thiazoles



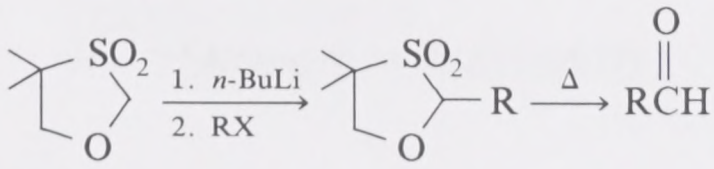
TL 4709 (1971)
JACS *95* 3408 (1973)
JOC *39* 1189, 1192 (1974)

7. Benzothiazoles



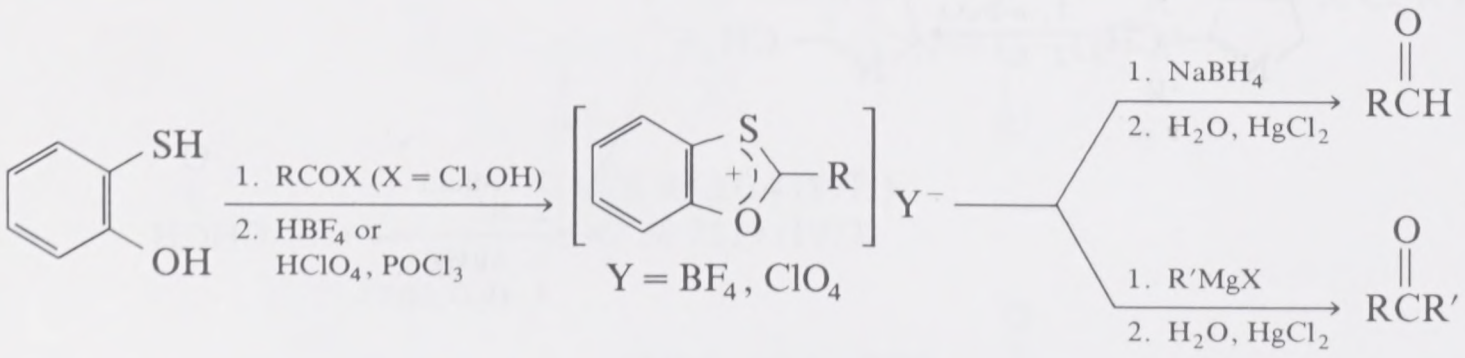
TL 5 (1978)

8. 1,3-Oxathiolane-3,3-Dioxides



TL 3375 (1979)

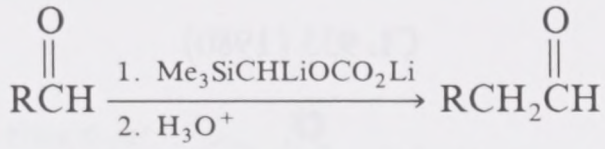
9. 1,3-Benzoxathiolium Salts



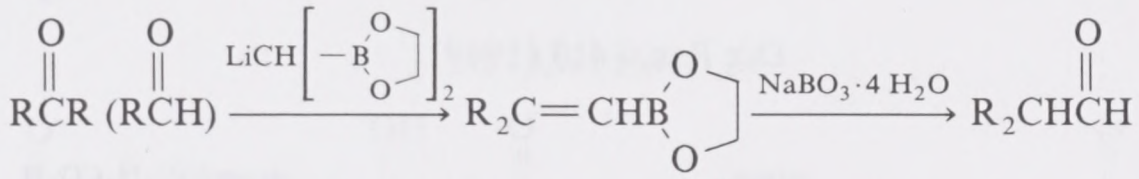
J Heterocyclic Chem *11* 507, 943 (1974)
Gazz Chim Ital *105* 907 (1975)
JCS Perkin I 323 (1976)

12. CARBONYL HOMOLOGATION

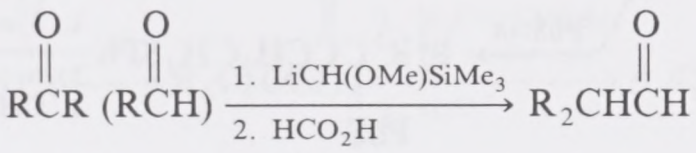
See also page 627, Section 4; page 709, Section 9; page 721, Section 10; page 729, Section 11; and page 737, Section 13.



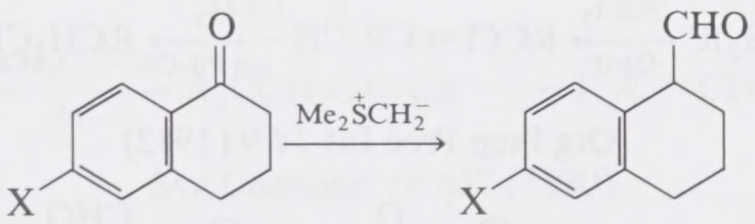
TL *28* 1847 (1987)



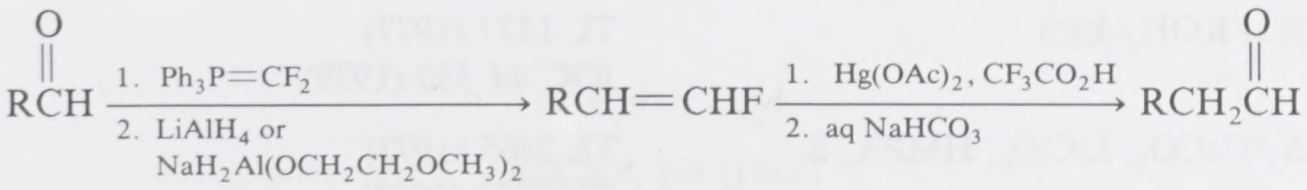
JACS *97* 5608 (1975); *99* 3196 (1977)
JOC *45* 1091 (1980)
Organomet *1* 20 (1982)



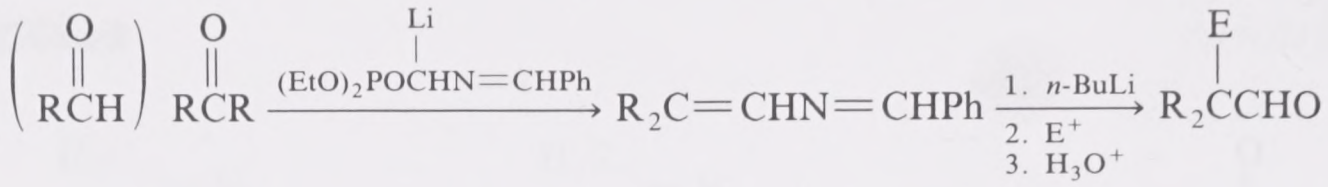
Organomet *1* 553 (1982)
JACS *107* 5391 (1985)



J Nat Prod *44* 557 (1981)
Syn Commun *12* 613 (1982)

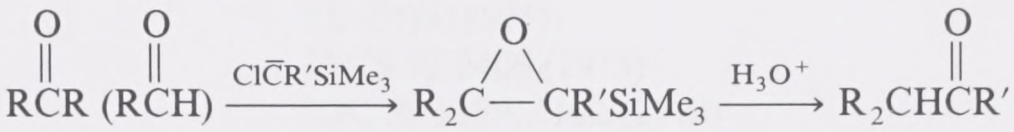


CL 651 (1980)



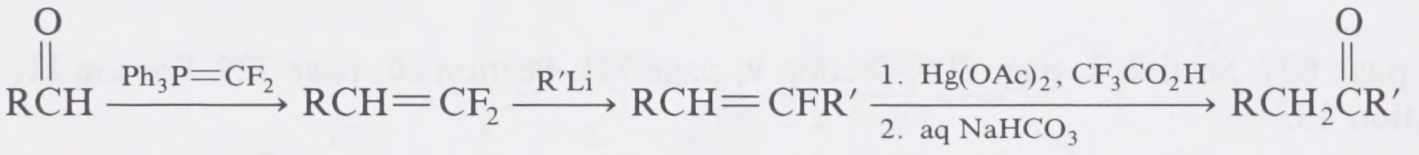
$E^+ = RX, RCHO$

See page 755, Section 10.

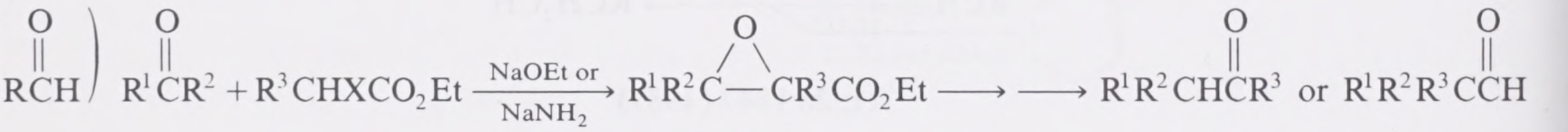


$R' = H, CH_3$

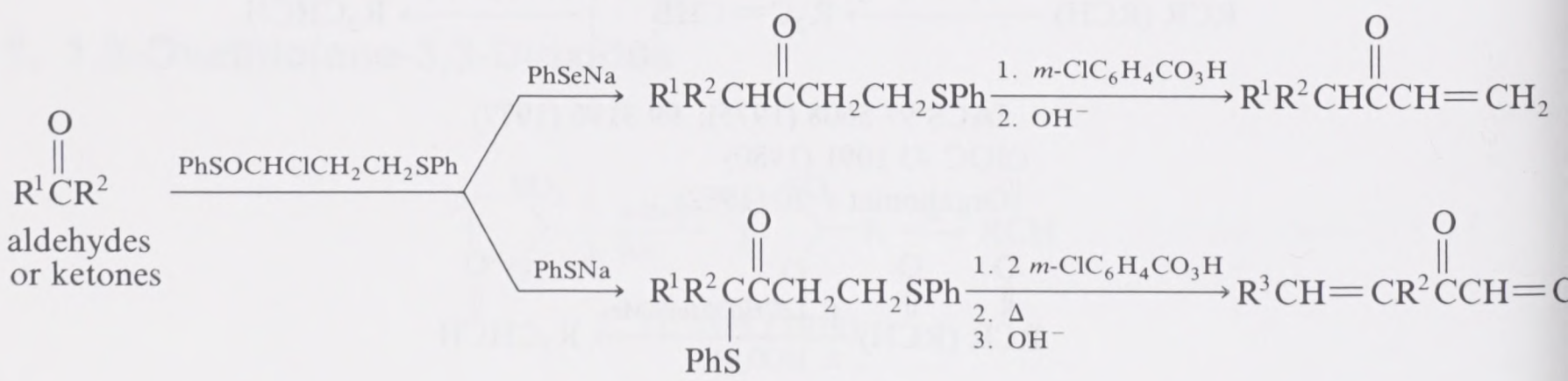
CC 513 (1977)
JACS *99* 4536 (1977)
Organomet *1* 893 (1982)
Tetr *39* 867 (1983)



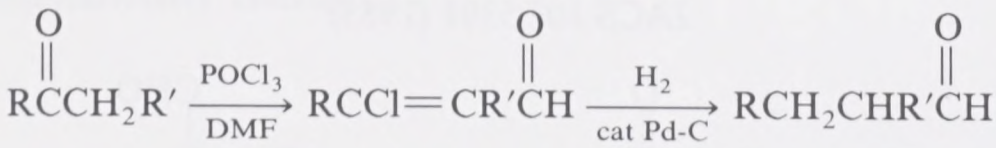
CL 935 (1980)



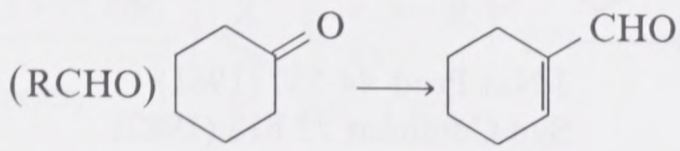
Org Rxs *5* 413 (1949)



TL *27* 2471 (1986)

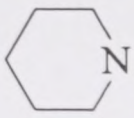


Org Prep Proc Int *14* 9 (1982)

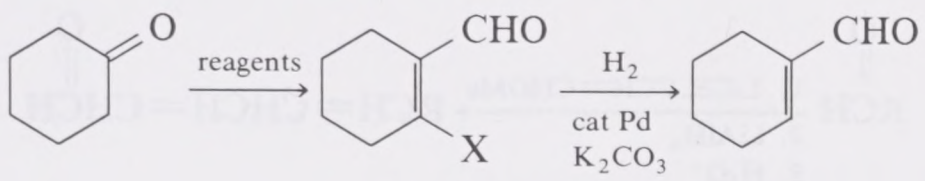


PhSOCHClLi/KOH/Δ — TL 1377 (1977); JOC *44* 450 (1979)

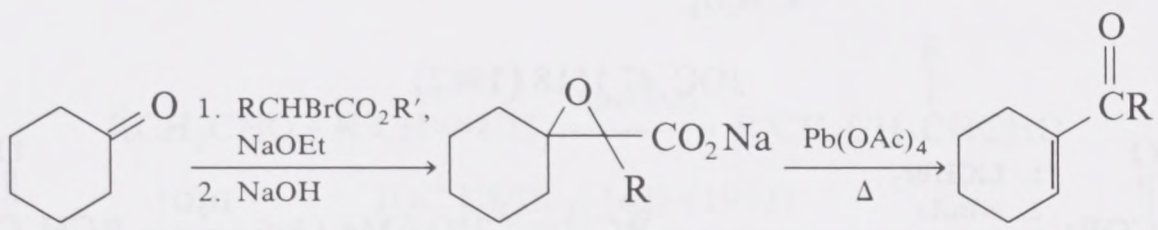
$LiCHCl_2$/Δ/$CaCO_3$, $LiClO_4$, HMPA, Δ — TL 2465 (1973); CC 1351 (1987)

CH_3NO_2,  $/TiCl_3$ Syn 196 (1974)

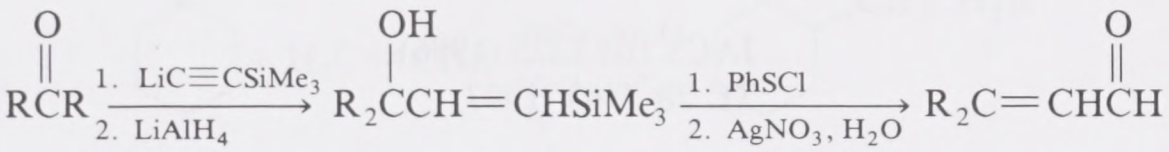
$TsNHNH_2/n$-BuLi/DMF TL 2287 (1976)



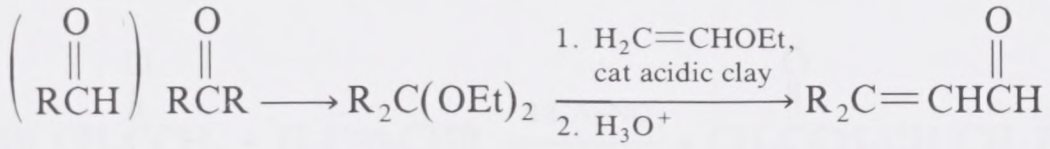
X	Reagents	
Cl	$COCl_2$, DMF	Coll Czech Chem Commun *24* 2385 (1959) Ber *93* 2743 (1960)
	$POCl_3$, DMF	Proc Chem Soc 227 (1958) Coll Czech Chem Commun *24* 2385 (1959) Ber *93* 2743 (1960) JOC *30* 1126 (1965); *48* 1921 (1983) (regioselectivity); *51* 2162 (1986)
Br	PBr_3 or $POBr_3$, DMF	Coll Czech Chem Commun *26* 3059 (1961)



TL 1321 (1979)

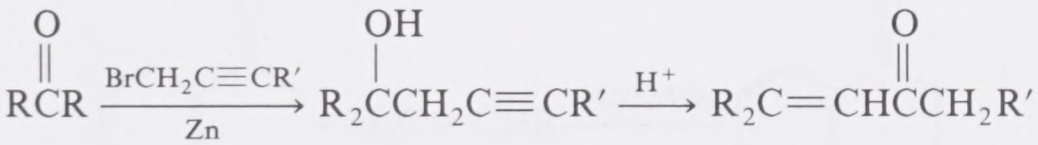


TL *22* 2021 (1981)

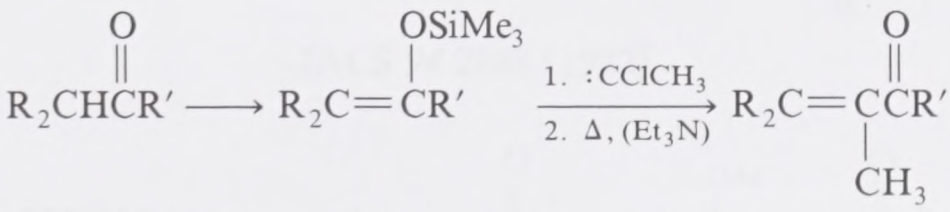


Syn 137 (1981)

See also page 173, Section 4, for analogous transformations.

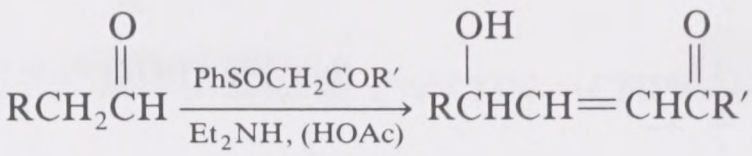


Syn Commun *10* 637 (1980)

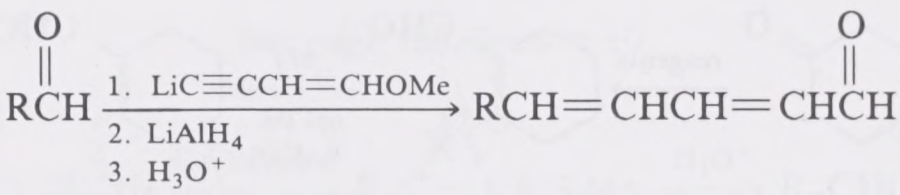


R′ = H or alkyl

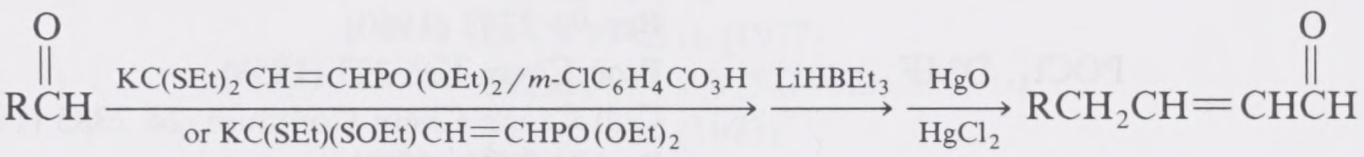
Syn 289, 291 (1981)
TL *22* 645 (1981)



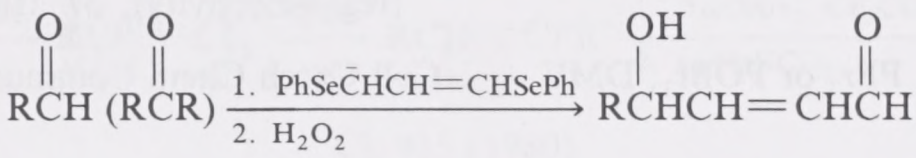
TL *28* 649 (1987)



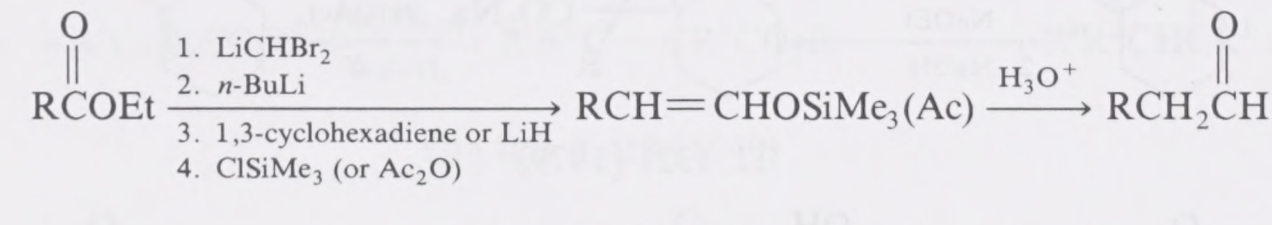
JCS 4082 (1956)
JOC *47* 4611 (1982)



Can J Chem *58* 2780 (1980)



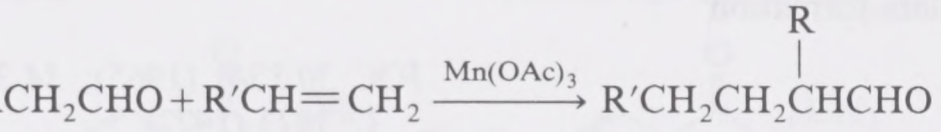
JOC *47* 1618 (1982)



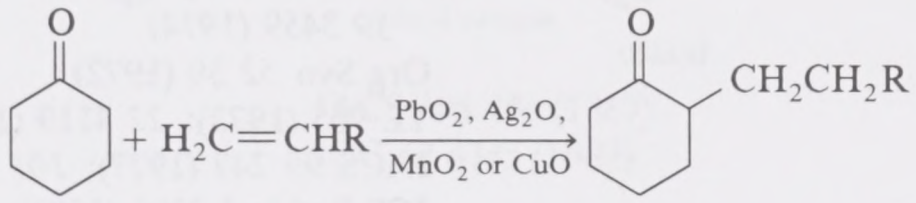
JACS *108* 1325 (1986)
TL *28* 2463 (1987)

13. ALKYLATION OF ALDEHYDES AND KETONES AND THEIR DERIVATIVES

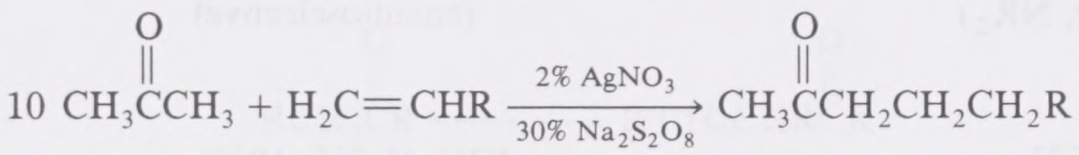
1. Free Radical Alkylation



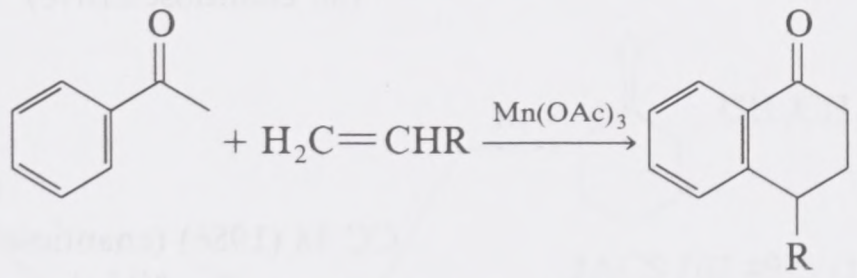
JOC USSR *8* 1422 (1972)



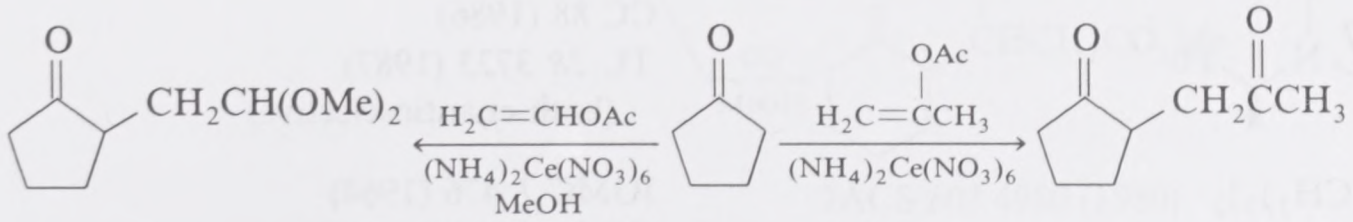
Syn 315 (1976)
Coll Czech Chem Commun *41* 746 (1976)



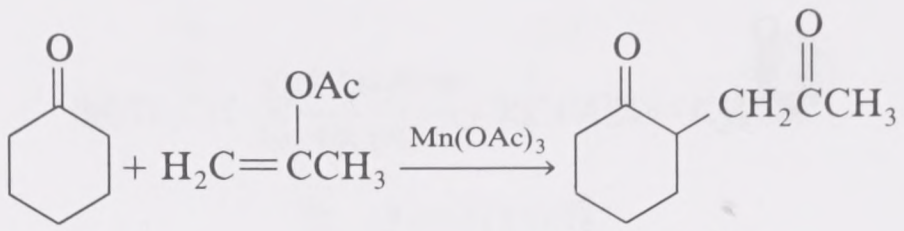
J Chem Res (S) 310 (1983)



JACS *94* 2888 (1972)



TL *28* 5357 (1987)



(low yields)

JOC *39* 3457 (1974)

2. Direct Enol or Enolate Alkylation

Reviews:

Rec Chem Prog *24* 43 (1963) (general); *28* 99 (1967) (general)
H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, California, 2nd ed (1972), pp 546–70 (general)
Tetr *32* 2979 (1976) (regiospecific preparation of ketone enolates and synthetic uses); *33* 2737 (1977) (structure and reactivity of alkali metal enolates)
Ber *114* 2866 (1981) (substituent effects on O vs C alkylation)
JOC *48* 4789 (1983) (stereochemistry and O vs C alkylation)
D. A. Evans in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 1 (stereoselective alkylation reactions of chiral metal enolates)

Bases for kinetic enolate formation

$(C_6H_5)_3CLi$

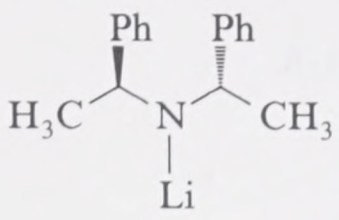
JOC *30* 1341 (1965); *34* 3070 (1969); *37* 3873 (1972)

$LiNR_2$

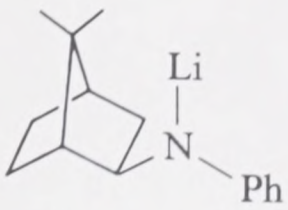
JOC *34* 2324 (1969); *36* 2361 (1971); *39* 3459 (1974)
Org Syn *52* 39 (1972)
TL 965 (1973); *22* 4119 (1981)
JACS *99* 247 (1977); *101* 934 (1979)
JCS Perkin I 2306 (1981)
Tetr *37* 3981 (1981)

$LiN(i\text{-}Pr)CHArCH_2X$
$(X = H, OMe, NR_2)$

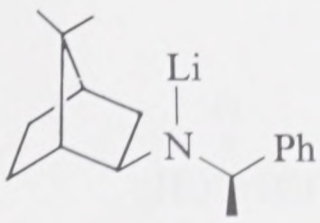
JACS *108* 543 (1986)
(enantioselective)



JOC *45* 755 (1980)
TL *23* 105 (1982); *27* 631, 2767 (1986)
(all enantioselective)



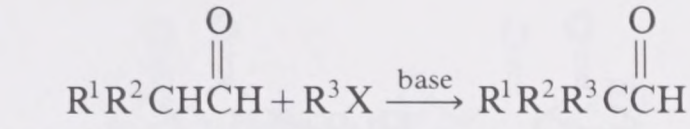
CC 88 (1986) (enantioselective)



CC 88 (1986)
TL *28* 3723 (1987)
(both enantioselective)

$LiN[Si(CH_3)_3]_2$

JOMC *1* 476 (1964)
CC 1497, 1498 (1969)



R^3 = allylic, benzylic, Me > 1° alkyl > 2° alkyl

Base

KH

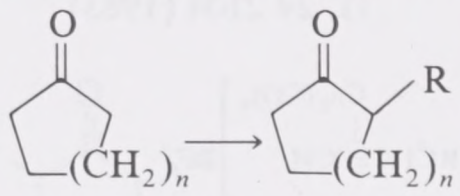
TL 491 (1978); *21* 4005 (1980)
JOC *47* 2479 (1982) (R^1 = SPh)

NaOH, *n*-Bu_4NI

TL 1273 (1973)
Chem Ind 731 (1978)
Ann 1585 (1979)

$KCPh_3$

JOC *50* 2668, 2676 (1985)



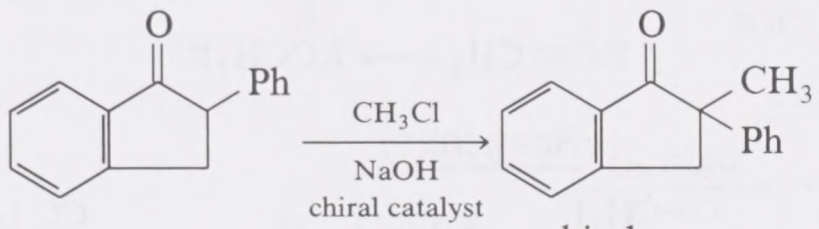
$n = 1, 2$

KO-*t*-Am, DME/RX (R = Me, $PhCH_2$)

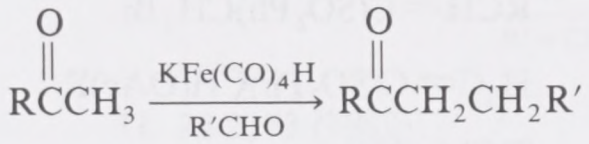
Syn Commun *8* 563 (1978)

K-Al_2O_3, hexane/*n*-BuBr

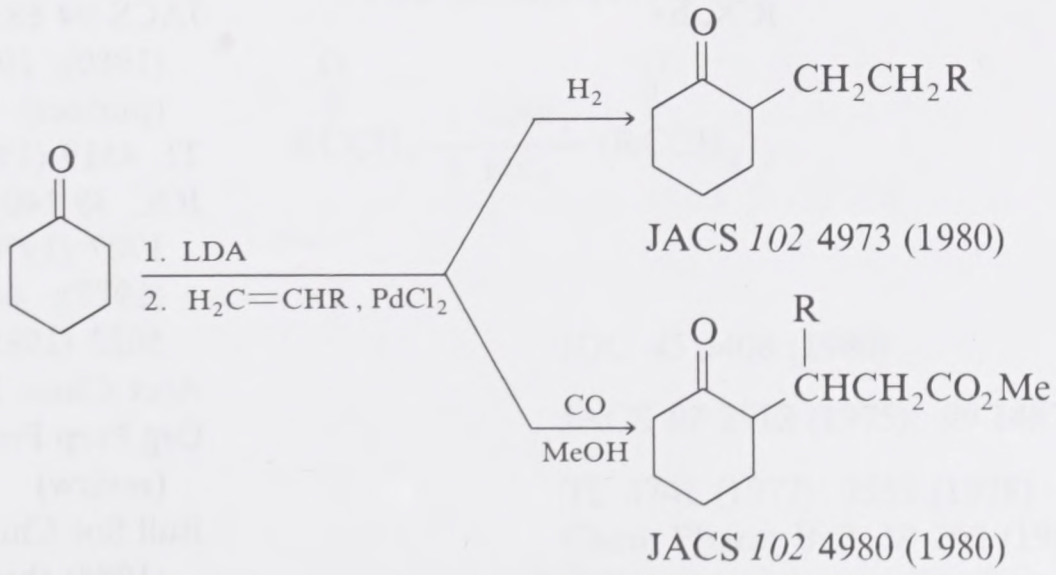
JOMC *204* 281 (1981)



JACS *106* 446 (1987)
JOC *52* 4745 (1987)

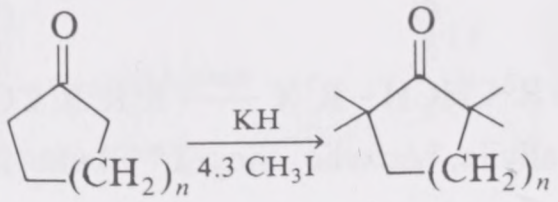


TL 2491 (1973)
JCS Perkin I 1273 (1975)



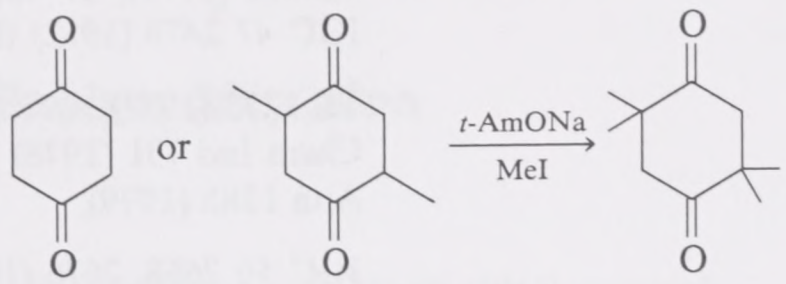
JACS *102* 4973 (1980)

JACS *102* 4980 (1980)

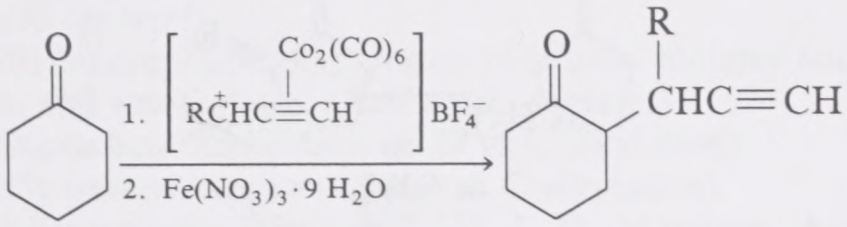


$n = 0–3$

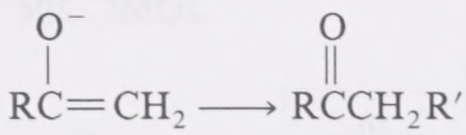
JOC *43* 1834 (1978)



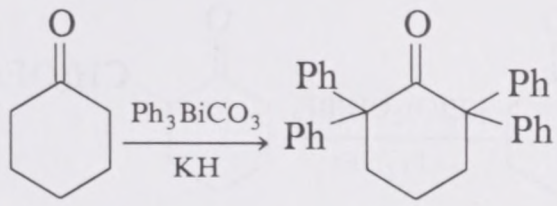
TL *24* 2104 (1983)



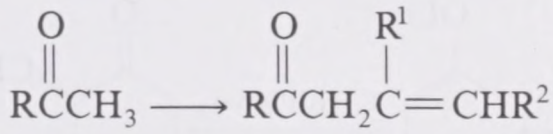
JACS *102* 2508 (1980)



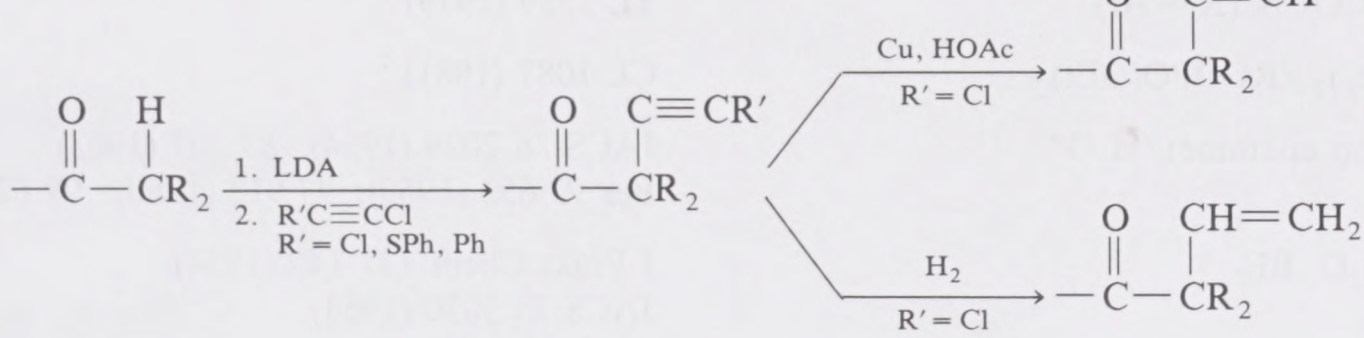
R′	Reagent(s)	
CH_3	CH_3I	CC 149 (1985) (stereochemistry)
$RCH{=}CHCH_2$	$RCH{=}CHCH_2OAc$, cat $Pd(DBA)_2$	CC 1158 (1981)
$H_2C{=}C(SO_2Ph)CHR$	$RCH{=}C(SO_2Ph)CH_2Br$	TL *27* 5095 (1986)
$RCH{=}C(SO_2Ph)CH_2$	$H_2C{=}C(SO_2Ph)CH(OAc)R$	TL *27* 5095 (1986)
CMe_2NO_2	$ClCMe_2NO_2$	JACS *101* 3378 (1979); *103* 4610 (1981) JOC *47* 1879 (1982)
Ph	Ph_3BiCO_3	CC 246 (1980)
aryl	R′X, $Ni(COD)_2$	TL 4519 (1973)
aryl, vinyl	R′X, hν	JACS *94* 683 (1972); *102* 7765 (1980); *107* 2183 (1985) (purines) TL 4519 (1973); *28* 91 (1987) JOC *38* 1407 (1973); *41* 1702, 1707 (1976); *42* 1481, 2481 (1977); *44* 2604 (1979); *46* 5022 (1981); *52* 3880 (1987) Acct Chem Res *11* 413 (1978) Org Prep Proc Int *10* 225 (1978) (review) Bull Soc Chim Belg *93* 547 (1984) (heterocycles)



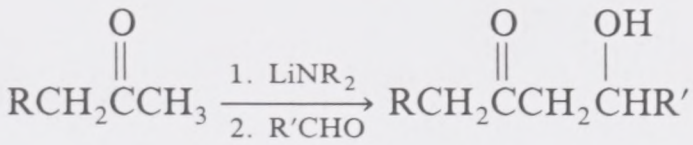
CC 246 (1980); 732 (1982)



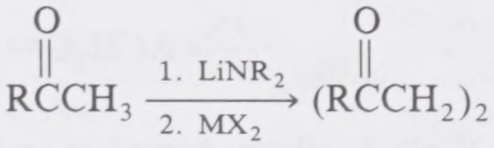
RLi (on enol silane)/$ZnCl_2$/$PhSeCH_2COR^1$/ MsCl, Et_3N (R^1 = H or Me, R^2 = H)	CC 434 (1981) JOC *47* 1632 (1982)
$MeNHCH_2CH_2NMe_2$/*n*-BuLi/$ZnCl_2$/ $ICH{=}CHR^2$, cat $Pd(PPh_3)_4$	CL 1007 (1987)
LDA/$PhSeCH_2CHO$/MsCl, Et_3N ($R^1 = R^2$ = H)	JACS *102* 7950 (1980) JOC *52* 2760 (1987)
LDA/$R^2CH(CHO)SiMe_2(t\text{-Bu})$/$BF_3 \cdot OEt_2$ (R^1 = H)	JACS *103* 6251 (1981)
LDA/$[R^2CH{=}C(OEt)R^1 - Fe(CO)_2C_5H_5]BF_4^-$/ HBF_4/NaI (R^1, R^2 = H, H; H, Me; Me, H)	JACS *102* 5930 (1980); *106* 7264 (1984) JOC *46* 4103 (1981)



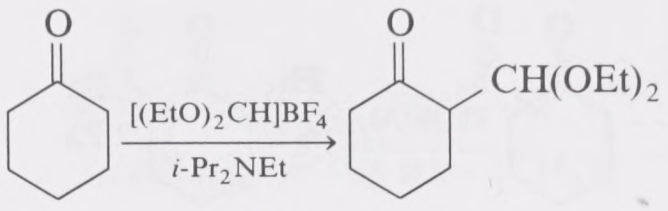
TL *23* 2373 (1982)
JACS *106* 3551 (1984)



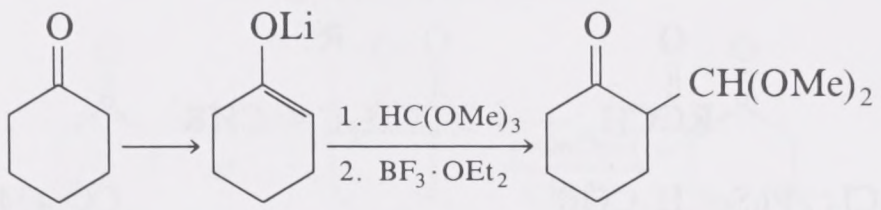
JOC *39* 3459 (1974)



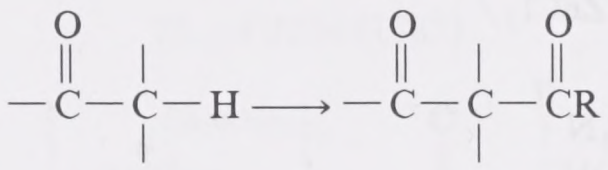
MX_2	
$FeCl_2$	JOC *45* 5408 (1980)
$CuCl_2$	JACS *97* 2912 (1975); *99* 1487 (1977)
$Cu(OTf)_2$	TL 3741 (1977); 3555 (1978) Chem Pharm Bull *28* 262 (1980) (inter- and intramolecular)

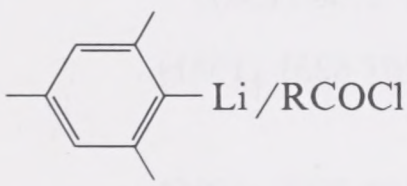


JOC *46* 2557 (1981)



TL *23* 3595 (1982)





TL 1187 (1977)
Helv *64* 716 (1981)

MeLi (on enol silane)/RCOCl — Helv *64* 716 (1981)

LDA/RCO_2CO_2Et — JOMC *127* C65 (1977)

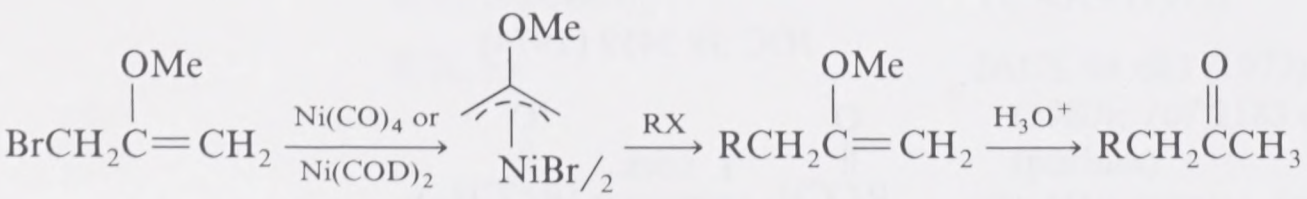
LDA/ArCOCN (R = Ar) — TL 1339 (1979)

$LiN(SiMe_3)_2/RCOPO(OEt)_2$ — CL 1087 (1981)

$RCOCl$ (on enamine)/H_3O^+ — JACS *76* 2029 (1954); *85* 207 (1963)
Ber *92* 652 (1959); *93* 913 (1960); *99* 823 (1966)

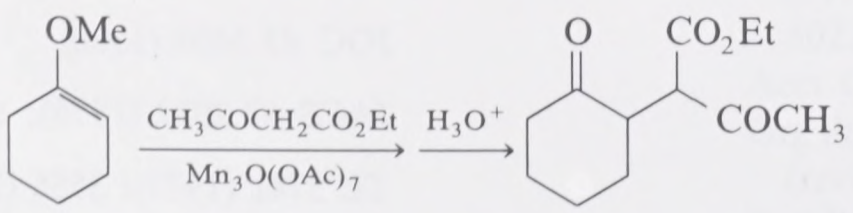
$(CH_3CO)_2O$, BF_3 — J Prakt Chem *141* 149 (1934)
JACS *75* 5030 (1953)
CC 85 (1979)
TL *23* 1115 (1982)

3. Enol Ethers



R = 1°, 2° alkyl; allylic; benzylic; aryl; vinylic

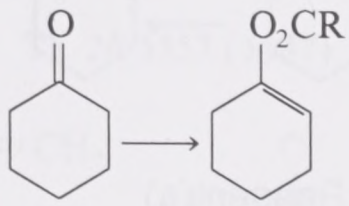
JACS *96* 3250 (1974)



TL *28* 175 (1987)

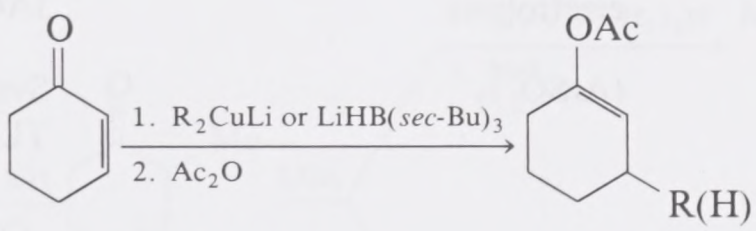
4. Enol Esters

4.1. Synthesis of Enol Esters

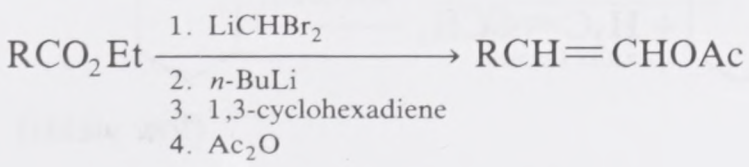


Review: JACS *102* 1966 (1980)

Ac_2O, NaOAc	Ber *42* 1161, 2014 (1909)
Ac_2O, KOAc	JACS *66* 1325 (1944); *74* 5381 (1952) BCSJ *59* 751 (1986)
Ac_2O, K_2CO_3	JOC *48* 2705 (1983)
Ac_2O, Et_3N, cat DMAP	Syn Commun *9* 157 (1979)
$LiN(SiMe_3)_2/Ac_2O$	JOC *47* 5088 (1982)
KH/AcCl, (DMAP)	Syn 504 (1979)
Ac_2O, cat TsOH	JACS *67* 1430 (1945) JOC *26* 3729 (1961); *28* 3362 (1963); *32* 1741 (1967); *48* 1921 (1983) (regioselectivity) JCS 2933 (1965)
Ac_2O, cat $HClO_4$	JOC *30* 2502 (1965); *32* 1741 (1967); *33* 943 (1968); *36* 2361 (1971) Tetr *23* 4143 (1967) Org Syn *52* 39 (1972)
$(PhCO)_2O$, cat $HClO_4$	JOC *34* 1962 (1969)
$H_2C{=}C(Me)OAc$, cat TsOH	Ind Eng Chem *41* 2920 (1949) JOC *28* 3362 (1963); *30* 1341, 2502 (1965); *33* 935 (1968); *36* 2361 (1971); *48* 1921 (1983) (regioselectivity)
$H_2C{=}C(Me)OAc$, cat TsOH, $Cu(OAc)_2$	BCSJ *59* 751 (1986)

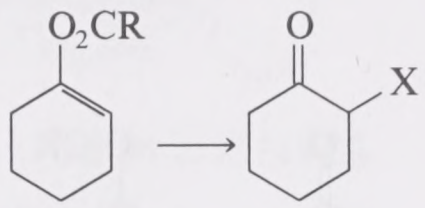


JOC *47* 5088 (1982)

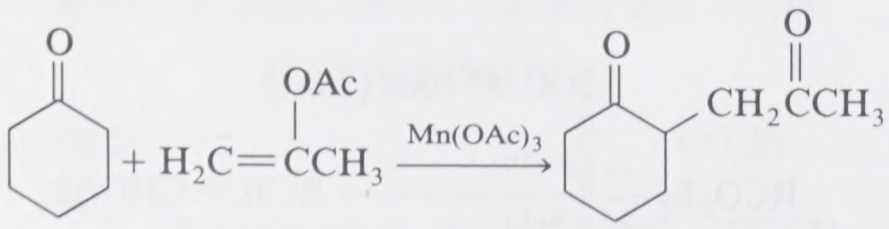


JACS *108* 1325 (1986)

4.2. Applications

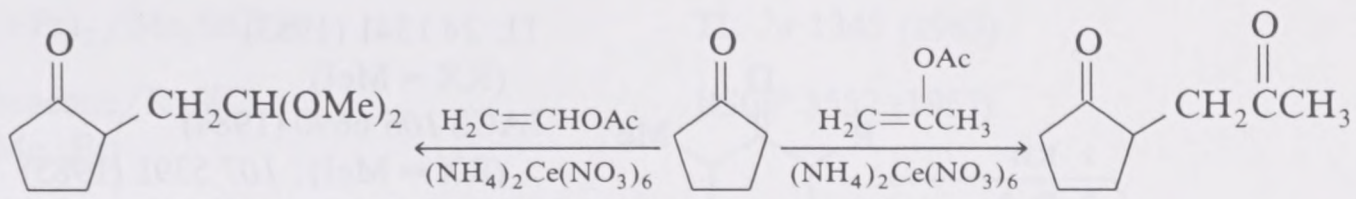


X	Reagent(s)	
R	MeLi/RX	JOC *30* 2502 (1965); *32* 1741 (1967); *33* 935, 943 (1968); *36* 2361 (1971); *51* 2408, 2416 (1986) Org Syn *52* 39 (1972) JACS *109* 3147 (1987)
	MeMgI/RX	JCS 2933 (1965)
	CH_2I_2, Zn-Cu/RX	JACS *102* 1966 (1980)
CH_3	MeLi/CH_2I_2, Zn-Cu	JOC *34* 1962 (1969)
$CH_2CH{=}CH_2$	$H_2C{=}CHCH_2OCO_2Me$, cat $Pd_2(DBA)_3 \cdot HCCl_3$, cat dppe, cat *n*-Bu_3SnOMe	TL *24* 4713 (1983)
$CH_2C{\equiv}CR$	$\overset{+}{C}H_2C{\equiv}CR$ ($Co_2(CO)_6$)	Syn Commun *10* 503 (1980)
COR	acylation or rearrangement	JACS *102* 1967 (1980) (review)
Br	Br_2	JACS *66* 1325 (1944); *67* 1430 (1945); *101* 2782 (1979) Org Syn Coll Vol *3* 127 (1955) JCS 907, 911 (1959); 1312, 3839 (1962); 2933 (1965) Tetr *21* 273 (1965) JCS Perkin I 126 (1978)
O_2CR	epoxidation electrolysis	JACS *102* 1967 (1980) (review) JACS *97* 6144 (1975)
$ArSO_3$	$(ArSO_3)_2$	Syn 760 (1985) TL *27* 5811 (1986)

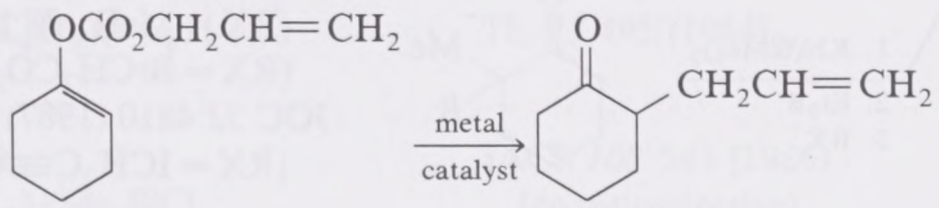


(low yields)

JOC *39* 3457 (1974)

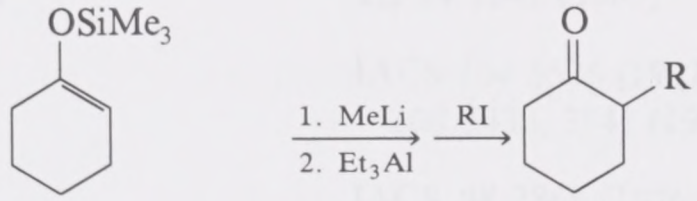


TL *28* 5357 (1987)



Metal	
Mo, Rh, Ni	CL 1721 (1984)
Pd	TL *24* 1793 (1983)

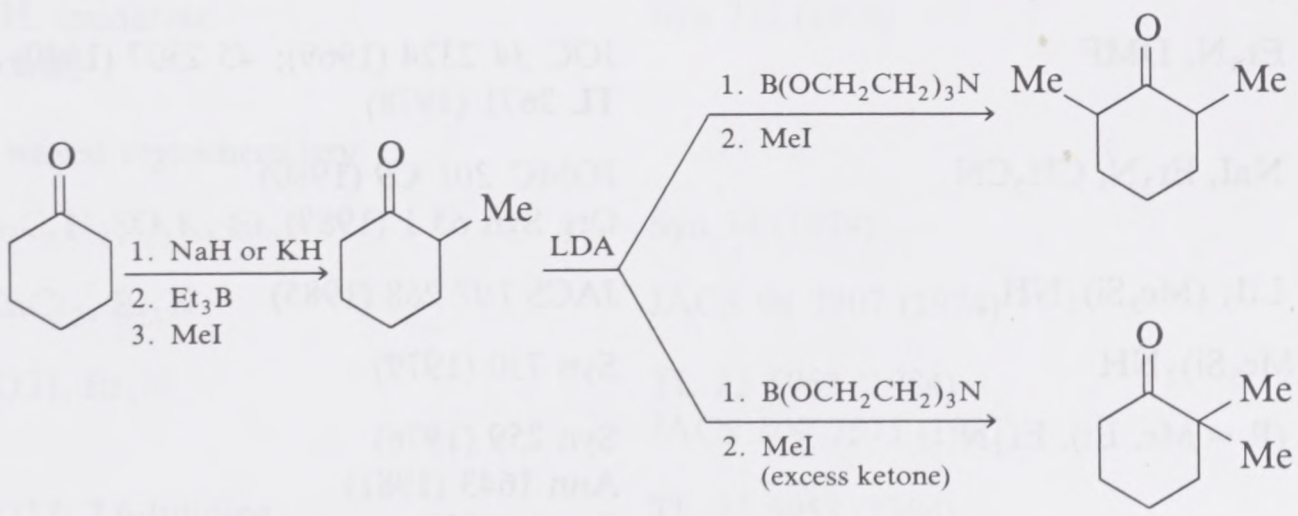
5. Enol Alanes



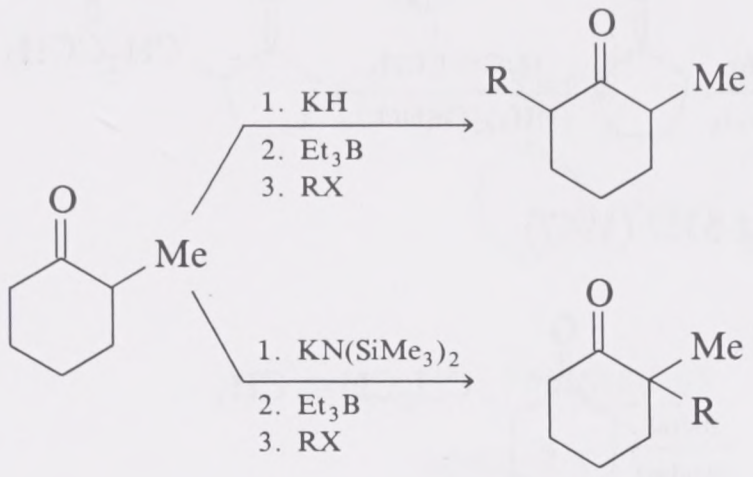
R = Me, *n*-Bu

TL 1117 (1969)

6. Enol Boranes

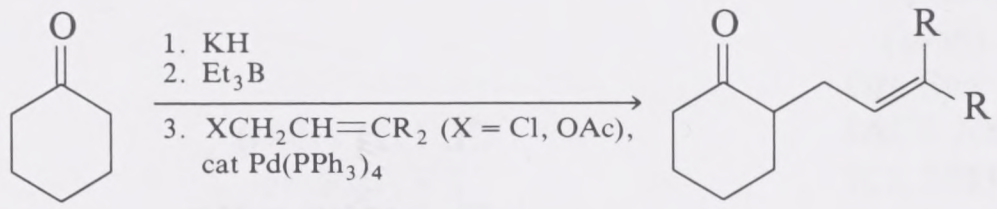


Syn Commun *8* 9 (1979)
TL 845 (1979)



TL *24* 1341 (1983)
(RX = MeI)
JACS *106* 6690 (1984)
(RX = MeI); *107* 5391 (1985)
(RX = MeI); *108* 7864 (1986)
($RX = H_2C{=}CHCH_2Br$)

TL *24* 1341 (1983)
(RX = MeI); *28* 1483 (1987)
($RX = BrCH_2CO_2Me$)
JOC *52* 4810 (1987)
[$RX = ICH_2C{\equiv}CPO(OEt)_2$]



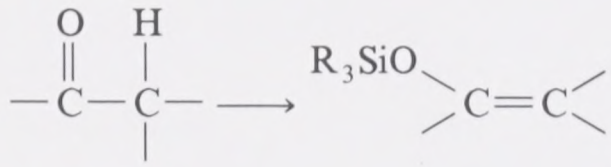
JOC *47* 3188 (1982); *48* 2427, 4098 (1983)
TL *24* 1341 (1983)

7. Enol Silanes

Reviews:

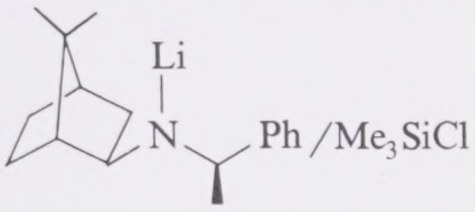
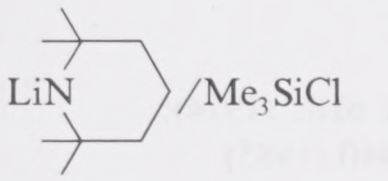
Syn 91 (1977); 1, 85 (1983)

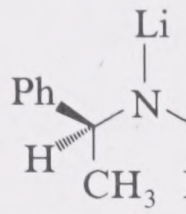
7.1. Preparation



Thermodynamic enol silane

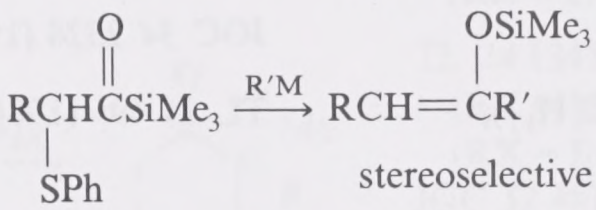
Me_3SiCl, Et_3N, DMF	JOC *34* 2324 (1969); *45* 2307 (1980) TL 2671 (1978)
Me_3SiCl, NaI, Et_3N, CH_3CN	JOMC *201* C9 (1980) Org Syn *65* 1 (1987)
Me_3SiCl, LiI; $(Me_3Si)_2NH$	JACS *107* 268 (1985)
Me_3SiI, $(Me_3Si)_2NH$	Syn 730 (1979)
R_3SiOTf (R = Me, Et), Et_3N	Syn 259 (1976) Ann 1643 (1981) Syn 1 (1982) (review)
NaH/Me_3SiCl, Et_3N	JACS *90* 4462 (1968)
$KH/Et_3B/Me_3SiCl$	TL *24* 1341 (1983)

$BrMgN(i\text{-}Pr)_2/Me_3SiCl$	TL *24* 1345 (1983)
Na, anthracene/R_3SiCl (R = Me, Et)	BSCF 3552 (1967)
Kinetic enol silane	
$LiN(i\text{-}Pr)_2/Me_3SiCl$	JOC *34* 2324 (1969); *45* 2307 (1980)
$LiN(i\text{-}Pr)_2$ or $LiN(t\text{-}C_4H_9)(t\text{-}C_8H_{17})$, Me_3SiCl, Et_3N	TL *25* 495 (1984)
$LiN(i\text{-}Pr)CHArCH_2X$ (X = H, OMe, NR_2)/Me_3SiCl	JACS *108* 543 (1986) (enantioselective)
	CC 88 (1986) TL *28* 3723 (1987) (both enantioselective)
	JACS *102* 3959 (1980)
$LiN(SiMe_3)_2/Me_3SiCl$	JOC *45* 2307 (1980)
$KN(SiMe_3)_2/Et_3B/Me_3SiCl$	TL *24* 1341 (1983)
$LiN(SiPhMe_2)_2/Me_3SiCl$	JACS *104* 5526 (1982); *108* 3435, 3841 (1986)
$LiN(i\text{-}Pr)_2/t\text{-}BuMe_2SiCl$	JACS *98* 2868 (1976) Helv *65* 385 (1982)
$LiN(SiMe_3)_2/t\text{-}BuMe_2SiCl$ (enones)	CC 564 (1973)
cat $n\text{-}Bu_4NF$, $Me_3SiCH_2CO_2Et$	JACS *98* 2346 (1976); *108* 3435, 3841 (1986)
cat $n\text{-}Bu_4NF$, $CH_3CH{=}C(OSiMe_3)COMe$	Syn 1089 (1982)
$(Me_3Si)_2NH$, imidazole (β-diketones)	Syn 722 (1976)
Unknown or mixed regiochemistry	
Me_3SiCl, $n\text{-}C_4H_9SO_3K$, Et_3N	Syn 34 (1979)
Me_3SiCl, $ZnCl_2$, Et_3N	JACS *96* 7807 (1974)
$t\text{-}BuMe_2SiOTf$, Et_3N	TL *25* 5953 (1984) JACS *109* 7575 (1987)
$t\text{-}BuMe_2SiOTf$; 2,6-lutidine	TL *25* 5953 (1984)
$i\text{-}Pr_3SiOTf$, Et_3N	TL *22* 3455 (1981)
Me_3SiNMe_2	TL 3553 (1974)



CH_3/Me_3SiCl TL *27* 631 (1986) (enantioselective)

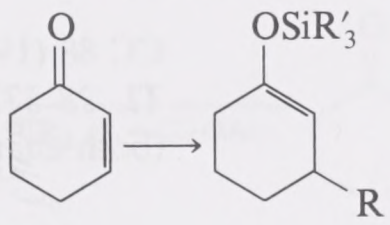
KH/Me_3SiCl, cat Et_3N, DME Syn 504 (1979)



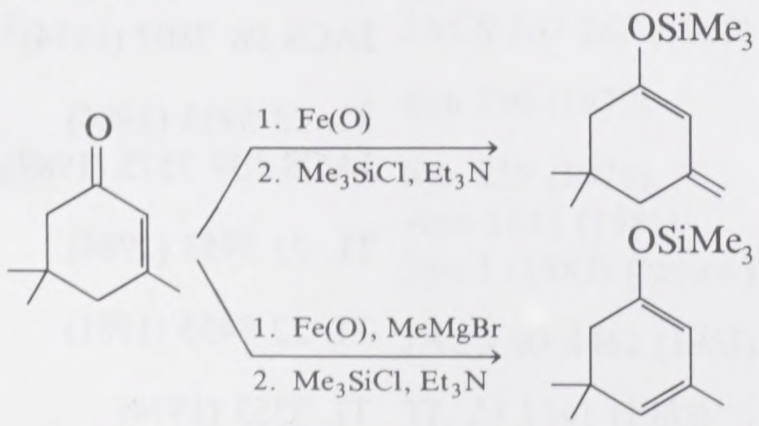
stereoselective

$R'M = LiAlH_4$, RLi, Me_3SnLi

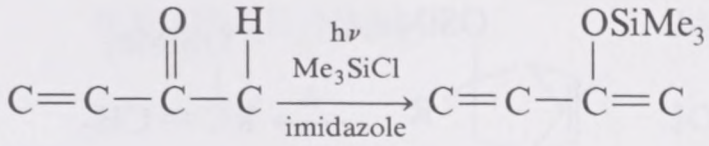
JOC *52* 513 (1987)



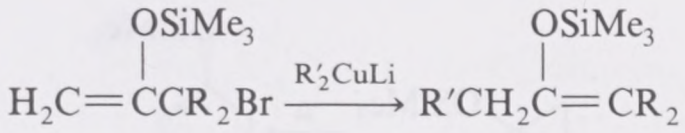
R	Reagents	
H	Li, NH_3, *t*-BuOH/Me_3SiCl	JACS *96* 6181 (1974); *107* 1440 (1985)
	$LiHB(sec\text{-}Bu)_3/Me_3SiCl$	JACS *107* 1440 (1985); JOC *52* 1870 (1987)
	Et_3SiH, cat $ClRh(PPh_3)_3$	TL 5035 (1972); Tetr *37* 4515 (1981)
	Et_3SiH, $EtMe_2SiH$ or $MePh_2SiH$; cat $[Pt(\mu\text{-}H)(SiR_3)PR_3]_2$	JOMC *191* 39 (1980)
alkyl, aryl	RMgBr, cat $CuBr \cdot SMe_2$, Me_3SiCl, HMPA (enals and enones)	TL *27* 4025 (1986)
	RCu, Me_3SiCl, HMPA or DMAP (enals and enones)	TL *27* 4029 (1986)
	RCu, Me_3SiCl, $Me_2NCH_2CH_2NMe_2$	TL *28* 27 (1987)
	R_2CuLi/Me_3SiCl	JACS *96* 6179 (1974); Tetr *37* 4027 (1981)
	$R_2CuLi/Ph_2SiMeCl$	JOC *52* 165 (1987)
	R_2CuLi, Me_3SiCl, HMPA or DMAP (enals or enones)	TL *27* 4029 (1986)
	R_2CuLi, Me_3SiCl	TL *26* 6015, 6019 (1985); *27* 1047 (1986); *28* 1973 (1987)
	(MeCuCN)Li, Me_3SiCl	TL *26* 6019 (1985)
	(MeCuCN)Li, *t*-$BuMe_2SiCl$	TL *28* 3589 (1987)
	R_2CuMgX/Me_3SiCl (enals)	JOMC *228* 321 (1982)



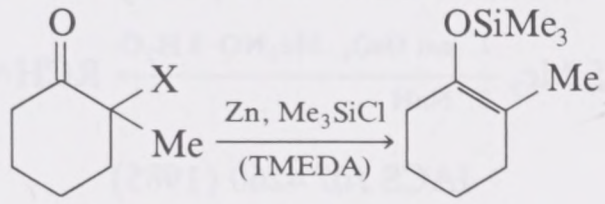
JACS *106* 7619 (1984)



JOC *51* 3335 (1986)

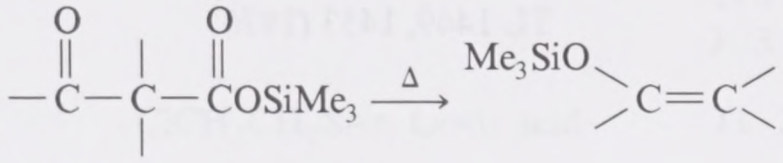


TL *21* 2325 (1980)

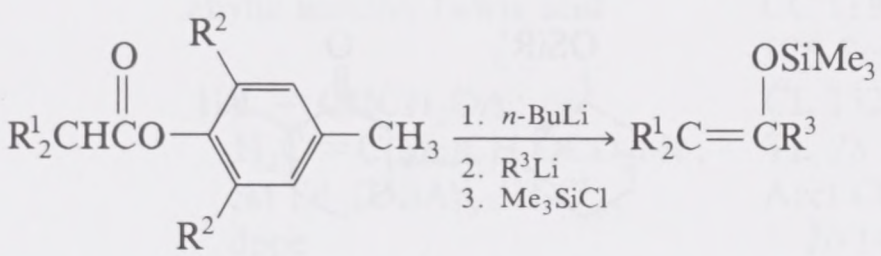


X = Cl, Br

Syn Commun *7* 327 (1977)
TL *24* 507 (1983)

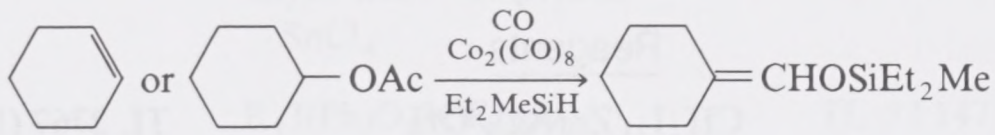


JACS *97* 1619 (1975)

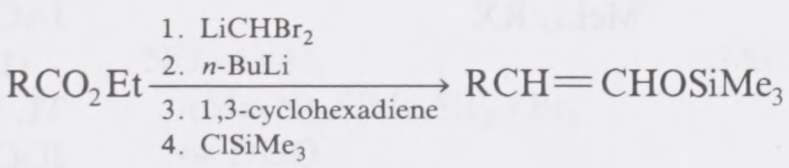


R^2 = *t*-Bu

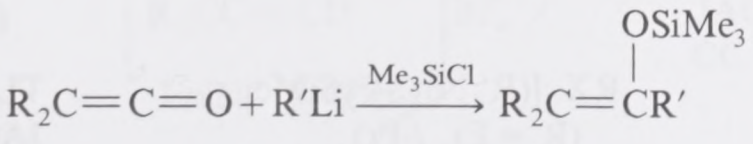
JACS *107* 5396 (1985)



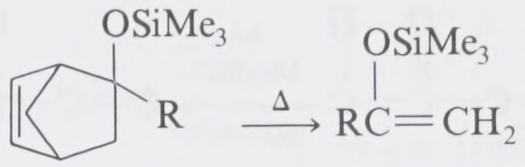
JACS *108* 7361 (1986)



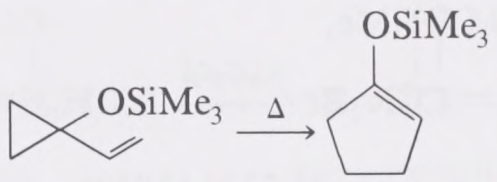
JACS *108* 1325 (1986)



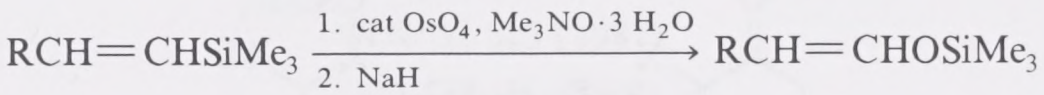
JACS *107* 5391 (1985)
JOC *50* 2105 (1985)



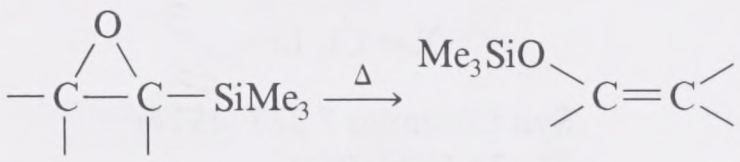
BSCF 1122 (1976)



JACS *95* 5311 (1973)



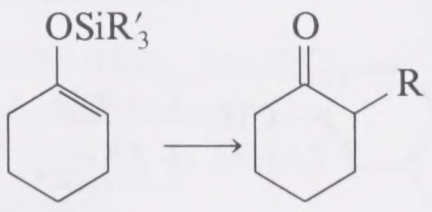
JACS *107* 4260 (1985)



JOMC *94* C21 (1975)
TL 1449, 1453 (1976)

7.2. Reactions

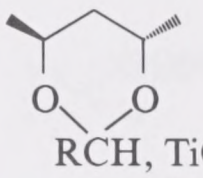
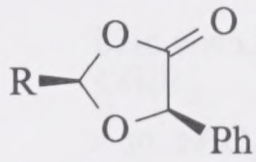
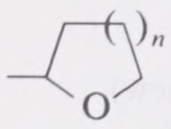
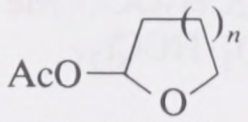
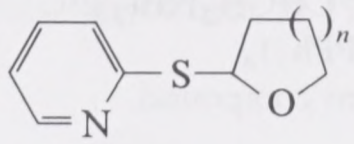
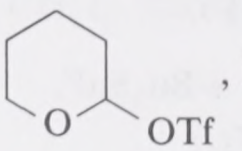
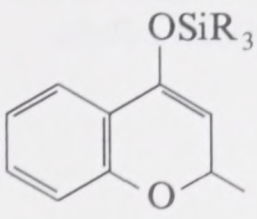
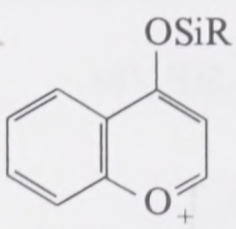
See also page 776, Section 21.

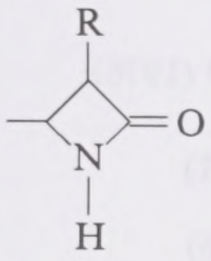
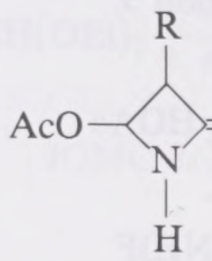
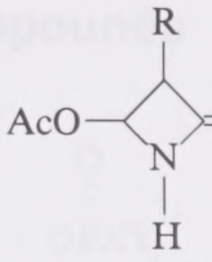
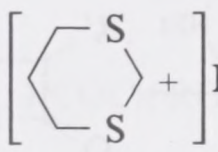


Reviews: Chimia 265 (1980)
Pure Appl Chem *55* 1749 (1983) (aldol review)

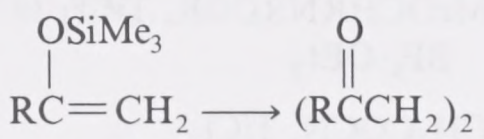
R	Reagents	
CH_3	CH_2I_2, Zn(Ag)/OH^-	TL 2767 (1973); 3327, 3333 (1974) JOC *39* 858 (1974)
1°, 2° alkyl; allylic; benzylic	MeLi/RX	JACS *90* 4464 (1968); *97* 1619 (1975); *101* 934 (1979) TL 1117 (1969) JOC *36* 2361 (1971); *51* 2408 (1986); *52* 165 (1987)
1° alkyl, allylic	$LiNH_2$, NH_3/RX	JOC *39* 2506 (1974); *40* 2156 (1975)
1° alkyl, benzylic, allylic	RX, $[(R'_2N)_3S]F_2SiMe_3$ (R′ = Et, *i*-Pr)	TL *21* 2085 (1980) JACS *102* 1223 (1980); *105* 1598 (1983)

1° alkyl, benzylic	RX, $(PhCH_2NMe_3)F$	JACS *104* 1025 (1982); *109* 1269 (1987) JOC *52* 3745 (1987)
2° and 3° alkyl, allylic, benzylic, RCHSR, RCHOR, CH_2NMeCO_2Me	RX; $SnCl_4$, $TiCl_4$, $ZnCl_2$, ZnI_2 or $FeCl_3$	TL 4183 (1977); 1455, 4925 (1978); 995, 1427, 1519, 2179, 4971 (1979); *21* 2010, 2033 (1980); *22* 1101, 2321 (1981); *23* 2399, 2601 (1982); *24* 323, 327, 419, 2095 (1983) Angew Int *17* 48 (1978); *18* 72 (1979); *21* 96 (1982) (review) BCSJ *52* 1241 (1979) JACS *101* 984 (1979); *106* 7630 (1984) Ber *113* 3734, 3741 (1980) Syn 941 (1980); 1003 (1981) JOC *45* 3559 (1980); *47* 3219 (1982) Syn Commun *11* 217 (1981) Tetr *37* 319, 4027 (1981) JCS Perkin I 1099 (1982)
CH_2CH_2SAr	$ClCH_2CH_2SAr$, Lewis acid	TL *24* 961 (1983)
C—C—XPh (X = S, Se)	Cl—C—C—XPh, $ZnBr_2$	TL *24* 5911 (1983)
allylic	allylic acetate, Lewis acid	CC 1180 (1981) JCS Perkin I 2079 (1982)
	$H_2C{=}CHCH_2OAc$ or $H_2C{=}C(Me)CH_2OCO_2Me$, cat $Pd_2(DBA)_3 \cdot HCCl_3$, dppe	CL 1325 (1983) TL *28* 2397 (1987) Acct Chem Res *20* 140 (1987) (review)
	n-BuLi/ $(R_2C{=}CHCH_2NEt_3)Br$, cat $Pd(PPh_3)_4$	JOMC *236* 409 (1982)
	allylic nitro compound, $SnCl_4$	CC 1285 (1986)
R_f	$R_fI(Ph)O_3SCF_3$, py	TL *23* 1471 (1982)
Ar	ArX (X = Br, I), *n*-Bu_3SnF, 3% $PdCl_2(PAr_3)_2$	JACS *104* 6831 (1982)
NO_2-Ar	NO_2-Ar-H, $[(Me_2N)_3S]Me_3SiF_2/Br_2$ or DDQ	JACS *107* 5473 (1985)
$CR_2C{\equiv}CH$	$\left[R_2\overset{+}{C}C{\equiv}CH\text{—}Co_2(CO)_6 \right] BF_4^- /$ $Fe(NO_3)_3 \cdot 9\,H_2O$	JACS *102* 2508 (1980) CC 1353 (1987)
CH_2OH	$RLi/H_2CO/H_2O$	JOC *49* 3685 (1984)

R	Reagents	
CHROH or CR_2OH	RCHO or R_2CO, various reagents	See page 647, Section 7.
CH_2OCH_2Ph	$H_2C(OCH_2Ph)_2$, cat Me_3SiOTf	TL *28* 517 (1987)
	$ClCH_2OCH_2Ph$, $TiCl_4$	TL *28* 517 (1987)
CHROR (chiral)	 RCH, $TiCl_4$	JACS *104* 7371, 7372 (1982); *106* 7588 (1984) JOC *52* 180 (1987)
CHROR	$RCH(OR)_2$, $TiCl_4$	CC 1691 (1986); 876 (1987) (both intramolecular) JACS *108* 3513 (1986) TL *28* 3747 (1987) (intramolecular)
	$RCH(OR)_2$, cat Me_3SiI	BCSJ *56* 3195 (1983)
	ClCHROR, cat Me_3SiX (X = I, OTf)	CL 405 (1983)
CR_2OR	$(RO)_2CR_2$, cat Me_3SiI	BCSJ *56* 3195 (1983)
	$(RO)_2CR_2$, cat $Me_3SiO_3SCF_3$	JACS *102* 3248 (1980)
	$(RO)_2CR_2$, $TiCl_4$	CL 15 (1974) JACS *109* 527 (1987) (chiral) TL *28* 4181, 4847 (1987) (both chiral)
$CHROCHPhCO_2H$	 , $BF_3 \cdot OEt_2$	JOC *49* 2513 (1984)
	 (n = 1, 2), Me_3SiOTf	TL *23* 2601 (1982)
	 (n = 1, 2), AgOTf	JACS *107* 4289 (1985)
	 , $BF_3 \cdot OEt_2$	CC 1245 (1987)
	 OTf^-	TL *28* 6355 (1987)
CH_2SR	$ClCH_2SR$, cat Me_3SiX (X = I, OTf)	CL 405 (1983)
CHRSAr	$RCH(SAr)_2$, $TiCl_4$	JACS *109* 7199 (1987)
	$NO_2CHRSPh$, $SnCl_4$	CC 947 (1987)

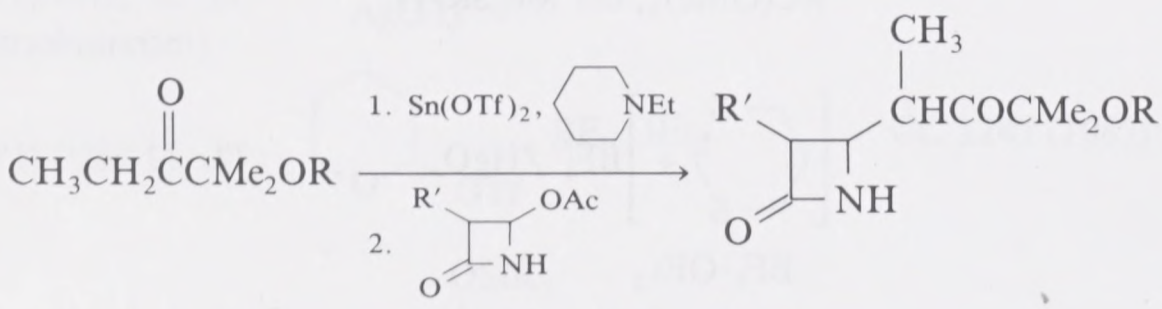
R_2CSR'	$R_2C(SR')_2$, $FeCl_3$ or $SnCl_4$	TL 4971 (1979) Syn Commun *11* 315 (1981)
$C(SPh)R^1CHR^2R^3$	$R^1C(SPh)=CR^2R^3$, $ROH \cdot 2\ TiCl_4$	TL *27* 3029 (1986)
CH_2NR_2	$R'OCH_2NR_2$, Me_3SiI or Me_3SiOTf	TL *23* 547 (1982) CL 405 (1983)
	$(R_2\overset{+}{N}=CH_2)Cl^-$ (R = Me, Et)	CC 269 (1986) TL *28* 6355 (1987)
	 , cat Me_3SiOTf	TL *28* 507 (1987)
	 , ZnI_2	CL 1343 (1985)
CHArNHAr	ArCH=NAr, cat Me_3SiOTf	CC 1053 (1987)
RCHNRCOR	MeOCHRNRCOR, $TiCl_4$ or $BF_3 \cdot OEt_2$	JACS *103* 1172 (1981)
$CH_3C(OH)CN$	CH_3COCN, $TiCl_4$	TL *22* 1171 (1981)
$CHRCH_2COR'$	$RCH=CHCOR'$, Lewis acid	See page 792, Section 2.
$CHR^1\overset{O}{\overset{\|}{C}}CH_2R^2$	$R^2CH_2C(NO_2)=CHR^1$, $SnCl_4/H_2O$	JACS *98* 4679 (1976); *106* 2149 (1984)
$CH(OR)_2$	$HC(OMe)_3$, cat MeSiOTf	JACS *102* 3248 (1980)
	$HC(OR)_3$, cat Me_3SiI	BCSJ *56* 3195 (1983)
	$HC(OMe)_3$, $SnCl_4$	TL *25* 2813 (1984)
	$HC(OMe)_3$, $TiCl_4$	CL 15 (1974)
	$MeLi/HC(OMe)_3/BF_3 \cdot OEt_2$	TL *23* 3595 (1982)
$CR(OMe)_2$	$RC(OMe)_3$, cat Me_3SiOTf	TL *27* 5099 (1986) (intramolecular)
CHO	 BF_4^-/HgO, $BF_3 \cdot OEt_2$	TL *22* 2829 (1981)
$COCH_3$	$(CH_3CO)BF_4$	JOC *46* 3771 (1981)
COR	RCOCl	CC 946 (1972) TL *28* 6355 (1987)
	RCOCl, $ZnBr_2$ or $TiCl_4$	Tetr *39* 841 (1983)
	RCOCl; $ZnCl_2$ or $SbCl_3$	JOC *47* 5099 (1982)
	RCOCl, $TiCl_4$ or $SnCl_4$	JOC *47* 3219 (1982)
	MeLi/RCOCl	TL 1187 (1977) Helv *64* 716 (1981)

R	Reagents	
CO_2CH_3	2 MeLi/chiral HNRR′/ CO_2/MeI	TL *27* 2767 (1986) (chiral)
CONHAr	$ArNCO/H_2O$	JOMC *164* 123 (1979)
COSMe	MeLi/COS/MeI	JOC *47* 3193 (1982)
halogen	See page 369, Section 1.	
OH	See page 488, Section 5.	
OAc	$Pb(OAc)_4/H_3O^+$ $Pb(OAc)_4$, KOAc, HOAc AgOAc, I_2	Syn Commun *6* 59 (1976) Tetr *39* 861 (1983) JOC *46* 2717 (1981)
O_2CPh	$Pb(O_2CPh)_4/(Et_3NH)F$	JOC *41* 1673 (1976)
O_3SAr	$(ArSO_3)_2$	JOC *50* 5148 (1985) TL *27* 5811 (1986)
SPh	PhSCl	CC 946 (1972) Tetr *37* 4027 (1981)
SOR (R = Me, Ph)	RSOCl	Syn 283 (1982)

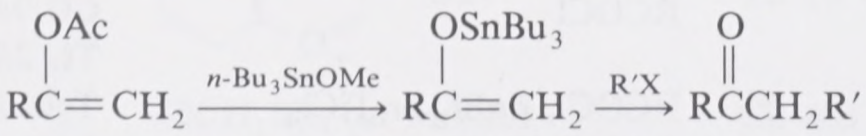


$Pb(OAc)_4$	TL *28* 873 (1987)
$Cu(OTf)_2$	TL 3741 (1977); 3555 (1978) Chem Pharm Bull *28* 262 (1980)
Ag_2O	JACS *97* 649 (1975)
PhIO, $BF_3 \cdot OEt_2$	CC 420 (1985) (R = Ar)

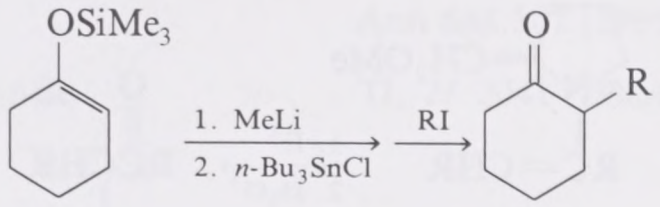
8. Enol Stannanes and Related Compounds



JOC *52* 5491 (1987)



JOMC *55* 273 (1973) (R′ = Me, Et, $PhCH_2$, $CH_2CH{=}CH_2$)
TL 3791 (1977) (R′ = 1° RI); *21* 2591 (1980) [R′X = allylic OAc, cat $Pd(PPh_3)_4$]
CL 939 (1982) [R′X = ArBr, cat $PdCl_2(PAr_3)_2$]
JACS *109* 7223 (1987) [R′X = heterocyclic iodide, cat $Pd(OAc)_2$-(*o*-Tol)$_3$P]



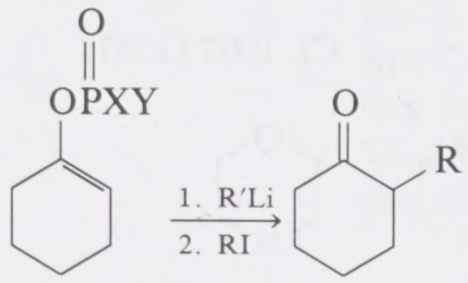
R = 1°, 2° alkyl

TL 1117 (1969)

$$n\text{-Bu}_3\text{SnCH}_2\text{CH(OEt)}_2 \xrightarrow[2.\ \text{PhCH}_2\text{Br}]{1.\ n\text{-BuLi}} \text{PhCH}_2\text{CH}_2\text{CH(OEt)}_2$$

JOMC *212* C31 (1981)

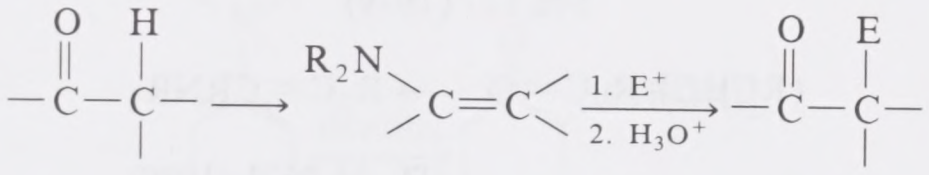
9. Enol Phosphorus Compounds



X	Y
Ph	Ph
Ph	OR
OR	OR

JOC *37* 3873 (1972)

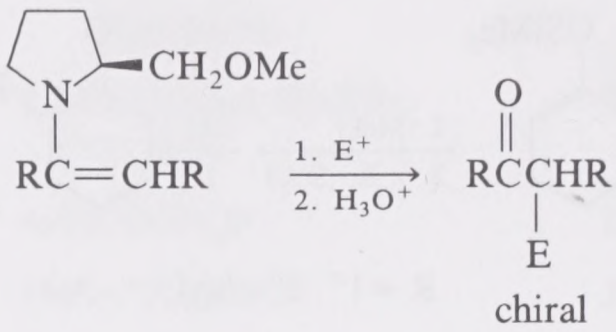
10. Enamines



$E^+ = X_2$, RX, RCOCl, RO_2CCl, Michael acceptors, etc.

Reviews:

Adv Org Chem *4* 1 (1963)
"Enamines: Synthesis, Structure and Reactions," Ed. A. G. Cook, Marcel Dekker, New York (1969); 2nd ed. (1987)
Syn 510 (1970); 517 (1983)
S. F. Dyke, "The Chemistry of Enamines," Cambridge Univ. Press, New York (1973)
Org Syn *53* 48, 59 (1973)
Org Syn Coll Vol *5* 808 (1973)
Acta Chem Scand B *32* 335 (1978)
Tetr *38* 1975, 3363 (1982)

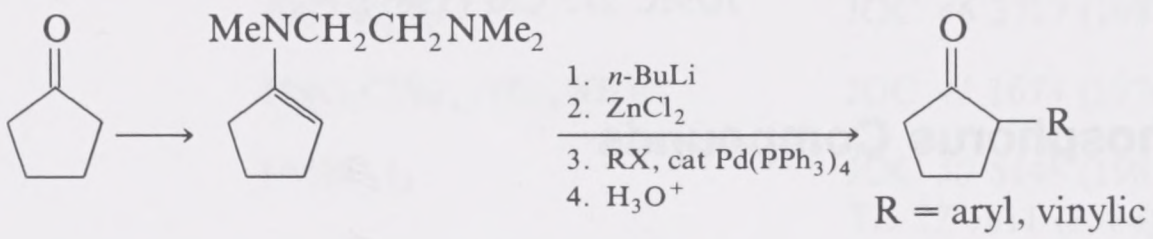


chiral

$\underline{E^+}$

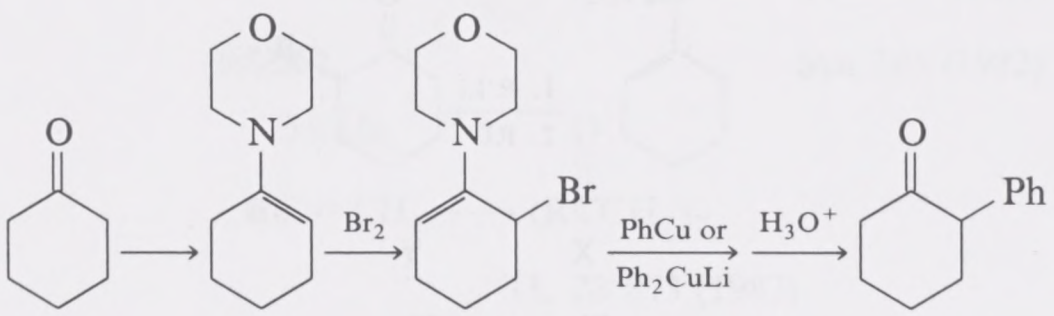
R_fI, Zn, Cp_2TiCl_2, ultrasound ($E = R_f$) JACS *107* 5186 (1985)

$ArCH{=}CHNO_2$ (conjugate addition) Helv *65* 1637 (1982)



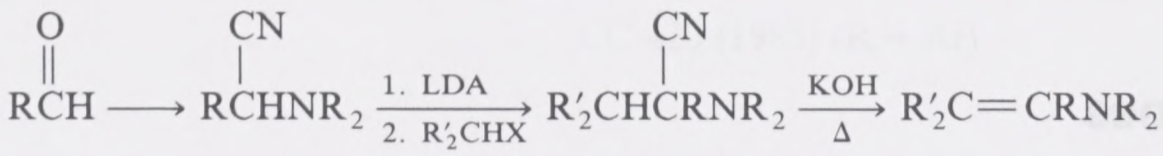
R = aryl, vinylic

CL 1007 (1987)



JOC *52* 3696 (1987)

Alternate syntheses of enamines and applications



Syn 127 (1979)

(RCHO) $R_2C{=}O \longrightarrow R_2C{=}CRNR_2$

$Ph_2POCHLiNMePh$ TL *21* 2671 (1980)



TL 2433 (1979)



JOC *39* 2814 (1974); *42* 2520 (1977); *44* 3391 (1979)



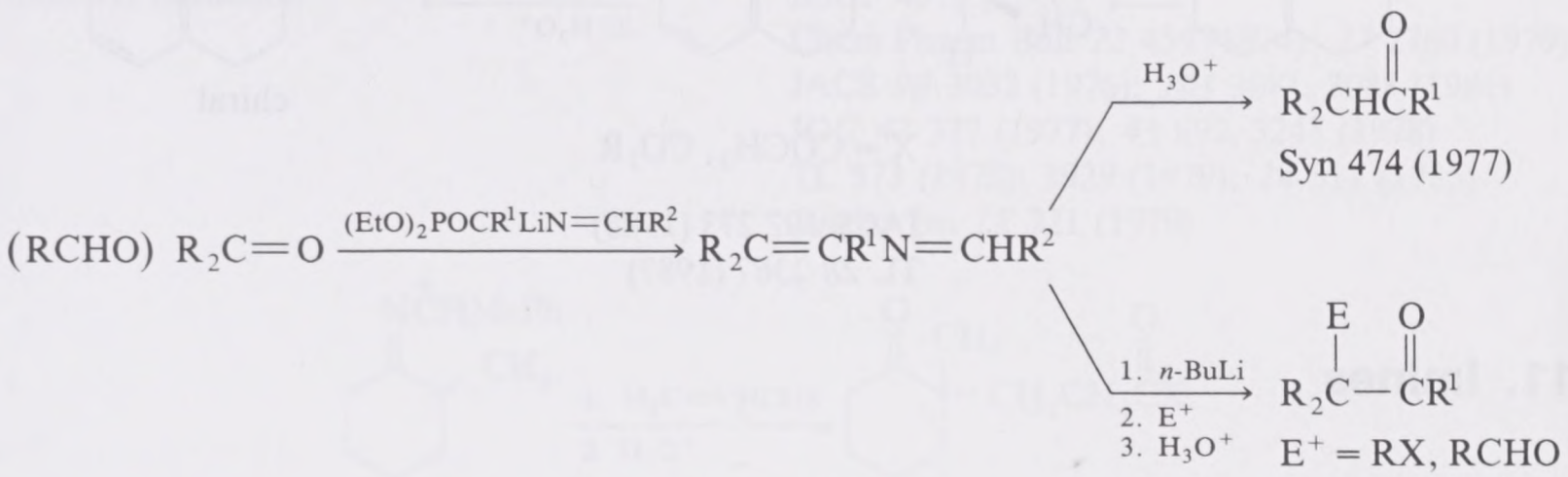
JOC *41* 3337 (1976); *42* 2520 (1977)



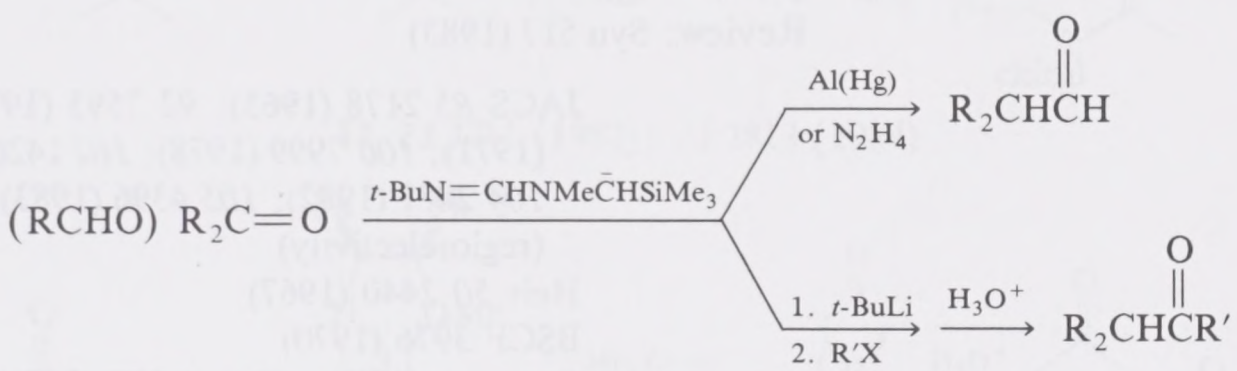
($X = CH_2$, O) Arch Pharm *305* 88 (1972)

$(PhO)_2POCLiArNHPh$ Ann *686* 107 (1965)

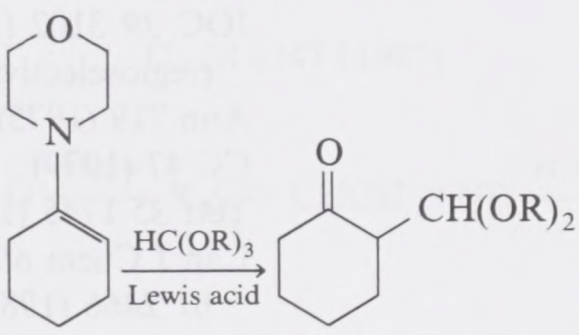
$(MeO)_2POCHN_2$, HNR_2, KO-*t*-Bu TL *21* 2041 (1980)



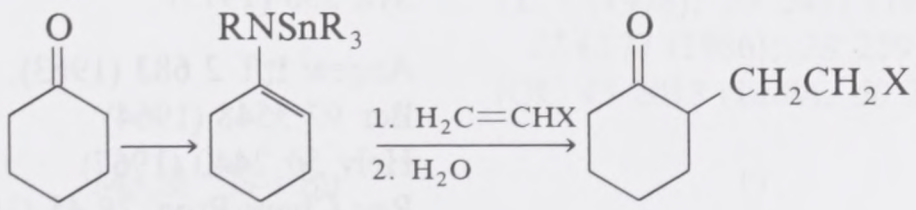
JOC *43* 782, 3792 (1978); *44* 3391 (1979); *46* 3567 (1981); *47* 1513 (1982); *52* 1962 (1987)
JACS *102* 5866 (1980); *106* 6431 (1984)
Syn Commun *11* 429 (1981)
Org Syn *65* 119 (1987)
TL *28* 503 (1987)
See also page 776, Section 21.



JACS *104* 877 (1982)

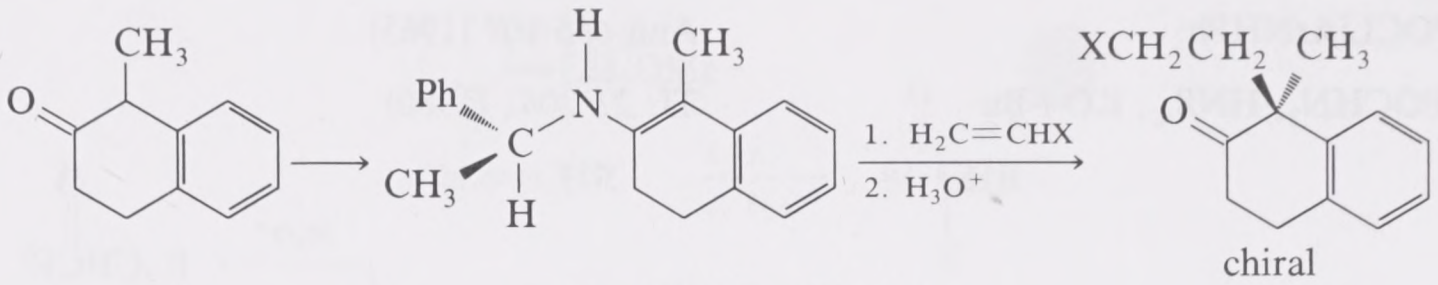


CL 1307 (1982)



X = CO_2R, CN

JOMC *186* C9 (1980)
TL *21* 4511 (1980)

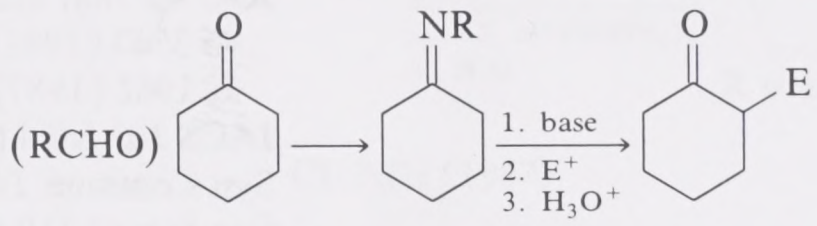


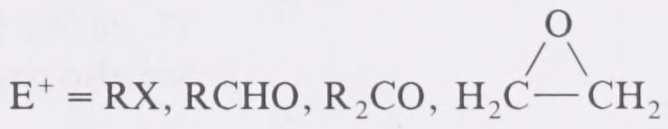
$X = COCH_3, CO_2R$

JACS *107* 273 (1985)
TL *28* 2367 (1987)

11. Imines

See also page 755, Section 10; and page 776, Section 21.





Review: Syn 517 (1983)

Alkylation

JACS *85* 2178 (1963); *92* 7593 (1970); *93* 5938 (1971); *100* 7999 (1978); *102* 1426, 5866 (1980); *104* 2081 (1982); *105* 4396 (1983) (regioselectivity)
Helv *50* 2440 (1967)
BSCF 3976 (1970)
Organomet Chem Syn *1* 237 (1971)
TL 1237 (1974); *24* 257, 511 (chiral), 3559 (regioselectivity) (1983)
JOC *39* 3102 (1974); *42* 2545 (1977); *46* 3157 (regioselectivity), 4631 (1981)
Ann 719 (1975)
CC 47 (1979)
Tetr *35* 1745 (1979)
Can J Chem *60* 1836 (1982) (chiral); *61* 2466 (1983)

Epoxide opening

JOC *32* 1679 (1972)
Ann 1075 (1973)
Syn 256 (1975)

Directed aldol

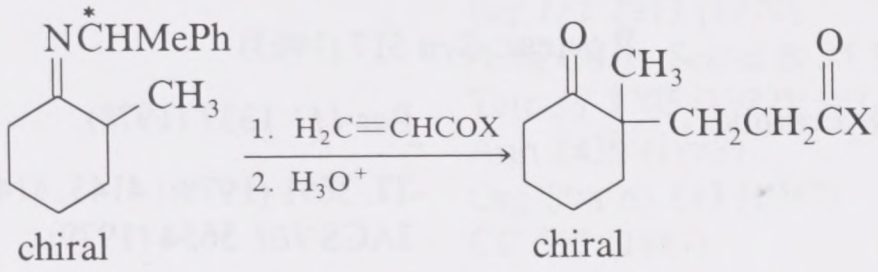
Angew Int *2* 683 (1963); *7* 7 (1968)
Ber *97* 3548 (1964)
Helv *50* 2440 (1967)
Rec Chem Prog *28* 45 (1967)
JOC *34* 1122 (1969)
JCS C 460 (1969)
TL 381 (1970)
JACS *102* 5866 (1980)

Regiochemistry

JACS *100* 292 (1978); *104* 2081 (1982)
JOC *43* 782, 3792 (1978)

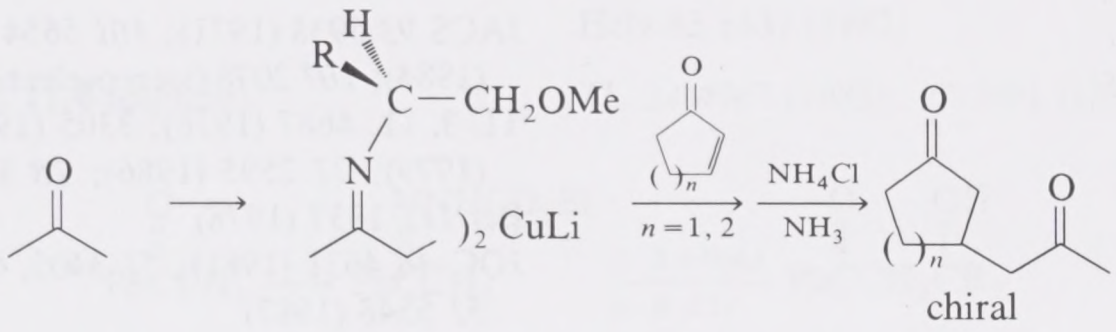
Asymmetric induction

BSCF 4571 (1968)
Chem Pharm Bull *22* 459 (1974); *27* 2760 (1979)
JACS *98* 3032 (1976); *103* 3081, 3088 (1981)
JOC *42* 377 (1977); *43* 892, 3245 (1978)
TL 573 (1978); 3929 (1979); *24* 511 (1983)
Angew Int *18* 221 (1979)

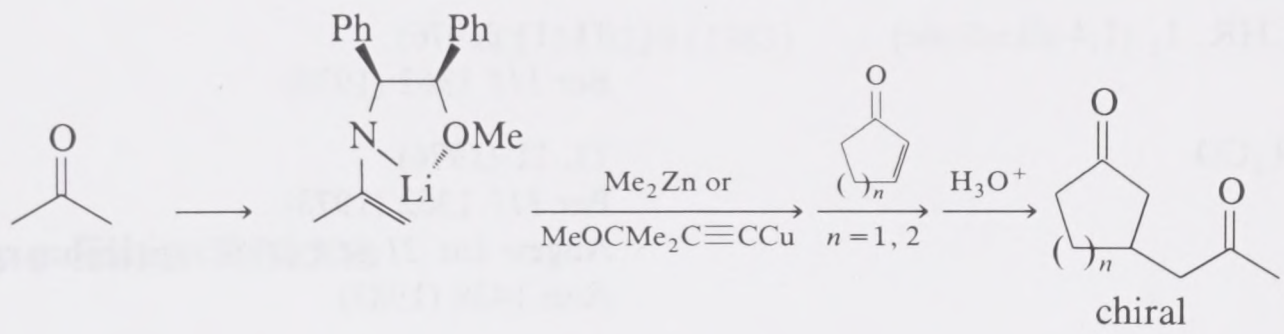


$X = CH_3, OCH_3$

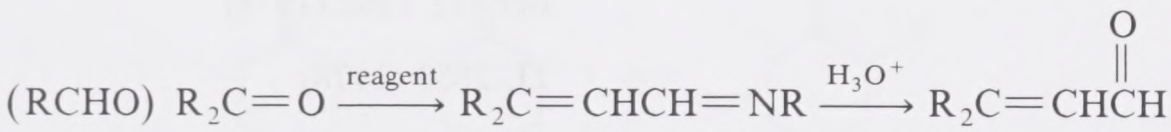
JACS *107* 273 (1985)



TL *23* 3711 (1982); *25* 2813 (1984)



TL *28* 6347 (1987)



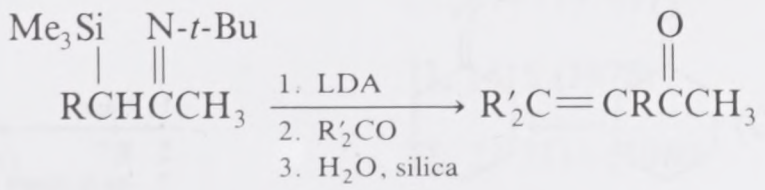
Reagent

$(EtO)_2POCHCH{=}NR$

JCS C 460 (1969)
JOC *43* 3788 (1978)

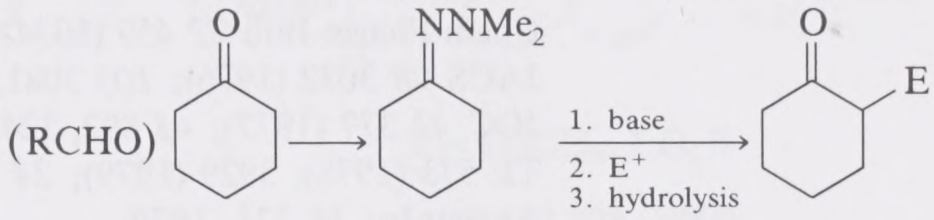
$Me_3SiCHCH{=}NR$

TL 7 (1976); *24* 2481 (1983); *26* 2391 (1985); *27* 6177 (1986); *28* 259 (1987)
JOC *45* 2013 (1980); *50* 2798 (1985)



TL *24* 2481 (1983)

12. Hydrazone Anions



Review: Syn 517 (1983)

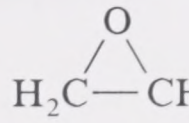
Preparation of dimethylhydrazones — Ber *111* 1337 (1978)

Deprotonation — TL 3691 (1978); 4145, 4149 (1979); *21* 3115 (1980)
JACS *101* 5654 (1979)

Hydrolysis — TL 3 (1976)

Electrophile:

RX — JACS *93* 5938 (1971); *101* 5654 (1979); *106* 4865 (1984); *107* 2078 (stereoselectivity), 5303, (1985)
TL 3, 11, 4687 (1976); 3305 (1977); 4145, 4149 (1979); *27* 2595 (1986); *28* 813, 5275 (1987)
Ber *111* 1337 (1978)
JOC *46* 4631 (1981); *51* 3405, 4212 (1986); *52* 5548 (1987)



, I_2 (1,4-alkadione) — TL 11 (1976)
Ber *111* 1362 (1978)

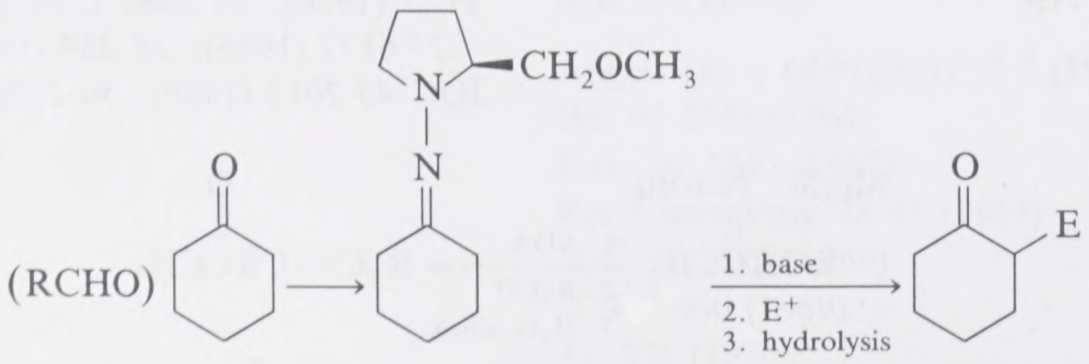
RCHO, R_2CO — TL 11 (1976)
Ber *111* 1362 (1978)
Angew Int *21* 864 (1982) (titanium species)
Ann 1439 (1983)

enone, CuX (1,4-addition) — TL 11 (1976); *21* 3115 (1980)
Ber *111* 1362 (1978)

RCOCl — TL 2853 (1978)

Me_3SiCl — TL 7 (1976)
Ber *111* 1362 (1978)

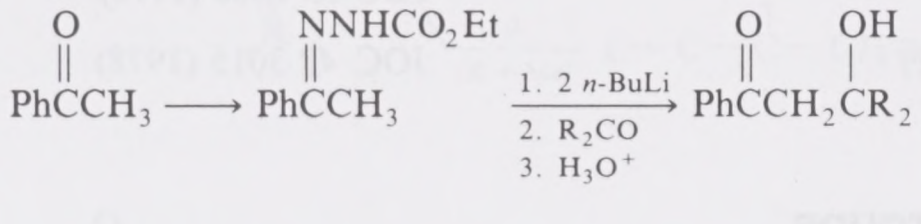
MeSSMe — TL 4687 (1976)



Review:

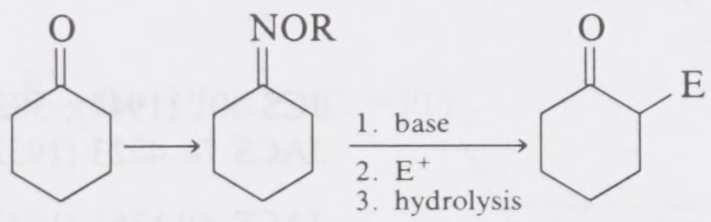
D. Enders in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 4 (Alkylation of Chiral Hydrazones)

$\underline{E^+}$	
RX	Angew Int *15* 549 (1976); *18* 397 (1979) TL 191 (1977) Ber *112* 2933 (1979) Acta Chem Scand B *35* 555 (1981) Tetr *38* 3705 (1982); *40* 1345 (1984) Ann 1439 (1983) Org Syn *65* 183 (1987) CC 358 (1987)
$RCHO, R_2CO$	Angew Int *17* 206 (1978) Ber *112* 3703 (1979)
$ArCH{=}CHNO_2$	Helv *65* 1637 (1982)
$RCH{=}CHCO_2R$ (1,4-addition)	TL *24* 4967 (1983); *27* 3491 (1986)



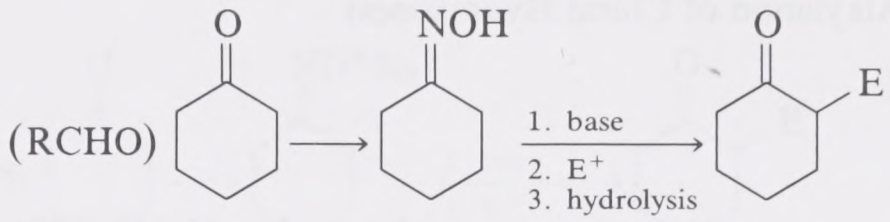
TL *24* 3239 (1983)

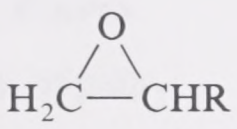
13. Oxime Ether Anions



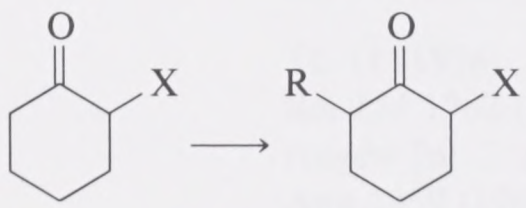
Preparation of oximes	TL 1415 (1978)
Deprotonation	TL 3889 (1975); 1415 (1978); *21* 3115 (1980)
Electrophile:	
RX	CC 674 (1976)
R_2CO	TL 1415 (1978)
enone, CuBr (1,4-addition)	TL *21* 3115 (1980)

14. Oxime Dianions



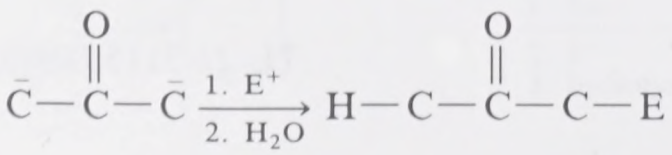
Deprotonation	TL 1439 (1976)
Electrophile:	
RX	JACS *91* 676 (1969) TL 1439, 4431 (1976) JOC *41* 439 (1976) JOMC *165* 1 (1979)
	JOMC *177* 35 (1979)
$RCHO, R_2CO$	JOC *41* 439 (1976) JOMC *165* 1 (1979)
RCO_2R (isoxazole)	JOC *35* 1806 (1970)
$RCONR_2$ (isoxazole)	JOC *43* 3015 (1978)

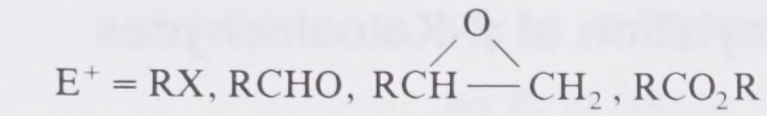
15. Blocking Groups



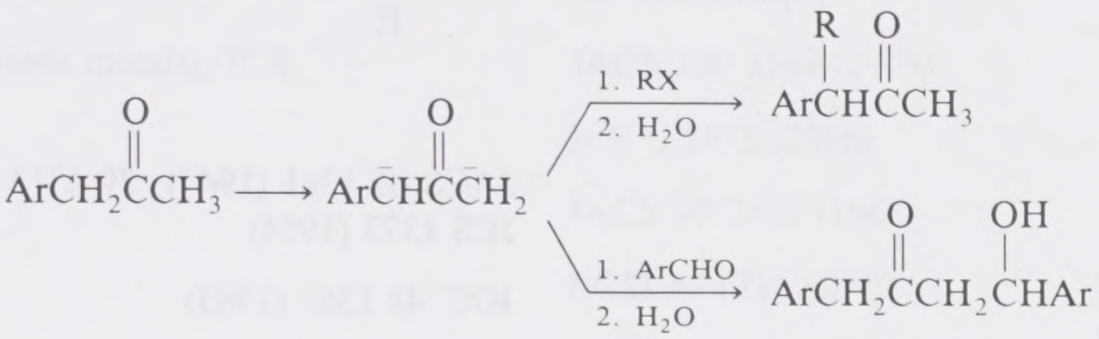
X	
$=CHNR_2$	JCS 501 (1944); 582 (1945) JACS *74* 4223 (1952)
$=CHOR$	JACS *69* 1361 (1947)
$=CHSR$	JOC *27* 1615, 1620 (1962); *32* 1741 (1967) JACS *105* 6975 (1983)
$(SR)_2$	JCS 1131 (1957)

16. Alkylation and Acylation of Carbonyl Dianions

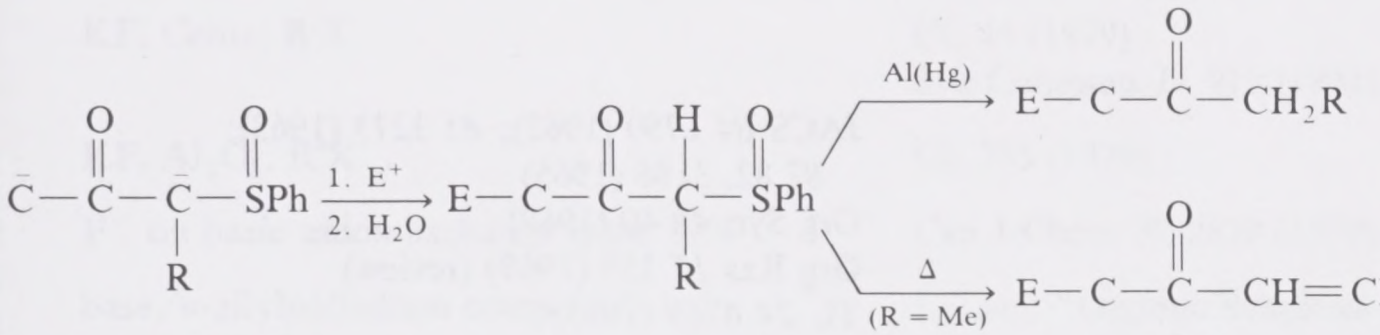




JACS *102* 2110 (1980)

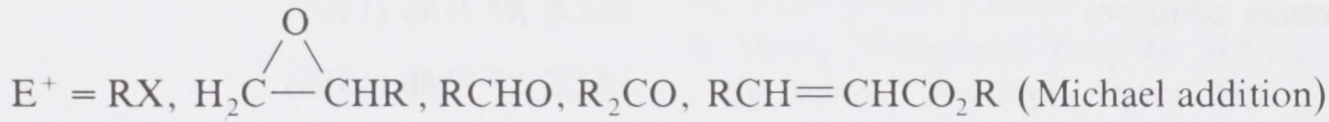


JOC *48* 2957 (1983)

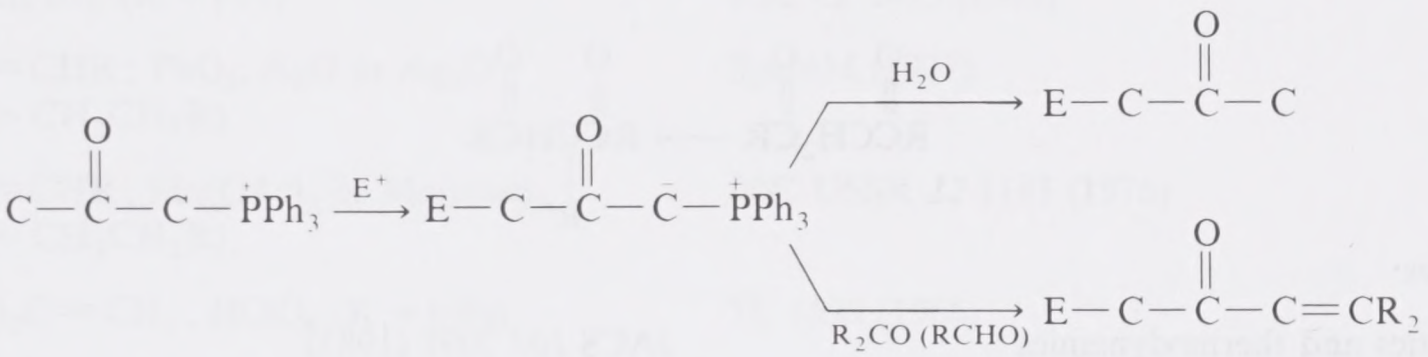


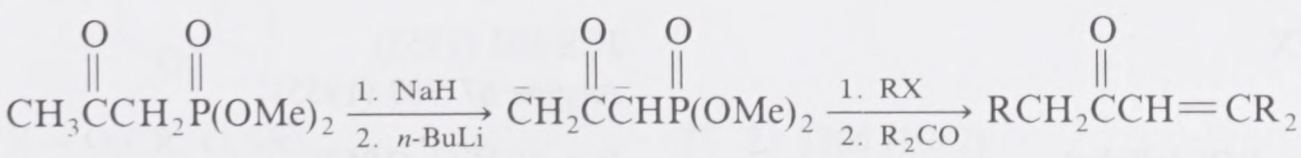
JOC *39* 732 (1974)
TL *28* 4629 (1987)

TL 107 (1974)
CC 497 (1974)
JACS *106* 721 (1984)



TL *28* 5677 (1987)

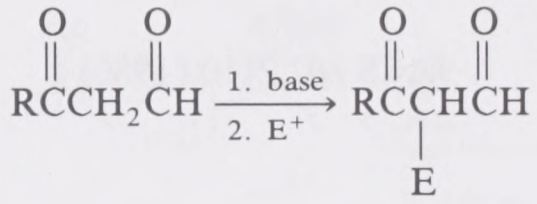




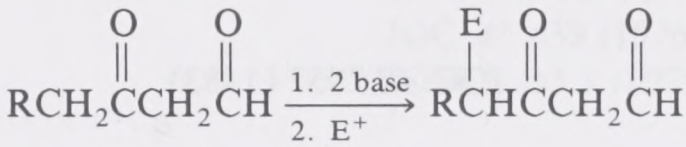
JOC *38* 4082 (1973); *41* 509 (1976)

JOC *38* 2909 (1973)

17. Alkylation and Acylation of β-Ketoaldehydes

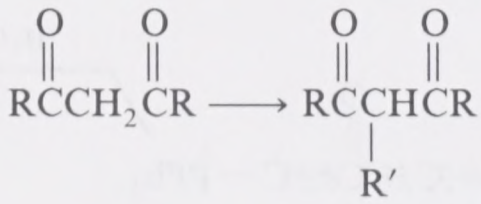


E^+	
RX	JACS *69* 1361 (1947); *79* 6313 (1957) JCS 1373 (1954)
$(Me_3S)BF_4$	JOC *48* 1362 (1983)



E^+	
RX	JACS *84* 1750 (1962); *85* 3273 (1963); *87* 82, 3186 (1965) Org Syn *48* 40 (1968) Org Rxs *17* 155 (1969) (review) TL *24* 4769 (1983)
RCHO, R_2CO	JACS *84* 1750 (1962); *87* 3186 (1965)
enone (Michael addition)	JACS *87* 3186 (1965)
RCO_2R	JACS *87* 3186 (1965)

18. Alkylation and Acylation of β-Diketones

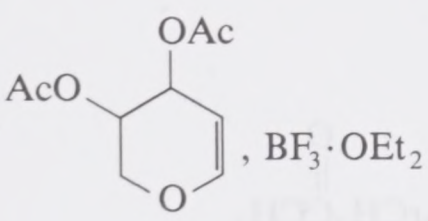
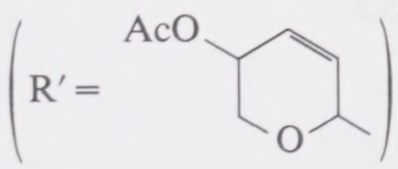


Reviews:

kinetics and thermodynamics	JACS *107* 2091 (1985)
ion pairing and reactivity	JACS *100* 3514 (1978); *106* 6759 (1984)
O vs C alkylation	Tetr *27* 4777 (1971)

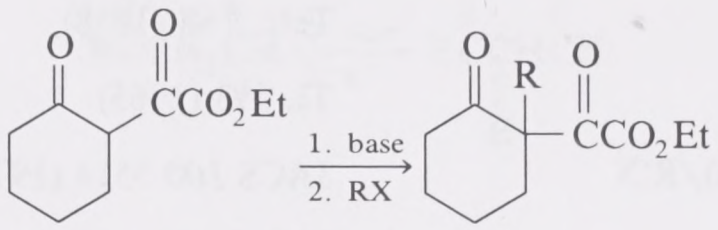
Reagent(s):

$NaH/(Me_3S)BF_4$	JOC *48* 1362 (1983)
NaOH, R_4NX (chiral), phase transfer	BCSJ *52* 3119 (1979)
KOH, R′X	JCS 803 (1953) Angew *67* 783 (1955)
KOH, Cu, R′X (allylic)	Ber *85* 1061 (1952)
K_2CO_3, MeI	Org Syn Coll Vol *5* 785 (1973)

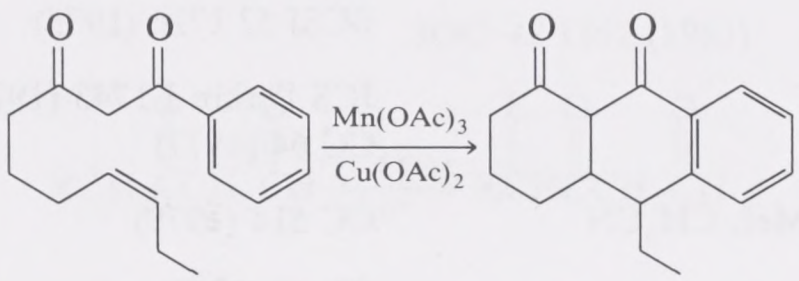
K_2CO_3, R′X	Tetr *38* 1279 (1982)
NaOMe/R′X	Ber *85* 61 (1952) JCS 811 (1953) Tetr *2* 88 (1958)
NaOEt/R′X	TL 593 (1965)
MOEt (M = various metals)/R′X	JACS *100* 3514 (1978)
KO-*t*-Bu/R′X	JCS C 1973 (1966)
TlOEt/R′I	JACS *90* 2421 (1968)
DBU, R′X	BCSJ *52* 1716 (1979)
R_4NF, R′X	JCS Perkin I 1743 (1977) CC 64 (1977)
n-Bu_4NCl, $KF \cdot 2\ H_2O$, MeI, CH_3CN	CC 514 (1979)
KF, Celite, R′X	CL 45 (1979) Syn Commun *11* 913 (1981)
KF, Al_2O_3, R′X	CL 755 (1979)
F^- on basic anion exchange resin, R′X	Can J Chem *57* 2629 (1979)
base/π-allylpalladium compound (R′ = allylic)	J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) Acct Chem Res *13* 385 (1980) CC 1162 (1982) (chiral) R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)
R′OH (allylic, benzylic), cat $Pd(acac)_2$, cat PPh_3	Tetr *37* 3009 (1981)
i-PrOH, BF_3 (R′ = *i*-Pr)	JOC *32* 2615 (1967)
$H_2C{=}CHR$; PbO_2, AgO or Ag_2O (R′ = CH_2CH_2R)	Syn 454 (1977)
$H_2C{=}CHR$, $Mn(OAc)_3$ or $Mn(acac)_3$ (R′ = CH_2CH_2R)	JOC USSR *12* 1183 (1976)
$(CH_3)_2C{=}CH_2$, $HClO_4$ (R′ = *t*-Bu)	TL 3599 (1966)
	CC 68 (1983)
	
Ph_4BiX (X = O_2CR, O_3SR), *N*-*t*-butyl-*N*′,*N*″-tetramethylquanidine (R′ = Ph)	TL *23* 3365 (1982)

$ArPb(OAc)_3$, py ($R' = Ar$) Austral J Chem *32* 1561 (1979)

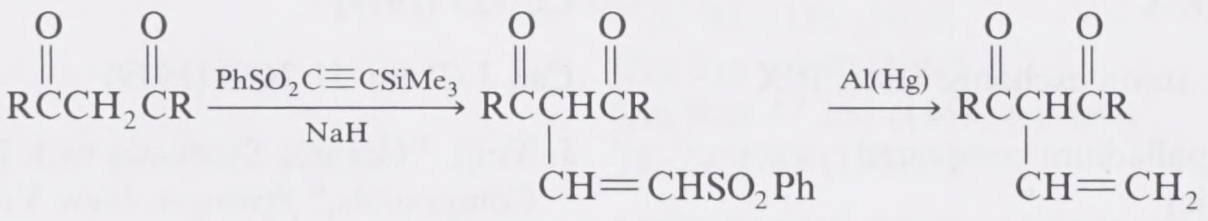
KO-*t*-Bu/NC-Ar-Br, NH_3, hν ($R' = ArCN$) Tetr *38* 3479 (1982)



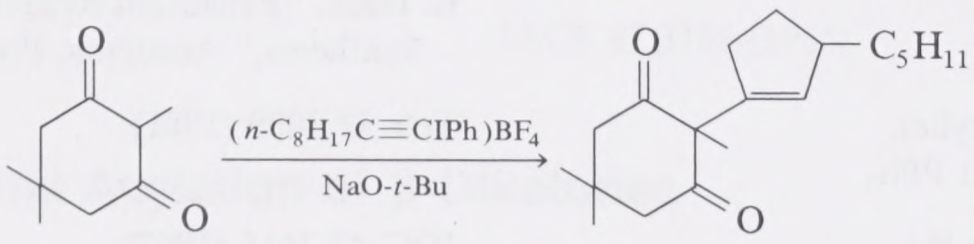
JACS *80* 5220 (1958)



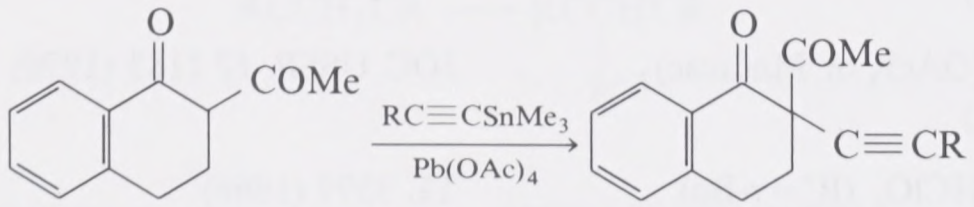
TL *28* 845 (1987)



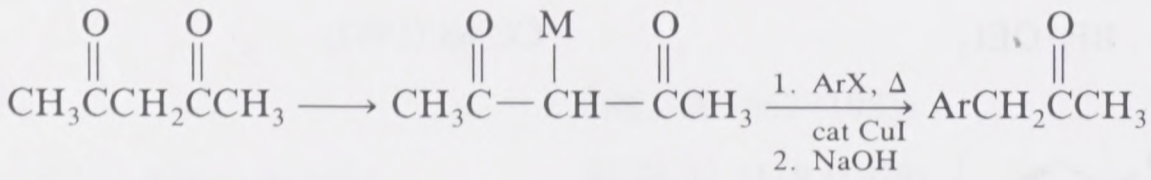
JOC *47* 4713 (1982)



JACS *108* 8281 (1986)

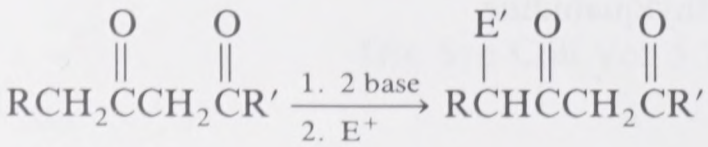


TL *27* 5025 (1986)



M = Na, K

CL 597 (1982)



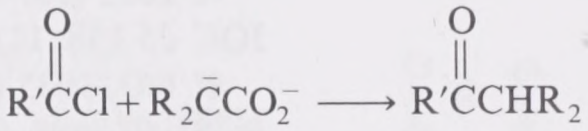
E^+	
RX	JACS *80* 6360 (1958); *81* 1160 (1959); *96* 1082 (1974) JOC *25* 158, 1110 (1960); *30* 61 (1965); *31* 663, 1035 (1966) BCSJ *40* 2698, 2909 (1967) Org Syn *47* 92 (1967) Org Rxs *17* 155 (1969) (review) Org Syn Coll Vol *5* 848 (1973) TL *28* 1997 (1987)
$RCHO, R_2CO$	JACS *80* 6360 (1958) JOC *26* 1344, 1716 (1961); *30* 1007 (1965) BCSJ *40* 2909 (1967) TL *28* 1997 (1987)
RCO_2R	JACS *80* 6360 (1958); *94* 8253 (1972); *95* 6865 (1973); *99* 1631 (1977) JOC *25* 538, 1110 (1960); *28* 725, 2266 (1963); *30* 1007, 4263 (1965); *46* 2260 (1981); *51* 4254 (1986) BCSJ *40* 2909 (1967) Ber *114* 2786 (1981) Syn Commun *12* 621 (1982) TL *28* 5615 (1987) (lactone)
$CH_3CONMeOMe$ ($E' = CH_3CO$)	TL *24* 1851 (1983)
CO_2	JACS *80* 6360 (1958) JOC *25* 1110 (1960); *31* 1032 (1966)
$RCH{=}CHCOX$ (X = R, OR) (Michael addition)	JOC *26* 1344 (1961); *28* 2266 (1963)

19. Alkylation and Acylation of β-Polyketones

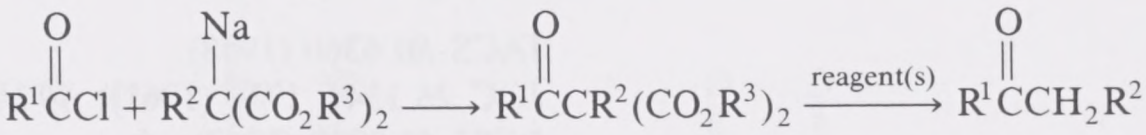
$$CH_3C(CH_2C)_nR \xrightarrow[2.\ E^+]{1.\ \text{base}} E'CH_2C(CH_2C)_nR$$

n	E^+	
2	RX, RCHO, R_2CO	JOC *30* 4263 (1965)
	RCO_2R	JOC *30* 4263 (1965); *46* 2260 (1981) JACS *85* 3884 (1963); *93* 6708 (1971); *94* 8253 (1972); *95* 6865 (1973) CC 442 (1979)
	CO_2	JOC *30* 4263 (1965) JACS *89* 6734 (1967); *91* 517 (1969); *98* 7733 (1976); *99* 1631 (1977)
2, 3	$CH_3CONMeOMe$ ($E' = COCH_3$)	TL *24* 1851 (1983)
3	RCO_2R	JACS *93* 6708 (1971); *95* 6865 (1973)
	CO_2	JACS *93* 6708 (1971)

20. Synthesis via β-Keto Acids, Esters, Amides and Imides



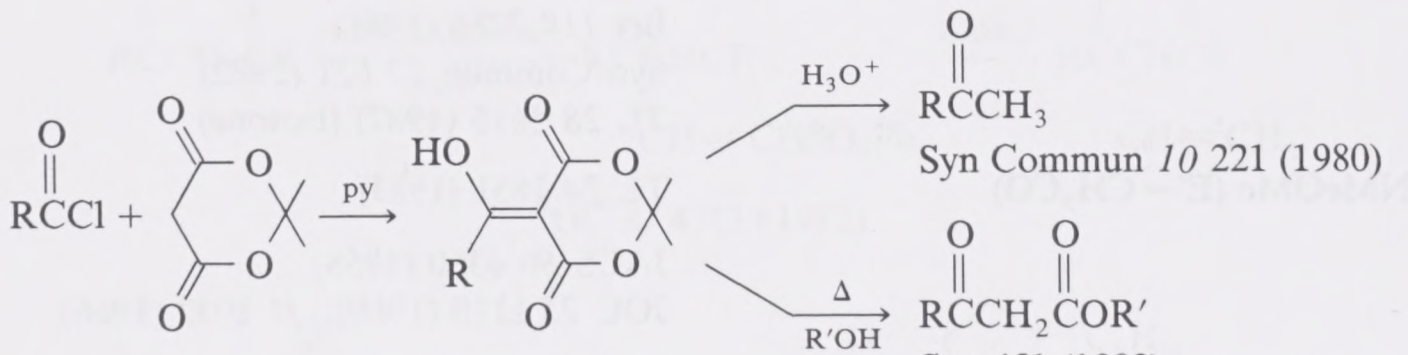
Compt Rend *286* 401 (1978)
Syn 284 (1982)



Reagent(s)

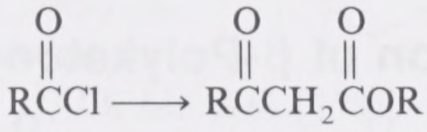
H_2, cat Pd-C ($R^3 = PhCH_2$) — JCS 325 (1950)

H^+ — JCS 322 (1950); JACS *74* 831 (1952)



Syn Commun *10* 221 (1980)

Syn 451 (1982)



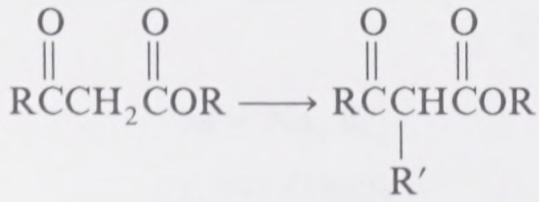
$LiCH_2CO_2R$ — See page 873, Section 2.

$LiO_2CCHLiCO_2R/H^+$ — JOC *44* 310 (1979); Org Syn *61* 5 (1983)

$NaCH(CO_2R)CO_2CH_2Ph/H_2$, cat Pd-C — JCS 2758 (1951)

$ROMgCH(CO_2R)_2$, Δ — J Prakt Chem 322 (1980)

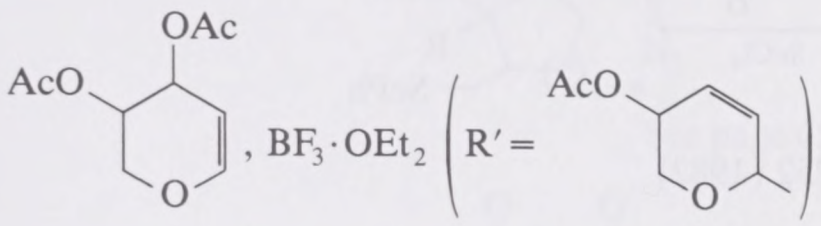
$BrMgO_2CCH(MgBr)CO_2R/H^+$ — Syn 143 (1978)



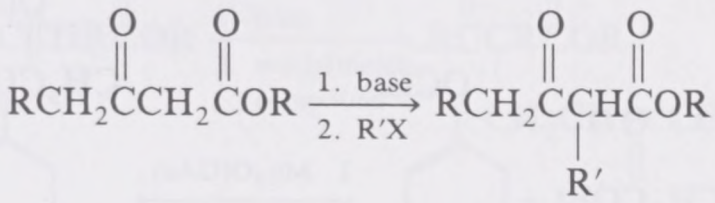
$R'OH$, BF_3 — JACS *62* 2389 (1940); *65* 552 (1943); Org Syn Coll Vol *3* 405 (1955)

R'_2O, BF_3 — JACS *62* 2389 (1940); *65* 552 (1943)

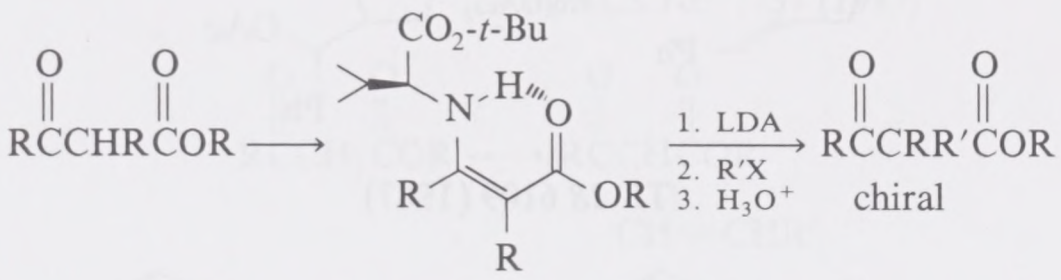
t-BuBr, $AgClO_4$ — Angew Int *5* 1044 (1966)



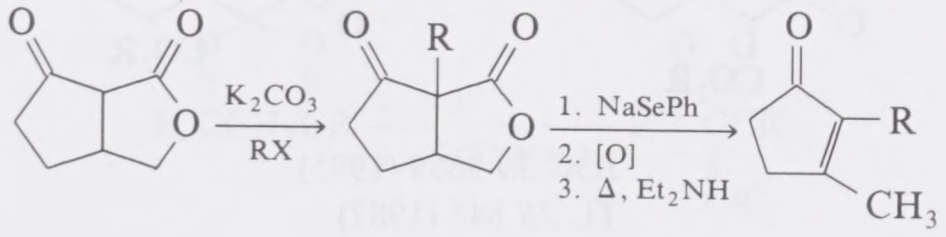
CC 68 (1983)



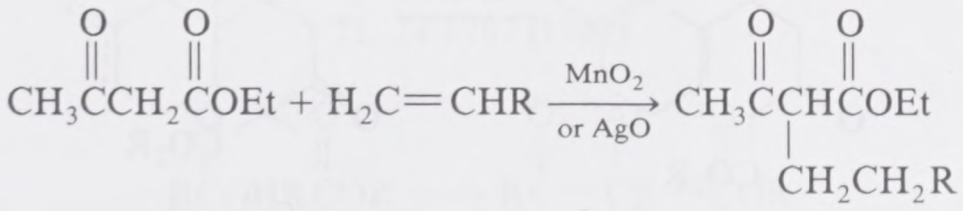
Newer Methods Prep Org Chem *2* 101 (1963)
Tetr *19* 1645 (1963) (rates); *27* 4777 (1971) (O vs C alkylation); *33* 2737 (1977) (review)
Org Syn *45* 7 (1965)
TL 593 (1965) (O vs C alkylation); 3679 (1968) (O vs C alkylation); 4903 (1972) (O vs C alkylation); *23* 1993 (1982) (copper enolate)
JOC *34* 1969 (1969) (O vs C alkylation); *35* 171 (1970) (stereochemistry); *48* 1362 (1983) (R′X = sulfonium salts)
Ann *736* 1 (1970) ($R'X = Me_2SO_4$)
BCSJ *49* 1126 (1976) (O vs C alkylation); *52* 1716, 3119 (1979)
CC 325 (1980)
Syn Commun *10* 279 (1980)
J Chem Res (S) 86 (1982)
JCS Perkin I 2293 (1983) (R′X = allylic halide, regiochemistry)



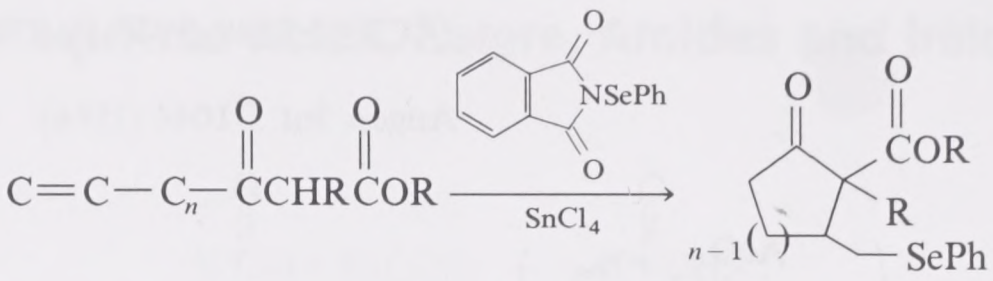
JACS *106* 2718 (1984)



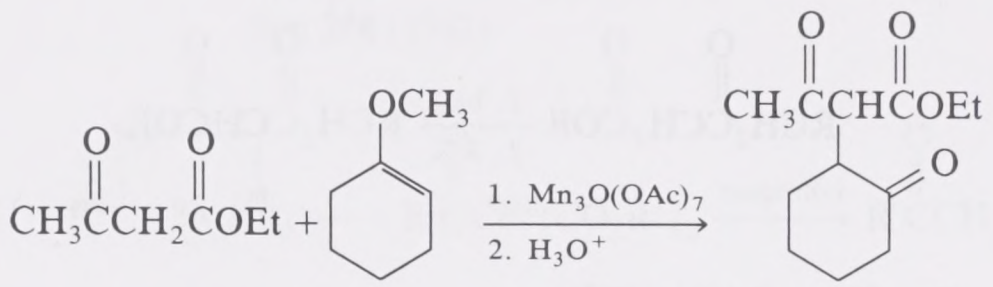
TL *22* 2447 (1981)



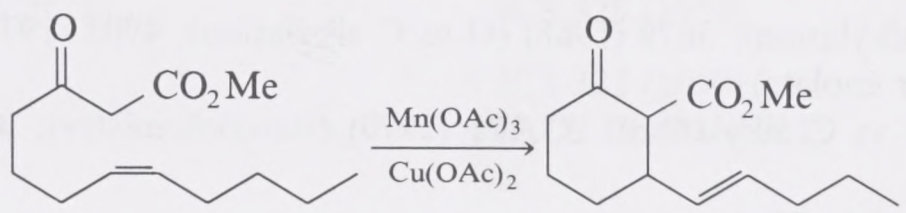
Syn 454 (1977)



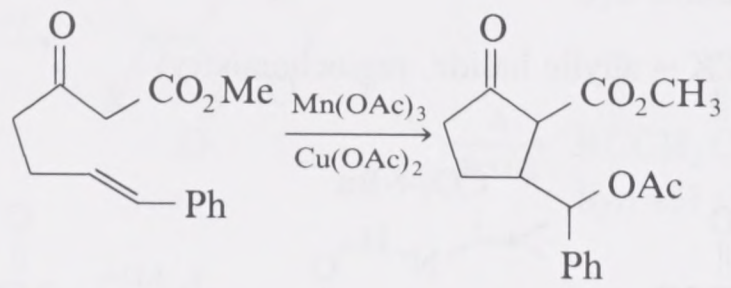
CC 1251, 1252 (1982)



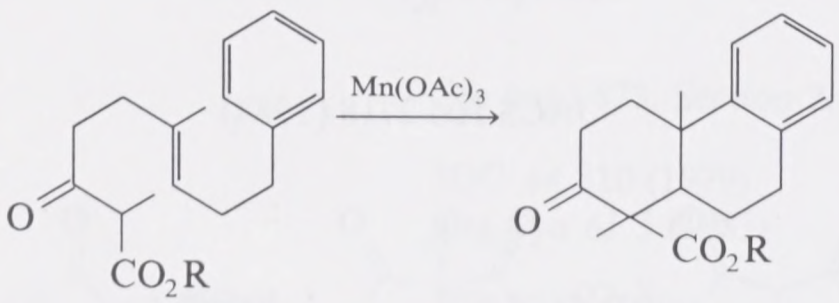
TL *28* 175 (1987)



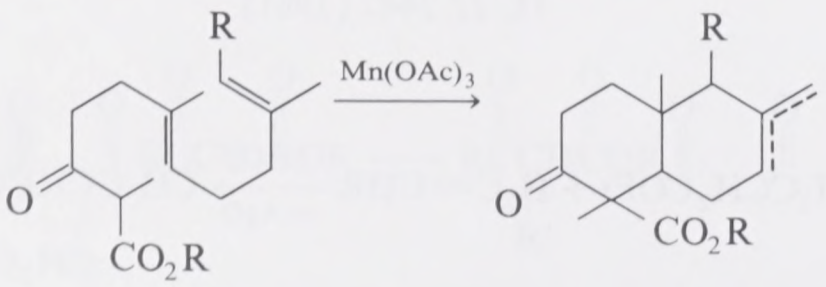
JOC *50* 3659 (1985)
TL *28* 845 (1987)



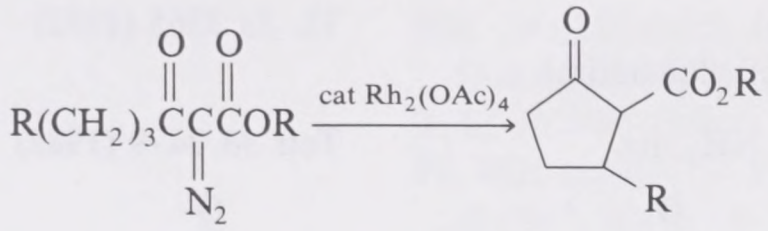
TL *28* 6109 (1987)



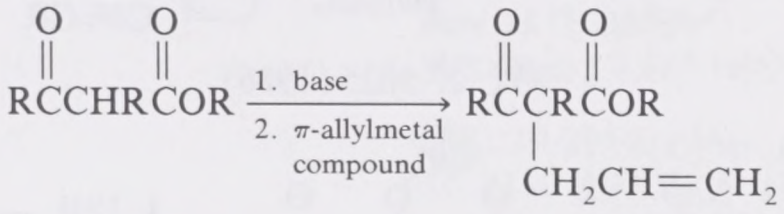
JOC *50* 3659 (1985)
TL *28* 845 (1987)



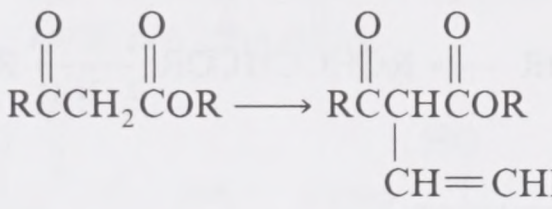
TL *28* 841 (1987)
JOC *52* 5487 (1987)



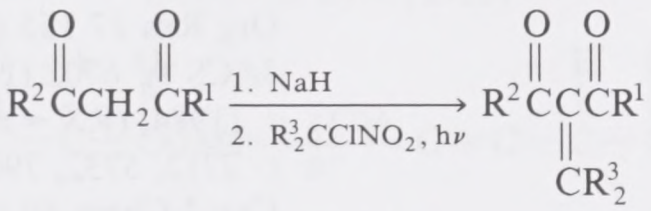
See page 653, Section 1.



Metal	
Pd	Tetr *33* 2615 (1977) (review) J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) (review) Acct Chem Res *13* 385 (1980) (review) R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985) (review)
Mo	JACS *104* 5543 (1982); *105* 3343 (1983); *109* 1469 (1987) Organomet *2* 1687 (1983) JOMC *252* 105 (1983)
W	JACS *105* 7757 (1983)

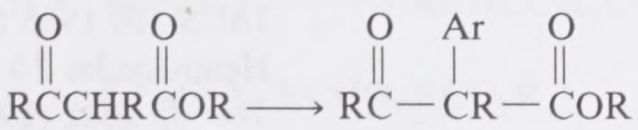


$PhSO_2C{\equiv}CSiMe_3$, KF, crown ether/Al(Hg) ($R' = H$)	JOC *47* 4713 (1982)
$R'CH{=}CHPb(OAc)_3$	CC 965 (1984)



R^1 = alkyl, OEt

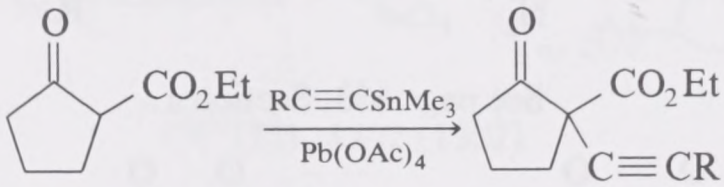
Syn 62 (1981)
TL *24* 1787 (1983)



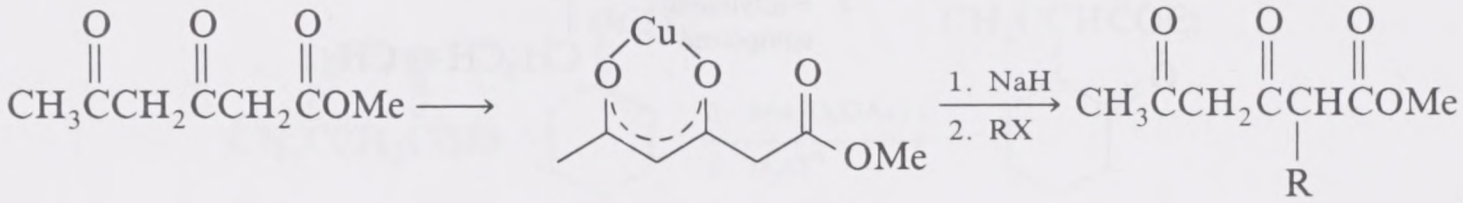
$ArPb(OAc)_3$	Austral J Chem *33* 113 (1980); *38* 1155 (1985) TL *23* 5365 (1982)

Ph_4BiX (X = O_2CR, O_3SR),
N-*t*-butyl-*N*′,*N*″-tetramethylquanidine — TL *23* 3365 (1982)

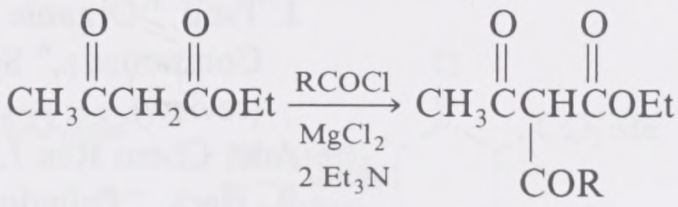
KO-*t*-Bu/ NC—Ar—Br, NH_3, hν — Tetr *38* 3479 (1982)



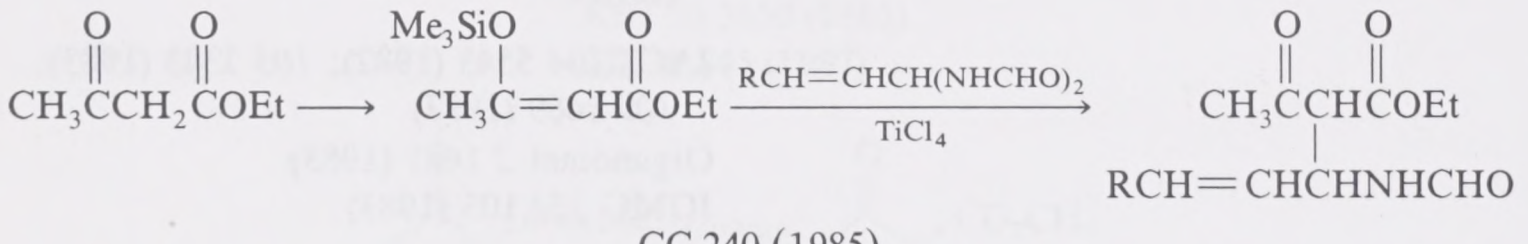
TL *27* 5025 (1986)



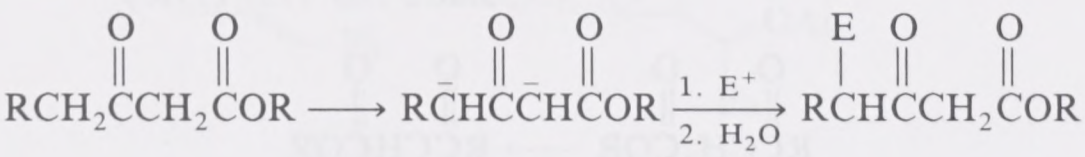
TL *28* 3715 (1987)



JOC *50* 2622 (1985)



CC 240 (1985)



$\underline{E^+}$

RX

JOC *29* 3249 (1964); *38* 3428 (1973); *39* 2648 (1974); *47* 381 (1982); *51* 4424 (1986); *52* 28, 192 (1987)
BCSJ *40* 2909 (1967)
Org Rxs *17* 155 (1969) (review)
JACS *92* 6702 (1970); *96* 1082 (1974); *106* 6006 (1984) (RX = allylic phosphate); *107* 196, 2122, 2712, 5732, 7967 (1985); *108* 8235 (1986)
Can J Chem *60* 673 (1982)
TL *24* 699 (1983); *26* 3059 (1985); *27* 131, 5555 (1986); *28* 731 (1987)
CC 265 (1986)

epoxide

JOC *38* 3428 (1973); *43* 788 (1978)
JACS *100* 1938 (1978)
Heterocycles *10* 111 (1978)
Tetr *35* 1601 (1979)
CL 337 (1985)
TL *28* 3597 (1987)

$RCHO$, R_2CO

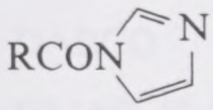
JOC *29* 3249 (1964); *47* 1779 (1982); *52* 4062 (1987)
BCSJ *40* 2909 (1967)
TL 4835 (1971); *27* 4713 (1986); *28* 5253, 5661 (1987)
CC 362 (1974)
JACS *104* 5528 (1982); *108* 2662 (1986)
Ann 1173 (1982)
JCS Perkin I 665 (1982)

RCO_2R

JOC *29* 3249 (1964)
TL 2405 (1972); *27* 1445, 2401, 3835 (1986); *28* 2017 (1987)
CC 362 (1974)
Can J Chem *52* 1343 (1974)
JACS *107* 7760 (1985) (lactone)

$RCONR_2$, $BF_3 \cdot OEt_2$

CL 1145 (1985)



JOC *51* 268 (1986)

RCN

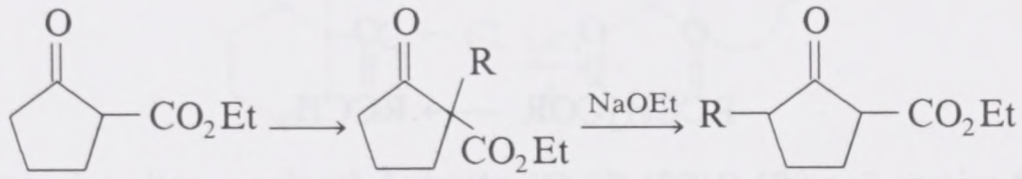
Can J Chem *52* 1343 (1974)

CO_2

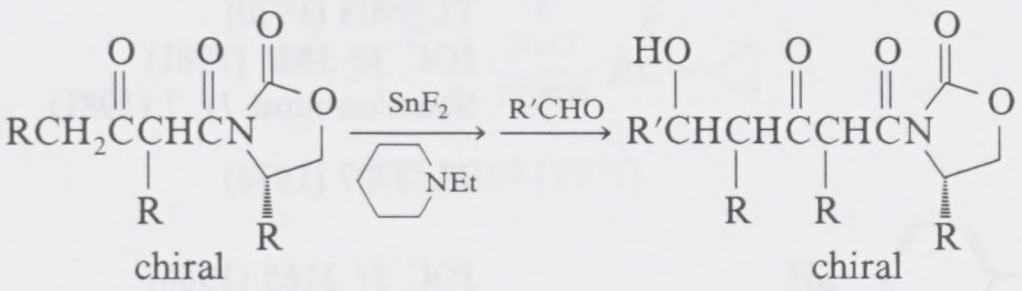
JOC *31* 1032 (1966)

$NCCO_2R$

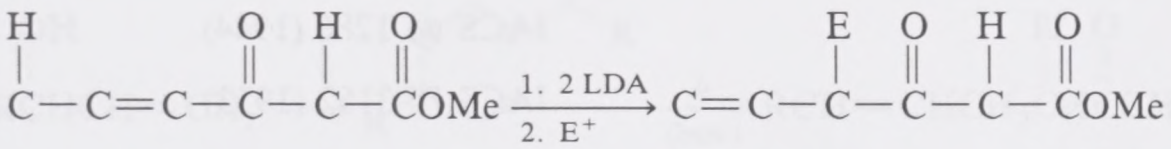
TL *28* 1051 (1987)



JOC *29* 2781 (1964); *52* 28 (1987)
JACS *106* 2064 (1984)

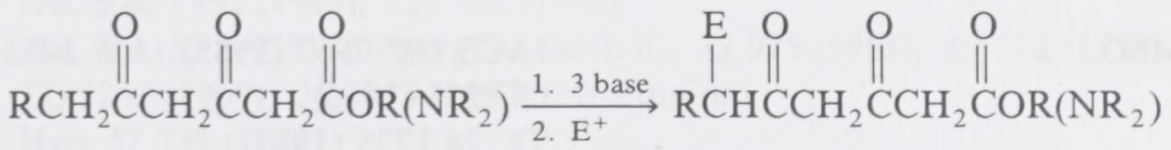


JACS *108* 2476 (1986)



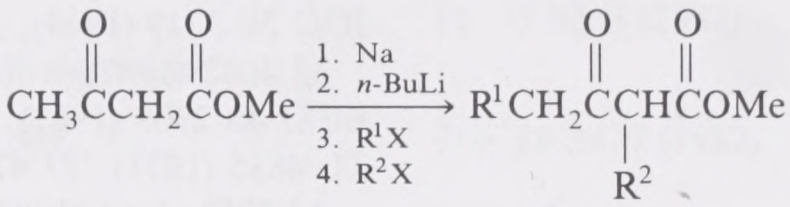
$E^+ = RX, H_2CO, RCHO, R_2CO$

Rec Trav Chim *102* 393 (1983)

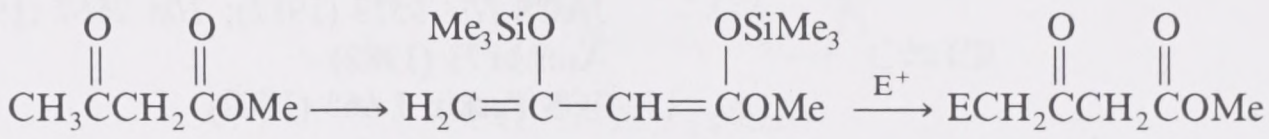


$E^+ = RX, RCHO, RCO_2R$

CC 362 (1974)
JOC *46* 2566 (1981)

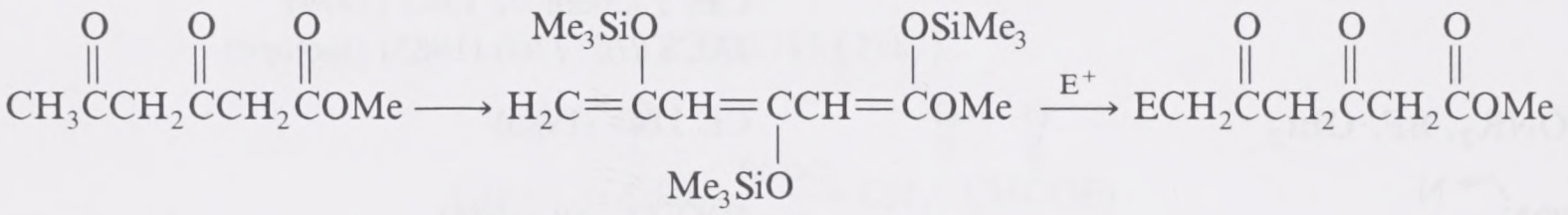


Syn Commun *11* 7 (1981)

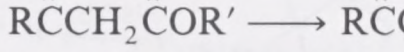


$E^+ = Br_2$, RCOCl, RCHO ($TiCl_4$), $RCH(OMe)_2$ ($TiCl_4$)

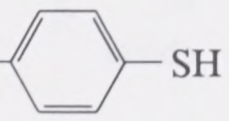
CC 578 (1979); 860 (1986)
Can J Chem *61* 688 (1983)



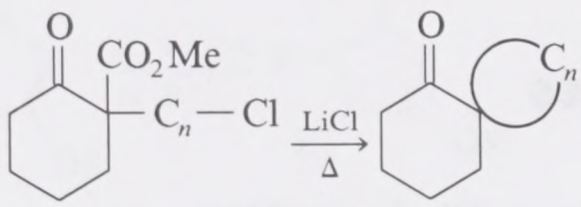
E^+	
RCHO, $TiCl_4$	JOC *51* 2423 (1986)
, $TiCl_4$, Ti(O-*i*-Pr)$_4$	JOC *52* 2105 (1987) (biaryl product)



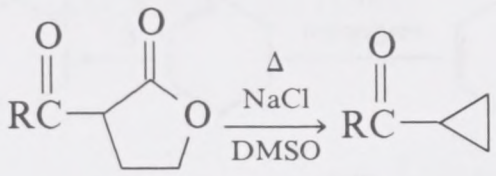
Review: Syn 893 (1982) (H_2O, salts and dipolar aprotic solvents)

H_2O, Δ	JOC *42* 459 (1977); *48* 2590 (1983)
B_2O_3	TL 3903 (1970) JOC *38* 3436 (1981) Syn Commun *11* 7 (1981)
Al_2O_3, aq dioxane	TL 2707 (1976)
cat Cs_2CO_3, 	JOC *51* 3165 (1986)
TsOH	JACS *66* 1286 (1944)
H_2SO_4	JACS *75* 3152 (1953)
CF_3CO_2H/Δ (R′ = *t*-Bu)	Syn 996 (1983)
H_2O, DMSO	TL 1091, 1095 (1974) JOC *43* 138 (1978); *52* 1880 (1987)
LiCl, H_2O, DMSO	JACS *107* 7967 (1985); *108* 3435 (1986) CC 265 (1986) TL *28* 1725 (1987) JOC *52* 1880 (1987)
LiCl, H_2O, DMF	TL *28* 5255 (1987)
LiCl, HMPA	CC 1351 (1987)

LiI·2 H_2O; 2,4,6-collidine	Org Syn *45* 7 (1965)
LiI·3 H_2O; 2,6-lutidine	JACS *107* 8066 (1985)
LiI·3 H_2O, DMF	JACS *106* 6690 (1984)
NaCl, H_2O, DMSO	TL 957 (1973); *28* 1439, 3131 (1987) JOC *51* 5450 (1986); *52* 28 (1987) JACS *109* 7477 (1987)
NaCl, H_2O, DMF	JACS *101* 7032 (1979)
$CaCl_2$·2 H_2O, DMSO	Syn 119 (1981) JOC *48* 2590 (1983)
$MgCl_2$, (RSH), HMPA or DMSO, Δ	Syn 119 (1981) TL *27* 3385 (1986)
Me_3SiI	Syn Commun *9* 233 (1979)
NaCN, HMPA	TL 3565 (1973)
DABCO	JOC *39* 2647 (1974)
DMAP, H_2O, Δ	TL *26* 3059 (1985)
~ 500°C	JOC *22* 1189 (1957)

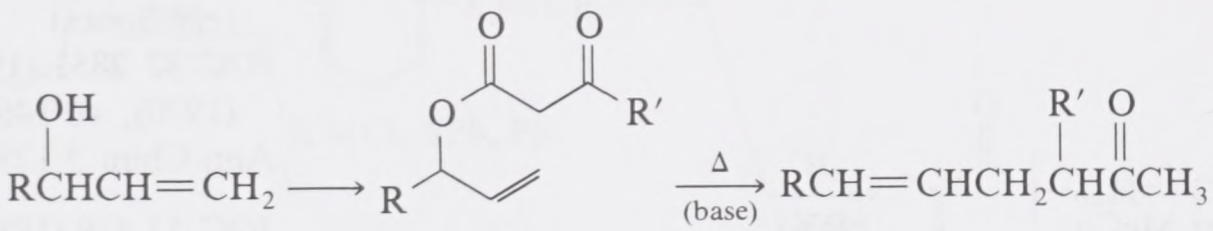


CC 30 (1981)

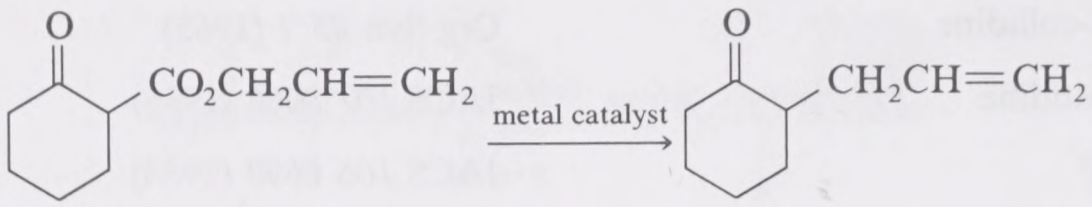


TL 4389 (1975)

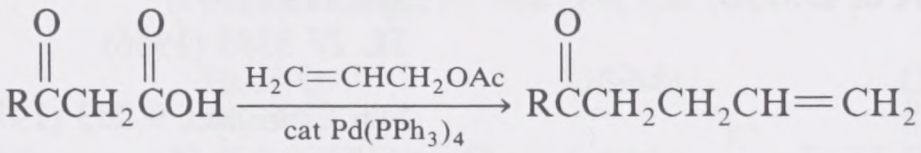
Carroll reaction



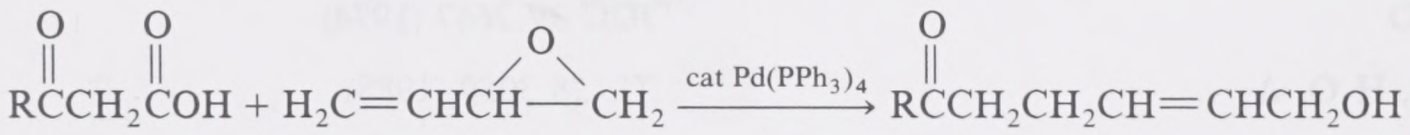
JCS 704, 1266 (1940); 507 (1941)
JACS *65* 1992 (1943); *102* 862 (1980)
JOC *23* 153 (1958) (propargylic alcohol); *33* 925 (1968); *49* 722 (1984)
TL 3253 (1969); *28* 4893 (1987) (on alumina)
Helv *57* 771 (1974)
CC 990 (1976)
Tetr *34* 2179 (1978)
Syn Commun *11* 237 (1981)
JCS Perkin I 2909 (1982)



Metal	
Mo, Rh, Ni	CL 1721 (1984)
Pd	TL *21* 3199 (1980); *23* 5279 (1982); *26* 5575 (1985) JACS *102* 6381 (1980) JOC *52* 2988 (1987)



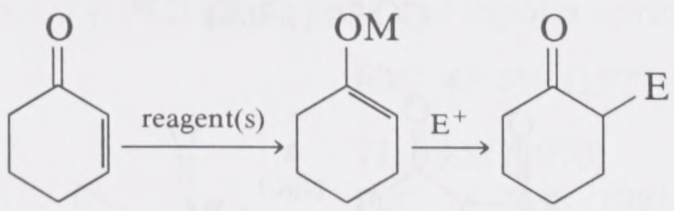
JOC *51* 421 (1986)



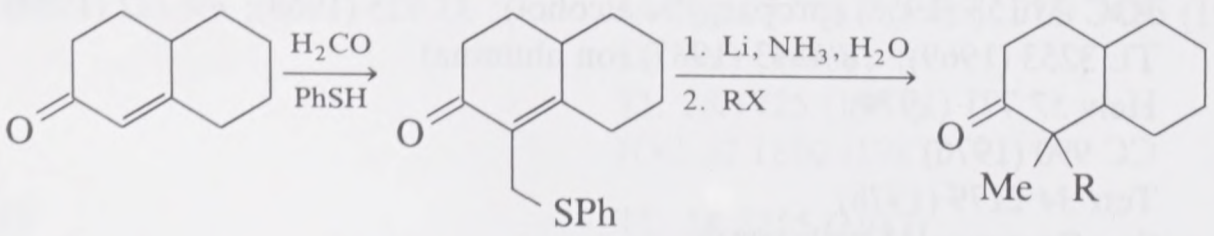
JOC *51* 5216 (1986)

21. Alkylation of Enones

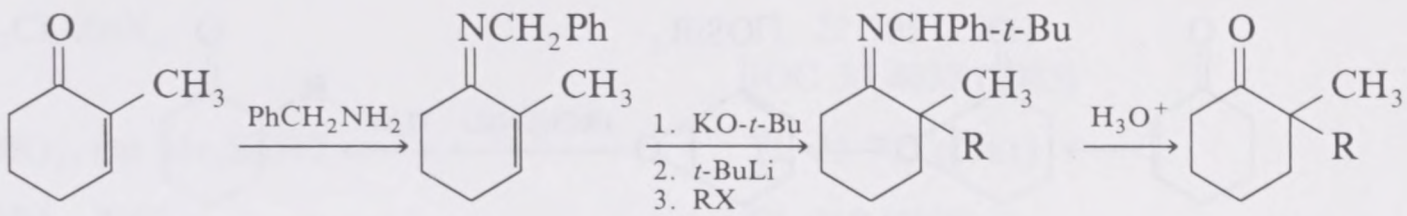
See also page 587, Section 1, and page 791, Section 15.



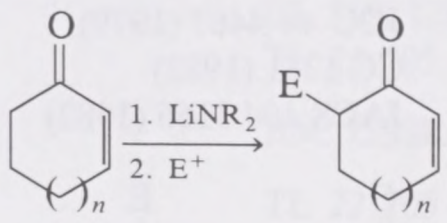
Reagent(s)	E^+	
Li, NH_3, *t*-BuOH	H_2O, RX, RCHO	JACS *87* 275 (1965); *89* 5464 (1967); *102* 1218, 1219 (1980) (enediones) JOC *32* 2851 (1967); *35* 1881 (1970); *40* 146 (1975) Ann Chim *5* 129 (1970)
i-Bu_2AlH, cat MeCu, HMPA/MeLi	RX	JOC *52* 439 (1987)
(Li)KHB(*sec*-Bu)$_3$	RX	JOC *41* 2194 (1976) JACS *107* 196 (1985)



JOC *49* 3685 (1984)

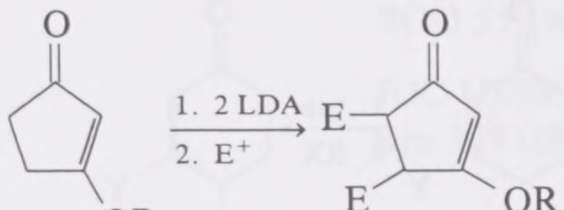


JACS *100* 292 (1978)



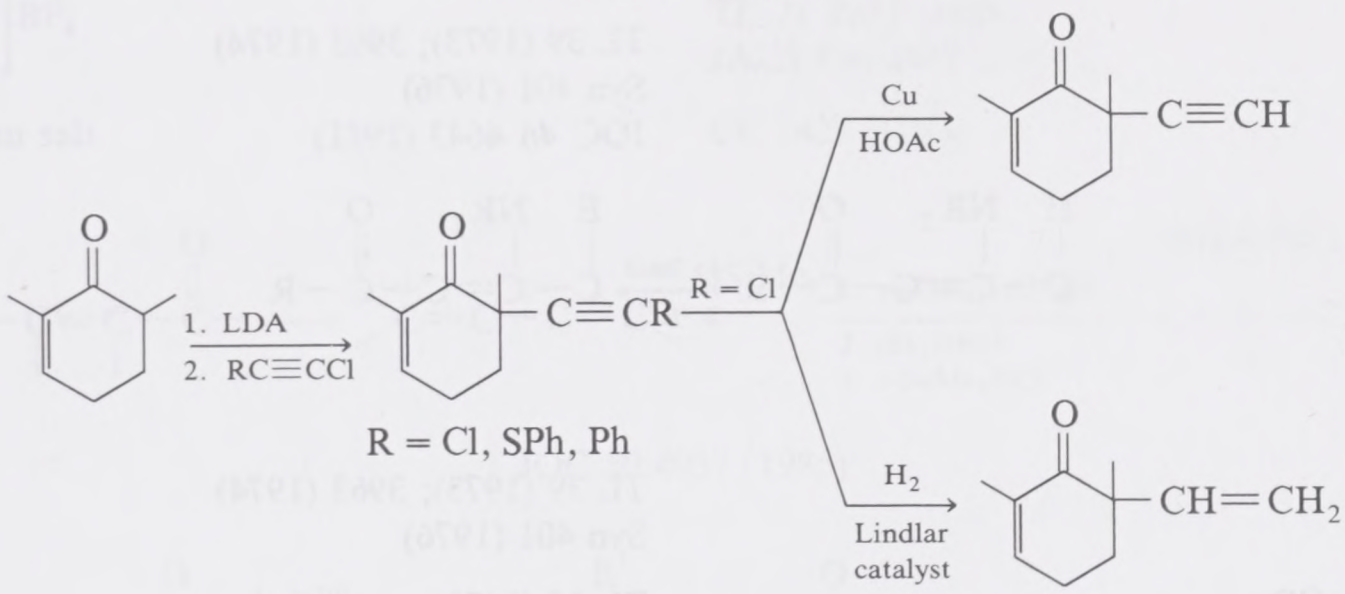
$n = 0, 1$; $E^+ = RX, RCHO, (MeO)_2CO$

TL 965 (1973); *22* 15 (1981); *23* 1631 (1982); *27* 4461 (1986); *28* 3027, 5441 (1987)
CC 564 (1973); 1720 (1987)
JOC *38* 1775 (1973); *40* 862 (1975); *44* 2593 (1979); *46* 4103, 4643 (1981); *48* 2318 (1983) (intramolecular alkylation); *52* 3346 (1987)
JACS *98* 2351 (1976); *106* 1443, 3539 (1984); *108* 1106 (1986)
Syn Commun *7* 345 (1977)
Tetr *35* 961 (1979)



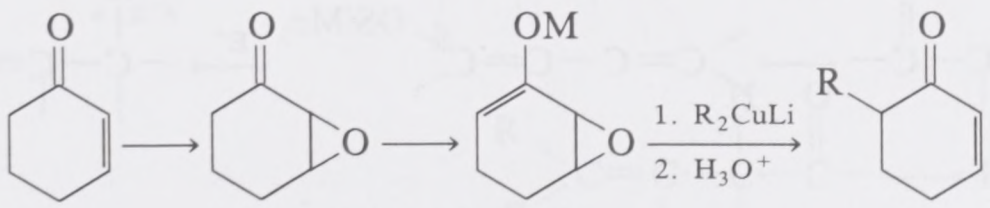
$E^+ = RX, RCHO$

CC 449 (1979)
JACS *105* 7203 (1983)



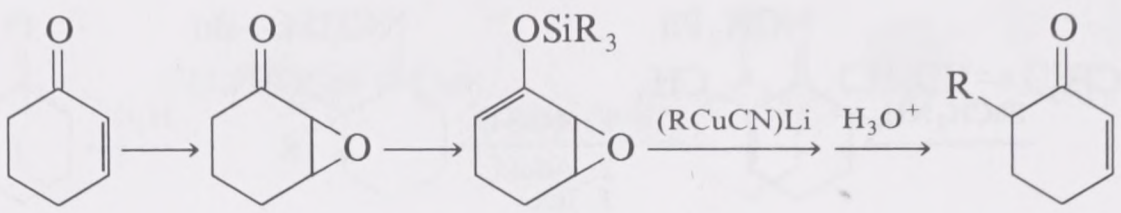
R = Cl, SPh, Ph

TL *23* 2373 (1982)



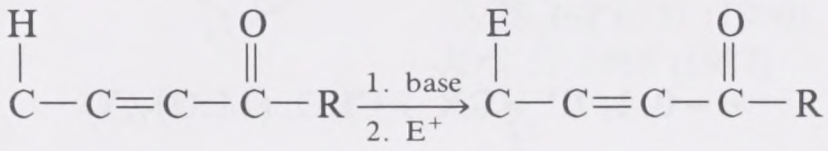
M = Li, $SiMe_3$

JACS *103* 2114 (1981)

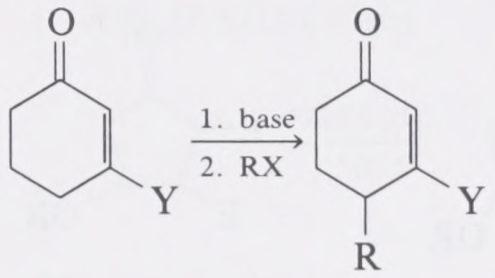


R = alkyl, aryl, not vinyl

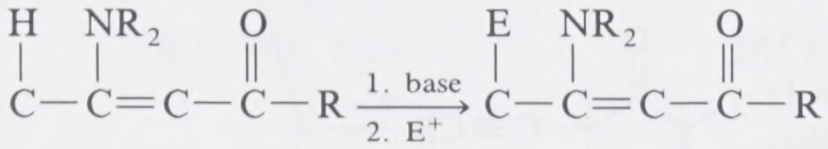
JOC *44* 4467 (1979)
CC 1331 (1982)
JACS *104* 3165 (1982)



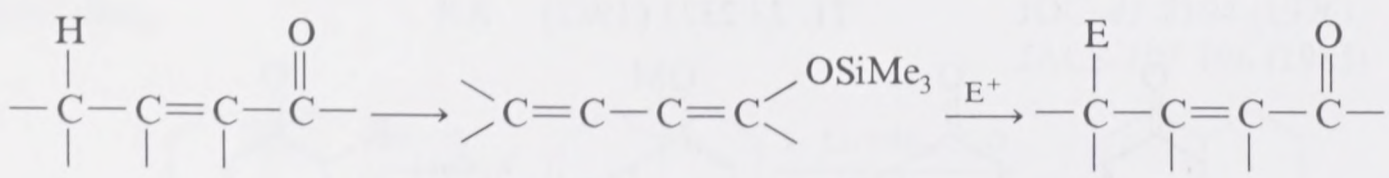
E^+	
RCHO	TL *21* 711 (1980)
RCHO, $ZnCl_2$	TL *26* 4097 (1985)
Br_2, $PhSO_2Cl$, PhSeBr	TL 4103 (1978)



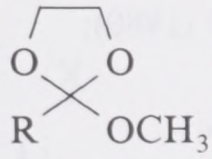
Y	
OR	TL *22* 15 (1981)
NR_2	TL 39 (1973); 3963 (1974) Syn 401 (1976) JOC *46* 4643 (1981)

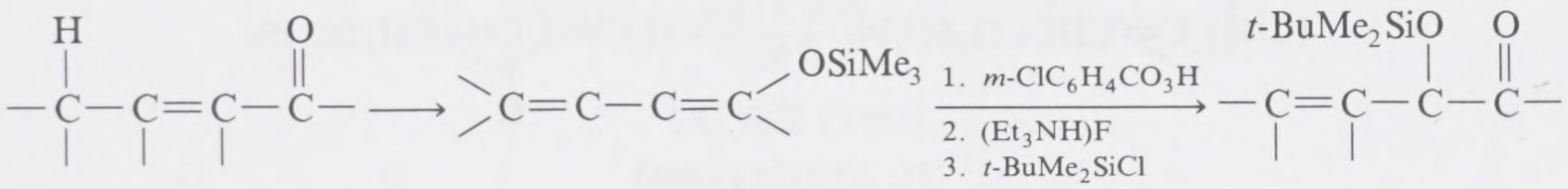


E^+	
RX	TL 39 (1973); 3963 (1974) Syn 401 (1976)
RCHO, R_2CO	TL 39 (1973)

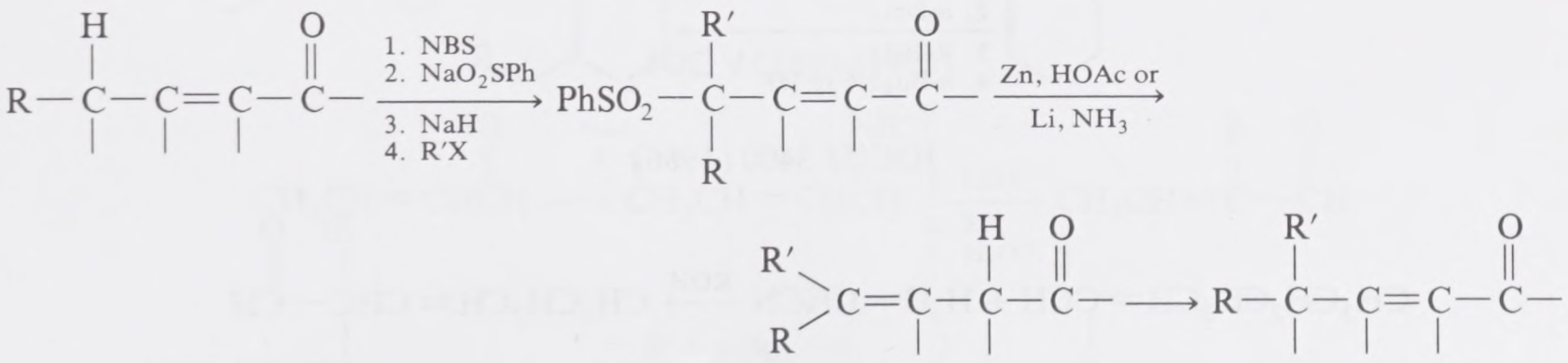


E^+	
PhSCl	TL 3205 (1979)
PhSCHClR, $ZnBr_2$	TL 3209 (1979); *22* 705 (1981); *24* 2913 (1983)

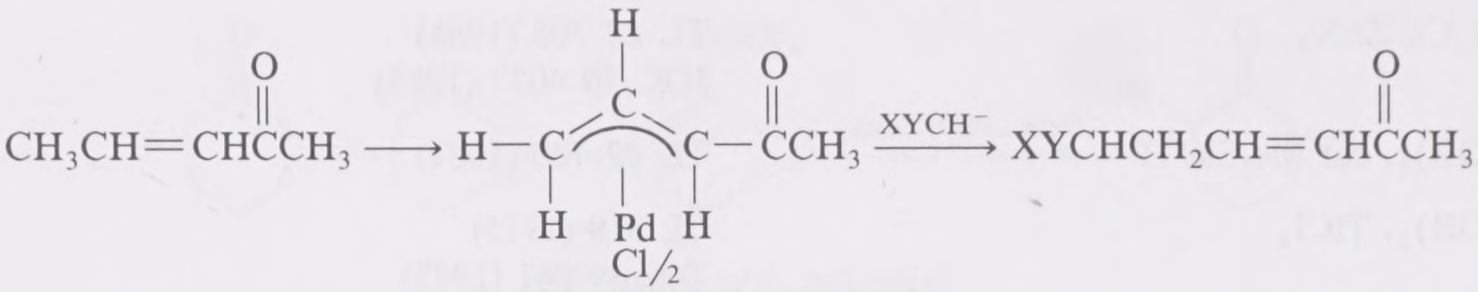
$ROCH_2Cl$, ZnX_2	TL *22* 705 (1981) JOC *50* 4037 (1985)
$RCH(OR)_2$, cat Me_3SiOTf	TL *22* 705 (1981)
$RCH(OR)_2$, $TiCl_4$	CL 319 (1975) Tetr *39* 841 (1983)
$RCH(OR)_2$, $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$	CL 319, 1201 (1975); 467 (1977) TL *22* 705 (1981)
$RCH(OR)_2$, $ZnCl_2$	JOC USSR *18* 1001 (1982)
$RCH(OR)_2$, $ZnBr_2$	TL *22* 705 (1981)
$R_2C(OR)_2$, $TiCl_4$	TL *22* 705 (1981)
RCHO, $TiCl_4$ or $BF_3 \cdot OEt_2$	TL *22* 705 (1981); *27* 4533 (1986) BCSJ *55* 1907 (1982) JOC *51* 3400 (1986)
$(RO)_3CH$, $BF_3 \cdot OEt_2$	BCSJ *55* 1907 (1987)
$(RO)_3CH$, $EtAlCl_2$	TL *27* 2703 (1986)
$(RO)_3CH$, $TiCl_4$	TL *22* 705 (1981) BCSJ *55* 1907 (1982)
$(RO)_3CH$, $ZnCl_2$	JOC USSR *18* 834 (1982) Syn 227 (1984)
 , $ZnCl_2$	Syn 227 (1984)
	TL *22* 2833 (1981) JACS *106* 4862 (1984)
pyridinium salt	CC 1425 (1983)



JOC *50* 4037 (1985)

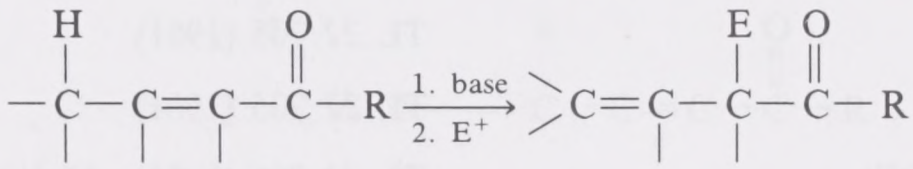


TL 2675 (1978)
JACS *102* 1602 (1980)

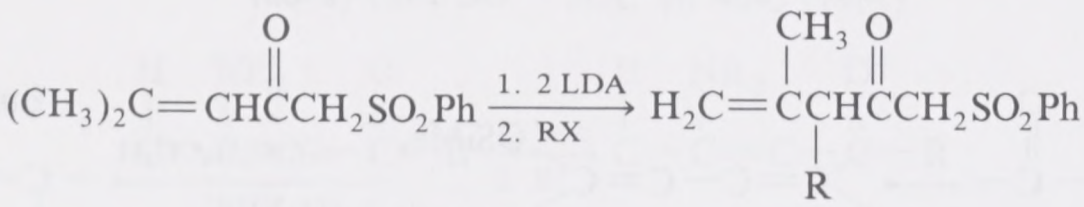


$X = CO_2R$; $Y = CO_2R$, CN, SO_2R

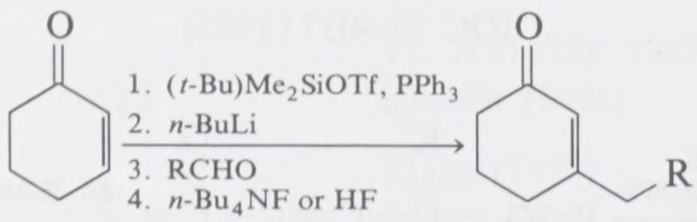
TL 1589 (1969); 2591 (1975)
Austral J Chem *30* 553 (1977)



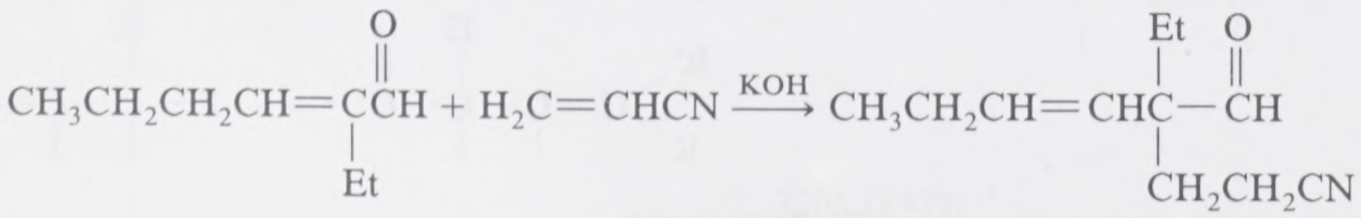
R	E^+	
H	RX	TL 1273 (1973); 1653 (1974)
alkyl	RX	JCS 1131 (1957); 4634, 4726 (1963) JACS *84* 284 (1962); *96* 7573 (1974); *108* 4556 (1986) Agric Biol Chem *28* 95 (1964) TL 1975 (1967); 459 (1968); 4103 (1978); *26* 4097 (1985) CC 611 (1969); 270 (1980); 75 (1986) JOC *35* 468 (1970); *51* 2408 (1986) CL 55 (1981) Syn Commun *12* 151 (1982)
	$RCHO, ZnCl_2$	TL *26* 4097 (1985)
	$RCOCl, RO_2CCl$	TL *26* 4097 (1985)



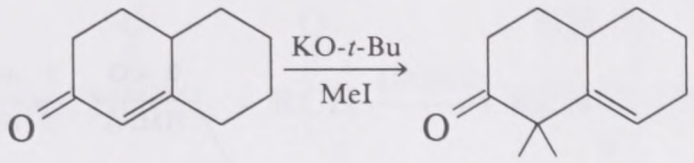
TL *27* 2725 (1986)



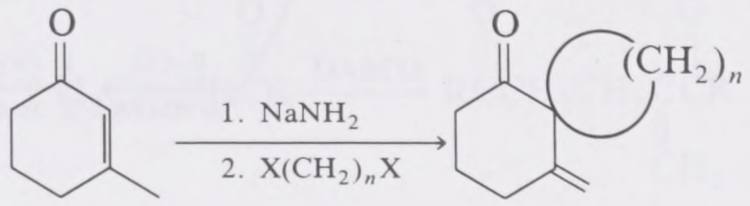
JOC *51* 3400 (1986)



JACS *66* 56 (1944)

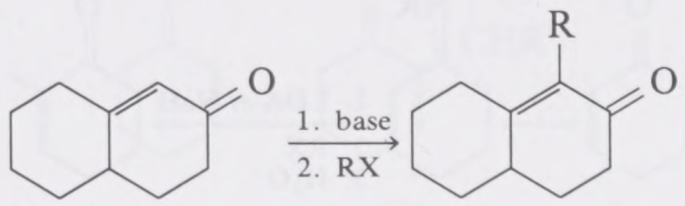


JACS *76* 2852 (1954); *79* 5542 (1957)
JCS 1131 (1957)
JOC *22* 602 (1957); *23* 841 (1958); *35* 186 (1970)

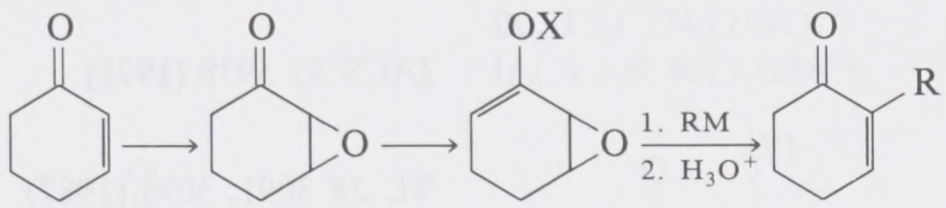


$n = 2, 4, 5$

JOC *31* 2171 (1966)

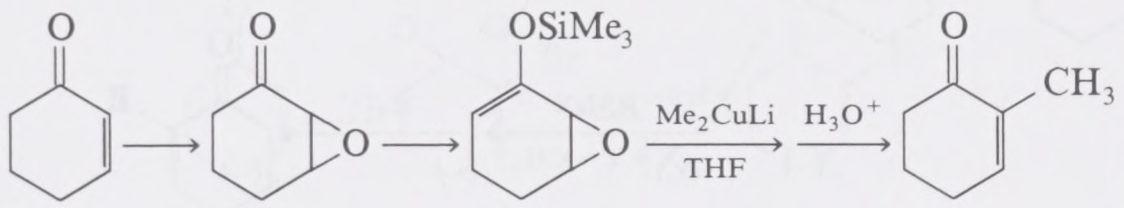


JACS *82* 2847 (1960); *108* 3841 (1986); *109* 3017 (1987)
JOC *32* 3008 (1967)

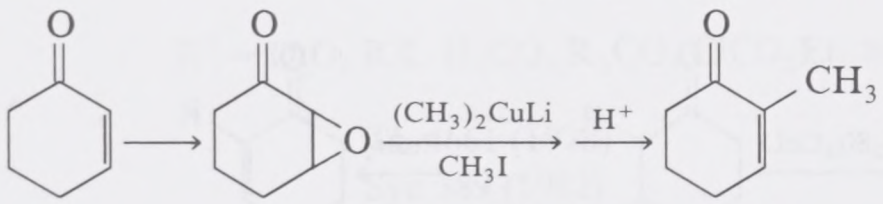


X	RM
Li	Ph_2CuLi, PhLi, PhMgBr
$SiMe_3$	Ph_2CuLi, $(H_2C{=}CH)_2$ CuMgBr

JACS *103* 2114 (1981)

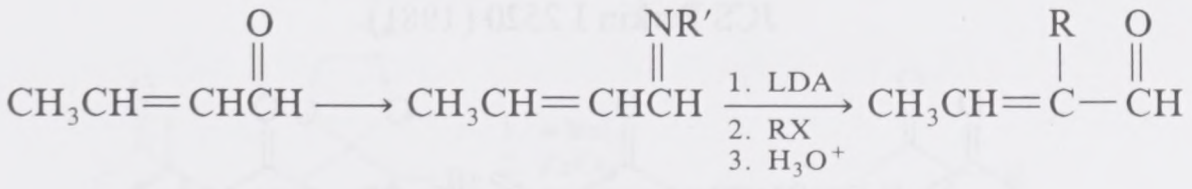


CC 1331 (1982)



(not general for other R's)

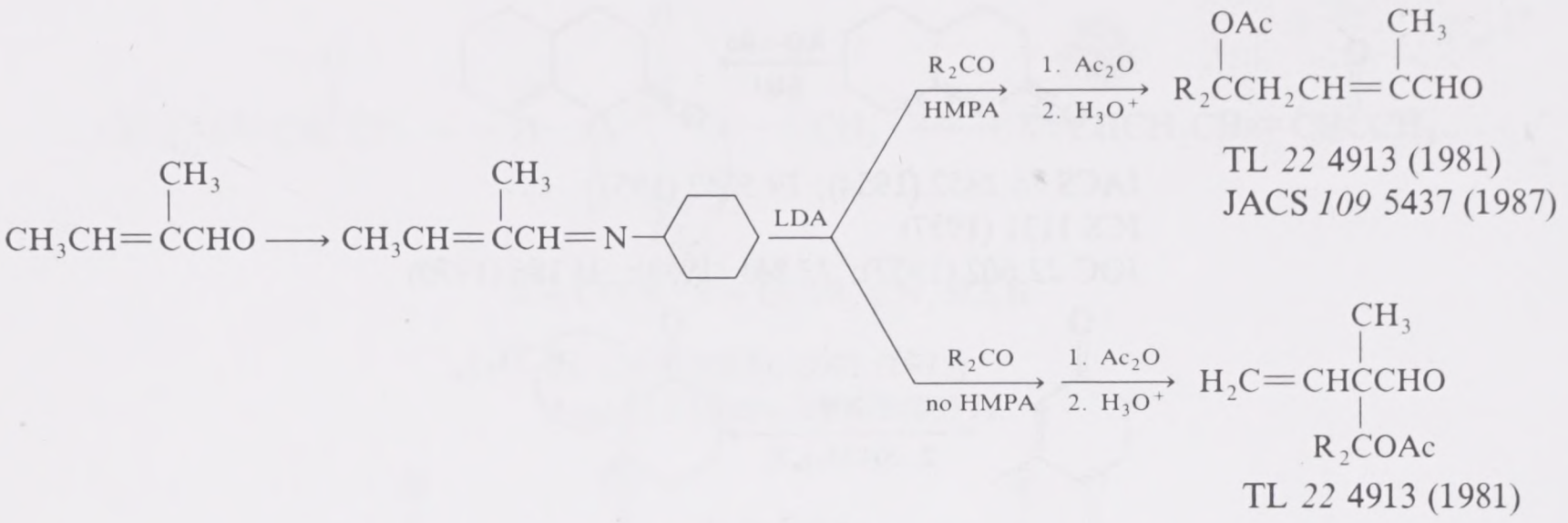
JOC *43* 1819 (1978)



$R' = t\text{-Bu}$,

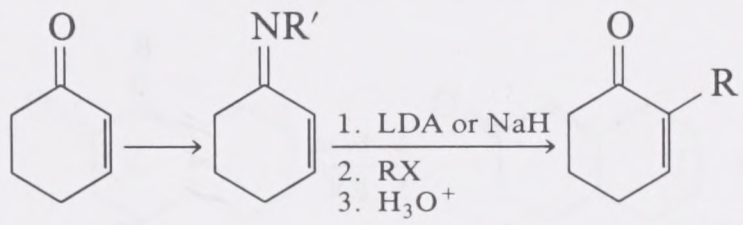


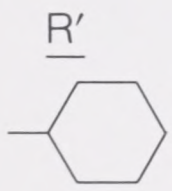
TL 1237 (1975); 597 (1976); *27* 4533 (1986)



TL *22* 4913 (1981)
JACS *109* 5437 (1987)

TL *22* 4913 (1981)

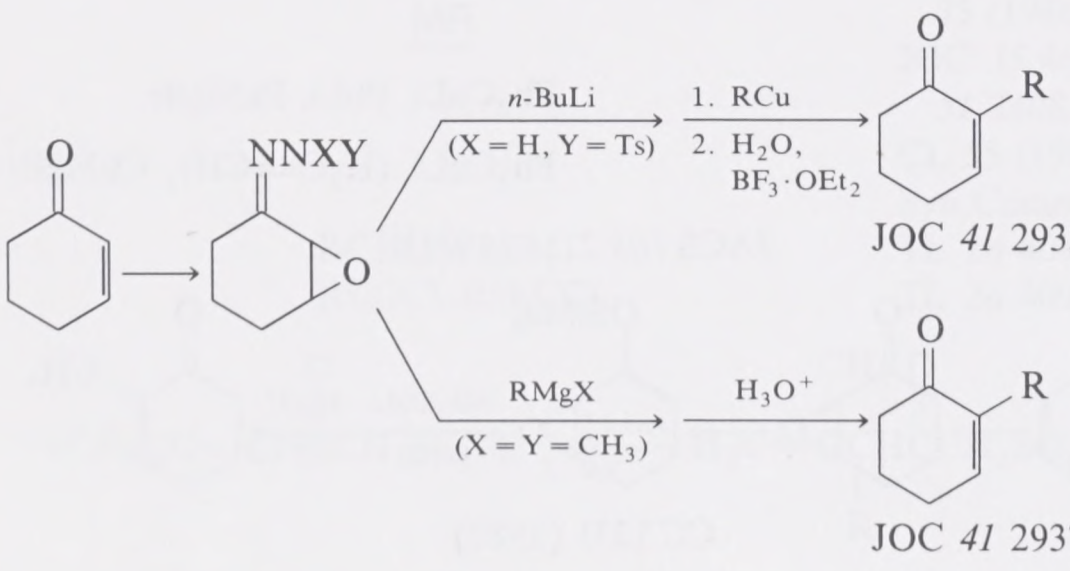




JACS *93* 5938 (1971)

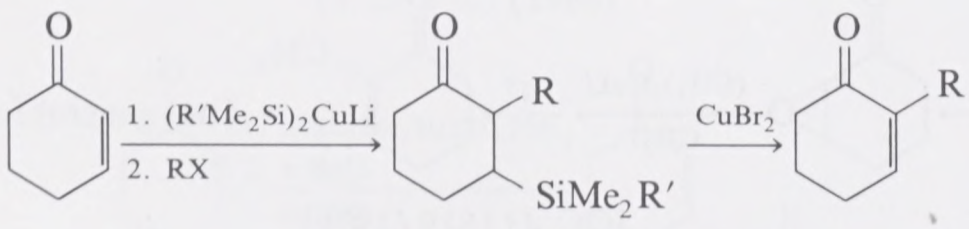
NMe_2

TL *28* 3091, 3095 (1987)

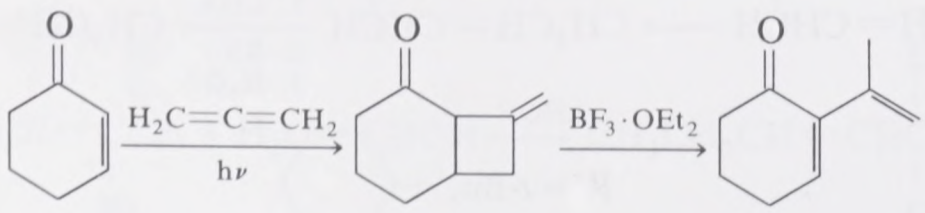


JOC *41* 2935 (1976)

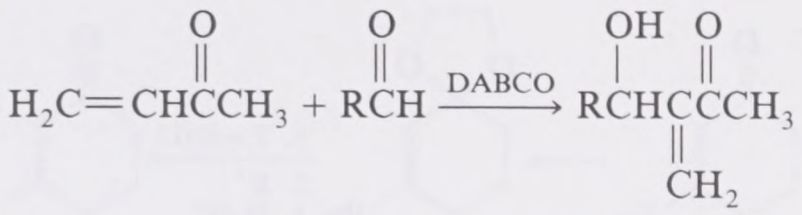
JOC *41* 2937 (1976)



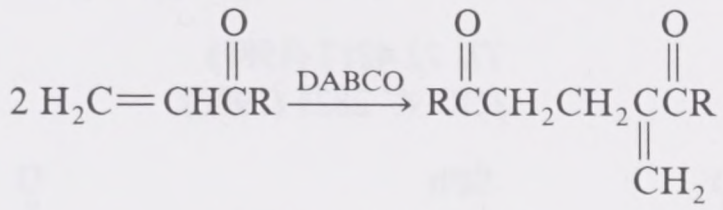
JCS Perkin I 2520 (1981)



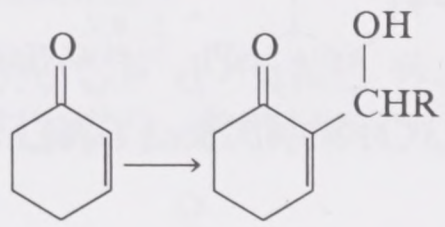
Syn 139 (1981)

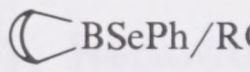


TL *27* 2031, 4307, 5007 (1986)



TL *28* 4591 (1987)

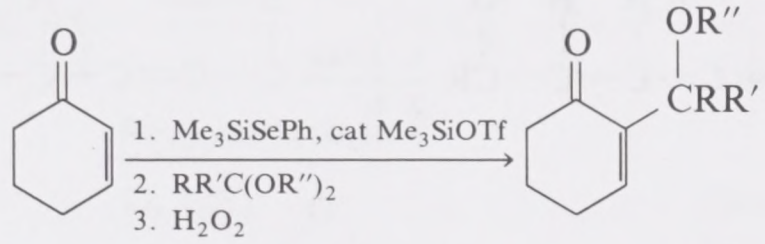




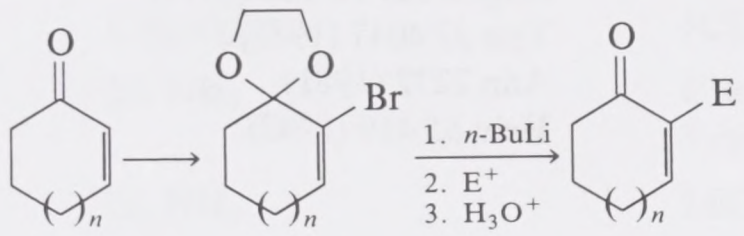
JOC *50* 730 (1985)

Me_2AlX (X = SMe, SPh or SeMe)/ RCHO/$NaIO_4$

TL *21* 361 (1980)
BCSJ *54* 274 (1981)
JACS *109* 8017 (1987)



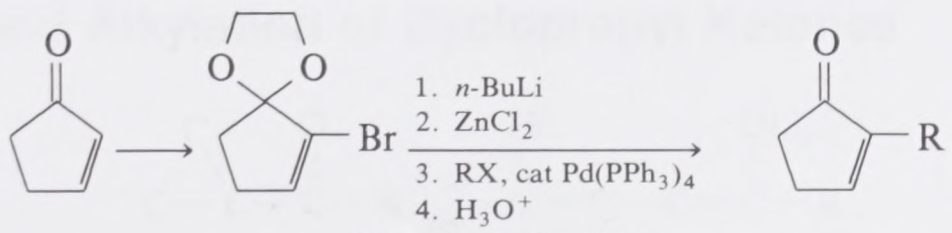
TL *22* 1809 (1981)



n = 0 or 1

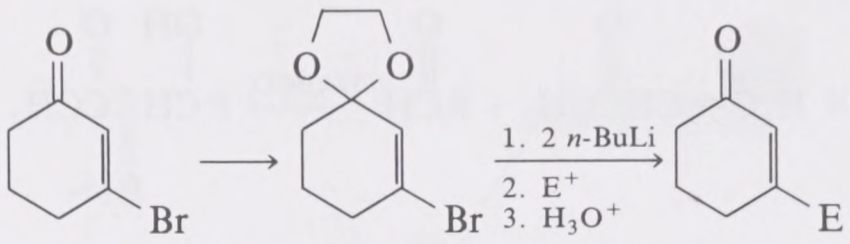
$E^+ = D_2O$, RX, H_2CO, R_2CO, $ClCO_2Et$, Me_2SiCl, $(MeS)_2$

TL 4661 (1978)
Syn 389 (1982)
JOC *47* 1855 (1982); *51* 1490 (1986)
JACS *108* 3385 (1986)



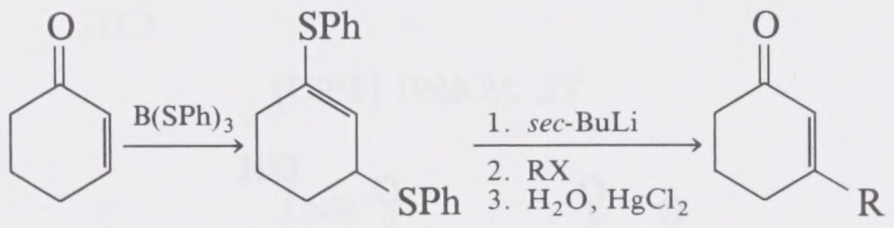
R = aryl, vinylic

CL 1007 (1987)

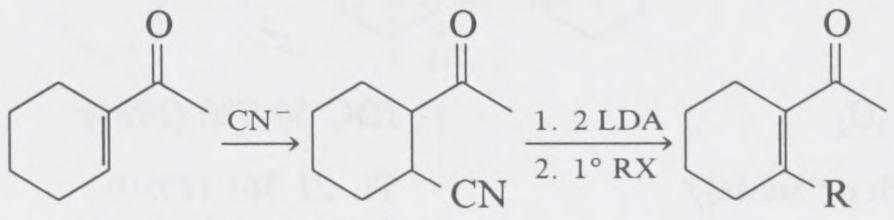


$E^+ = MeI, RCHO, R_2CO, CO_2, Me_3SiCl$

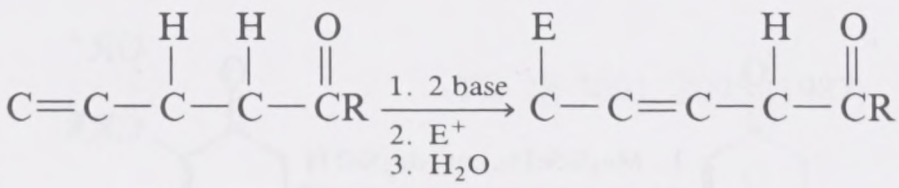
TL *22* 4217 (1981)
JOC *47* 2825 (1982)



JOC *41* 2506 (1976)



TL 3187 (1977)

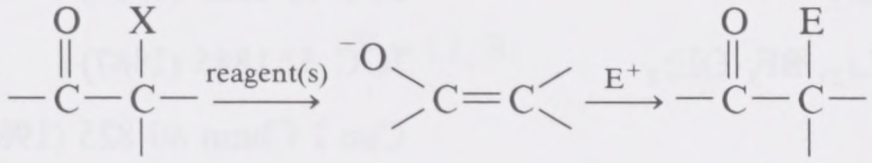


$E^+ = H_2O, D_2O, RX, RCH(O)CH_2, RCHO, R_2CO$

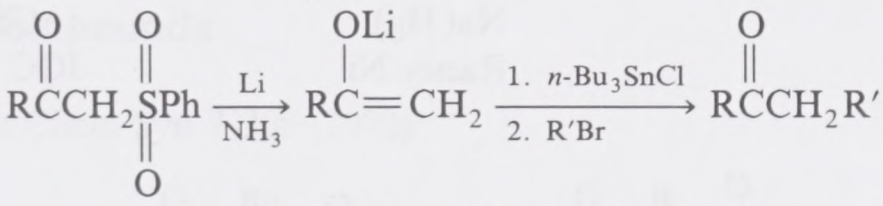
Angew Int *16* 320 (1977)
Tetr *37* 4047 (1981)
Ann 2272 (1981)
Helv *65* 419 (1982)

14. ALKYLATION OF α- AND β-SUBSTITUTED CARBONYL COMPOUNDS

1. Reduction of α-Substituted Ketones to Enolates



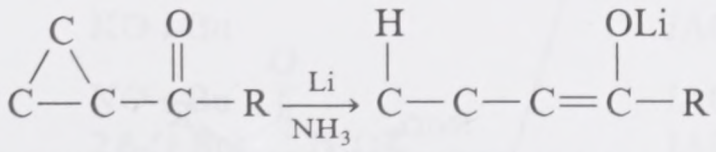
X	Reagent(s)	
Br	Li, NH_3	Chem Ind 118 (1963) Tetr *20* 357 (1964)
	Zn	JACS *89* 5727 (1967) Ann 459 (1982)
	CH_3MgBr	JCS 2933 (1965)
OH, OAc	Li, NH_3	Chem Ind 118 (1963) Tetr *20* 357 (1964)
CN	Li, NH_3	JACS *104* 2198 (1982)
HgCl	Li, NH_3	JOC *29* 1868 (1964)



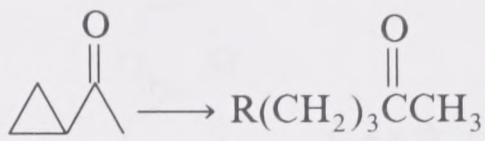
R′ = allylic, benzylic, propargylic

JOC *50* 3846 (1985)

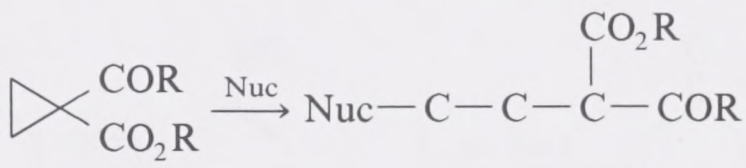
2. Reduction and Alkylation of Cyclopropyl Ketones



JOC *31* 3794 (1966); *35* 374, 2361 (1970); *52* 3000, 4634 (1987)
TL 2879 (1974)
Austral J Chem *33* 1061 (1980)
JACS *107* 7724, 7732 (1985); *108* 4149 (1986)



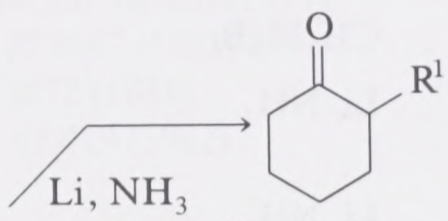
R_2CuLi	TL *24* 4543 (1983)
$R_2CuCNLi_2 \cdot BF_3$	TL *24* 5521 (1983)
$(\mathbf{RCH{=}CH}CuC{\equiv}CC_3H_7)Li$	JCS Perkin I 683 (1983)



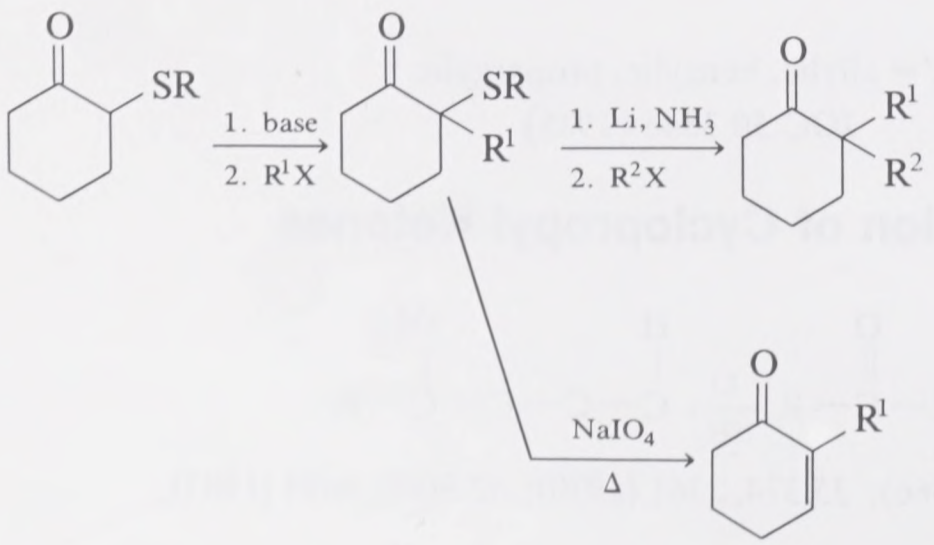
Review: Acct Chem Res *12* 66 (1979)

Nuc	
R_2CuLi	TL 529 (1975); 3857 (1976) Can J Chem *60* 825 (1982)
$(RCuCH_2SOCH_3)Li$, $BF_3 \cdot OEt_2$	JOC *52* 1885 (1987)
$[RCu(CN)CH_2SOCH_3]Li_2$	JOC *52* 1885 (1987)
$[RCu(CN)CH_2SOCH_3]Li_2$, $BF_3 \cdot OEt_2$	JOC *52* 1885 (1987)
Et_2AlCN (Nuc = CN)	Can J Chem *60* 825 (1982)

3. Reduction and Alkylation of Ketones Containing Sulfur in the α-Position

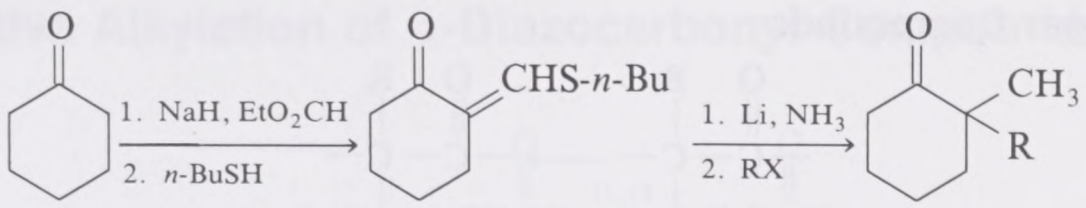


Li, NH_3	Syn Commun *3* 265 (1973)
lithium 1-dimethyl-aminonaphthalenide	TL *22* 3377 (1981)
Na(Hg)	JACS *107* 7724, 7732 (1985)
Raney Ni	JOC *50* 2589 (1985)

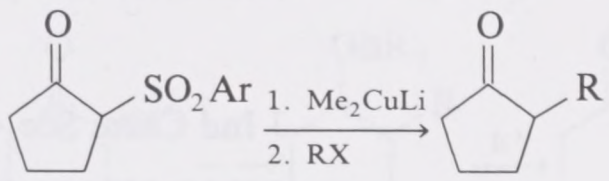


Angew Int *12* 586 (1973)
Syn Commun *3* 265 (1973)
TL 3955 (1973); *22* 3377 (1981)

JACS *108* 3385 (1986)



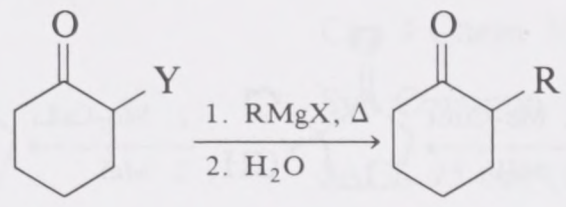
JACS *93* 1027 (1971); *104* 2198 (1982)



JACS *107* 1239 (1985)

4. Substitutive Alkylation of α-Halocarbonyl Compounds

4.1. Organomagnesium Compounds



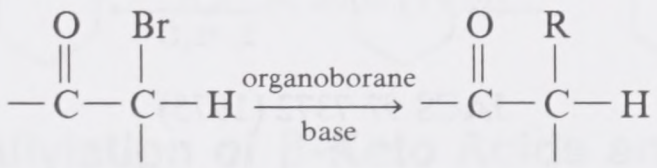
Y = Cl, Br

R

alkyl (low yields)	JACS *56* 1990 (1934); *73* 1993 (1951) Compt Rend *198* 941 (1934) JOC *37* 4090 (1972)
aryl	JACS *66* 1550 (1944); *70* 495 (1948); *71* 3313 (1949); *72* 1995 (1950) JOC *12* 737 (1947); *19* 1363 (1954); *24* 843 (1959)
vinylic	TL *22* 2243 (1981) Tetr *37* 3967 (1981) JCS Perkin I 225 (1987)

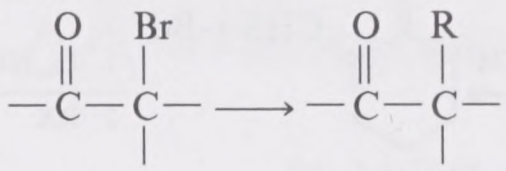
4.2. Organoboron Compounds

Review: Organomet Chem Syn *1* 305 (1972)



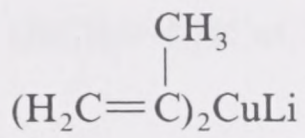
Organoborane	Base	
R_3B	KO-*t*-Bu	JACS *90* 6218 (1968)
R-9-BBN	KO-*t*-Bu	JACS *91* 2147, 4304 (1969)
	$2,6\text{-}(t\text{-Bu})_2C_6H_3OK$	JACS *91* 6852 (1969) JOC *51* 3398 (1986) (R = vinylic)

4.3. Organocopper Compounds



Me_2CuLi

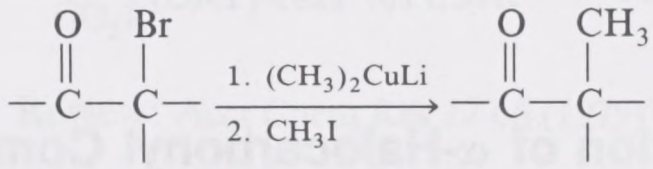
TL 177 (1971)
JOMC *153* 259 (1983)



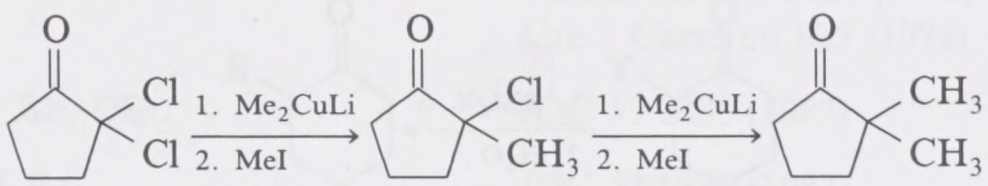
J Ind Chem Soc *45* 1026 (1968)

(MeCuCN)Li

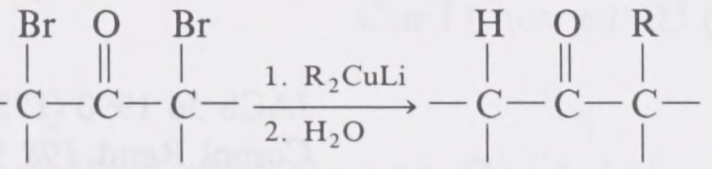
JOMC *153* 259 (1983)



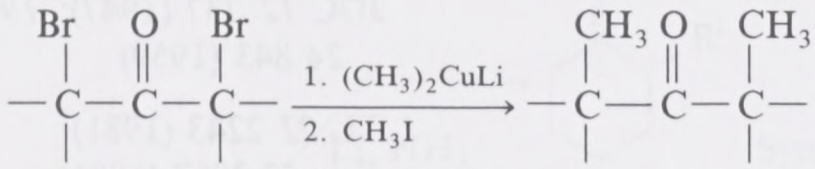
JACS *95* 3076, 7788 (1973)
Tetr *31* 1223, 1227 (1975)



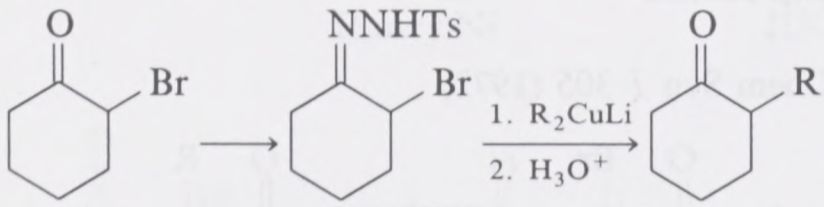
JOC *45* 2036 (1980); *48* 4763 (1983)
JACS *105* 2435 (1983)



JACS *95* 3076, 7788 (1973) (both R = Me)
Tetr *31* 1223, 1227 (1975) (both R = Me)
TL *27* 4671 (1986) (R = Ph)

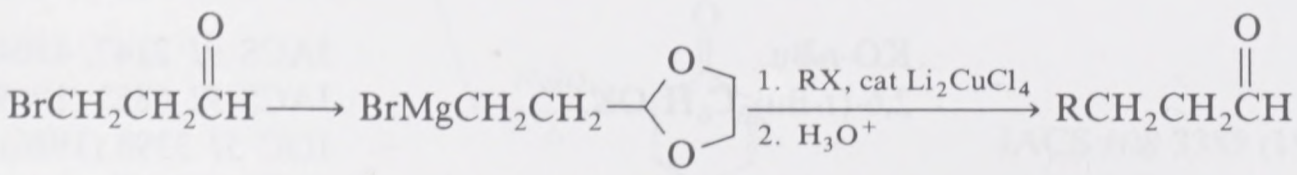


JACS *95* 3076, 7788 (1973)
Tetr *31* 1223, 1227 (1975)



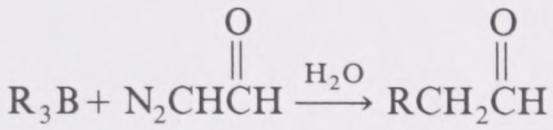
JACS *97* 7372 (1975)

5. Substitutive Alkylation of β-Halocarbonyl Compounds

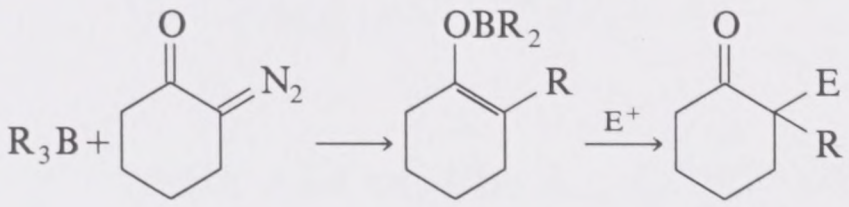


JOC *48* 1767 (1983)

6. Substitutive Alkylation of α-Diazocarbonyl Compounds

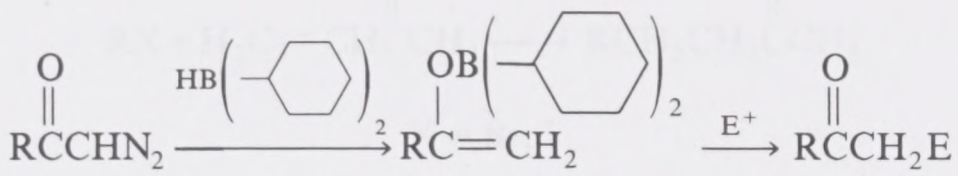


Can J Chem *48* 868 (1970)



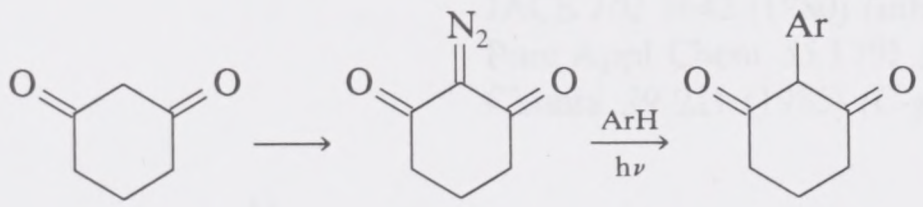
E^+	
H_2O or D_2O	JACS *90* 5936 (1968); *91* 6195 (1969) CC 139 (1969) Can J Chem *49* 2371 (1971)
NCS or NBS	Can J Chem *50* 2387 (1972)
PhSeCl	Syn Commun *10* 667 (1980)
$(Me_2N{=}CH_2)I$	JACS *95* 602 (1973)
2 RLi/R′X (E = R′)	JOC *36* 1790 (1971)
$Me_2NCH_2CH_2OLi$/R′X (E = R′)	Syn Commun *10* 139 (1980)
R′CN/H_3O^+ (E = COR′)	Syn Commun *12* 189 (1982)

For other reactions of boron enolates see page 647, Section 7.



$E^+ = (Me_2N{=}CH_2)I$, RCHO, R_2CO

JOC *52* 1347 (1987)



JOC *44* 4906 (1979)

7. Decarboxylation-Allylation of β-Keto Acids and Esters

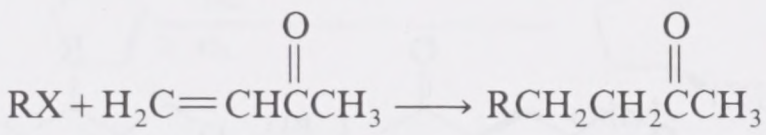
See page 768, Section 20.

15. 1,4-ADDITION TO α,β-UNSATURATED CARBONYL COMPOUNDS

See also page 724, Section 2; and page 746, Section 7.1.

1. Free Radical and Related Addition Reactions

See also page 814, Section 16.



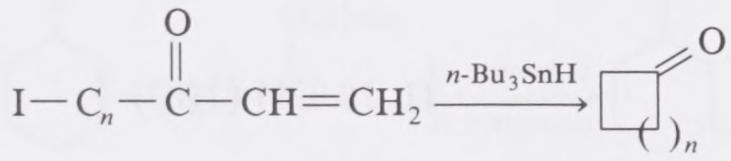
X = Br, I

n-Bu_3SnH

TL *28* 5853 (1987) (C-glycosides)
Ann 427 (1987)

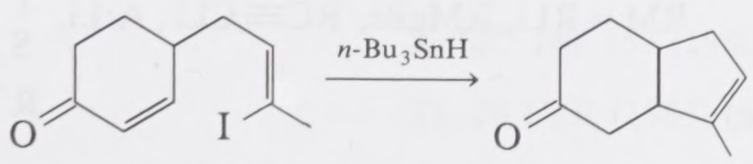
vitamin B_{12}, reductant

JACS *102* 3642 (1980) (intramolecular)
Pure Appl Chem *55* 1791 (1983) (review)
Chimia *39* 211 (1985) (C-glycosides)

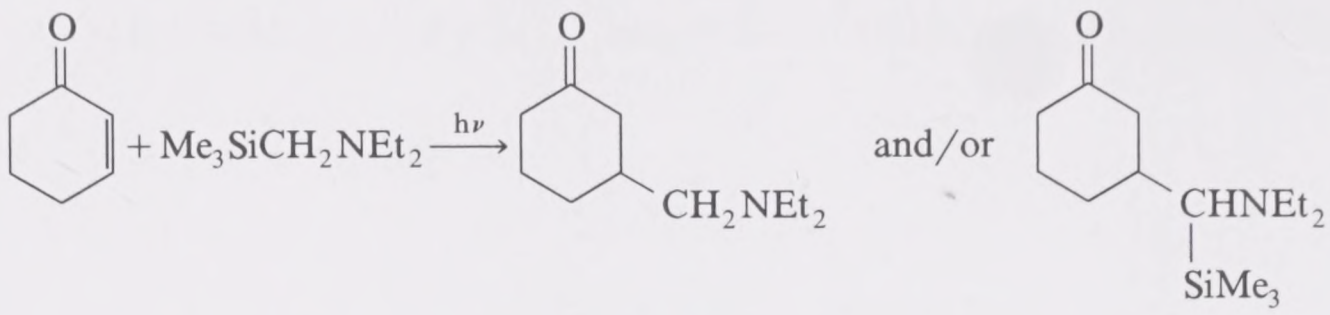


n = 7, 11, 15

JACS *108* 2787 (1986)



TL *24* 1871 (1983)

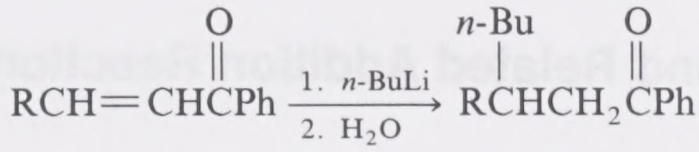


JACS *109* 4421 (1987)

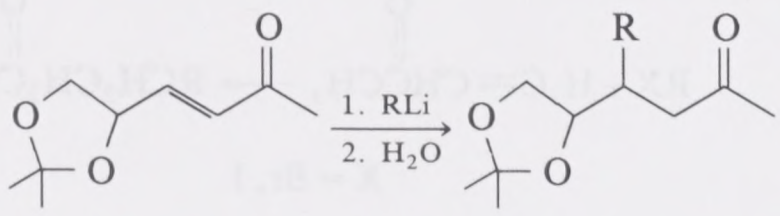
2. Michael and Michael-like Addition Reactions

Reviews of and key references to the Michael reaction:

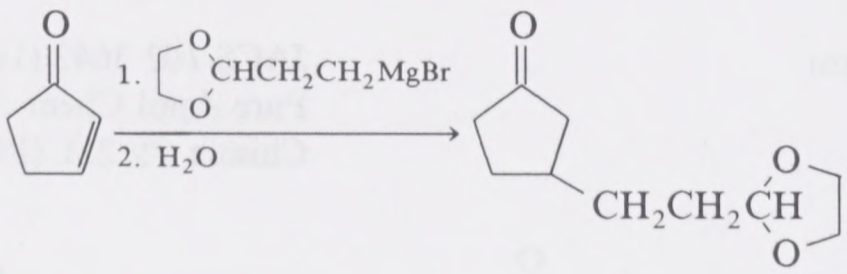
Org Rxs *10* 179 (1959) (review)
Syn 107 (1979) (phase transfer)
JOC *44* 2239 (1979) (asymmetric); *48* 4642 (1983) (annulation)
Angew Int *19* 1013 (1980) (high pressure); *20* 770 (1981) (high pressure, F^- catalyzed)
K. Tomioka and K. Koga in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Part A, Chpt 7 (asymmetric additions, review)
TL *24* 3841 (1983) (high pressure)



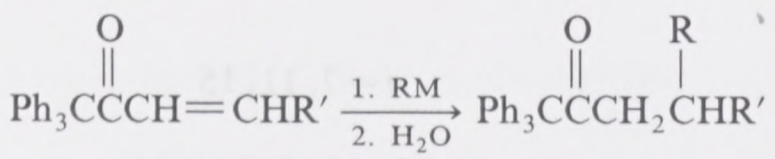
JOC *49* 1144 (1984)



TL *28* 2525 (1987)



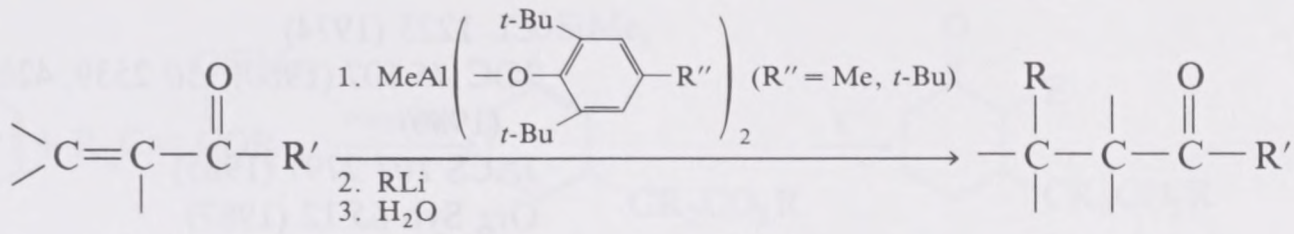
TL *28* 3217 (1987)



RM = RLi, RMgBr, RC≡CLi, ArLi,

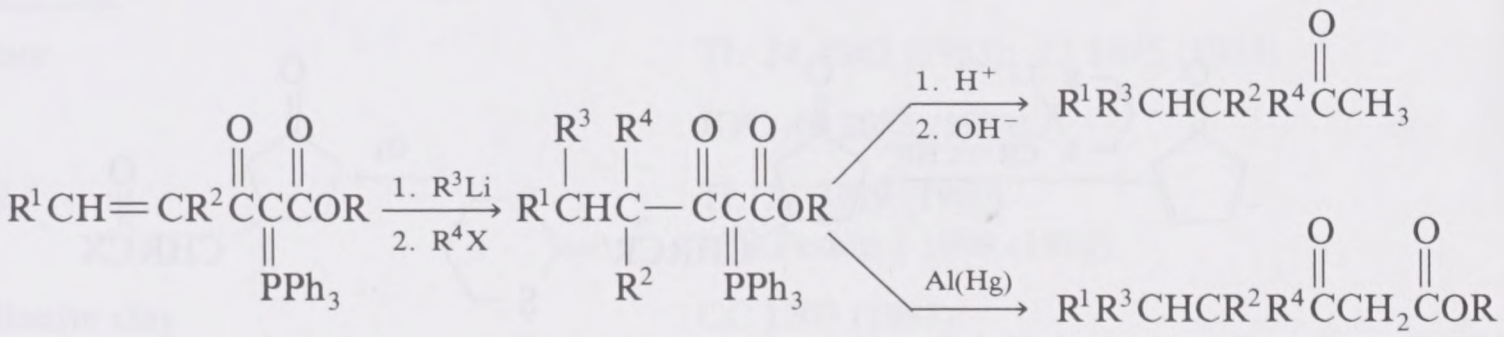


Helv *68* 264 (1985)

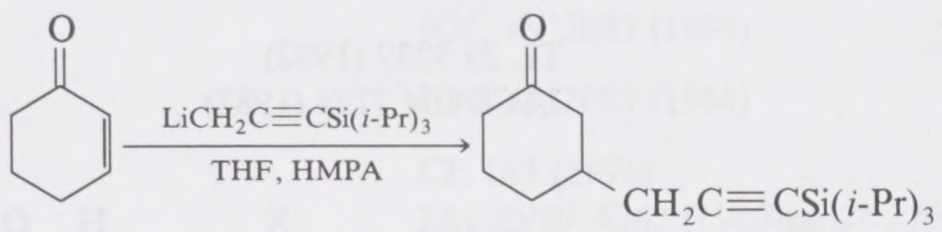


R = 1°, 2°, 3° alkyl; aryl; vinylic; ester enolate

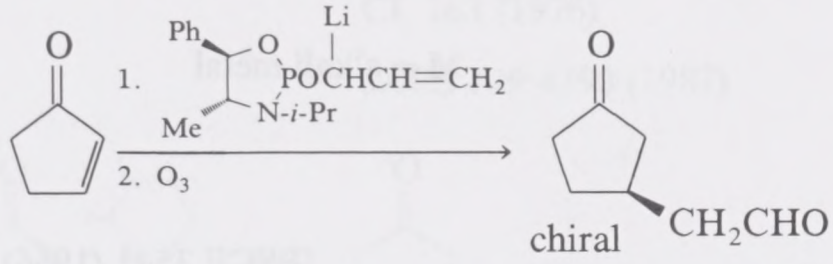
TL *28* 5723 (1987)



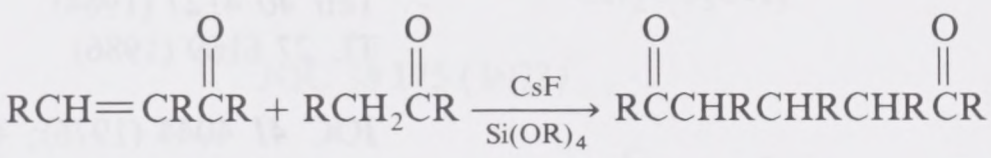
JOC *47* 4955, 4963 (1982); *52* 1381 (1987) (intramolecular)



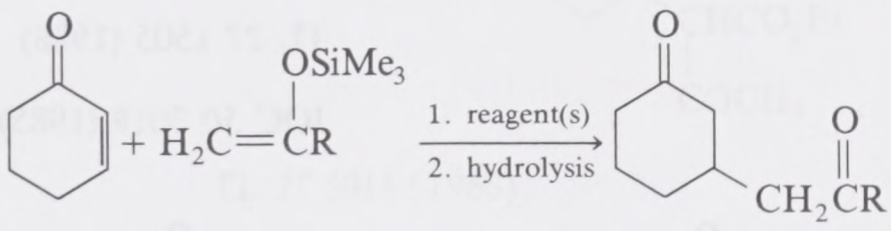
TL *23* 719 (1982)



JACS *109* 5026 (1987)



CC 122 (1981)
Tetr *39* 117, 999 (1983)



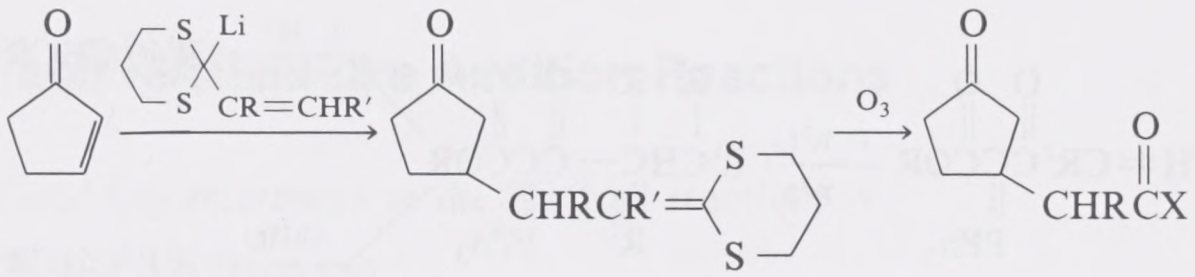
Reagent(s)	
montmorillonite clay	CC 1203 (1987)
cat $(Ph_3C)ClO_4$	CL 953 (1985); 1017 (1986)
CsF	JOMC *184* 157 (1980)
$BF_3 \cdot OEt_2$, ROH	TL *26* 6201 (1985) (also methyl enol ethers used)
$SnCl_4$	JACS *107* 2797 (1985)

$TiCl_4$

CL 1223 (1974)
JOC *45* 607 (1980); *50* 2539, 4266 (1985); *51* 279 (1986)
JACS *107* 2797 (1985)
Org Syn *65* 12 (1987)

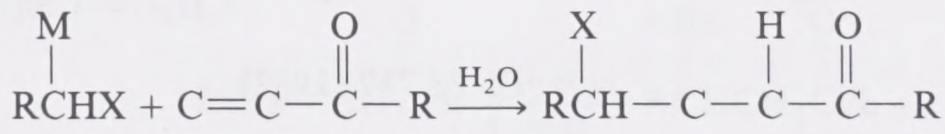
$TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$

CL 1223 (1974)
BCSJ *49* 779 (1976)
JOC *43* 2720 (1978); *50* 4266 (1985)



X = R′, OEt

TL *23* 3237 (1982)
JACS *104* 7174 (1982)



M = alkali metal

X

COR

BSCF 3543 (1966)
JOC *42* 183 (1977)
Tetr *40* 4127 (1984)
TL *27* 6169 (1986)

CO_2R

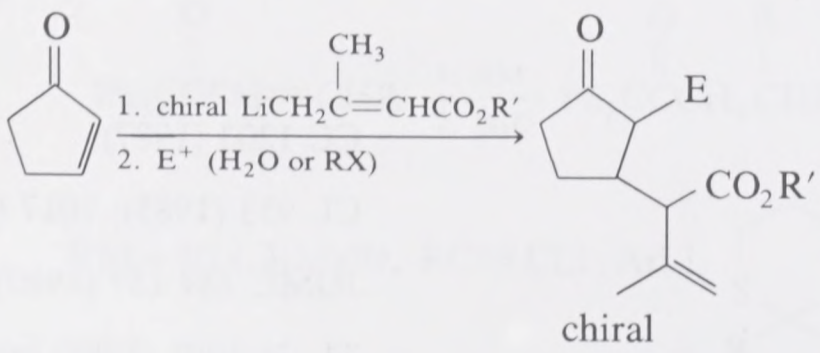
JOC *41* 4044 (1976); *47* 3464 (1982); *50* 3022 (1985)
J Polym Sci, Polym Chem Ed *17* 3509 (1979)
TL *27* 3927 (1986) (intramolecular)

CS_2Me

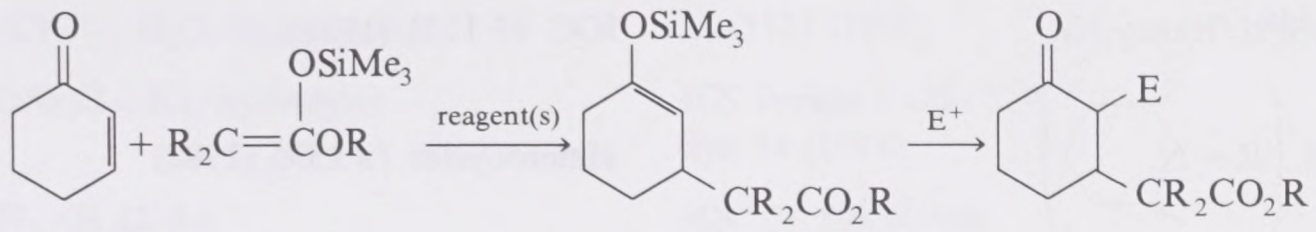
TL *27* 1505 (1986)

$CONR_2$

JOC *50* 3019 (1985)



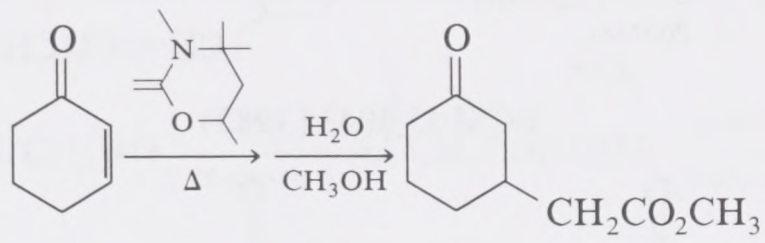
TL *24* 4975 (1983)



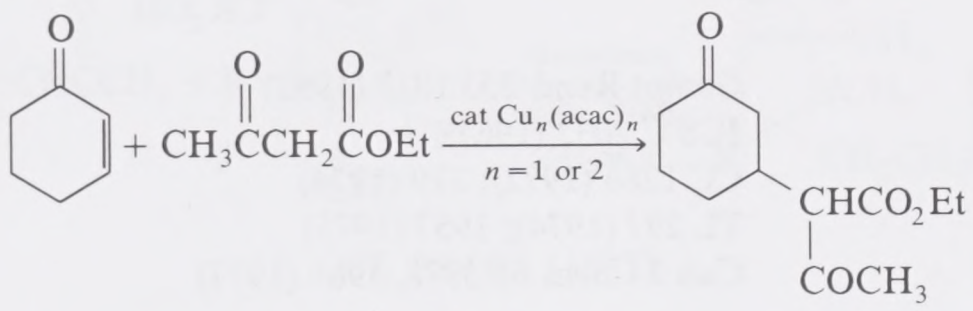
E^+ = NBS; PhSeCl; H_3O^+; PhSCHClR, $ZnBr_2$; RX, $[(Me_2N)_3S]Me_3SiF_2$

Reagent(s)

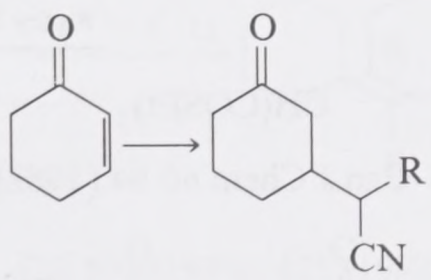
high pressure	TL *24* 4943 (1983); *25* 1075 (1984)
CH_3NO_2	JOC *49* 2083 (1984)
Δ, CH_3CN	TL *21* 3779 (1980) JCS Perkin I 1099 (1982)
montmorillonite clay	CC 1203 (1987)
cat $(Ph_3C)ClO_4$	CL 1817 (1986)
cat $[(Me_2N)_3S]Me_3SiF_2$	JOC *49* 2083 (1984)
cat Me_3SiCl, CH_3NO_2	JOC *49* 2083 (1984)
$TiCl_4$	CL 163 (1976) JACS *102* 4262 (1980); *107* 2797 (1985) JOC *45* 237 (1980); *51* 279 (1986)
$TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$	CL 163 (1976)
ZnI_2	JACS *109* 4390 (1987)



JOC *38* 175 (1973)



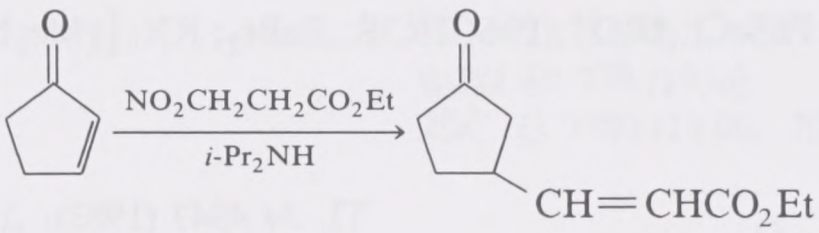
TL *27* 5015 (1986)

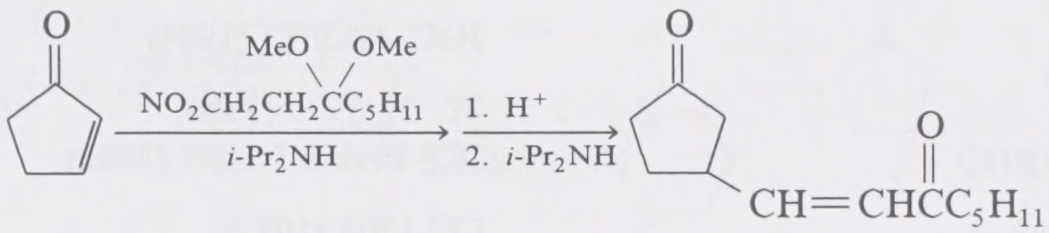


ArCHLiCN	Syn Commun *11* 85, 335 (1981) TL *22* 2171 (1981)

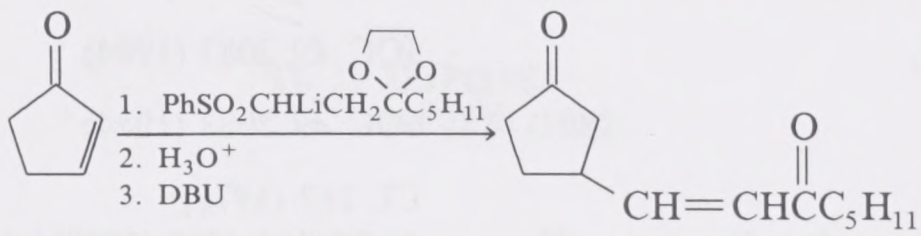
RCLi(CN)SPh/Raney Ni — JOC *47* 1131 (1982)

RCHLiCN (R = N) — Heterocycles *19* 1395 (1982)

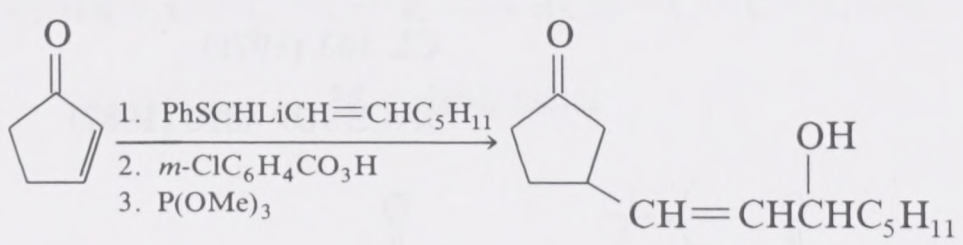




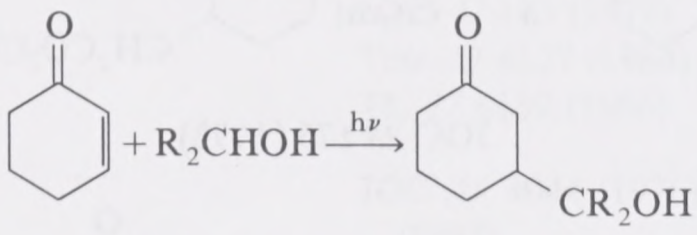
TL 2371 (1978)



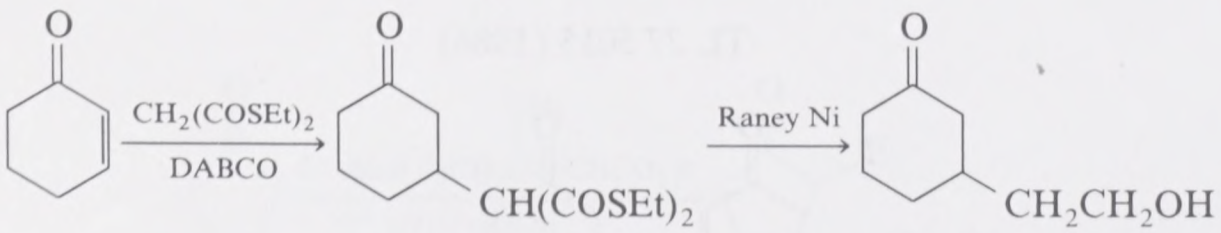
CL 607 (1982)



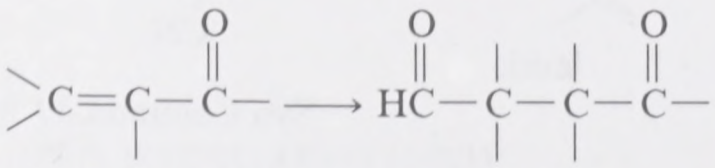
BCSJ *55* 3043 (1982)



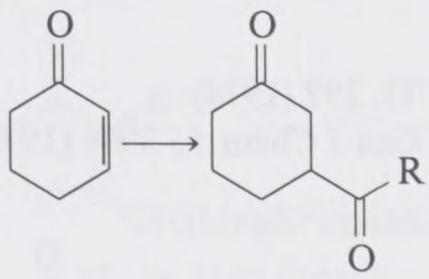
Compt Rend *255* 1817 (1962)
JCS C 2032 (1967)
CC 1286 (1972); 319 (1974)
TL 297 (1974); 1957 (1975)
Can J Chem *55* 3978, 3986 (1977)



Can J Chem *60* 94 (1982)



$LiC(SPh)_3/CrCl_2$, H_2O/hydrolysis	TL 3533 (1978)
$ArSCHLiSOAr/I_2$, KI/hydrolysis	JCS Perkin I 1284 (1981) Syn 74 (1981)
$TsCHLiSCH_3/H_2O$, hν	JOC *51* 508 (1986)



See subsequent sections on organometallic compounds and page 709, Section 9.

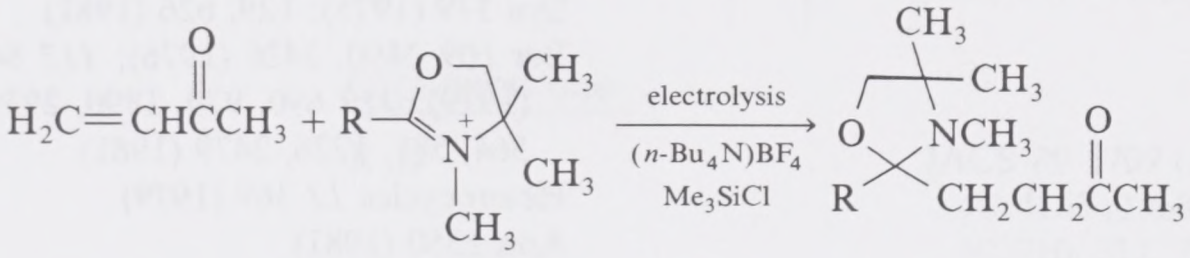
$$R_2CHNO_2 + H_2C{=}CHX \xrightarrow{\text{base}} R_2\overset{\displaystyle NO_2}{\overset{|}{C}}CH_2CH_2X$$

$$X = COR, CN, CHO, SOPh, SO_2Ph, CO_2Me$$

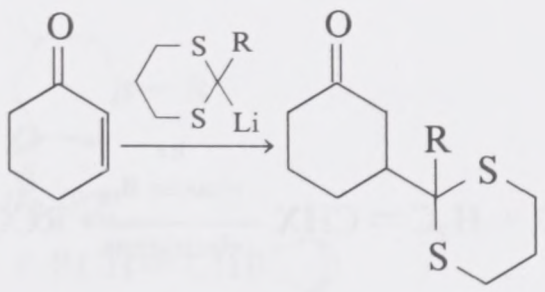
Org Syn Coll Vol *4* 652 (1963)
TL 2371 (1978); *23* 2957, 3521 (1982)
CL 1673 (1981) (chiral base)
Angew Int *19* 1013 (1980) (high pressure)
Syn 841 (1982)
JOC *47* 5017 (1982); *50* 3692 (1985); *52* 1601 (1987) (KF-alumina as base)
Syn Commun *12* 339 (1982)
CC 635 (1982)
BCSJ *56* 1885 (1983) (KF-alumina as base)

$$RCCH{=}CHR + R'CH_2NO_2 \xrightarrow[\text{18-crown-6}]{\text{KF}} RCCH_2CHRCHR' \xrightarrow[\text{silica gel}]{KMnO_4} RCCH_2CHRCR'$$

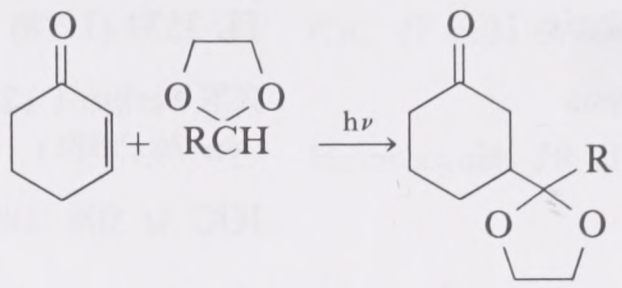
CC 635 (1982)



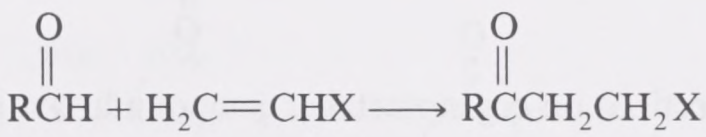
TL *28* 4411 (1987)



CC 100 (1979); 421 (1982)
Helv *65* 385 (1982)
Tetr *38* 3285 (1982)



TL 297 (1974)
Can J Chem *55* 3986 (1977)



X = COR, CN, CO_2R, SO_2Ph

Review: Angew Int *15* 639 (1976)

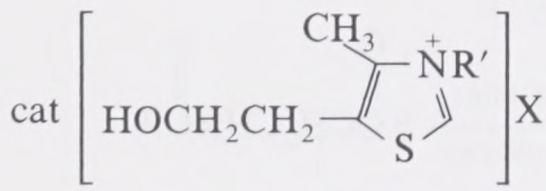
Reagent(s)

hν (R = Me, *n*-Pr, Ph)

Syn Commun *6* 417 (1976)
Can J Chem *55* 3986 (1977)

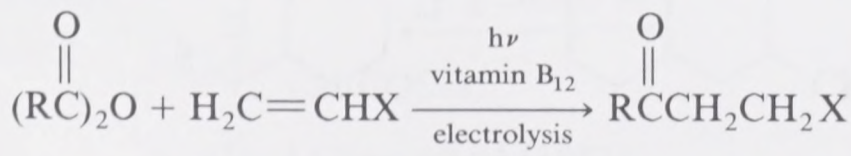
cat NaCN (R = aryl, heterocyclic)

TL 1461 (1973)
Angew Int *12* 81 (1973)
Ber *107* 210, 2453 (1974); *109* 534, 541 (1976)
Org Syn *59* 53 (1980)



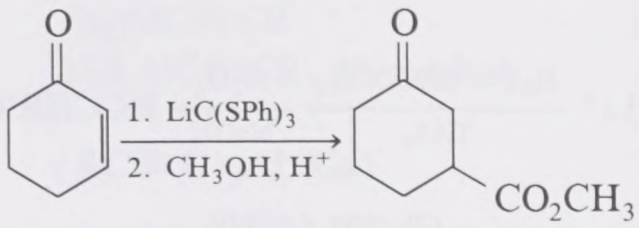
CH_2Ph; X = Cl, I), base
(R = alkyl, aryl, heterocyclic)

TL 4505 (1974)
Org Syn *65* 26 (1987)
Angew Int *13* 539 (1974);
17 131 (1978)
Syn 379 (1975); 129, 626 (1981)
Ber *109* 2890, 3426 (1976); *112* 84, 1410, 2419 (1979); *113* 690, 979, 1890, 2939 (1980); *114* 564, 581, 1226, 2479 (1981)
Heterocycles *12* 369 (1979)
Ann 1550 (1981)
CC 1447 (1986)
JOC *51* 2712 (1986); *52* 2213 (1987)

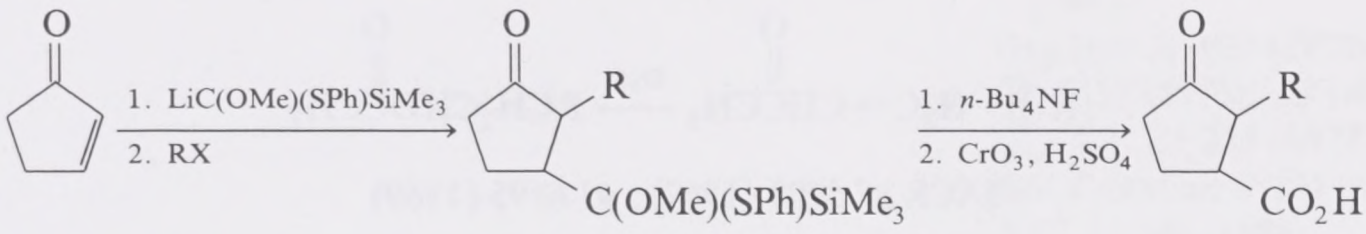


X = CHO, COR, CO_2R, CN

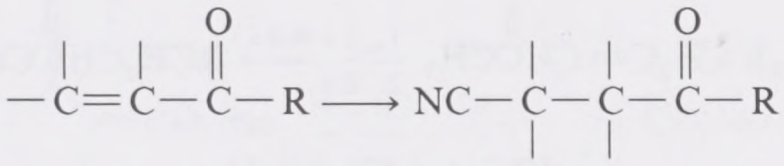
JACS *105* 7200 (1983)



CC 216 (1975)



TL *28* 2147 (1987)

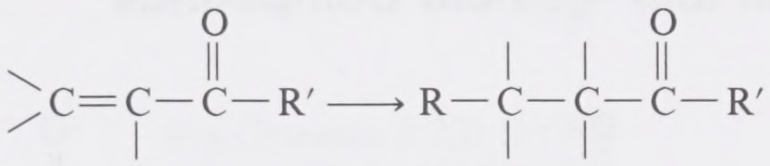


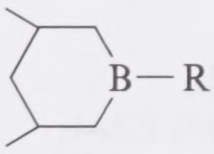
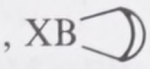
LiCN	TL *28* 4189 (1987)
NaCN, NH_4Cl	TL *28* 3061 (1987)
KCN	TL *28* 2537 (1987)
t-BuNC, $TiCl_4$ (R = alkyl)	JACS *104* 6449 (1982)
t-BuNC, $EtAlCl_2$ (R = H)	JACS *104* 6449 (1982)
HCN·py (R = alkyl)	JOC *51* 902 (1986)

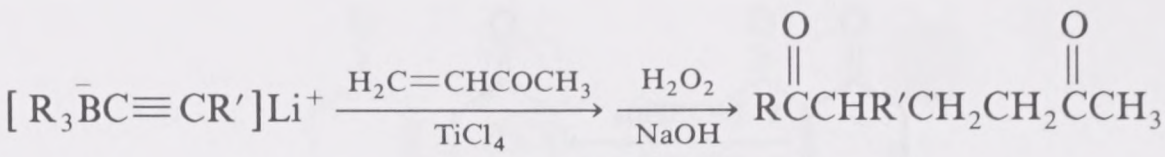
See also page 800, Section 4.

3. Organoboron Compounds

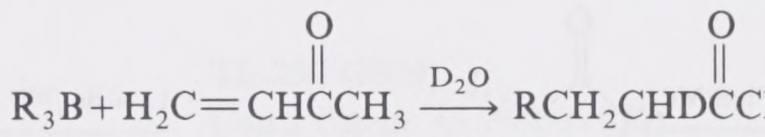
Review: Angew Int *11* 692 (1972)



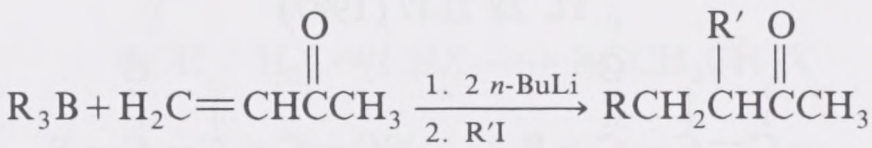
R′	Organoborane	
H	R_3B	JACS *89* 5709 (1967); *90* 4165 (1968); *92* 710, 712, 714 (1970)
alkyl	R_3B	JACS *89* 5708 (1967); *90* 4166 (1968); *92* 712, 714 (1970)
		JACS *93* 3777 (1971); *95* 6757 (1973)
	Ph_2BR	JOMC *156* 101 (1978)
	E-RCH=CHB 	JACS *98* 7832 (1976)
	Z-XCR=CHB  , XB  (X = Br, I)	JACS *107* 5225 (1985)
	$(RC{\equiv}C)_3B$	TL 2627 (1972); 235 (1976)
	RC≡CB	JACS *99* 954 (1977)



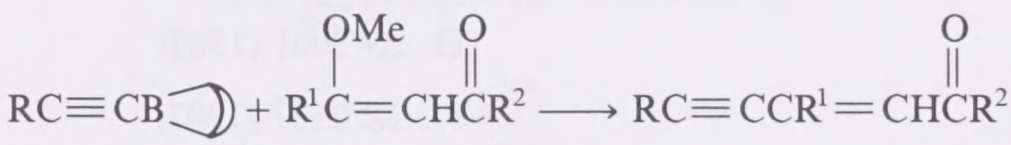
CL 221 (1980)



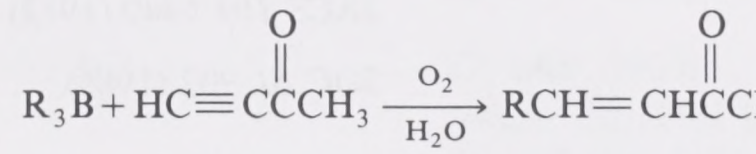
JACS *89* 5708 (1967); *91* 6195 (1969)



JOC *36* 1790 (1971)

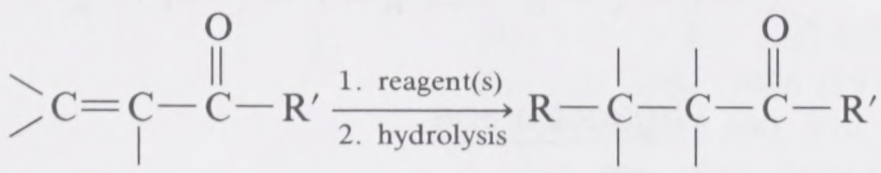


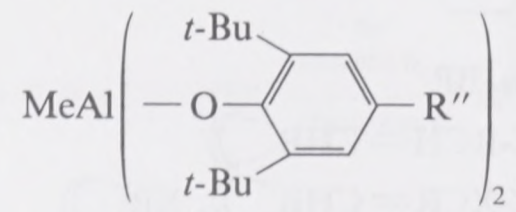
JOC *42* 3106 (1977)



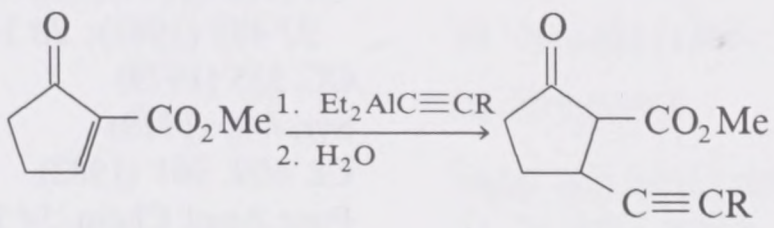
JACS *92* 3503 (1970)

4. Organoaluminum and -gallium Compounds

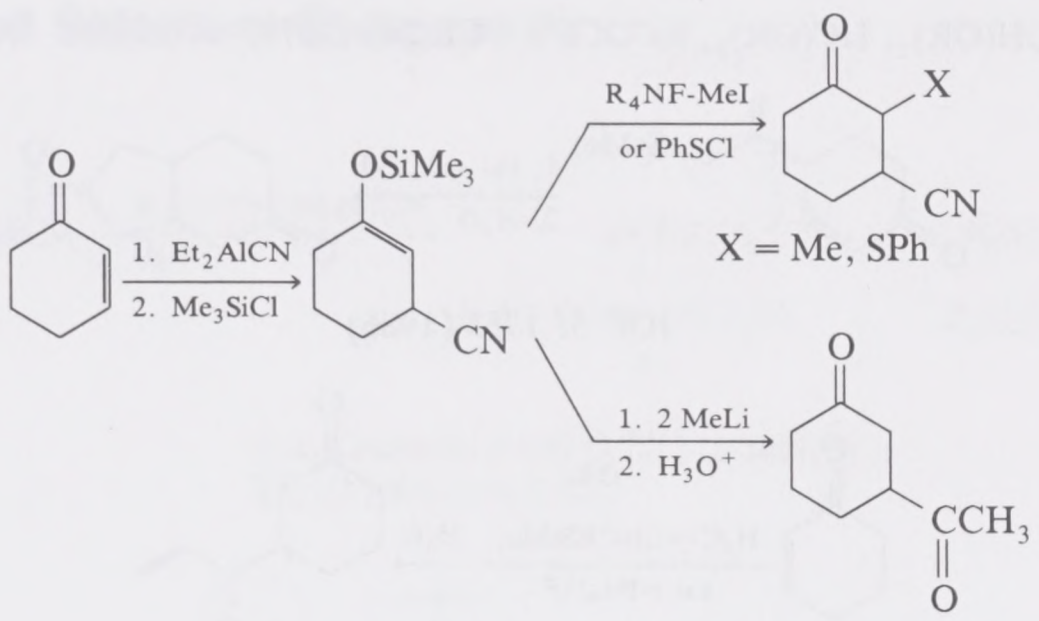


R	Reagent(s)	
CH_3	$(CH_3)_3Al$ or $LiAl(CH_3)_4$, $Ni(acac)_2$	JOC *39* 3297 (1974) Austral J Chem *28* 801, 817 (1975)
CH_3 or Ph	R_2AlI (R = Me, Ph)	JOC *44* 4792 (1979)
1°, 2°, 3° alkyl; aryl; vinylic; ester enolate	 (R″ = Me, *t*-Bu)/RLi	TL *28* 5723 (1987)
E-CH=CHR	[*E*-RCH=CHAlMe(*i*-Bu)$_2$]Li	TL 4083 (1972); 765 (1975) JOC *44* 71, 1438 (1979)

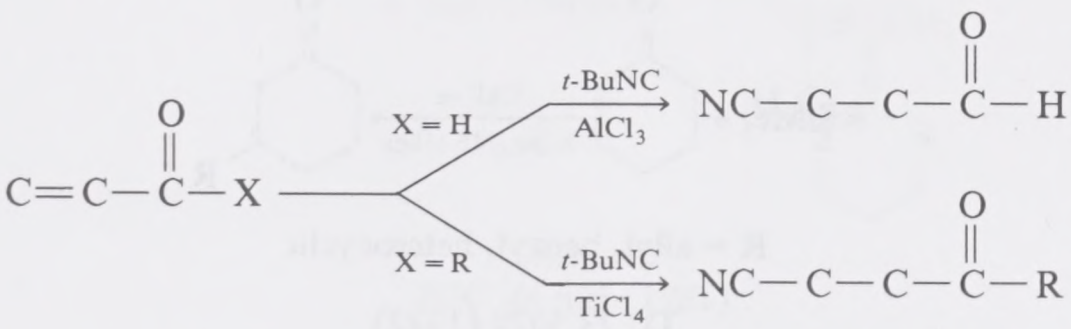
$RC\equiv C$	$Et_2AlC\equiv CR$	JACS *93* 7320 (1971)
	$Me_2AlC\equiv CR$, Ni catalyst	JACS *100* 2244 (1978) JOC *45* 3053 (1980)
	$(RC\equiv C)_3Al$ (Ga)	TL 2627 (1972)
CN	Et_2AlCN or Et_3Al-HCN	JACS *94* 4635, 4644, 4654, 4672 (1972) Org Syn *52* 100 (1972) TL 5113 (1973); *28* 1439 (1987) Org Rxs *25* 255 (1977) Syn Commun *8* 231 (1978) JOC *51* 902 (1986)



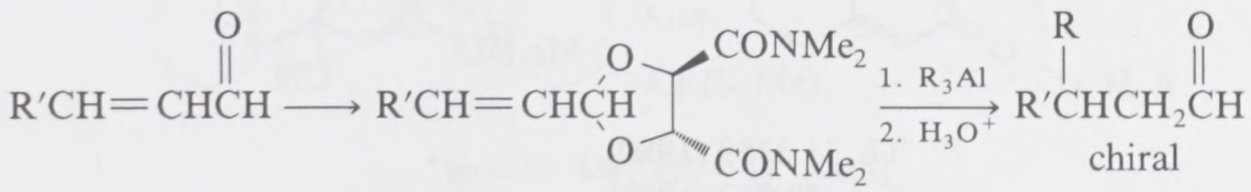
TL *27* 2885 (1986)



Syn Commun *8* 231 (1978)
See also TL *21* 3389 (1980)

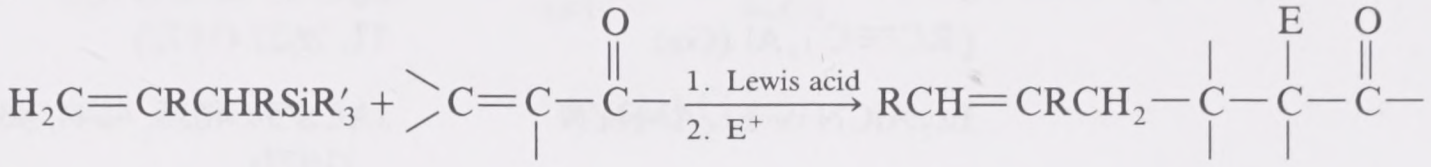


JACS *104* 6449 (1982)

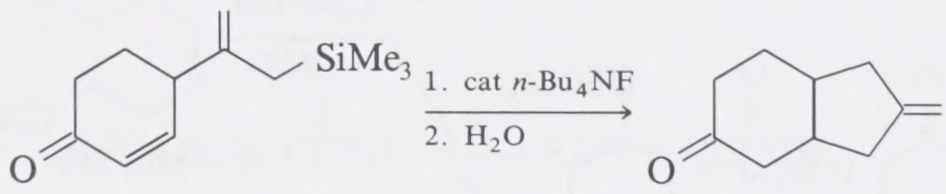


JACS *106* 5004 (1984)

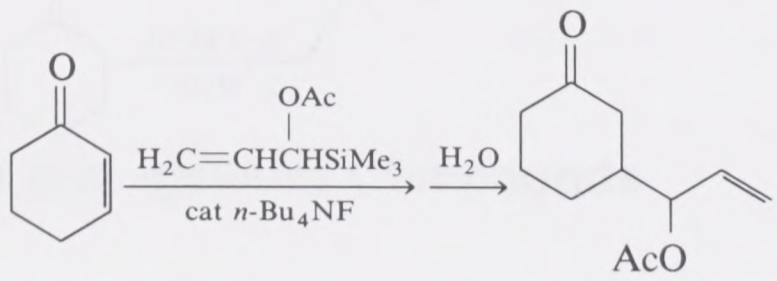
5. Organosilicon Compounds



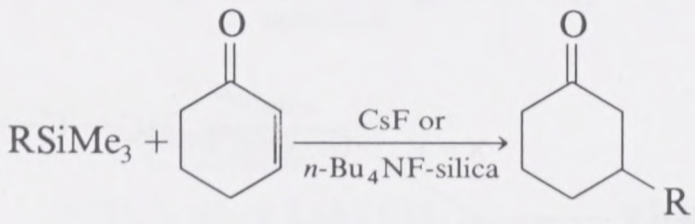
E^+	
H_2O	JACS *99* 1673 (1977); *104* 1124 (1982) (intramolecular); *106* 721 (1984); *107* 2568 (1985); *108* 3835 (1986) TL 1385 (1977); 4557 (1979); *21* 955, 4557 (1980); *22* 485 (1981); *28* 1483, 5441, 5793, 6413 (1987) CC 525 (1979) Syn 446 (1979) CL 609, 961 (1982) Pure Appl Chem *54* 1 (1982) (review) JOC *49* 4214 (1984) Org Syn *62* 86 (1984)
RCHO, R_2CO, $RCH(OR)_2$, $HC(OR)_3$, RCOCl	CL 245 (1979)



JOC *51* 1753 (1986)

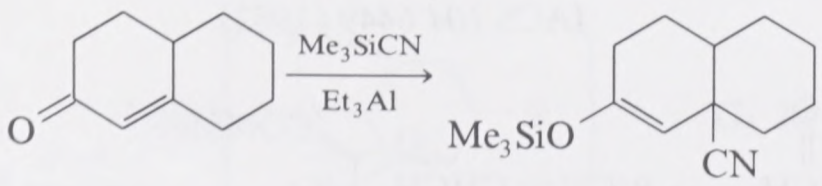


TL *28* 4649 (1987)



R = allyl, benzyl, heterocyclic

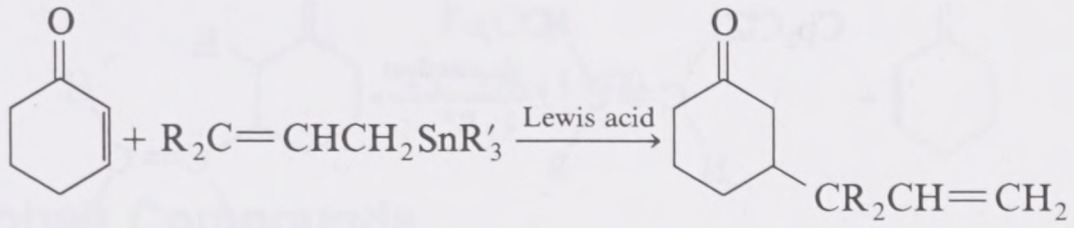
TL *23* 5079 (1982)



TL *21* 3389 (1980)
Tetr *39* 967 (1983)
See also Syn Commun *8* 231 (1978)

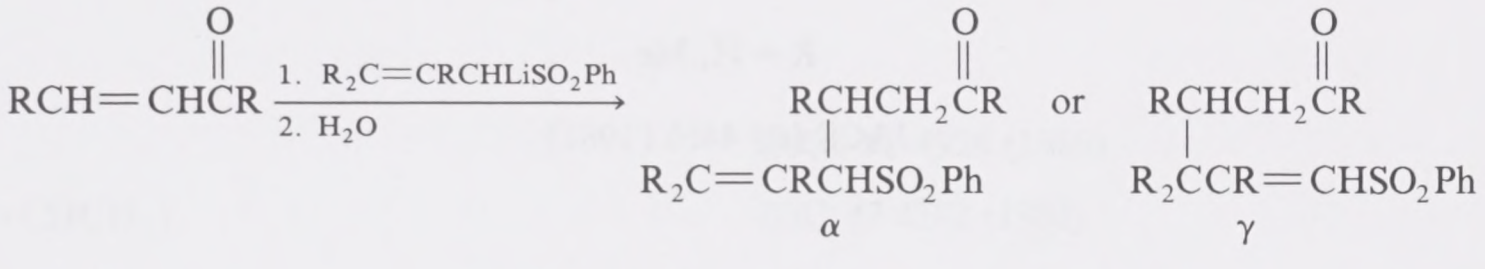
6. Organotin Compounds

See also page 805, Section 13.

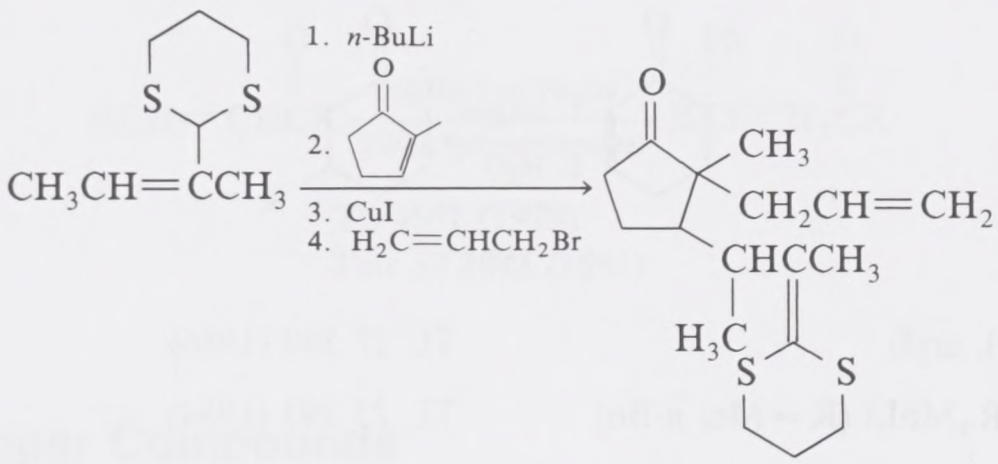


Lewis acid	
$BF_3 \cdot OEt_2$	TL *28* 1483 (1987)
$AlCl_3$	TL *28* 1483 (1987)
$(Et_2Al)_2SO_4$	CL 977 (1979)
$TiCl_4$	JACS *102* 2112 (1980) (intramolecular) TL *28* 1483 (1987)

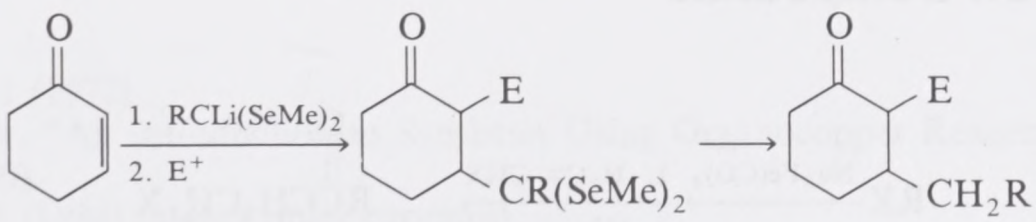
7. Sulfur and Selenium Compounds



Syn Commun *8* 483 (1978) (α and γ)
TL *22* 1905 (1981) (α)



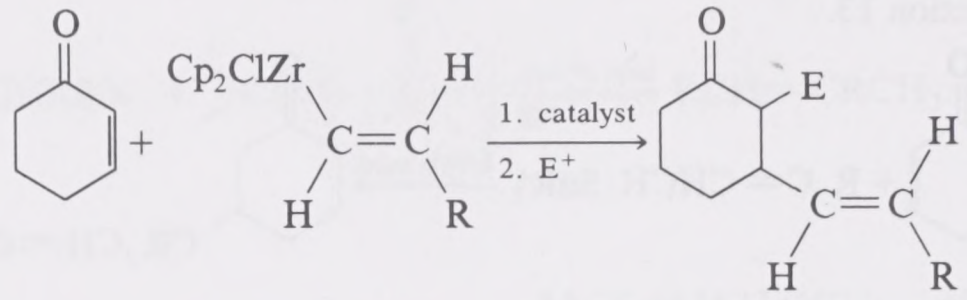
JOC *46* 825 (1981)



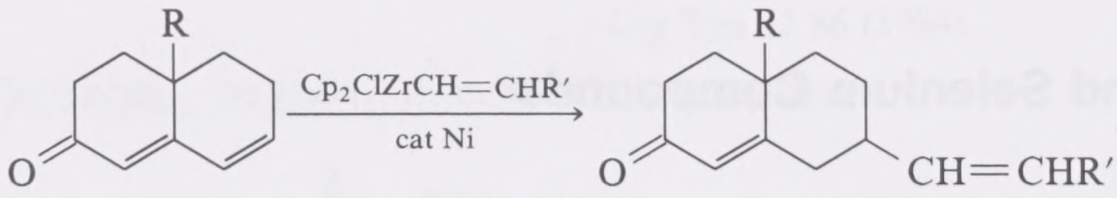
R = H, Me; $E^+ = H^+$, MeI

TL *22* 1623 (1981)

8. Organozirconium Compounds



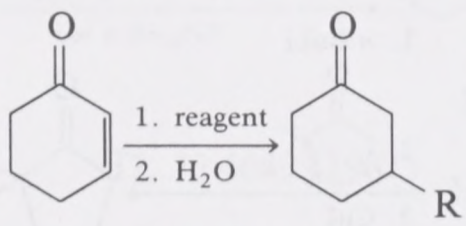
Catalyst	E^+	
CuO_3SCF_3, LiI	H^+	TL 1303 (1977)
$Ni(acac)_2$, *i*-Bu_2AlH	H^+	JACS *99* 8045 (1977); *102* 1333 (1980); *103* 4466 (1981)
		TL 4383 (1978)
	CH_2O	TL 4381 (1978)



R = H, Me

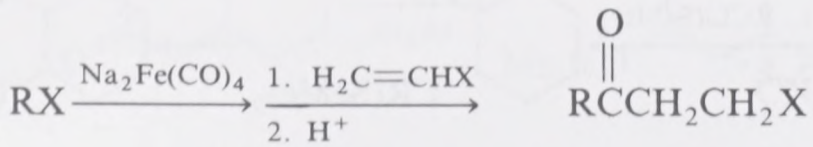
JACS *103* 4466 (1981)

9. Organomanganese Compounds



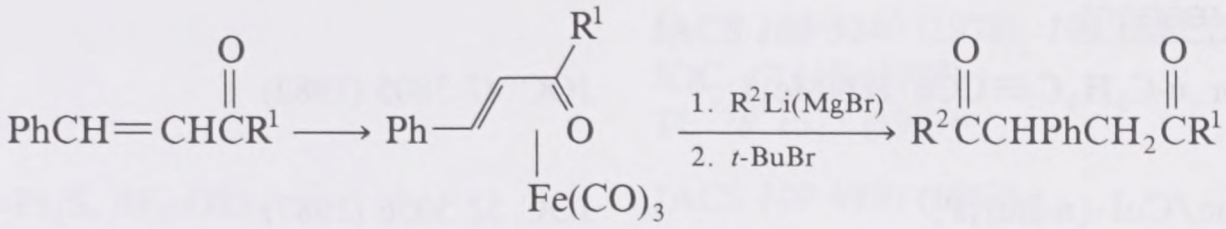
Reagent	
R_2Mn (R = 1° alkyl, aryl)	TL *27* 569 (1986)
RMnCl, R_2Mn or R_3MnLi (R = Me, *n*-Bu)	TL *25* 293 (1984)

10. Organoiron Compounds



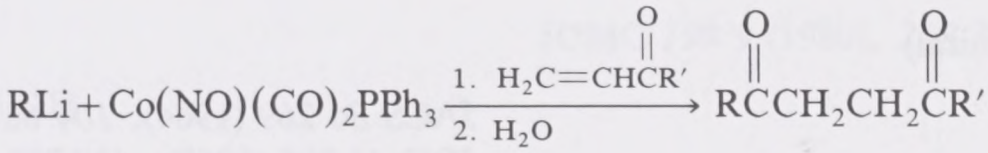
X = CO_2R, COR, CN

JACS *99* 5222 (1977)



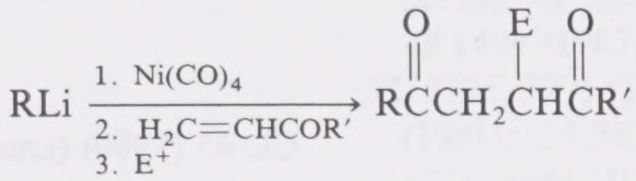
CC 226 (1987)

11. Organocobalt Compounds



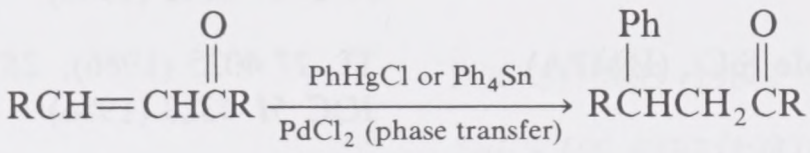
JOC *50* 4955 (1985)

12. Organonickel Compounds



E^+	
H_2O	JACS *91* 4926 (1969)
$H_2C{=}CHCH_2I$	JOC *47* 4382 (1982)

13. Organopalladium Compounds

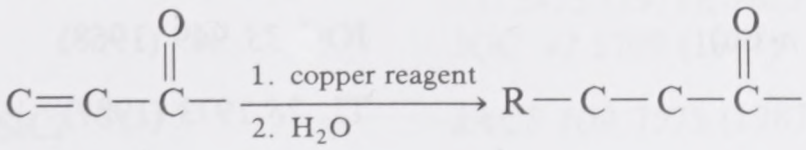


TL 4591 (1979)
Tetr *37* 2941 (1981)

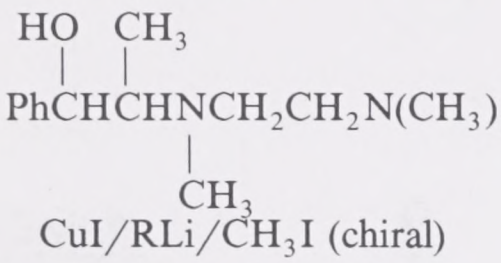
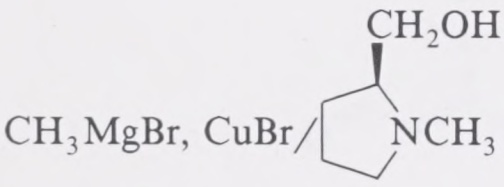
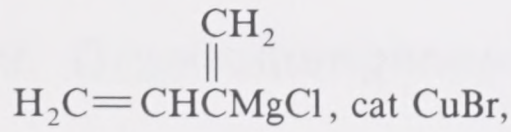
14. Organocopper Compounds

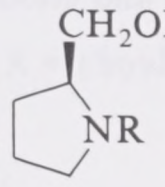
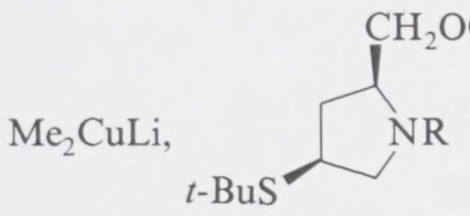
Reviews:

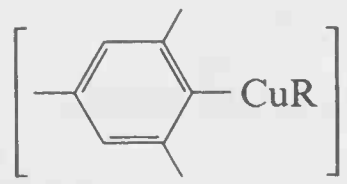
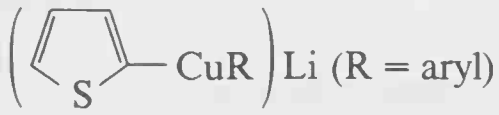
Org Rxs *19* 1 (1972)
G. H. Posner, "An Introduction to Synthesis Using Organocopper Reagents," J. Wiley, New York (1980)
Tetr *40* 5005 (1984) (higher order cuprates)



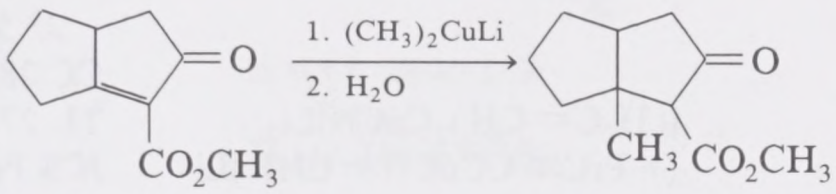
Copper reagent

RX, Li, CuI or n-$C_3H_7C{\equiv}CCu\cdot P(NMe_2)_3$, ultrasound	JOC *47* 3805 (1982)
Li, naphthalene/$CuI\cdot(n\text{-}Bu)_3P$, n-Bu_3P/RBr	JOC *52* 5056 (1987)
	JACS *108* 7114 (1986)
RMgX, CuX	JACS *86* 269 (1964); *104* 6879 (1982) JOC *33* 305 (1968); *42* 1709 (1977) BSCF 568 (1969) TL 3361 (1979); *28* 357, 3061 (1987) CL 45 (1980) (chiral ligand) JOMC *220* 295 (1981) Helv *64* 1575, 2489 (1981)
	CL 45 (1980) (enantioselective)
RMgX, $CuBr\cdot SMe_2$	JACS *106* 1443 (1984)
RMgX, CuI, $BF_3\cdot OEt_2$	JOC *51* 5311 (1986)
RMgX, cat CuBr	Org Syn *65* 203 (1987)
	TL *24* 1003 (1983)
RMgX, cat $CuBr\cdot SMe_2$	JOC *47* 5045 (1982)
RMgX, cat $CuBr\cdot SMe_2$, Me_3SiCl, (HMPA)	TL *27* 4025 (1986); *28* 5669 (1987) JOC *51* 4323 (1986)
$Zn(CH_2CH_2CO_2R)_2$, cat $CuBr\cdot SMe_2$, Me_3SiCl	JACS *106* 3368 (1984); *109* 8056 (1987)
$Zn(CH_2CH_2CO_2R)_2$, cat $CuBr\cdot SMe_2$, $BF_3\cdot OEt_2$, HMPA	JOC *51* 4323 (1986)
RCu	JOC *33* 949 (1968) TL *28* 2525 (1987)
$RCu\cdot n\text{-}Bu_2S$ (R = 2-pyridyl)	Tetr *38* 1509 (1982)
$RCu\cdot n\text{-}Bu_3P$	JOC *31* 3128 (1966); *33* 949 (1968); *52* 3346 (1987) (R = vinyl) Tetr *38* 1509 (1982)
$RCu\cdot 2\ n\text{-}Bu_3P$	TL *21* 1247 (1980)
$RCu[P(OR')_3]_3$ (R′ = Me, n-Bu)	JOC *33* 949 (1968)
RCu, n-Bu_3P, $BF_3\cdot OEt_2$	TL *28* 1973 (1987)

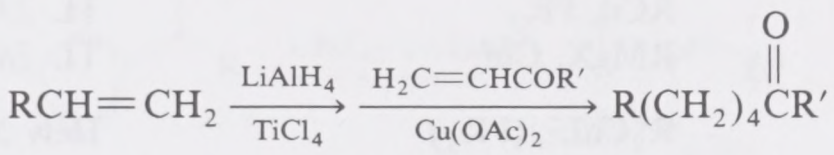
$RCu \cdot BF_3$	JACS *100* 3240 (1978), *104* 6081 (1982) JOC *47* 119 (1982) TL *28* 2525 (1987)
$ROCH_2Cu$, *i*-Pr_2S, $BF_3 \cdot OEt_2$	JACS *109* 4930 (1987)
$RCu \cdot AlCl_3$	CC 1193 (1980); 703 (1982) (β-cyclopropyl-α,β-enones) TL *21* 4073 (1980)
RCu, Me_3SiCl, (HMPA)	TL *27* 4029 (1986); *28* 2525 (1987)
R_2CuMgX	JOMC *199* 9 (1980); *228* 321 (1982) (enals)
Me_2CuMgX, 	TL *22* 3601 (1981) (enantioselective)
$R_2CuMgX \cdot COD$	TL *21* 1311 (1980)
R_2CuLi	JOC *31* 3128 (1966); *33* 949 (1968); *35* 186 (1970); *41* 3629, 4031 (1976); *44* 4481 (1979); *48* 1404 (1983); *51* 4779 (1986) TL 2875, 3795 (1971); 3361, 3365 (1979); *22* 3585 (1981); *23* 3823 (1982) (chiral R); *28* 2525, 4251, 4943 (1987) Tetr *35* 2645 (1979) (α-haloenones); *36* 2305 (1980) (enals); *37* 1385 (enals), 3981, 4027 (1981); *38* 1509 (1982) CC 643 (1981) (enals) JACS *107* 2149 (1985); *109* 5731 (1987)
Me_2CuLi, 	TL *24* 3517 (1983) (enantioselective)
$[Me_3Si(PhS)CH]_2CuLi$	JOC *51* 3983 (1986)
$(ROCH_2)_2CuLi$, *i*-Pr_2S	JACS *109* 4930 (1987)
R_2CuLi, $BF_3 \cdot OEt_2$	Tetr *37* 3981 (1981) JACS *103* 194 (1981); *108* 3443 (1986) TL *28* 4061 (1987)
R_2CuLi, Me_3SiCl, (HMPA)	TL *26* 6015, 6019 (1985); *27* 1047, 4029 (1986)
$(ROCH_2)_2CuLi$, *i*-Pr_2S, Me_3SiCl	JACS *109* 4930 (1987)
$(ROCH_2)_2CuLi$, *i*-Pr_2S, $BF_3 \cdot OEt_2$	JACS *109* 4930 (1987)
$(H_2C{=}CHCH_2)_2CuLi$	JOC *34* 3615 (1969)
$(RCH{=}CH)_2CuLi$	Can J Chem *48* 1626 (1970) Helv *54* 1939 (1971) JACS *93* 7318 (1971); *94* 9256 (1972) TL 2455 (1971); 2627 (1972) JOC *42* 1709 (1977)
$(H_2C{=}CH)_2CuLi$, Me_3SiCl	JACS *109* 7575 (1987)

$(C_6H_5)_2CuLi$	TL 1579, 1583 (1970); *28* 3065 (1987)
polymer-$PPh_2 \cdot R_2CuLi$	JOC *44* 2705 (1979)
(MeCuR)Li	TL *21* 3151 (1980)
(PhCuR)Li (R = 2-pyridyl)	Tetr *38* 1509 (1982)
(ArCuR)Li	Tetr *34* 3023 (1978) Acta Chem Scand B *32* 483 (1978)
	TL *22* 192 (1981) JOC *46* 192 (1981) (enals and enones)
	TL *23* 3823 (1982)
	TL *25* 5959 (1984) (R = vinyl); *28* 945 (1987) JOMC *285* 437 (1985)
	TL *25* 5959 (1984) (R = vinyl)
(n-PrC≡CCuR)Li (or MgX)	JACS *94* 7210 (1972); *106* 8296 (1984) JOC *44* 3661 (1979)
(t-BuC≡CCuR)Li	JOC *38* 3893 (1973); *44* 1006 (1979)
[n-C_5H_{11}C≡CCu**CH=CHSn(n-Bu)$_3$**]Li	TL *28* 3065 (1987)
($MeOCMe_2C$≡CCuR)Li	JOC *43* 3418 (1978)
(Me_2NCH_2C≡CCuR)Li	JOC *44* 1006 (1979)
(Me_3SiC≡CCu**CH_2CH=CROSiMe_3**)M (M = Li, MgBr)	TL *25* 5307 (1984) JACS *107* 5495 (1985)
(Me_3SiC≡CCu**CH_2CH=CROSiMe_3**)Li, Me_3SiCl, HMPA	TL *27* 4029 (1986)
[Me_3SiC≡CCu**CH=C=CROSiMe_2(t-Bu)**]Li	TL *28* 1299 (1987)
(RCuCN)Li (or MgX)	CC 88 (1973) TL 3879 (1977); *22* 2985 (1981)
(RCuCN)Li, Me_3SiCl	TL *26* 6019 (1985) (enals)
$(R_2CuCN)Li_2$	TL *23* 3755 (1982); *28* 2525 (1987) JOC *49* 3938 (1984); *51* 1293 (1986)
$(R_2CuCN)Li_2$, $BF_3 \cdot OEt_2$	TL *25* 5959 (1984) (R = Ph) JOC *52* 4647 (1987)
	TL *28* 3911 (1987)
$(RCuCH_2SO_2R')Li$ (R′ = Me, Ph)	CC 358 (1982)
$(RCuCH_2SOCH_3)Li$	JOC *52* 1885 (1987)
$[RCu(CN)CH_2SOCH_3]Li_2$	JOC *52* 1885 (1987)

(RCuSR′)Li (R′ = Ph, chiral R′)	JACS *95* 7788 (1973) Syn 662 (1974) Acta Chem Scand B *34* 443 (1978) TL 3849 (1980)
(RCuOR′)Li (R′ = *t*-Bu, chiral R′)	JACS *95* 7788 (1973) TL 1815 (1973); *22* 1329 (1981) Acta Chem Scand B *34* 443 (1978)
$(RCuNCy_2)Li$	JACS *104* 5824 (1982)
$(RCuNR'_2)Li$ (chiral amides)	JOC *51* 4953 (1986) JACS *109* 2041 (1987)
(MeCuX)Li (X = chiral alkoxide or amide)	Bull Soc Chim Belg *87* 369 (1978) (enantioselective)
$(RCuPPh_2)Li$	JACS *104* 5824 (1982)
Me_3CuLi_2	TL 2659 (1976)
Me_3CuLi_2, Me_3Cu_2Li, or $Me_5Cu_3Li_2$	JOC *42* 1099 (1977)
$Me_5Cu_3Li_2$	CC 643 (1981) (enals) JOC *47* 2572 (1982) (enals)
$(PhMe_2Si)_2CuLi$	TL *28* 965 (1987) (enal)

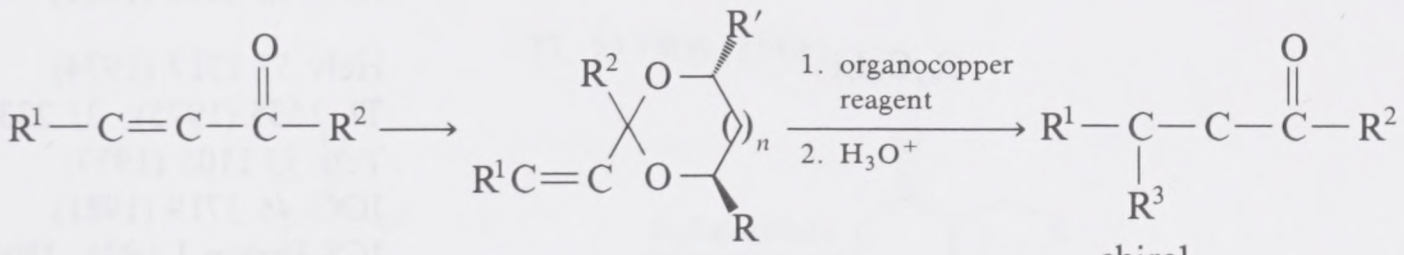


JACS *109* 6199 (1987)



R′ = H, Me

CL 167 (1979)



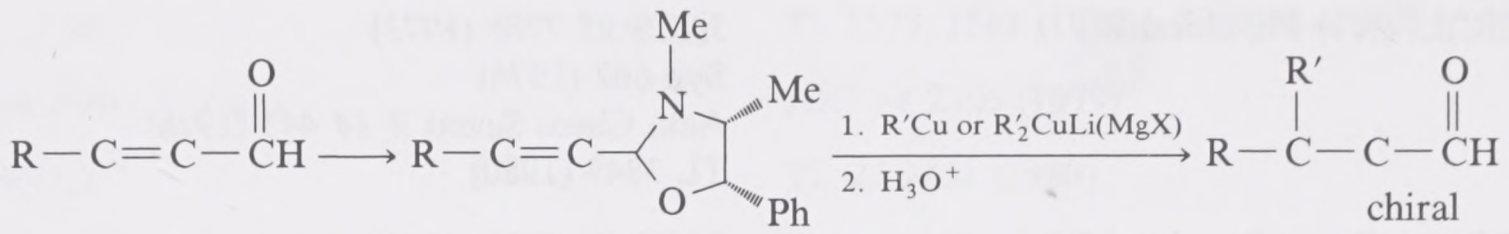
chiral

$n = 0, 1$

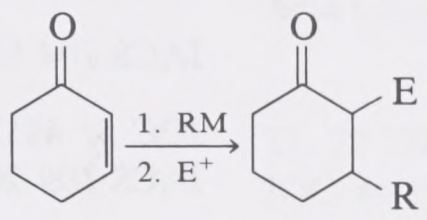
R^2 = H, alkyl

Organocopper Reagent

PhCu, $BF_3 \cdot OEt_2$	TL *27* 3143 (1986)
R^3Cu, CuBr, *n*-Bu_3P (R^3 = aryl, vinylic)	TL *28* 2363 (1987)
Me_2CuLi, $BF_3 \cdot OEt_2$	TL *25* 3083 (1984)



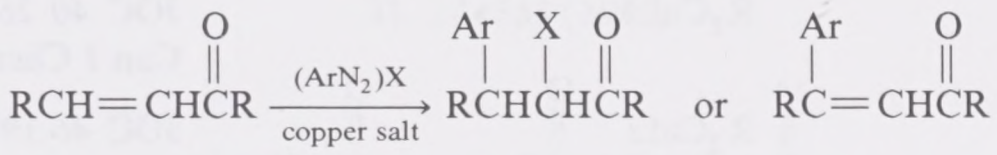
TL *24* 373, 585 (1983)



Review: Syn 364 (1985)

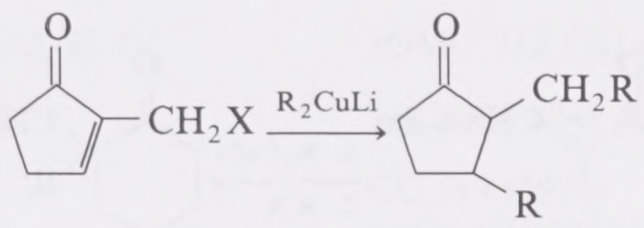
E^+	RM	
R′X	RMgX, cat CuI·*n*-Bu_3P	JACS *103* 4136 (1981); *108* 3435 (1986); *109* 6199 (1987)
	RMgX, $CuBr \cdot SMe_2$	JOC *44* 3731 (1979)
	R_2CuLi	JOC *38* 4450 (1973); *29* 275 (1974)
		JACS *95* 6867 (1973); *97* 107 (1975); *101* 938 (1979)
		TL 2591 (1974); 4867 (1976); *27* 5103, 6295 (1986)
		CC 28 (1984)
	$[(H_2C{=}CH)_2CuCN]Li_2$	TL *27* 5103 (1986)
	(*n*-PrC≡CCu**CH**=**CHR**)Li	JCS Perkin I 1407 (1981)
		TL *23* 327 (1982)
R′CHO	RCu, PR_3	TL *23* 4057 (1982)
	RMgX, CuI	TL *28* 2489 (1987)
R′CHO ($ZnCl_2$)	R_2CuLi, (PR_3)	Helv *57* 1317 (1974)
		JACS *96* 7114 (1974); *97* 6260 (1975)
		Tetr *35* 425 (1979)
		JOC *46* 2932 (1981)
R′COCl	R_2CuLi	Helv *57* 1317 (1974)
		TL 1535 (1975); *21* 2337 (1980)
		Tetr *33* 1105 (1977)
		JOC *46* 3719 (1981)
		JCS Perkin I 1994, 2394 (1981)
$ClCO_2Me$	RMgX, CuI	JCS Perkin I 1516 (1981)
		TL *23* 703 (1982)
	R_2CuLi	JOC *40* 1488 (1975)
	(*n*-PrC≡CCu**CH**=**CHR**)Li	TL 4087 (1976)
CO_2/CH_2N_2	R_2CuLi	Tetr *35* 425 (1979)
		CL 57 (1982)
		JACS *106* 2954 (1984)
$H_2C{=}C(SMe)SOMe$	R_2CuLi	JOC *44* 3755 (1979)

Br_2	Ph_2CuLi $R_2CuLi(MgX)$	JACS *101* 934 (1979) JOMC *228* 321 (1982) (on enals)
PhSSPh	(*n*-PrC≡CCu**CH**=**CHR**)Li	TL 4091 (1976)
PhSCl	(RCH=CHCuSPh)Li	TL 4091 (1976)
MeSOCl	R_2CuLi	CL 1159 (1981)
PhSeBr	RMgX, CuI $(CH_3)_2C$=CHMgBr, cat CuI R_2CuLi	Tetr *38* 1959 (1982) JOC *50* 2539 (1985) JOC *39* 2133 (1974) JACS *97* 5434 (1975)



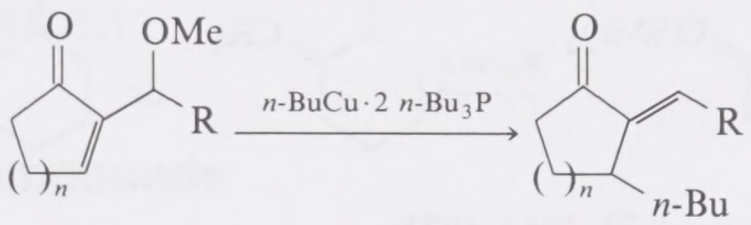
X = halogen

Org Rxs *11* 189 (1960); *24* 225 (1976)



X = Cl, OAc, SPh

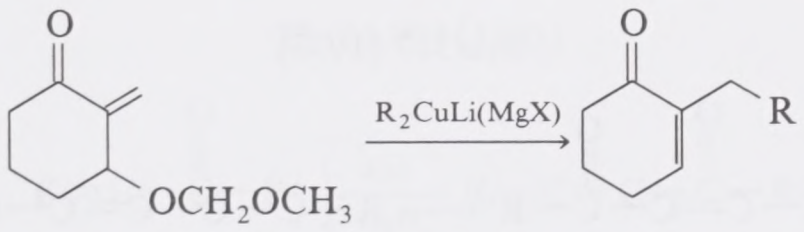
TL *21* 3237 (1980)



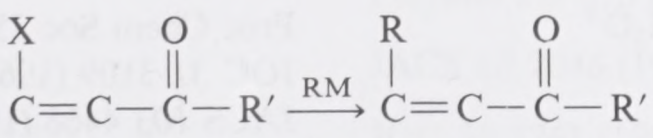
$n = 1, 2$

R = Ph, OMe

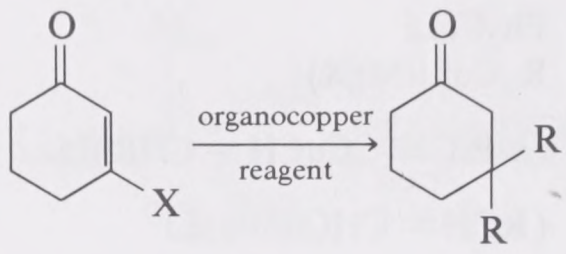
TL *22* 1809 (1981)



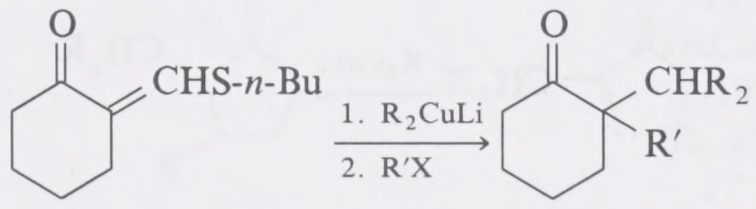
TL *22* 119 (1981)
CL 1189 (1981)



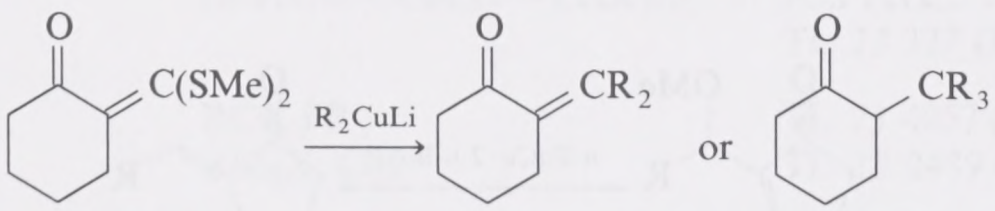
See page 185, Section 1; page 191, Section 2; page 192, Section 3; and page 206, Section 14.



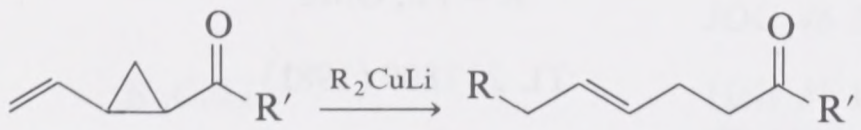
X	Organocopper Reagent	
Cl	R_2CuLi	JOC *41* 636 (1976)
Cl, Br	$[PhSCu(CH_2)_nCuSPh]Li_2$ ($n = 4, 5$)	TL 1245 (1977) (spiro product)
Cl, Br, I	R_2CuLi	JOC *40* 2694 (1975) Can J Chem *60* 1256 (1982)
OMs	R_2CuLi	JOC *46* 197 (1981)
OAc	R_2CuLi	TL 2071 (1973)
SR	R_2CuLi	CC 907 (1973) JOC *52* 110 (1987)



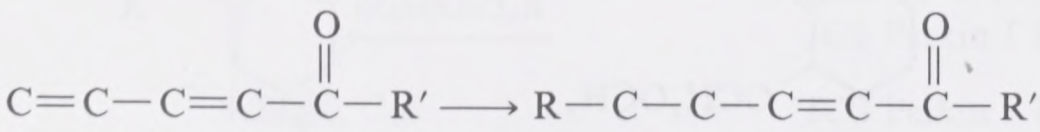
JOC *39* 275 (1974)



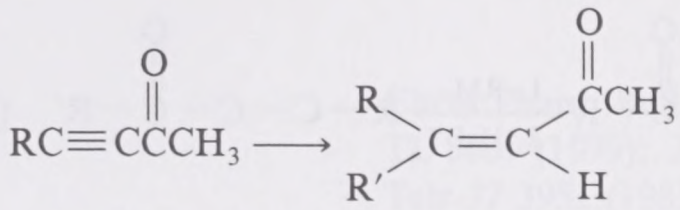
TL 3817 (1973)
Acta Chem Scand B *33* 460 (1979)



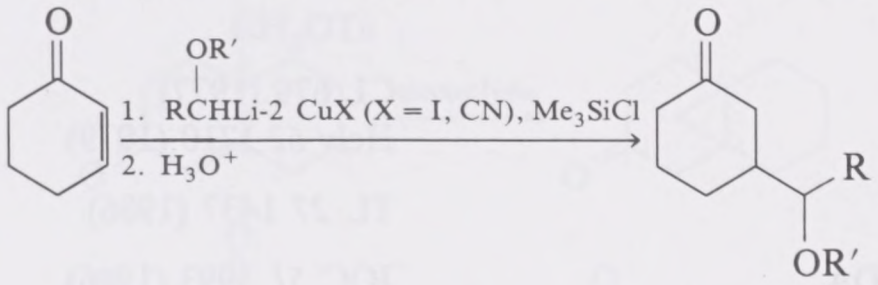
Syn 317 (1975)



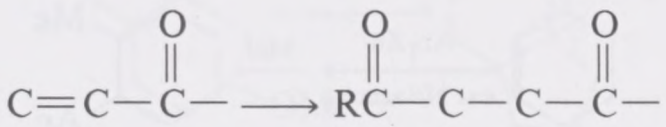
RMgX, cat $CuCl/H_3O^+$	JACS *81* 4069 (1959)
RMgX, cat $CuBr \cdot SMe_2/H_3O^+$	JCS Perkin I 2840 (1979)
RMgX, cat $Cu(OAc)_2 \cdot H_2O/H_3O^+$	Proc Chem Soc 356 (1962) JOC *31* 3109 (1966) JACS *103* 4466 (1981)
R_2CuLi/H_3O^+	TL 3795 (1971)



See page 233, Section 2.17.



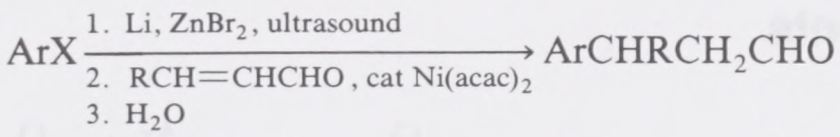
TL *27* 4553 (1986)



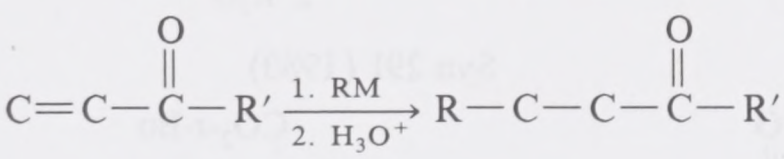
$(R_2CuCN)Li_2$, CO	JACS *107* 4551 (1985)
(RCuCN)Li, CO	TL *27* 1473 (1986)
n-$Bu_3SnCH(OEt)_2$, *n*-BuLi/CuI/H_3O^+	JOMC *212* C31 (1981)
$[RC(SPh)_2]_2CuLi/H_2O$, $CuCl_2$	JACS *94* 8641 (1972)
$(H_2C{=}COR')_2CuLi/H_3O^+$	CC 519 (1975)
(R' = Me, Et; R = Me)	JACS *97* 3822 (1975) JOC *44* 4781 (1979)
$(R'CH{=}CSiMe_3)_2CuLi/(HOCH_2)_2$, TsOH/ *m*-$ClC_6H_4CO_3H$/aq $HClO_4$ or $BF_3{\cdot}OEt_2$-CH_3OH (R = $R'CH_2$)	TL 3365 (1974) JOC *44* 4781 (1979)

15. Organozinc Compounds

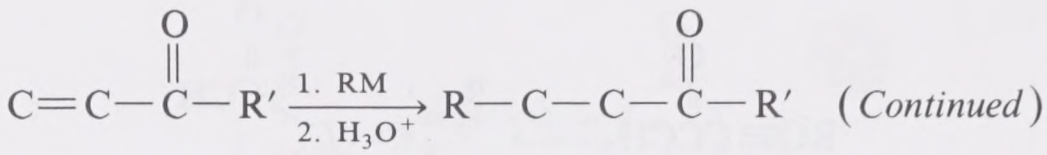
See also page 805, Section 14.



TL *26* 829 (1985)

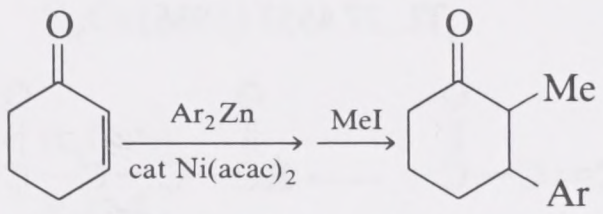


RM	
Et_2Zn	Polymer J *9* 595 (1977)
Ph_2Zn	JACS *63* 2046 (1941)
R_2Zn, cat $Ni(acac)_2$	JOC *50* 5761 (1985) JACS *109* 4752 (1987)



(*Continued*)

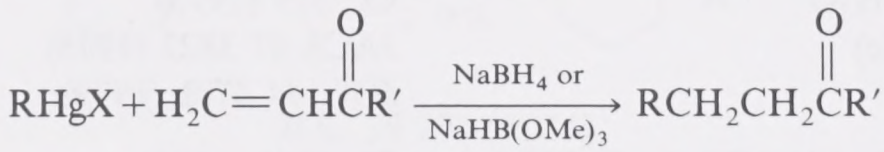
RM	
$(EtO_2CCH_2CH_2)_2Zn$, Me_3SiCl, cat $CuBr \cdot SMe_2$	JACS *106* 3368 (1984)
R_3ZnLi	CL 679 (1977) Helv *62* 1710 (1979)
Me_2RZnLi	TL *27* 1437 (1986)
3 RMgX, $ZnCl_2 \cdot$ TMEDA	JOC *51* 3993 (1986)



JOC *50* 5761 (1985)

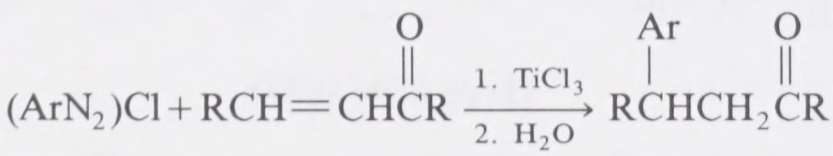
16. Organomercury Compounds

See also page 805, Section 13, and page 67, Section 2.16.

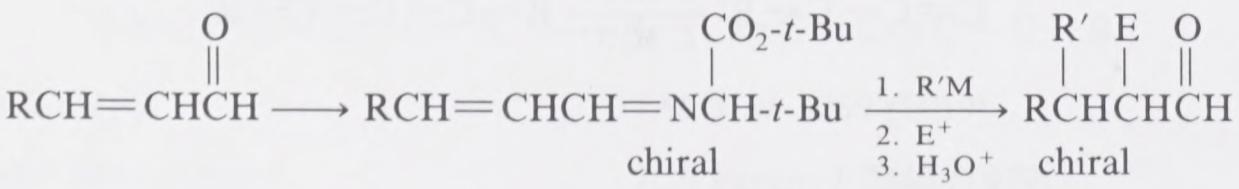


Angew Int *20* 965 (1981)
JOC *47* 2231 (1982) (intramolecular)
TL *23* 931 (1982)
Syn 735 (1982)
Ber *117* 2132 (1984)
Tetr *41* 4025 (1985)
Ann 427 (1987)

17. Other Reagents



Syn 291 (1980)



$E^+ = H^+, RX$

Review:

K. Tomioka and K. Koga, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Chpt 7

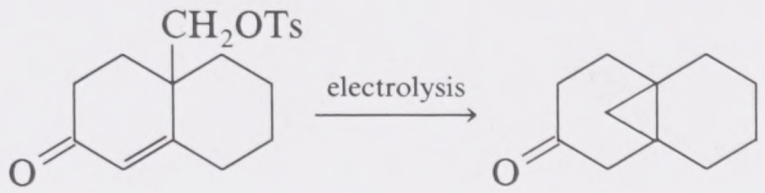
R′M

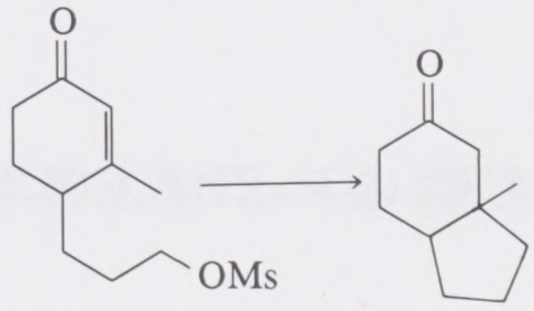
R′MgX

Chem Pharm Bull *27* 771 (1979)
TL 3009 (1979); *21* 4005 (1980)
Tetr *37* 3951 (1981)

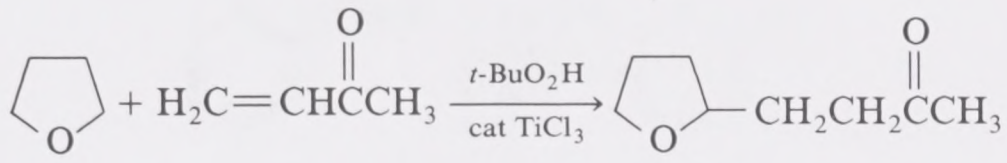
$KCH(CO_2Et)_2$

Chem Pharm Bull *27* 2437 (1979)

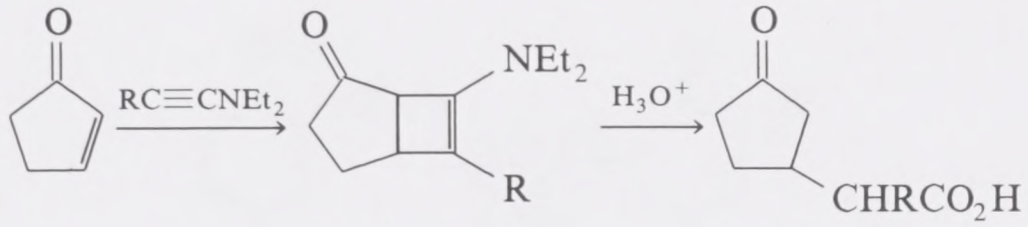




JOC *46* 5455 (1981)

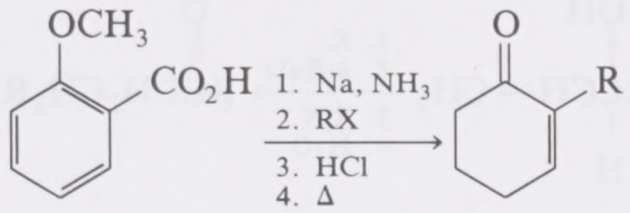


Tetr *38* 393 (1982)

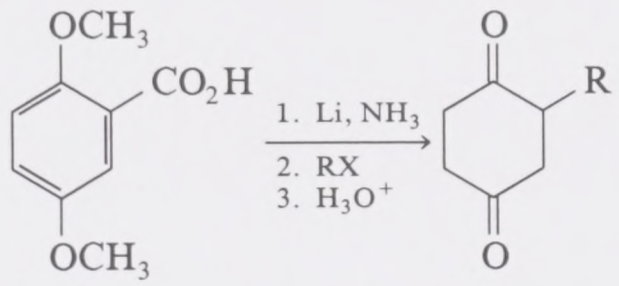


TL *23* 1821 (1982)

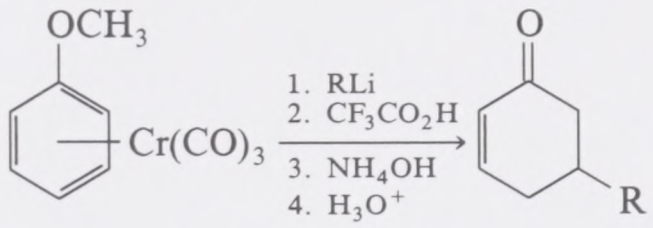
16. MISCELLANEOUS REACTIONS



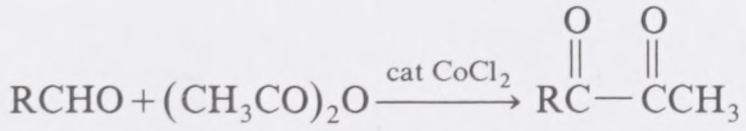
Org Syn *61* 59 (1983)



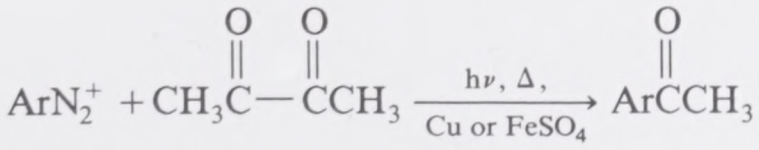
Syn 374 (1979)
JOC *45* 1722 (1980); *52* 2297 (1987)



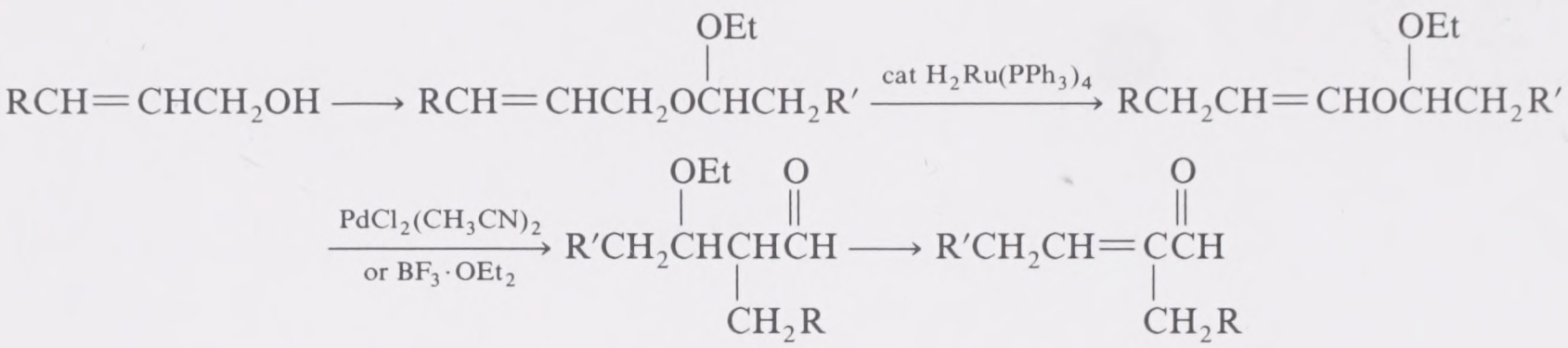
JOC *44* 3275 (1979)



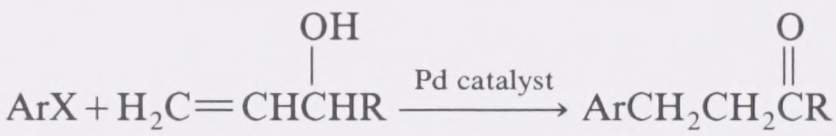
CC 692 (1987)



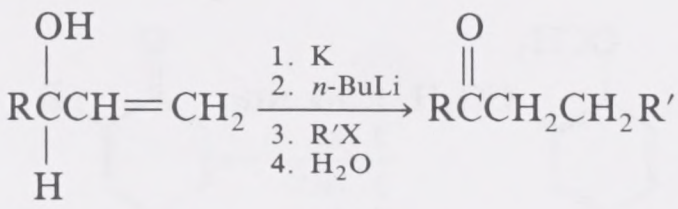
TL *23* 1831 (1982)



CL 1361, 1435 (1981)



JOC *41* 265, 273, 1206 (1976)
Tetr *35* 329 (1979)
Syn Commun *11* 579 (1981)
TL *22* 2479 (1981)



TL *28* 2587 (1987)

NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

GENERAL REFERENCES

"The Chemistry of Carboxylic Acids and Esters," Ed. S. Patai, Interscience, New York (1969)

"The Chemistry of Acyl Halides," Ed. S. Patai, Interscience, New York (1972)

"The Chemistry of Acid Derivatives," Ed. S. Patai, J. Wiley, New York (1979)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E4 (acid derivatives), G. Thieme, Stuttgart-New York (1983)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E5 (acids and derivatives), Part 1, G. Thieme, Stuttgart-New York (1985)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E5 (acids and derivatives), Part 2, G. Thieme, Stuttgart-New York (1985)

1. OXIDATION, SUBSTITUTION AND ADDITION

1. Alkanes

$$ArCH_3 \longrightarrow ArCO_2H$$

O_2, KO-*t*-Bu, DMF	JOC *28* 410 (1963)
NaOCl, cat $RuCl_3 \cdot 3\ H_2O$, cat *n*-Bu_4NBr	JOC *51* 2880 (1986)
HNO_3	Org Syn Coll Vol *3* 820, 822 (1955)
PbO_2, KOH	Org Syn Coll Vol *5* 617 (1973)
CrO_3, HOAc	JACS *78* 1689 (1956)
$Na_2Cr_2O_7$, H_2SO_4	Org Syn Coll Vol *1* 392, 543 (1941) JOC *23* 1236 (1958)
$Na_2Cr_2O_7$/HCl	Org Syn Coll Vol *5* 810 (1973)
$KMnO_4$	Org Syn Coll Vol *1* 159 (1941); *2* 135 (1943); *3* 740 (1955)
(*n*-Bu_4N)MnO_4, py	CC 253 (1978)

$$ArCH_3 \longrightarrow ArCH_2OAc$$

$Na_2S_2O_8$, $Cu(OAc)_2$	Syn 477 (1980)
$K_2S_2O_8$, $Cu(OAc)_2$	JCS Perkin I 669 (1979)
$Pb(OAc)_4$	JCS 3943 (1954) JACS *91* 138 (1969) Syn 567 (1973) (review)
$Mn(OAc)_3$	JACS *91* 138 (1969)
$Co(OAc)_3$	JACS *91* 6830 (1969)
$Pd(OAc)_2$	Syn 567 (1973) (review)
$Hg(OAc)_2$	JOC *50* 3070 (1985)

$Ce(NH_4)_2(NO_3)_6$, HOAc	JOC *31* 2033 (1966); *42* 3682 (1977)
DDQ, HOAc	TL *28* 5403 (1987)

$$ArCH_3 \xrightarrow{CrO_2(OAc)_2} ArCH(OAc)_2$$

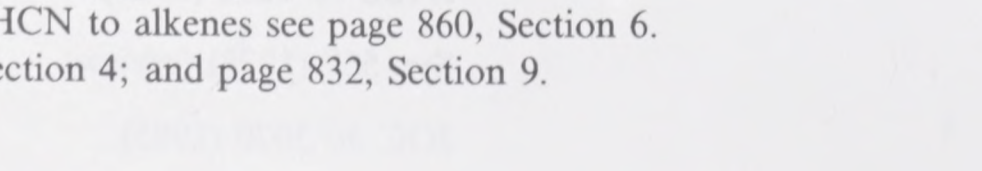
Syn 567 (1973) (review)

$$R_3CH \longrightarrow R_3CO_2CR'$$

$Pb(OAc)_4$, LiCl, CF_3CO_2H	JCS Perkin I 2576 (1976) JOC *50* 2759 (1985)
CrO_3, Ac_2O, HOAc	JOC *50* 2759 (1985)
$Pd(O_2CCF_3)_2$	JACS *109* 8109 (1987)

$$R_3CH \xrightarrow[CH_3CN]{Br_2} \xrightarrow{H_2O} R_3CNHCCH_3 \quad (O \text{ above } C)$$

Syn 632 (1977)



CC 688 (1981)

2. Arenes

$$ArH \longrightarrow ArO_2CR$$

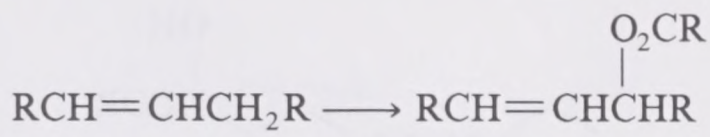
$(RCO_2)_2$; O_2, I_2, $CuCl_2$ or Lewis acid	Syn 1 (1972) (review)
$Pb(OAc)_4$	Syn 567 (1973) (review)
$K_2S_2O_8$, cat $Pd(O_2CCF_3)_2$	JACS *109* 8109 (1987)

$$RC_6H_5 \longrightarrow RCO_2H$$

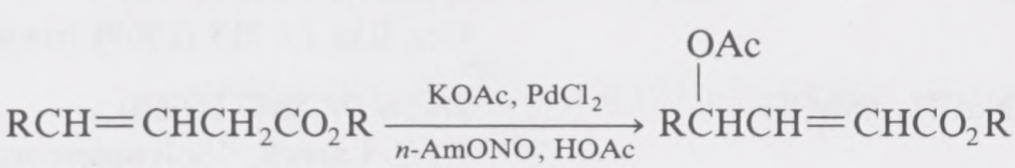
O_3/H_2O_2	JOC *42* 1254 (1977) JACS *98* 122 (1976); *108* 2343 (1986); *109* 5524 (1987)
$NaIO_4$, cat $RuCl_3 \cdot H_2O$	JOC *46* 3936 (1981)

3. Alkenes

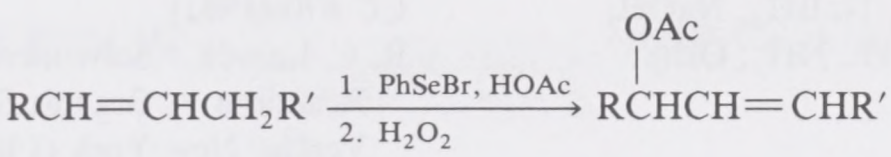
For alkenol → lactone see page 941, Section 8.
For the addition of HCN to alkenes see page 860, Section 6.
See also page 325, Section 4; and page 832, Section 9.



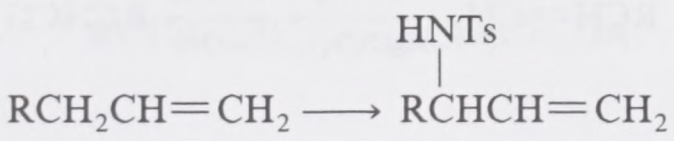
t-$C_4H_8O_3CC_6H_5$, Cu(I) or Cu(II)	JACS *80* 756 (1958); *81* 5819 (1959); *84* 774, 4969 (1962); *86* 3753 (1964); *108* 8230 (1986) Org Syn *48* 18 (1968) Syn 1 (1972) (review) TL *28* 1561 (1987)
cat $PdCl_2$, $CuCl_2$, HOAc, NaOAc, (PPh_3)	Angew Int *21* 366 (1982)
$Pb(OAc)_4$	Ann *481* 263 (1930) JOC *29* 3353 (1964) Syn 567 (1973) (review)
$Hg(OAc)_2$	JCS 2381 (1951) JOC *29* 3353 (1964) TL 3719 (1965); 4203 (1966); 3483 (1970) JACS *94* 2320 (1972) Syn 567 (1973) (review) R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1986), pp 190–196
$Mn(OAc)_3$, cat KBr	JCS C 2355 (1971)



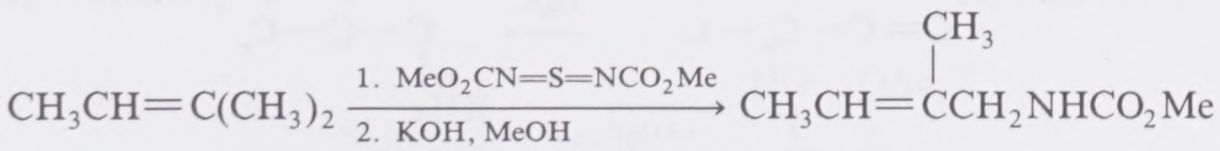
TL *22* 131 (1981)



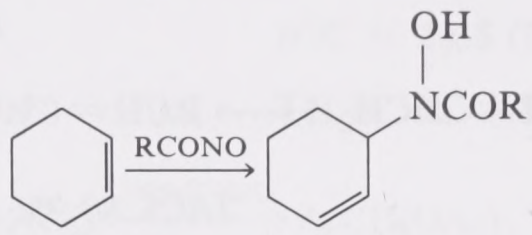
JACS *106* 1446 (1984)



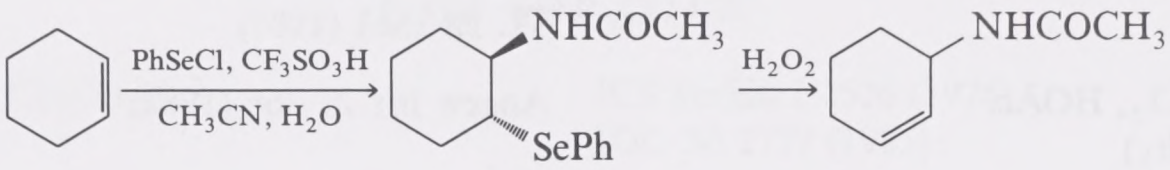
$TsN{=}S{=}NTs$	JOC *41* 176 (1976)
$TsN{=}Se{=}NTs$	JACS *98* 269 (1976)



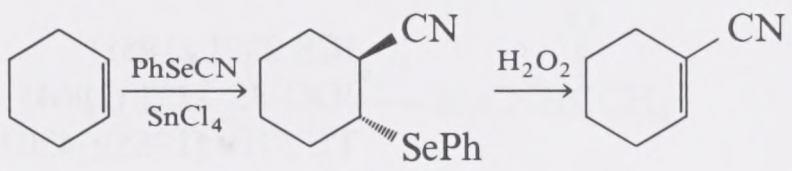
JOC *48* 3561 (1983)
Org Syn *65* 159 (1987)



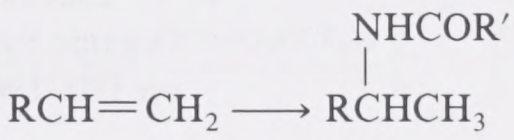
Tetr *37* 4007 (1981)



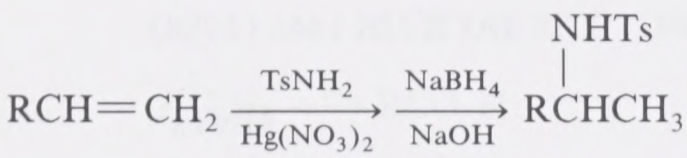
CC 546 (1981)
JOC *46* 4727 (1981)



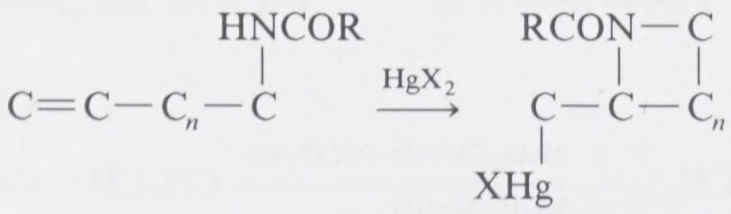
CC 871 (1982)



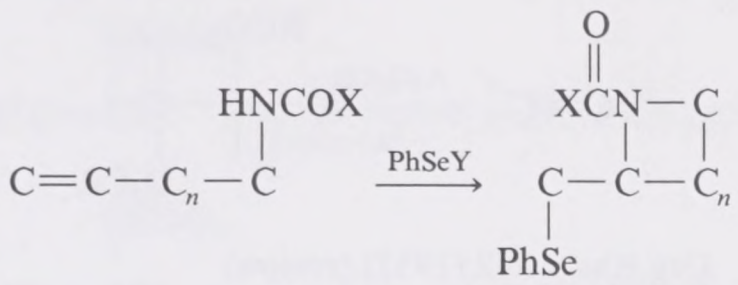
H_2SO_4, R′CN/H_2O	JACS *70* 4045 (1948) Org Rxs *17* 213 (1969) (review)
$Hg(NO_3)_2$, R′CN/$NaBH_4$, NaOH	JACS *91* 5647 (1969) R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)
$Hg(NO_3)_2$, R′CONH$_2$/$NaBH_4$, NaOH, *n*-BuNH$_2$ (R′ = Me, Ph, NH$_2$, OEt)	CC 670 (1981) R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)



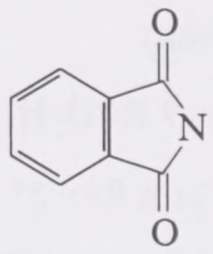
CC 1178 (1981)
R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)



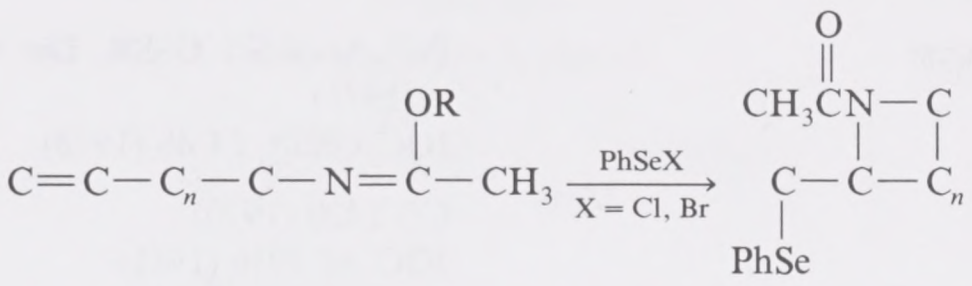
R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)
JOC *52* 4717 (1987)



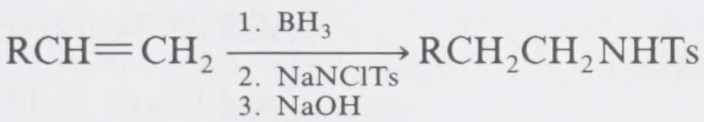
X	Y	
R	Cl, Br	JOC *51* 1724 (1986)
OR	Cl	CC 379 (1978) JOC *45* 2120 (1980)



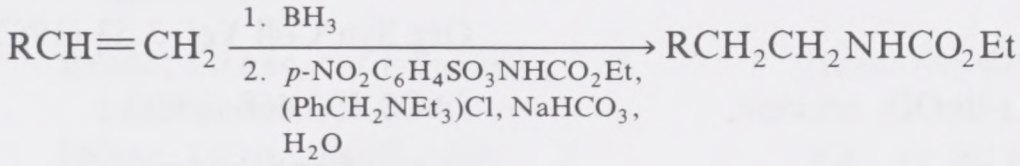
JACS *101* 3704 (1979)
Tetr *37* 4097 (1981)
TL *24* 1357 (1983)



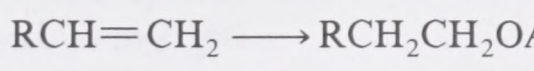
JCS Perkin I 1837 (1986)



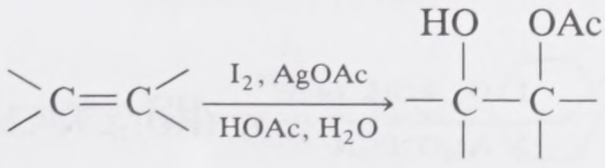
TL 181 (1978)



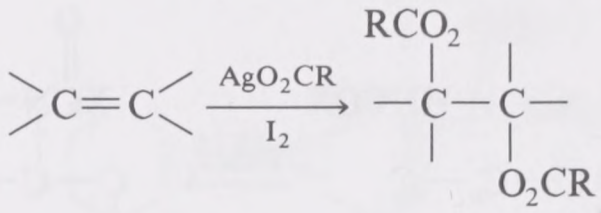
Syn Commun *11* 475 (1981)



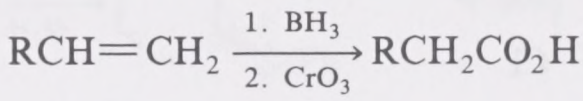
$BH_3/Hg(OAc)_2/I_2$	JOC *39* 834 (1974)
$BH_3/Pb(OAc)_4$ or $PhI(OAc)_2$	BCSJ *51* 901 (1978)
BH_3/HOAc, NaOAc, electrolysis	CL 1021 (1974)
$LiAlH_4$, $TiCl_4/Pb(OAc)_4$	TL 1405 (1979)



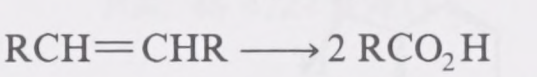
JACS *109* 6403 (1987)



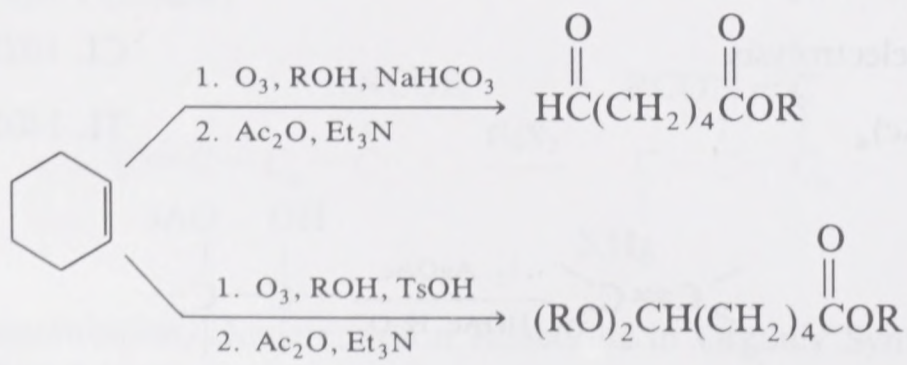
Org Rxs *9* 332 (1957) (review)
Adv Org Chem *1* 117 (1960) (review)
JCS C 1327 (1966)
JOC *50* 3070 (1985); *52* 2226, 5574, (1987)



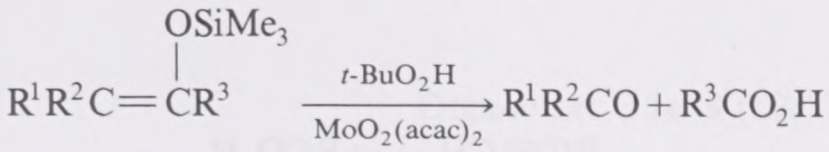
CC 122 (1968)

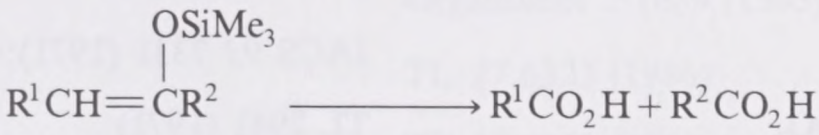


O_3/H_2O_2	Chem Rev *27* 437 (1940); *58* 925 (1958)
$O_3/K_2Cr_2O_7$, H_2SO_4	JACS *108* 4603 (1986)
O_3/H_2, Lindlar catalyst	Bull Acad Sci USSR, Div Chem Sci *25* 1790 (1976) JOC USSR *14* 48 (1978)
NaOCl, cat $RuCl_3$	CC 1420 (1970) JOC *46* 3936 (1981) JACS *103* 464 (1981) TL *28* 3061, 5441, 6331 (1987)
$NaIO_4$, cat RuO_4	JACS *85* 3419 (1963)
$NaIO_4$, cat $KMnO_4$	Can J Chem *33* 1701 (1955); *34* 1413 (1956) JACS *107* 7967 (1985)
$NaMnO_4$, *t*-BuOH, H_2O	JOC *26* 3734 (1961)
$KMnO_4$, H_2O	Org Syn Coll Vol *2* 53 (1943)
$KMnO_4$, Na_2CO_3, *t*-BuOH, acetone	JACS *108* 468 (1986)
$KMnO_4$, KNO_3, K_2CO_3	JOC *26* 3734 (1961)
$KMnO_4$, R_4NCl (phase transfer)	TL 1511 (1974) JOC *42* 3749 (1977) Org Syn *60* 11 (1981)
$KMnO_4$, dimethyl polyethylene glycol	JOC *43* 1532 (1978)
(*n*-Bu_4N)MnO_4, py	CC 253 (1978)

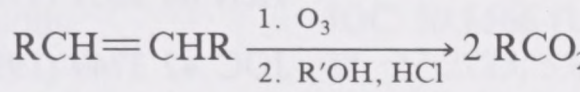


TL *23* 3867 (1982)



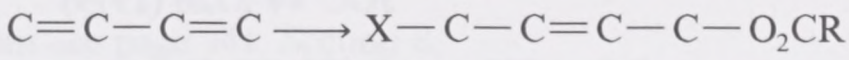


TL *22* 2595 (1981)



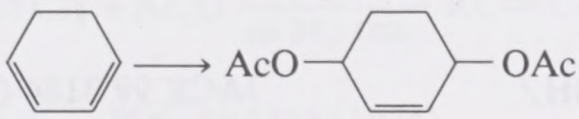
Angew Int *17* 939 (1978)

4. Dienes

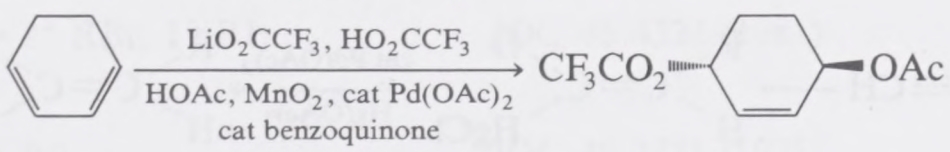


X = halogen

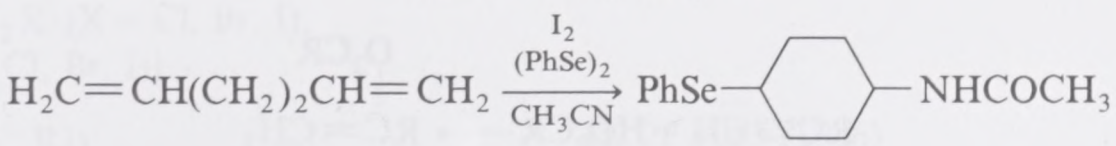
See page 325, Section 4.



Stereochemistry	Reagents	
cis	HOAc, LiOAc, LiCl, cat $Pd(OAc)_2$, benzoquinone	JACS *103* 4959 (1981)
	HOAc, LiOAc, LiCl, MnO_2, cat $Pd(OAc)_2$, cat benzoquinone	JOC *49* 4619 (1984)
	HOAc, LiOAc, $LiClO_4$, LiCl, cat $Pd(OAc)_2$, cat hydroquinone, electrolysis	CC 1236 (1987)
trans	HOAc, LiOAc, cat $Pd(OAc)_2$, benzoquinone	JACS *103* 4959 (1981)
	HOAc, LiOAc, MnO_2, cat $Pd(OAc)_2$, cat benzoquinone	JOC *49* 4619 (1984)
	HOAc, LiOAc, $LiClO_4$, cat $Pd(OAc)_2$, cat hydroquinone, electrolysis	CC 1236 (1987)
	HOAc, O_2, cat $Pd(OAc)_2$, cat hydroquinone, cat Co(II) *meso*-tetraphenylporphyrin	JACS *109* 4750 (1987)



TL *25* 2717 (1984)



CC 87 (1982)

5. Alkynes

$$RC{\equiv}CH \longrightarrow RCO_2H$$

$Tl(NO_3)_3$ — JACS *93* 7331 (1971); *95* 1296 (1973)

$NaIO_4$ or NaOCl, cat RuO_2 — TL 2941 (1971)

PhIO, cat $RuCl_2(PPh_3)_3$ — Helv *64* 2531 (1981)

$KMnO_4$, HOAc, H_2O, Aliquat 336 — JOC *42* 3749 (1977)

$KMnO_4$, HOAc, H_2O, Adogen-464 — Syn 462 (1978)

$$RC{\equiv}CR \longrightarrow 2\,RCO_2H$$

O_3 — Chem Rev *27* 437 (1940) (review)

$KMnO_4$, H_2O — JOC *44* 2726 (1979)

$$RC{\equiv}CH \longrightarrow RCH_2CO_2H$$

BH_3/*m*-$ClC_6H_4CO_3H$ — JACS *89* 291 (1967)

n-BuLi/Me_3SiCl/$\left(\text{C}_6\text{H}_{11}\right)_2$BH/ H_2O_2, NaOH — JACS *99* 3184 (1977); *106* 6006 (1984)

$$RC{\equiv}CR' \xrightarrow[CH_3OH]{PhI(OH)OTs} RR'CHCO_2CH_3$$

TL *28* 2845 (1987)

$$RC{\equiv}CSiMe_3 \xrightarrow[R'OH]{\text{cat } OsO_4,\ t\text{-}BuO_2H} RC(=O)-C(=O)OR'$$

R′ = H or alkyl

TL *27* 1947 (1986)

$$RC{\equiv}CX \xrightarrow[\text{cat } RuCl_2(PPh_3)_3]{PhIO} RC(=O)-C(=O)X$$

X = OR, NR_2

TL *23* 3661 (1982)

$$RC{\equiv}CH \longrightarrow \begin{matrix} R & & H \\ & C{=}C & \\ H & & HgCl \end{matrix} \xrightarrow[Hg(OAc)_2]{\text{cat } Pd(OAc)_2} \begin{matrix} R & & H \\ & C{=}C & \\ H & & OAc \end{matrix}$$

JACS *102* 1966 (1980)

$$RC{\equiv}CH + HO_2CR' \longrightarrow \begin{matrix} & O_2CR' \\ & | \\ RC{=}CH_2 & \end{matrix}$$

Review: JACS *102* 1966 (1980)

Reagent(s)	
cat $[Ru(CO)_2(OAc)]_n$	Organomet *2* 1689 (1983)
cat $Ru_3(CO)_{12}$	Organomet *2* 1689 (1983)
cat $RuCl_3 \cdot 3\ H_2O$, (PR_3)	TL *27* 6323 (1986)
cat $RuCl_2(PMe_3)$(*p*-cymene)	TL *27* 6323 (1986)
cat bis(η^5-cyclooctadienyl)ruthenium, cat PR_3, (cat maleic anhydride)	JOC *50* 1566 (1985); *52* 2230 (1987) TL *27* 2125, 5389 (1986)
cat $PdCl_2(PhCN)_2$, Et_3N	TL *25* 5323 (1984) (intramolecular)
cat $Hg(OAc)_2$	JACS *77* 939 (1955); *103* 5459 (1981) (intramolecular)
cat $HgO\text{-}BF_3 \cdot OEt_2\text{-}MeOH$	JACS *56* 1802 (1934)

For intramolecular reactions see page 941, Section 8.

$$RC{\equiv}CH + Ac_2O \xrightarrow[\text{cat } BF_3 \cdot OEt_2]{\text{cat } Hg(OAc)_2} R\overset{\overset{\displaystyle OAc}{|}}{C}{=}CH_2$$

JOC *38* 4254 (1973)

$$RC{\equiv}CR \xrightarrow[\text{2. Zn}]{\text{1. } Hg(OAc)_2,\ HOAc} \begin{matrix} H \\ R \end{matrix}\!\!>C{=}C<\!\!\begin{matrix} R \\ OAc \end{matrix}$$

JOC *47* 3707 (1982)

6. Alkyl Halides

See also page 966, Section 3.

$$RX \longrightarrow RO\overset{\overset{\displaystyle O}{\|}}{C}R'$$

NaO_2CR', HMPA (RX = 1° RBr; 1° RI; allylic Cl; benzylic Cl)	JOC *39* 3721 (1974)
KO_2CR', alumina (RX = 1°, 2° RBr; 1° R_2SO_4)	Syn Commun *10* 279 (1980)
CsO_2CR', DMF (RX = 2° RBr; 1° RI; 1°, 2° ROMs)	JOC *46* 4321 (1981)
$Hg(O_2CR')_2$, cat $B(O_2CR')_3$ [RX = 1° RI; 3° RX (X = Cl, Br, I); $H_2C{=}CHCH_2X$ (X = Cl, Br, I), $PhCH_2X$ (X = Cl, Br, I)]	JOC *39* 3721 (1975)
$R'CO_3H$ (RX = 3° RI)	TL *27* 6055 (1986)
$PhI(OAc)_2$ (RX = 3° RI)	TL *27* 6055 (1986)

$$R_2C{=}CHI \xrightarrow{Cu(OAc)_2} R_2C{=}CHOAc$$

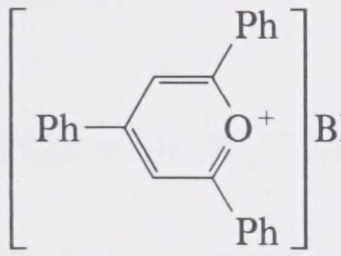
JOMC *93* 415 (1975)

$$R_3CX \xrightarrow[CH_3CN]{(NO_2)BF_4} \xrightarrow{H_2O} R_3CNHC(=O)CH_3$$

JOC *45* 165 (1980)

7. Amines

$$RCH_2NH_2 \longrightarrow RCH_2OC(=O)R'$$



$BF_4^-/R'CO_2Na$ CC 701 (1977)

$R'COCl/N_2O_4/\Delta$ Org Syn Coll Vol *5* 336 (1973)

8. Nitro Compounds

$$RCH_2NO_2 \xrightarrow[2.\ MoO_5\cdot py\cdot HMPA]{1.\ LDA} RCO_2H$$

TL *22* 5235 (1981)

9. Ethers

$$RCH_2OR \xrightarrow[Cu(I)\ or\ Cu(II)]{t\text{-}BuO_3CR'} RCH(O_2CR')OR$$

Syn 1 (1972) (review)

$$(RCH_2)_2O \longrightarrow RCOCH_2R$$

CrO_3, HOAc
Helv *42* 1124 (1959)
CC 752 (1966) ($Me > RCH_2$)
Carbohydr Res *12* 147 (1970)
JACS *107* 5289 (1985)

H_2CrO_4 JCS 221, 227 (1959)

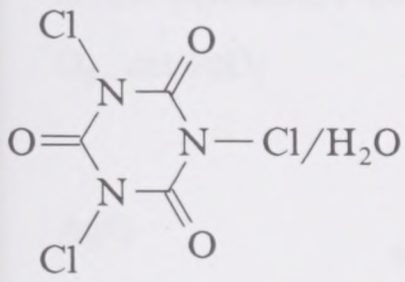
$(PhCH_2NEt_3)MnO_4$ Angew Int *18* 69 (1979)

$Zn(MnO_4)_2$, silica gel — JACS *105* 7755 (1983)

RuO_4 — JACS *80* 6682 (1958)
JOC *28* 2729 (1963)
TL *28* 435 (1987)

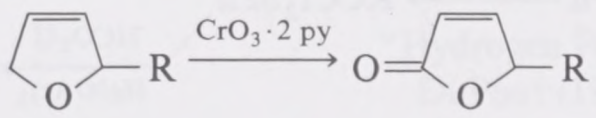
$NaIO_4$, cat RuO_2 — Syn Commun *10* 205 (1980)
JACS *102* 3904 (1980); *107* 1308 (1985)
JOC *52* 83 (1987)

$NaIO_4$, cat $RuCl_3 \cdot H_2O$ — JOC *46* 3936 (1981); *51* 1015 (1986)

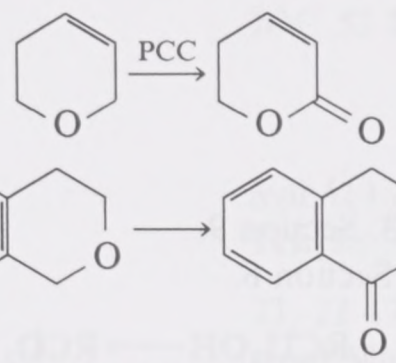


TL 5819 (1968)

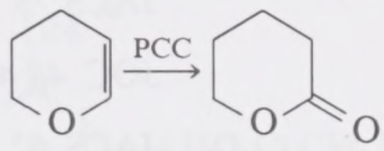
Tetr *27* 2671 (1971)



TL *28* 5819 (1987)



JOC *49* 1647 (1984)



TL *27* 4011 (1986)

$$ROR' \longrightarrow ROCR''$$

Ac_2O, NaI — TL *28* 2537 (1987)

Ac_2O, Me_3SiCl ($R' = CH_3$, CH_2SCH_3) — TL *24* 1189 (1983)

Ac_2O, $FeCl_3$ — JOC *39* 3728 (1974)

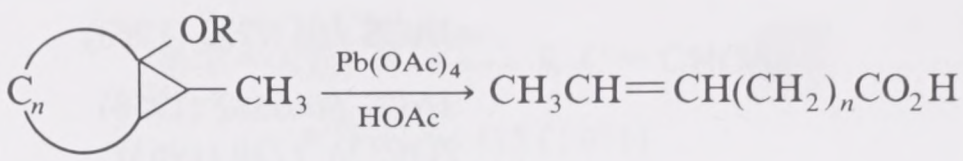
R″COCl, NaI — TL *23* 681 (1982); *28* 2537 (1987)

$$ROTHP \xrightarrow[HOAc]{AcCl} ROAc$$

Syn 567 (1972)

$$R_3COMe \xrightarrow[CH_3CN]{(NO_2)BF_4} \xrightarrow{H_2O} R_3CNHCCH_3$$

JOC *45* 165 (1980)

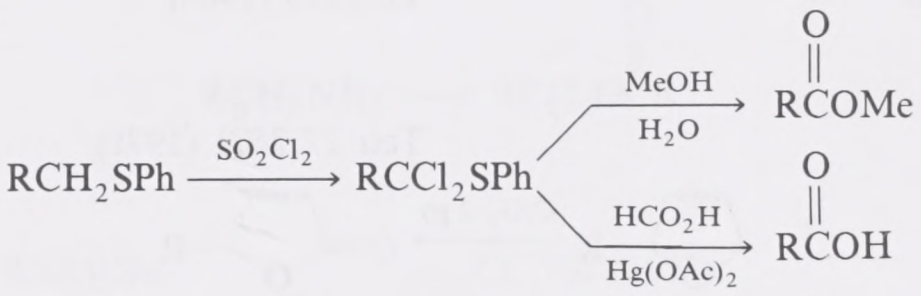


R = H, $SiMe_3$

n = 3–5

TL 4013 (1977)
JACS *107* 4230 (1985)

10. Sulfides



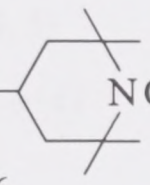
CC 857 (1982)

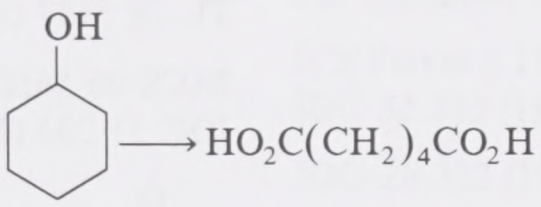
11. Alcohols

For alcohol → ester see also page 963, Section 9.
For alkenol → lactone see page 941, Section 8.

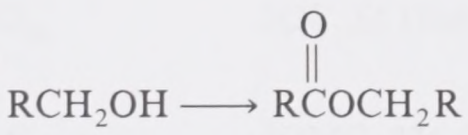
$RCH_2OH \longrightarrow RCO_2H$

CrO_3, HOAc	JACS *78* 2255 (1956)
CrO_3, H_2SO_4	JOC *48* 4404 (1983)
$K_2Cr_2O_7$, H_2SO_4	JACS *82* 2498 (1960)
$(C_5H_5NH)_2Cr_2O_7$ (PDC), DMF (non-allylic)	TL 399 (1979); *28* 5311, 6069 (1987) JACS *104* 1774 (1982); *109* 5437 (1987) JOC *50* 2607 (1985) CL 85 (1986)
$KMnO_4$	JCS 633 (1939); 2685 (1950) BCSJ *36* 1264 (1963) TL *28* 5263 (1987)
$KMnO_4$ (phase transfer)	TL 1511 (1974) JACS *109* 7280 (1987)
$NaMnO_4 \cdot H_2O$	TL *22* 1655 (1981)
(n-Bu_4N)MnO_4, py (benzylic)	CC 253 (1978)
$Zn(MnO_4)_2 \cdot 6\ H_2O$	J Biol Chem *241* 3970 (1966) JOC *50* 5480 (1985)
$Cu(MnO_4)_2 \cdot 8\ H_2O$	JOC *47* 2790 (1982)
$NaIO_4$, cat $RuCl_3 \cdot H_2O$, H_2O, CH_3CN, CCl_4	JOC *46* 3936 (1981); *50* 5696 (1985)

$NaIO_4$, cat RuO_2, H_2O, CH_3CN, CCl_4	TL *28* 6425 (1987)
H_5IO_6, cat $RuCl_3 \cdot H_2O$, H_2O, CH_3CN, CCl_4	JOC *50* 1560 (1985)
$RuCl_3$, $K_2S_2O_8$	TL *28* 4965 (1987)
RuO_4	JACS *80* 6682 (1958)
cat $K_2Ru_2O_4$, K_2SO_5	CC 58 (1979)
cat $RuO_2 \cdot 2\ H_2O$, electrolysis	JOC *51* 155 (1986)
nickel peroxide, NaOH	JOC *27* 1597 (1962)
O_2, cat PtO_2	Ber *89* 1648 (1956) Tetr *9* 67 (1960) JOC *52* 4898 (1987)
AgO	TL 5685 (1968)
HNO_3	Org Syn Coll Vol *1* 168 (1941)
H_2O_2	"Hydrogen Peroxide in Organic Chemistry," DuPont (1962), p 57
NaOCl, cat  , KBr, Aliquat 336	JOC *52* 2559 (1987)
electrolysis [$Ni(OH)_2$ anode]	Syn 513 (1979) Tetr *38* 3299 (1982)
Pseudomonas aeruginosa (R = allene, enantioselective)	TL *21* 1711 (1980) Appl Microbiol Biotechnol *21* 258 (1985)



HNO_3	Rec Trav Chim *24* 19 (1905) JACS *52* 3235 (1930) Org Syn Coll Vol *1* 18 (1941)
$KMnO_4$	Ber *41* 575 (1908), *55B* 3526 (1922) J Chem Ed *10* 113 (1933)



$Ca(OCl)_2$	TL *23* 35 (1982)
KI, H_2O, electrolysis	TL 165 (1979)
$Na_2Cr_2O_7$, H_2SO_4	Org Syn Coll Vol *1* 138 (1941)
t-BuO_2H, cat $(PhCH_2NMe_3)OMoBr_4$	TL *25* 4417 (1984)
cat $H_2Ru(PPh_3)_4$	TL *22* 5327 (1981) JOC *52* 4319 (1987)

cat $Ru_3(CO)_{12}$, $PhC{\equiv}CPh$ — TL *22* 1541 (1981)

cat $PdCl_2$, K_2CO_3, CCl_4 — CL 1171 (1981)

$$2\,RCH_2OMR'_3 \xrightarrow{NBS} RC(=O)CH_2R$$

$$RCH_2OMR'_3 + R''CHO \xrightarrow{NBS} R''C(=O)CH_2R$$

$\underline{R'_3M}$	
Me_3Si	JOC *43* 371 (1978)
n-Bu_3Sn	JACS *98* 1629 (1976)

$$RCH_2OH \longrightarrow RC(=O)R'$$

$CrO_3 \cdot 2$ py, Ac_2O, *t*-BuOH (R′ = *t*-Bu)	JOC *49* 4735 (1984) TL *27* 3049 (1986)
$(COCl)_2$-DMSO, $Et_3N/(CH_3)_2C(OH)CN$, $Et_3N/(COCl)_2$-DMSO, Et_3N/MeOH (R′ = Me)	JOC *51* 3023 (1986)

$$RCH_2OH \xrightarrow[MnO_2]{NaCN \text{ or } KCN} RC(=O)CH_3$$

$\underline{R}$	
aryl	TL *28* 5157 (1987)
vinylic	JACS *90* 5616 (1968) JOC *51* 253 (1986)

$$ROH \longrightarrow ROCR'$$

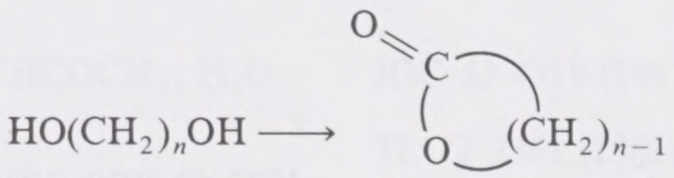
MsCl, Et_3N/CsO_2CEt (R′ = Et)	JOC *46* 4321 (1981)
$Zn(O_2CR')_2$ (R′ = Me, Ph), PPh_3, $EtO_2CN{=}NCO_2Et$	Syn Commun *16* 611 (1986)

12. Diols

$$RCH(OH)-CH(OH)R \longrightarrow RCO_2H$$

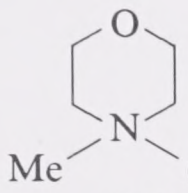
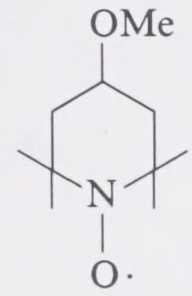
$KMnO_4$	JOC *50* 3007 (1985)
$NaIO_4/AgNO_3$, KOH	JACS *107* 3285 (1985)
$NaIO_4$, cat $RuCl_3 \cdot H_2O$	JOC *46* 3936 (1981)

NaOCl, cat $RuCl_3 \cdot 3\ H_2O$	CC 1420 (1970)
cat $RuO_2 \cdot 2\ H_2O$, electrolysis	JOC *51* 155 (1986)
H_2O_2, cat $Na_2WO_4 \cdot 2\ H_2O$-H_3PO_4	JOC *51* 1599 (1986)
t-BuO_2H, cat $VO(acac)_2$	TL *24* 5009 (1983)
t-BuO_2H, cat $Mo(CO)_6$, cat $[C_5H_5N(CH_2)_{15}CH_3]Cl$, $MgSO_4$	Syn 59 (1986)

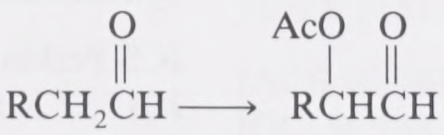


Review: Heterocycles *14* 661 (1980) ($n = 4$)

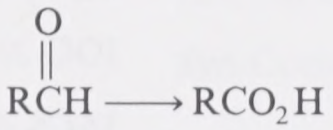
O_2, cat Pt ($n = 4$)	TL 3899 (1973); 4045 (1976) JACS *98* 3379 (1976); *102* 3964 (1980)
$NaBrO_3$ ($n = 4$–6)	CL 1097 (1983)
NIS, AgOAc ($n = 4$, 5)	JOC *52* 5472 (1987)
$AgCO_3$, Celite ($n = 4$–6)	Tetr *31* 171, 987 (1975) TL 4045 (1976); *22* 3721, 3725 (1981) JOC *43* 1086 (1978); *50* 3017 (1985); *52* 325 (1987) JACS *104* 5523 (1982) JCS Perkin I 1579 (1983)
MnO_2 ($n = 4$, 5; allylic)	JACS *98* 4312 (1976) TL 111 (1978) Syn Commun *13* 237 (1983)
$BaMnO_4$ ($n = 4$)	JCS Perkin I 1579 (1983) JOC *52* 325 (1987)
$KMnO_4$ ($n = 4$)	JOC *28* 323 (1963); *42* 1623 (1977)
CrO_3, py ($n = 4$, 6)	JACS *76* 527 (1954) JOC *28* 323 (1963) TL *27* 1445 (1986)
$Na_2Cr_2O_7$, H_2SO_4 ($n = 4$, 5)	JOC *28* 323 (1963); *45* 1828 (1980)
copper chromite ($n = 4$, 5)	JACS *68* 1385 (1946); *69* 1545 (1947)
H_2O_2, $[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$ ($n = 4$–6)	JOC *52* 1868 (1987)
cat $Ru_3(CO)_{12}$, $PhC{\equiv}CPh$ ($n = 4$, 5)	JOMC *226* Cl (1982)
cat $RuO_2 \cdot 2\ H_2O$, electrolysis ($n = 4$, 5)	JOC *51* 155 (1986)
cat $RuCl_2L_3$ or $Ru_2Cl_4L_3$, $PhCH{=}CHCOCH_3$, Et_3N ($n = 4$, 5)	TL *24* 2677 (1983)
cat $H_2Ru(PPh_3)_4$, $PhCH{=}CHCOPh$ ($n = 5$)	J Mol Catal *7* 337 (1980)

cat $H_2Ru(PPh_3)_4$, $PhCH{=}CHCOCH_3$ ($n = 4, 5$)	TL *27* 365 (1986) JOC *51* 2034 (1986)
cat $H_2Ru(PPh_3)_4$, CH_3COCH_3 ($n = 4, 5$)	TL *22* 5327 (1981) JOC *52* 4319 (1987)
 , cat $RuCl_2(PPh_3)_3$/ Ag_2CO_3, Celite ($n = 5$)	TL *27* 3311 (1986)
Cl_2,  ($n = 4, 5$)	JOC *50* 3930 (1985)
$Ni(O_2CR)_2$, Br_2 ($n = 4$)	Syn Commun *10* 881 (1980) JOC *46* 4806 (1981)
Raney Ni ($n = 4$)	JOC *21* 1325 (1956)
horse liver alcohol dehydrogenase ($n = 4, 5$) (chiral)	CC 469 (1977); 515 (1980) JACS *104* 4659 (1982); *106* 1461 (1984); *107* 2521 (1985) Can J Chem *60* 2007 (1982) Org Syn *63* 10 (1984)

13. Aldehydes



$Pb(OAc)_4$	JACS *79* 1938 (1957) Compt Rend *250* 4174 (1960)
$Pb(OAc)_4$, BF_3	BSCF 4083 (1968)



air	JOC *51* 449 (1986)
O_2, cat Mn(II) stearate	JOC *52* 287 (1987)
$KMnO_4$	Org Syn Coll Vol *2* 315, 538 (1943) JACS *106* 3297 (1984); *107* 199 (1985)
$KMnO_4$, 18-crown-6	JACS *94* 4024 (1972) TL *27* 4537 (1986)
$KMnO_4$, $MgSO_4$	JACS *109* 7122 (1987)
$KMnO_4$, *t*-BuOH, 5% (K)NaH_2PO_4	TL *27* 4537 (1986) JACS *109* 7575 (1987)

$NaMnO_4 \cdot H_2O$	TL *22* 1655 (1981)
$(PhCH_2NEt_3)MnO_4$, CH_2Cl_2, HOAc	Monatsh *110* 1471 (1979)
$(n\text{-}Bu_4N)MnO_4$, py (R = Ar)	CC 253 (1978)
$Cu(MnO_4)_2 \cdot 8\ H_2O$	JOC *47* 2790 (1982)
cat $(PhCH_2NMe_3)OMoBr_4$, $t\text{-}BuO_2H$	TL *25* 4417 (1984)
$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, H_2O_2, $CeCl_3 \cdot 7\ H_2O$, $n\text{-}Bu_4NCl$, K_2CO_3	TL *25* 173 (1984)
cat $H_2Ru(PPh_3)_4$, $PhCH{=}CHCOCH_3$, H_2O	JOC *52* 4319 (1987)
cat $RuCl_2(PPh_3)_4$, PhIO	TL *22* 2361 (1981)
$NaIO_4$, cat RuO_2	JOC *52* 622 (1987)
$NaIO_4$, cat $RuCl_3 \cdot H_2O$, CCl_4, CH_3CN, H_2O	JOC *46* 3936 (1981)
cat $RuO_2 \cdot 2\ H_2O$, electrolysis	JOC *51* 155 (1986)
RuO_4	JACS *80* 6682 (1958)
CrO_3, Ac_2O	JACS *86* 2612 (1964)
$K_2Cr_2O_7$, H_2SO_4	JACS *80* 3022, 3030 (1958); *107* 199 (1985); *108* 1039 (1986)
$(C_5H_5NH)_2Cr_2O_7$	TL 399 (1979) JOC *50* 2095 (1985)
$(bipy)H_2CrOCl_5$	Syn Commun *10* 951 (1980)
$(phen)_2H_2CrOCl_5$	Syn Commun *10* 951 (1980)
$(bipy)CrOCl_5$	Syn Commun *10* 951 (1980)
Ag_2O	JACS *73* 2590 (1951); *92* 336 (1970); *106* 1029 (1984); *107* 7978 (1985) Org Syn Coll Vol *4* 919 (1963) Tetr *24* 6583 (1968) JOC *44* 1022 (1979); *50* 2981 (1985); *51* 956 (1986) Syn 74 (1981) JCS Perkin I 461 (1982)
AgO	TL 5685 (1968)
AgO, NaCN	JACS *90* 5616 (1968)
$AgNO_3$, NaOH, H_2O_2, H_2O, O_2	Ber *93* 2743 (1960)
NBS, H_2O	JACS *78* 1689 (1956)
$NaClO_2$, $CH_3CH{=}C(CH_3)_2$	JOC *45* 1175 (1980)
$NaClO_2$, $(K)NaH_2PO_4$, $CH_3CH{=}C(CH_3)_2$	Tetr *37* 2091 (1981) JOC *50* 470 (1985) JACS *109* 6719 (1987) TL *28* 5759, 5763 (1987)

$NaClO_2$, NaH_2PO_4, $(CH_3)_2C{=}CH_2$	JACS *106* 7217 (1984) TL *27* 3533 (1986)
$NaClO_2$, H_2O_2, NaH_2PO_4	JOC *51* 567 (1986)
$NaClO_2$, H_2NSO_2OH	Acta Chem Scand *27* 888 (1973) JOC *51* 3007 (1986)
$NaClO_2$, HOAc	Methods Carbohydr Chem *3* 182 (1963)
$NaClO_2$, resorcinol, acetate buffer	Acta Chem Scand *27* 888 (1973)
$Ca(OCl)_2$	TL *23* 3131 (1982)
HNO_3	Org Syn Coll Vol *1* 166 (1941)
H_2O_2	"Hydrogen Peroxide in Organic Chemistry," DuPont (1962), p 56
nickel peroxide, NaOH (R = Ar)	Chem Pharm Bull *26* 299 (1978)
$CF_3C(OH)(O_2H)CF_3$	TL *21* 685 (1980)
$NaHSO_3/Ac_2O$, $DMSO/H_2O$	TL *27* 3995 (1986)

$$\underset{\text{RCH}}{\overset{\text{O}}{\overset{\|}{}}} \longrightarrow \underset{\text{RCX}}{\overset{\text{O}}{\overset{\|}{}}}$$

Cl_2	Org Syn Coll Vol *1* 155 (1941)
$(PhCO_2)_2$, CCl_4	JACS *69* 2916 (1947)
NBS, hν	TL 3809 (1979)

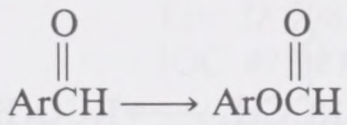
$$2\,\underset{\text{RCH}}{\overset{\text{O}}{\overset{\|}{}}} \longrightarrow \underset{\text{RCOCH}_2\text{R}}{\overset{\text{O}}{\overset{\|}{}}}$$

RCH_2ONa	Org Syn Coll Vol *1* 104 (1941)
$B(OH)_3$	JOC *38* 1433 (1973)
$Al(OR)_3$	Chem Zentr *77* 1309, 1554, 1556 (1906) Org Syn Coll Vol *1* 104 (1941) JACS *69* 2605 (1947); *74* 5133 (1952) JOC *33* 3310 (1968)
cat $H_2Ru(PPh_3)_4$, H_2O	JOC *52* 4319 (1987)
cat $Ru_3(CO)_{12}$, H_2O, $PhC{\equiv}CPh$	TL *22* 1541 (1981)

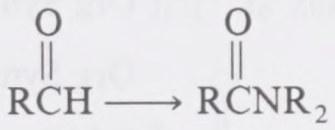
$$\underset{\text{RCH}}{\overset{\text{O}}{\overset{\|}{}}} \longrightarrow \underset{\text{RCOR}'}{\overset{\text{O}}{\overset{\|}{}}}$$

NaOCl, HOAc, MeOH	TL *23* 4647 (1982)
HOCl, R′OH	TL *23* 4647 (1982)
t-BuOCl/R′OH, Et_3N or py	JOC *47* 1360 (1982)
t-BuO_2H, cat $(PhCH_2NMe_3)OMoBr_4$, R′OH	TL *25* 4417 (1984)
O_2, cat HCl, hν, R′OH (R = Ph)	CL 475 (1974)

O_3, KOH, R′OH	TL 1627 (1978)
$NaHSO_3/Ac_2O$, DMSO/R′OH	TL *27* 3995 (1986)
H_2SO_5, R′OH	JOC *33* 2525 (1968)
$(NH_4)_2S_2O_8$, H_2SO_4, MeOH	Tetr *37* 2091 (1981)
KCN, $PhNO_2$, R′OH, phase transfer catalyst (R = aryl)	Tetr *38* 337 (1982)
NaCN or KCN, MnO_2, CH_3OH (R = vinylic)	JACS *90* 5616 (1968) Ber *103* 3774 (1970) JOC *51* 253, 3070 (1986)
Me_3SiCl, cat $ZnI_2/H_3O^+/MnO_2$, MeOH	Tetr *37* 2091 (1981)
PDC, CH_3OH	TL *28* 3235 (1987)
NBS, $R'OSiMe_3$	JOC *43* 371 (1978)
NBS, $R'OSn(n\text{-}Bu)_3$	JACS *98* 1629 (1976)
NBS, hν/R′OH	TL 3809 (1979)
I_2, CH_3OH, KOH	JCS C 1693 (1968) JOC *50* 2707 (1985)
cat $Ru_3(CO)_{12}$, RCH_2OH (R′ = R), $PhC{\equiv}CPh$	TL *22* 1541 (1981)
cat $H_2Ru(PPh_3)_4$, R′OH	JOC *52* 4319 (1987)
electrolysis, R′OH	JOC *50* 4967 (1985)
electrolysis, NaCN, MeOH	BCSJ *55* 335 (1982)



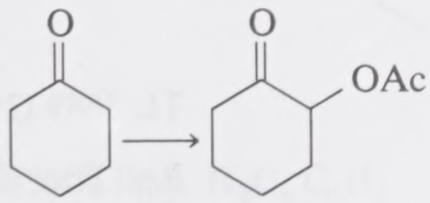
m-$ClC_6H_4CO_3H$, KF	TL *22* 3895 (1981)
H_2O_2, SeO_2	TL *27* 6299 (1986)



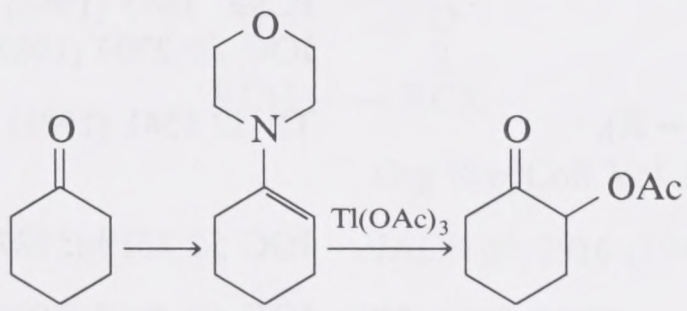
NBS, hν/RNH_2	TL 3809 (1979)
$Me_3SiCN/LDA/Ph_2P(O)ONMe_2/H_3O^+$	TL *23* 3255 (1982)
$NaHSO_3/Ac_2O$, $DMSO/HNR_2$	TL *27* 3995 (1986)

14. Ketones

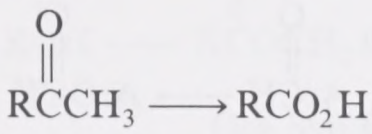
See also page 929, Section 7.



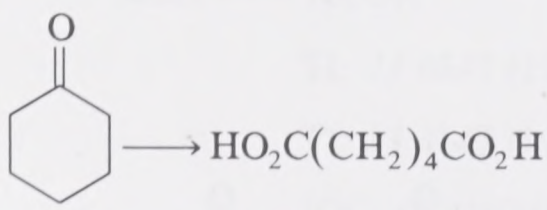
$Pb(OAc)_4$	JCS 4426 (1955) Austral J Chem *13* 121 (1960) Syn 567 (1973) (review) JACS *107* 5576 (1985)
$Pb(OAc)_4$, hν	JCS C 2484 (1969)
$Pb(OAc)_4$, cat $BF_3 \cdot OEt_2$	JCS 4472 (1961) Syn 567 (1973) (review)
$Hg(OAc)_2$	Naturwiss *35* 125 (1948) Ann *561* 165 (1949); *581* 59 (1953) Helv *35* 1615 (1952) JCS 3512 (1953); 705 (1954) JACS *79* 4465 (1957) Ber *93* 1374 (1960) JOC *28* 1705 (1963) Syn 567 (1973) (review) R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1985), p 205 (review)



JOC *33* 3359 (1968)

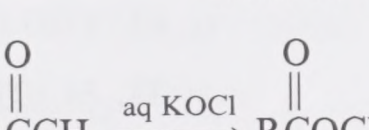


$HNO_3/KMnO_4$ (R = aryl)	Org Syn Coll Vol *3* 791 (1955)
$Na_2Cr_2O_7$, HOAc (R = aryl)	Org Syn Coll Vol *3* 420 (1955)
NaOCl (R = aryl)	Org Syn Coll Vol *2* 428 (1943)
KOCl (R = vinylic)	Org Syn Coll Vol *3* 302 (1955)
Br_2, NaOH/HCl (R = 1°, 2° alkyl)	Org Syn Coll Vol *5* 8 (1973) JACS *107* 2033 (1985)
I_2, py/NaOH (R = aryl)	JACS *66* 894 (1944)
$C_6F_5I(O_2CCF_3)_2$, H_2O, C_6H_6 (R = aryl)	CC 202 (1987)



KO_2 (phase transfer)	TL 3689 (1978)
HNO_3	Rec Trav Chim *24* 19 (1905)

$KMnO_4$	Ber *39* 2202 (1906)
$Zn(MnO_4)_2$, silica gel	JACS *105* 7755 (1983)
$C_6H_5I(O_2CCF_3)_2$, H_2O, C_6H_6	CC 202 (1987)

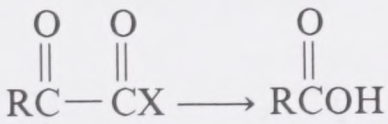


Reviews:

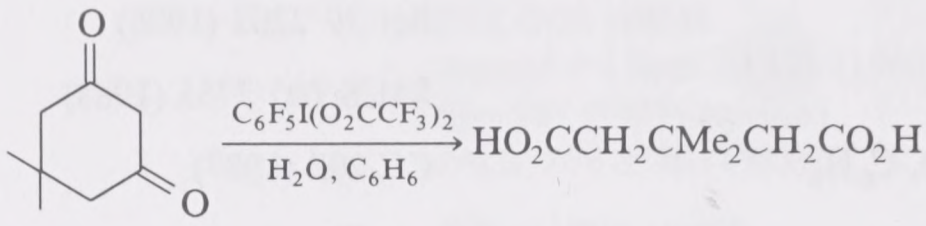
Chem Rev *45* 385 (1949)
Org Rxs *9* 73 (1957)
P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, pp 577–589
Quart Rev *21* 429 (1967)
B. Plesnicar, "Oxidation in Organic Chemistry," Ed. W. S. Trahanovsky, Academic Press, New York (1978), pp 254–262
Tetr *37* 2697 (1981)

RCO_3H	Org Rxs *9* 73 (1957) (review)
m-$ClC_6H_4CO_3H$	JOC *50* 2759 (1985)
m-$ClC_6H_4CO_3H$, $NaHCO_3$	JOC *52* 3560 (1987) TL *28* 4773 (1987)
m-$ClC_6H_4CO_3H$, cat Li_2CO_3	JOC *52* 5700 (1987)
m-$ClC_6H_4CO_3H$, cat TsOH	JOC *50* 2489 (1985)
CF_3CO_2H	TL *28* 3061 (1987)
H_2O_2, $(CF_3CO)_2O$	JACS *77* 188 (1955); *107* 5717 (1985) Tetr *6* 253 (1959)
98% H_2O_2, $(CF_3CO)_2O$, Na_2HPO_4	Tetr *37* 3981 (1981) JOC *47* 3871 (1982)
H_2O_2, $PhSeO_2H$	CC 870 (1977)
H_2O_2, CF_3COCF_3	TL 2741 (1970)
$Me_3SiOSO_3OSiMe_3$	JOC *44* 4969 (1979)

JACS *107* 5570 (1985)

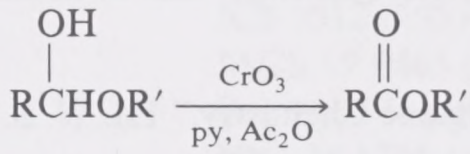


X	Reagent(s)	
R, ONa	$Ca(OCl)_2$, H_2O, HOAc, CH_3CN	TL *23* 3135 (1982)
R	HIO_4	JCS 1467 (1935) JACS *81* 37 (1959)
R (R = Ph)	$C_6F_5I(O_2CCF_3)_2$, H_2O, C_6H_6	CC 202 (1987)

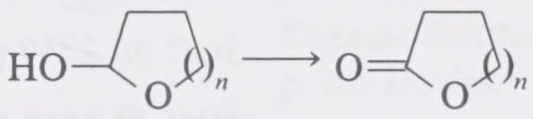


CC 202 (1987)

15. Hemiacetals and Lactols



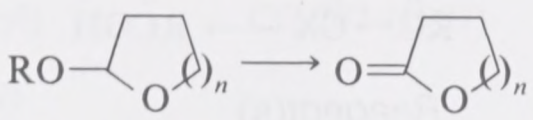
TL *27* 3049 (1986)



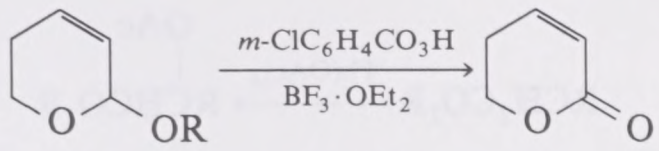
$n = 1, 2$

CrO_3, HOAc	TL *27* 2757 (1986)
PCC	JACS *105* 3720 (1983) CC 1512 (1985) TL *26* 771 (1985); *27* 2757 (1986)
PCC, Al_2O_3	JOC *52* 3541 (1987)
PCC, NaOAc, Al_2O_3	TL *28* 6437 (1987)
PCC, NaOAc, molecular sieves	JACS *109* 7488 (1987)
PDC, molecular sieves	CC 1714 (1987) TL *28* 5457 (1987)
PDC, HOAc, molecular sieves	JACS *109* 7534 (1987)
Ag_2CO_3, Celite	CC 1720 (1987)
Br_2, $Ba(O_2CPh)_2$, H_2O	TL *28* 1073 (1987)

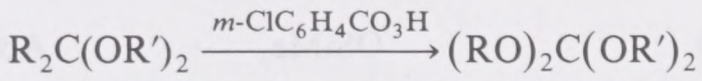
16. Acetals



n	Reagent(s)	
1	*m*-$ClC_6H_4CO_3H$, $BF_3 \cdot OEt_2$	TL 419 (1978) JACS *109* 7534 (1987)
2	H_2CrO_4	TL *27* 2703 (1986); *28* 671 (1987)

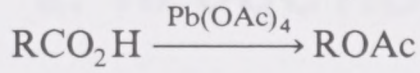


TL *23* 3781 (1982)
CC 1714 (1987)

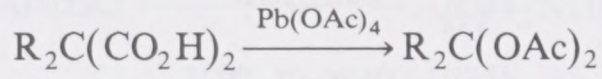


JACS *104* 1769 (1982)

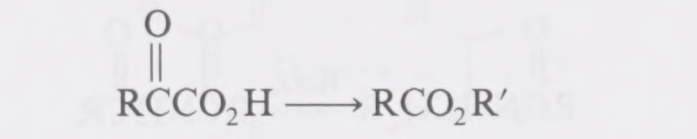
17. Carboxylic Acids



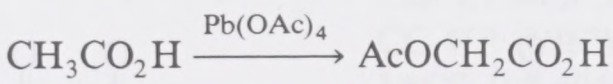
Org Rxs *19* 279 (1972) (review)
TL 549 (1976); *27* 5319 (1986); *28* 781, 4143, 4147 (1987)
CC 1797 (1987)



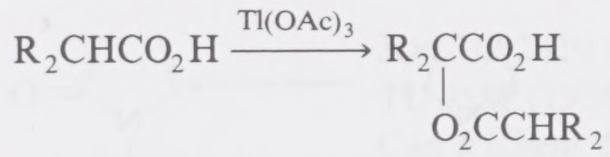
Org Rxs *19* 279 (1972) (review)



R′	Reagents	
H	$Pb(OAc)_4/H_3O^+$	JACS *62* 1597 (1940)
Me, Et	NIS, R′OH	JOC *52* 3165 (1987)

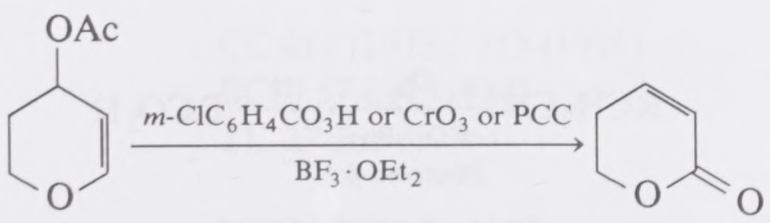


JOC *16* 533 (1951)

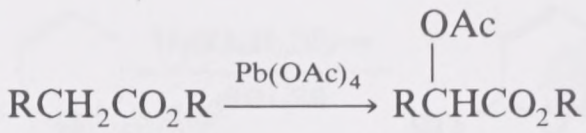


TL 5285 (1970)

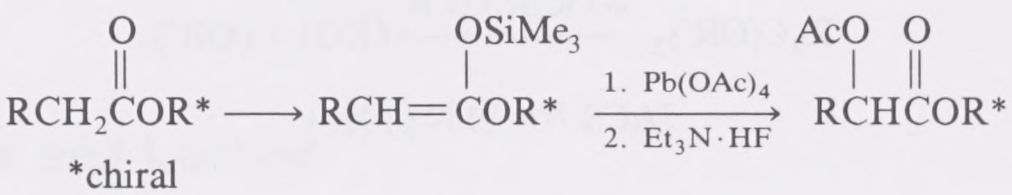
18. Esters



TL *23* 3781 (1982)

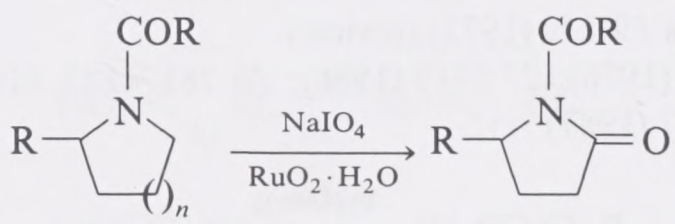


Proc Acad Sci USSR, Chem Sec *129* 995 (1959)
TL 2769 (1970) (lactones)
Syn 567 (1973) (review)



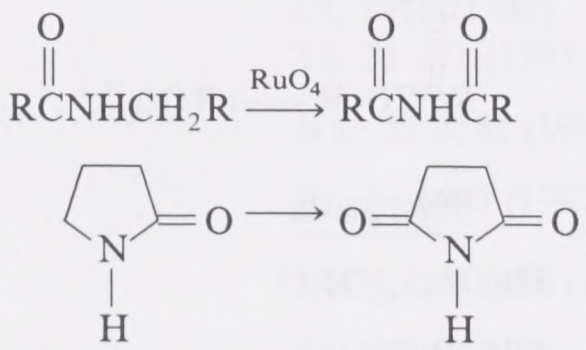
Helv *68* 216 (1985)

19. Amides

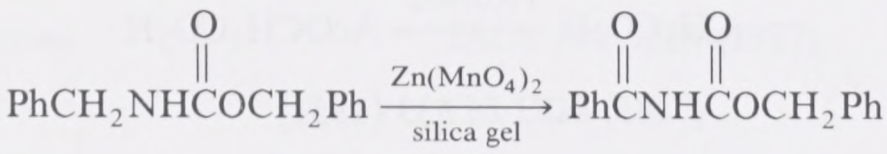


$n = 1, 2$

CC 71 (1975)

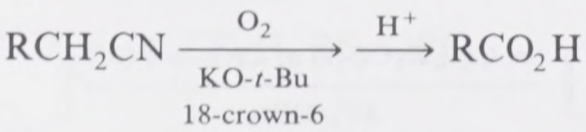


JACS *80* 6682 (1958)



JACS *105* 7755 (1983)

20. Nitriles



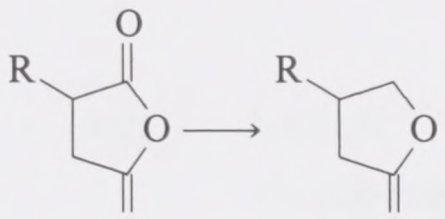
JOC *45* 3630 (1980)

2. REDUCTION

$$R_2C{=}O \xrightarrow[\text{aq } H_2SO_4,\ CH_3CN]{R'_3SiH} R_2CHNHCOCH_3$$

$$ArCHO \longrightarrow ArCH_2NHCOCH_3$$

JOC *39* 2740 (1974)

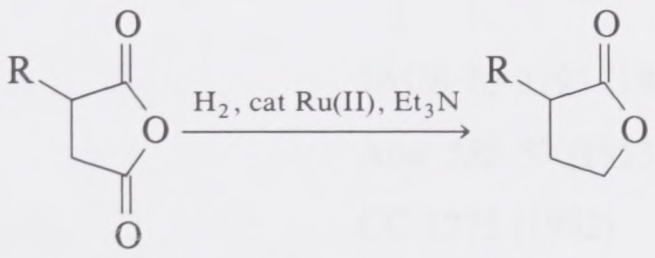


Na, C_2H_5OH — JCS 478 (1936)

$NaBH_4$ — JOC *35* 3574 (1970)
TL 4651 (1976); *28* 451, 455 (1987)
Can J Chem *56* 1524 (1978) (review)
CC 458 (1982)
JACS *108* 4943 (1986)

$KHB(sec\text{-}Bu)_3$ — CC 458 (1982)

$LiAlH_4$ — JOC *32* 3919 (1967)
TL 3589 (1968)
Can J Chem *56* 1524 (1978) (review)



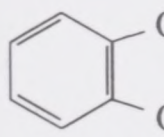
CC 412 (1975); 315 (1976)
BCSJ *57* 897 (1984)
TL *27* 365 (1986)

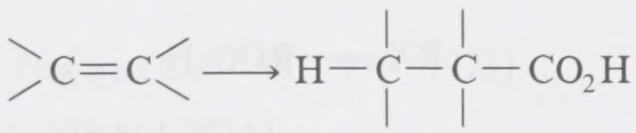
3. CARBONYLATION, CARBOXYLATION AND RELATED REACTIONS

See also page 211, Section 6, for the synthesis of α,β-unsaturated nitriles, carboxylic acids and derivatives.

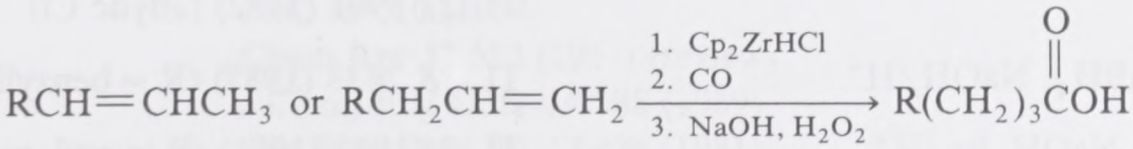
1. Carboxylic Acids

$$ArH \longrightarrow ArCO_2H$$

CO, $Pd(OAc)_2$	CC 220 (1980)
CO, cat $Pd(OAc)_2$, *t*-BuO_2H, $H_2C{=}CHCH_2Cl$	JOMC *256* C35 (1983)
CO_2, cat $Pd(OAc)_2$, *t*-BuO_2H	JOMC *266* C44 (1984)
$ClCOCOCl$, $(AlCl_3)/H_2O$	Ber *41* 3558 (1908); *44* 202 (1911); *45* 1186 (1912) JACS *70* 1079 (1948) Org Syn *44* 69 (1964)
 CCl_2, $AlCl_3/H_2O$	Ber *96* 1382 (1963)



CO, BF_3, H_2O	JACS *70* 3793 (1948)
CO, $NiCl_2$ or $Ni(CO)_4$	Ann *582* 53 (1953)
9-BBN/CO, $KHB(O\text{-}i\text{-}Pr)_3/H_2O_2$, $NaOAc/AgNO_3$, NaOH	CC 1273 (1982)
HCO_2H, H_2SO_4	JOC USSR *2* 256 (1966)



JACS *97* 228 (1975)

$$H_2C{=}CHCH{=}CH_2 \xrightarrow[i\text{-PrMgBr}]{Cp_2TiCl_2} \xrightarrow[2.\ H^+]{1.\ CO_2} H_2C{=}CHCH(CH_3)CO_2H$$

CC 180, 342 (1981)
JOMC *224* 327 (1982)

$$RCH_2CH{=}CH_2 \xrightarrow[2.\ IO_4^-\text{ or Ce(IV)}]{1.\ R'COCOCOR'} RCH{=}CHCH_2CO_2H$$

R′	
OEt	JACS *102* 2473 (1980); *106* 1092, 3797 (1984) JOC *47* 4201 (1982)
o-C_6H_4	TL *23* 1399 (1982)

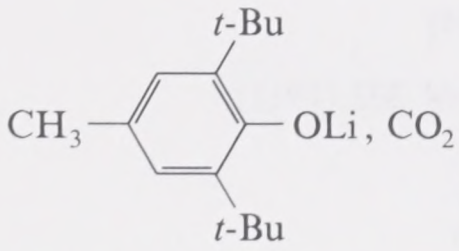
$$\begin{matrix}(CH_3)_3COH \\ \text{or} \\ (CH_3)_3CCl \\ \text{or} \\ (CH_3)_2C{=}CH_2\end{matrix} \xrightarrow[H_2SO_4]{H_2C{=}CCl_2} \xrightarrow{H_2O} (CH_3)_3CCH_2\overset{\overset{O}{\|}}{C}OH$$

Angew Int *4* 956 (1965); *5* 870 (1966); *19* 171 (1980) (review)
CL 1107 (1980)
Acta Chem Scand B *34* 621 (1980)

$$R_2C{=}CRCH_2OH + H_2NCOR + CO \xrightarrow[\text{cat } HRh(CO)(PPh_3)_3]{H_2,\ CO} R_2CHCHR\overset{\overset{HNCOR}{|}}{C}HCO_2H$$

TL *23* 2491 (1982)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CCO_2H$$



n-BuLi/CO_2/H^+ — JACS *101* 5364 (1979)

EtMgX/CO_2/H^+ — JACS *65* 2208 (1943)

$$RX \longrightarrow RCO_2H$$

RLi/CO_2/H^+ — JACS *108* 806, 1311 (1986) (both R = aryl)

Mg/CO_2/H^+ — Org Syn Coll Vol *1* 361 (2° RCl), 524 (3° RCl) (1941); *3* 553 (1955) (ArBr)
JOC *18* 432 (1953) (2° RCl, benzylic Cl)
Org Syn *59* 85 (1980) (3° RCl)
Syn 587 (1982) (1° RCl)
TL *23* 3901 (1982) (allylic Cl)

CO, $CoCl_2$, $NaBH_4$, NaOH/H^+ — TL *28* 2633 (1987) (R = benzylic)

CO, $Co_2(CO)_8$, NaOH, hν/H^+ — TL *22* 1013 (1981) (R = aryl, vinylic)

CO, NaOH, C_6H_6, (n-$C_{12}H_{25}NMe_3$)Cl, cat $Co(CO)_3NO$	JOMC *212* C23 (1981) (R = benzylic)
CO, KOH, n-BuOH, ($PhNMe_3Br$), cat $Co_2(CO)_8$	JOMC *232* 59 (1982) (R = 2° benzylic)
CO, NaOH, CH_2Cl_2 or C_6H_6, cat $Pd(PPh_3)_4$	Organomet *1* 775 (1982) (R = 1° benzylic)
CO, NaOH, t-AmOH, ($PhCH_2NEt_3$)Cl, cat $Pd(Ph_2PCH_2CH_2PPh_2)_2$	Organomet *2* 801 (1983) (R = vinylic)
CO, $Ca(OH)_2$, MeOH, cat $PdCl_2(PPh_3)_2$	TL *28* 2721 (1987) (R = aryl)
CO, H_2O, n-Bu_3N, cat $PdCl_2(PPh_3)_2$, Δ	JOC *46* 4614 (1981) (R = aryl)
CO_2, cat Pd, electrolysis	CL 169 (1986) (R = aryl)
$(RS)_3CLi$/hydrolysis or esterification	Angew Int *6* 442 (1967) (R = alkyl) Ber *105* 487 (1972) (R = alkyl)

$$ArI + CO \xrightarrow[\substack{\text{cat } PdCl_2(PR_3)_2 \\ i\text{-PrOH}}]{Ca(OH)_2} ArCHCO_2H \quad (OH)$$

TL *28* 2721 (1987)

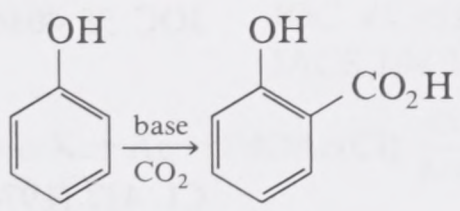
$$ArI + CO + H_2O \xrightarrow[\text{base}]{\text{cat } PdCl_2(PR_3)_2} ArCCO_2H \quad (O)$$

Base

Et_3N	CC 837 (1985)
$Ca(OH)_2$	J Mol Catal *41* 379 (1987)

$$R_3COH \xrightarrow[H_2SO_4]{HCO_2H} R_3CCOH \quad (O)$$

Org Syn Coll Vol *5* 739 (1973)



Org Syn Coll Vol *2* 557 (1943)
JOC *19* 510 (1954)
Chem Rev *57* 583 (1957) (review)
J Chem Eng Data *14* 388 (1969)
Org Prep Proc Int *13* 426 (1981)

$$RSPh \xrightarrow[\text{naphthalene}]{Li} \xrightarrow{CO_2} RCO_2H$$

JOC *43* 1064 (1978) (lithiation)
JACS *107* 196 (1985)
Tetr *42* 2803 (1986) (lithiation)

$$ArNH_2 \longrightarrow (ArN_2)BF_4 \xrightarrow[NaOAc]{\text{cat } Pd(OAc)_2} \xrightarrow{H_2O} ArCO_2H$$

TL *21* 2877 (1980)
JOC *45* 2365 (1980)

$$RCH_2NO_2 \xrightarrow[2.\ H_3O^+]{1.\ CO_2,\ Mg(OCH_3)_2} RCHCO_2H \quad (NO_2)$$

JACS *85* 616 (1963)

$$ArSiMe_3 \xrightarrow[KO\text{-}t\text{-}Bu]{CO_2} ArCOH \quad (O=)$$

Angew Int *20* 265 (1981)

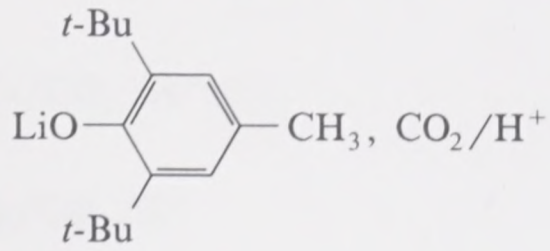
$$ArCR(ArCHO) \xrightarrow[\text{electrolysis}]{CO_2} ArCCO_2H \quad (O=,\ OH,\ R)$$

Angew Int *22* 492 (1983)
CL 453 (1984)
BCSJ *58* 1723 (1985)
TL *27* 3429 (1986)

See also page 863, Section 4.

$$-C(=O)-C(H)- \longrightarrow -C(=O)-C(CO_2H)-$$

$NaNH_2/CO_2/H^+$ — JACS *66* 1768 (1944); *106* 4186 (1984)

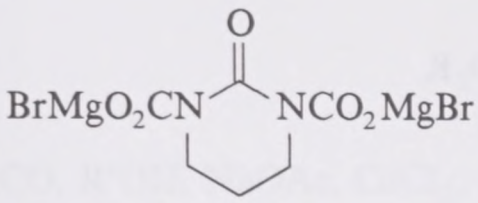


JOC *38* 4086 (1973)

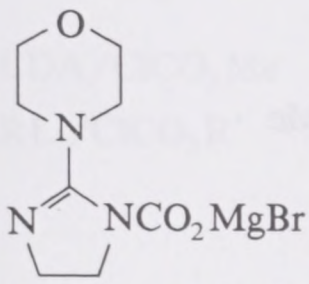
CO_2, DBU — CL 427 (1974)

CO_2, $MgCl_2$, NaI, CH_3CN, Et_3N — JOC *50* 4877 (1985)

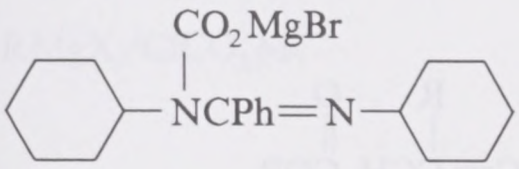
CO_2, $Mg(OCH_3)_2$ — JACS *81* 2598 (1959)
JOC *31* 1747 (1966); *38* 2489 (1973) (lactone); *52* 1686 (1987)
Tetr *38* 2797 (1982) (lactone)



TL *21* 1967 (1980)



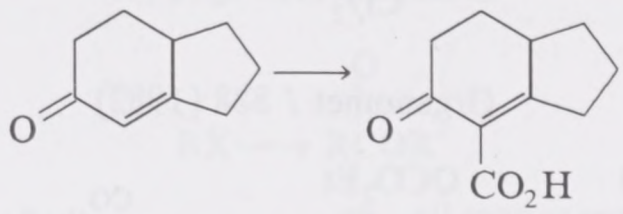
CC 326 (1980)



BCSJ *55* 3949 (1982)

$HOCO_2CuL_3$ (L = Et_3P, *t*-BuNC)

JACS *102* 431 (1980)

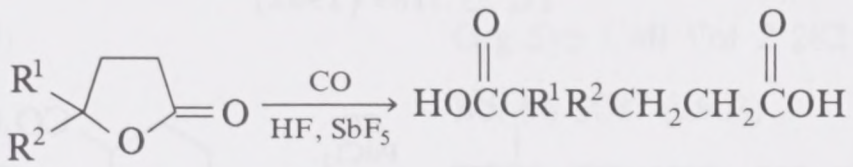


NaH, $DMSO/CO_2$

JOC *38* 3239 (1973)

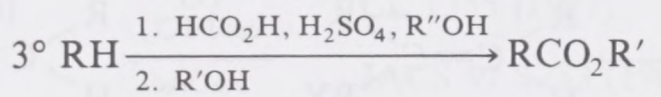
$Mg(OCH_3)_2$, CO_2

JACS *107* 7184 (1985)

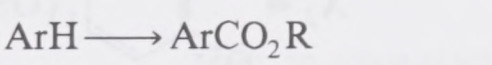


CC 767 (1981)

2. Esters



J Gen Chem USSR *33* 3206 (1963)
JOC USSR *1* 1596 (1965); *2* 256 (1966)

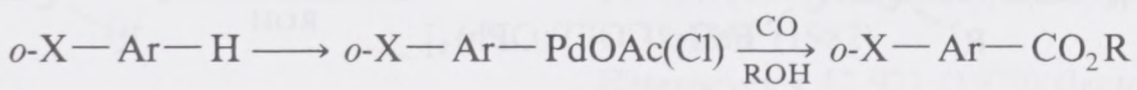


n-BuLi/$ClCO_2Et$

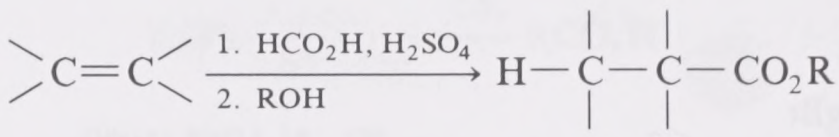
JACS *106* 3286 (1984)

$Tl(O_2CCF_3)_3/CO$, cat Li_2PdCl_4, ROH

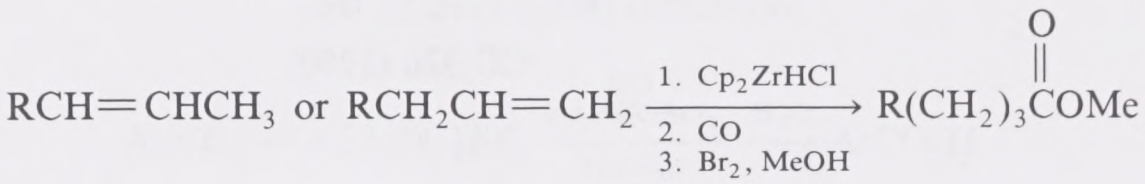
JOC *45* 363 (1980)
JACS *104* 1900 (1982)



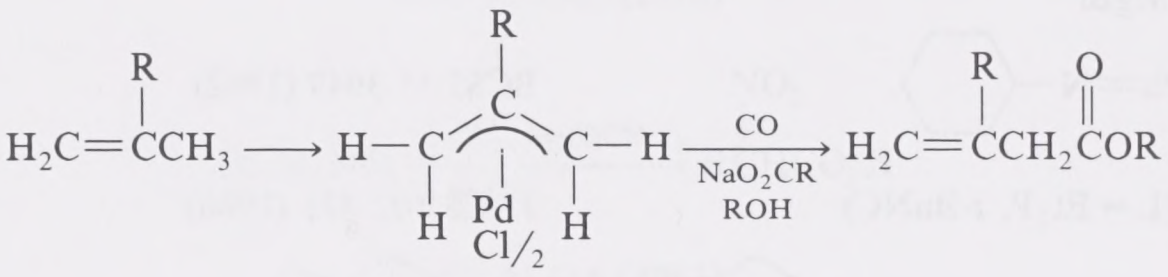
X	
NHCOR	JOC *46* 4416 (1981)
$CHRNR'_2$	JOMC *182* 537 (1979) BCSJ *52* 142, 957 (1979)
$CH_2CH_2NMe_2$	TL *27* 1971 (1986)



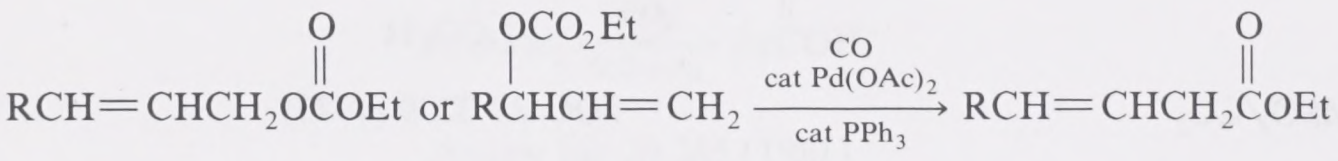
JOC USSR *1* 1814 (1965); *2* 256 (1966)



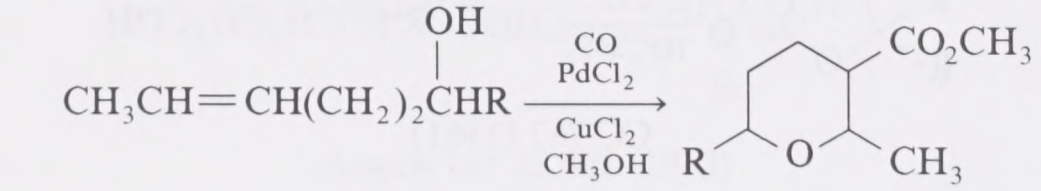
JACS *97* 228 (1975)



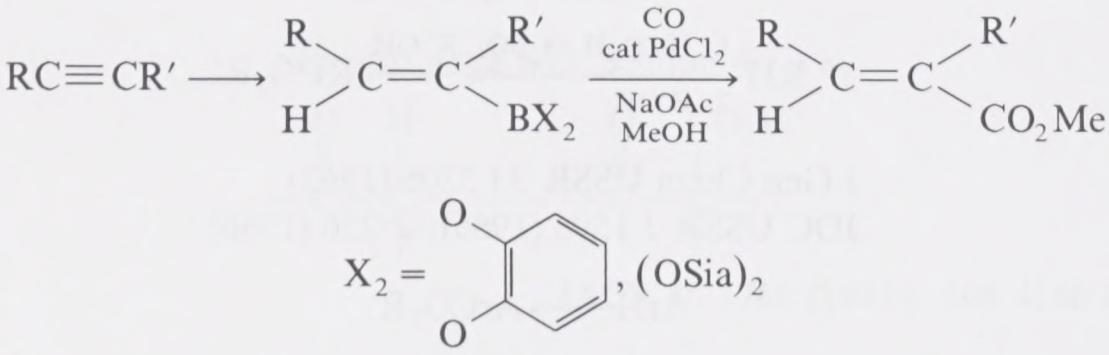
Organomet *1* 888 (1982)



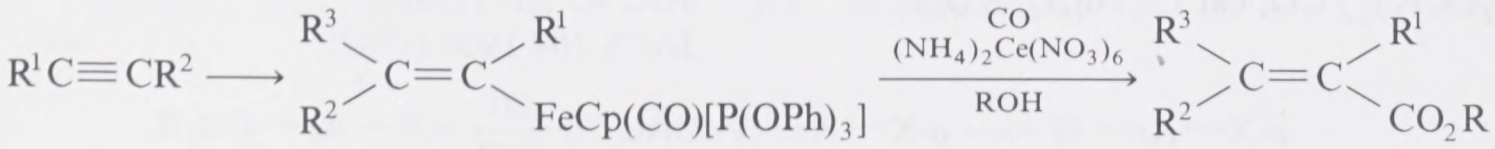
TL *23* 5189 (1982)



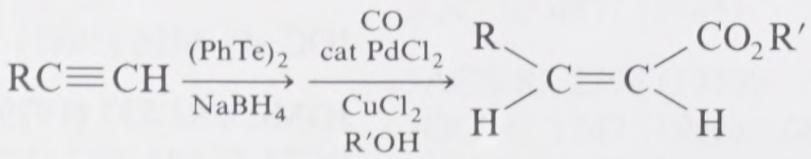
JACS *106* 1496 (1984)



CL 879 (1981)



JACS *108* 1940 (1986)



JOC *52* 4859 (1987)

$$RC{\equiv}CH \longrightarrow RC{\equiv}CC(=O)OR'$$

CO, R′OH, NaOAc, $CuCl_2$, cat $PdCl_2$	TL *21* 849 (1980); *28* 1857 (1987) JACS *108* 800 (1986)
LDA/$ClCO_2Me$	JOC *52* 2378 (1987)
RLi/$ClCO_2R'$	CC 1290 (1982) JOC *47* 4611 (1982) Org Syn *64* 108 (1985); *65* 47 (1987) TL *28* 2941 (1987)
RMgX/$ClCO_2Me$	Org Syn *60* 81 (1981) JOC *52* 1889 (1987)

$$RC{\equiv}CH \longrightarrow RCH{=}CHCO_2R$$

See page 215, Section 2.

$$RX \longrightarrow RCOR'$$

$LiC(OMe)_2CN/H_3O^+$ (R = 1° alkyl)	TL *22* 4279 (1981)
$Mg/NCC(OEt)_3/H_3O^+$ (R = 1°, 2° alkyl; aryl)	TL *22* 1509 (1981)
$Mg/OC(OEt)_2$ (R = aryl)	Org Syn Coll Vol *2* 282 (1943)
Mg/$ClCO_2Et$ (R = aryl)	Ber *36* 3087 (1903)
Mg or $Li/MnI_2/ClCO_2Et$ (R = 1° alkyl, aryl, vinylic)	BSCF 570 (1977)
$Na_2Fe(CO)_4/(CO)/I_2$, R′OH (R = 1° alkyl)	JACS *95* 249 (1973)
$Fe(CO)_5$, NaOR′ (R = 1° alkyl)	CL 1355 (1977)
$Ni(CO)_4$, NaOR′ (R = 1° alkyl, aryl, vinylic)	JACS *91* 1233 (1969); *92* 6314 (1970); *104* 6646 (1982)
$(Ph_3P)_2Ni(CO)_2$, Et_3N (R = vinylic; lactone)	JACS *104* 6879 (1982)
CO, R′OH, Pd catalyst (R = benzylic, aryl, vinylic, heterocyclic)	JOC *39* 3318 (1974); *40* 532 (1975); *47* 3630 (1982) (lactone) BCSJ *48* 2075, 2091 (1975) JACS *98* 5832 (1976); *102* 4193 (1980) TL 133 (1979) (lactone); *21* 3885 (1980); *23* 4361 (1982) Heterocycles *12* 921 (1979) (lactone) CL 369 (1980)
CO, $Ti(OR')_4$, cat $Pd(PPh_3)_4$ (R = 1° alkyl, aryl, vinylic)	JOC *50* 2134 (1985)
CO, $Zr(OR')_4$, cat $Pd(PPh_3)_4$, cat $[ClRh(H_2C{=}CHCH_2CH_2CH{=}CH_2)]_2$ (R = aryl, vinylic)	JOC *50* 2134 (1985)

CO, MeOH, cat $PtCl_2(PPh_3)_2$, K_2CO_3 (R = 1°, 2° alkyl; aryl) — CC 351 (1986)

CO, $M(OR')_4$ (M = Ti, Zr), cat $[ClRh(H_2C{=}CHCH_2CH_2CH{=}CH_2)]_2$ (R = benzylic) — JOC *50* 2134 (1985)

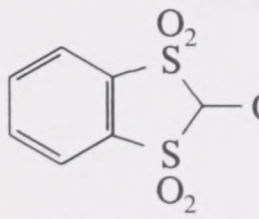
CO, HCO_2R', cat $[ClRh(H_2C{=}CHCH_2CH_2CH{=}CH_2)]_2$, cat KI (R = 1° alkyl; 1°, 2° benzylic) — CC 167 (1986)

CO, HCO_2R', cat $[ClRh(H_2C{=}CHCH_2CH_2CH{=}CH_2)]_2$, cat $Pd(PPh_3)_4$, cat KI (R = aryl) — CC 167 (1986)

$Mg/Fe(CO)_5/I_2$, R′OH (R = 1° alkyl, aryl) — TL 1477 (1978)

NaOH, $MeSCH_2SO_2Me/SOCl_2$/MeOH (R = 1° alkyl, benzylic, allylic) — TL *22* 4499 (1981)

NaOH, $MeSCH_2SO_2Tol$ (phase transfer)/ H_2O_2, HOAc/MeOH, H^+ (R = 1° alkyl, benzylic, allylic) — CL 767 (1983)



$OCH_2CH_2SiMe_3$, Cs_2CO_3/ BCl_3/R′OH (R = 1° alkyl) — JACS *106* 2469 (1984)

$$ArCH_2X \xrightarrow[\substack{\text{cat } Pd(dppe)_2\\(R_4N)HSO_4}]{CO} ArCH_2\overset{\overset{O}{\|}}{C}OCH_2Ar$$

Organomet *1* 775 (1982)

$$ArX + CO + ROH \xrightarrow[NEt_3]{\text{cat } PdCl_2(PR_3)_2} Ar\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OR$$

CL 567 (1985)
J Mol Catal *32* 115 (1985); *34* 317 (1986)
JOC *52* 5733 (1987)

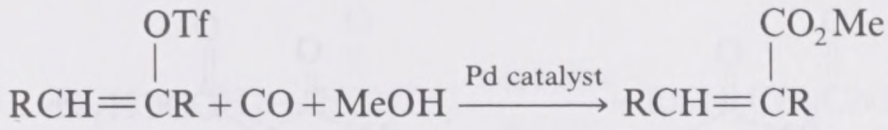
$$RX \longrightarrow R(CH_2)_nCO_2R$$

$n = 1, 2$

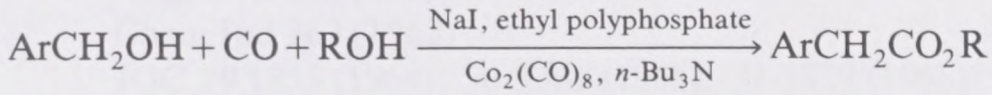
See page 873, Section 2.

$$ArOTf + CO + ROH \xrightarrow{\text{Pd catalyst}} ArCO_2R$$

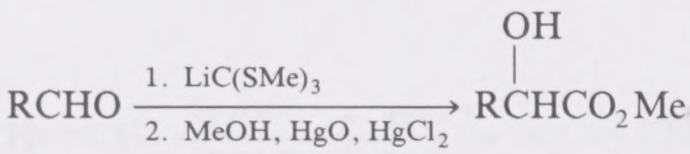
TL *27* 3931 (1986)
CC 904 (1987)



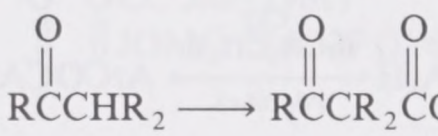
TL *26* 1109 (1985)
CC 1002 (1987)

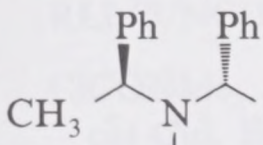


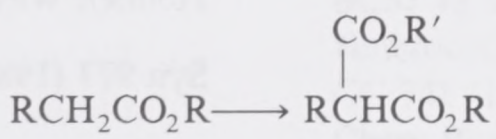
BCSJ *55* 643 (1982)



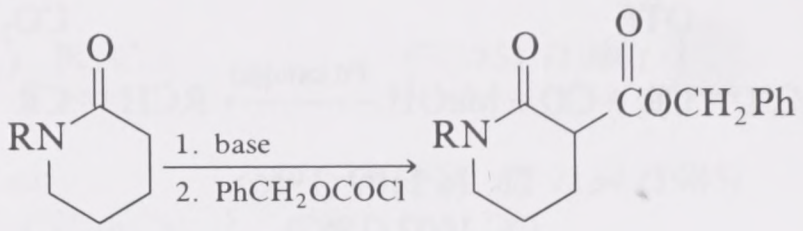
TL *28* 475 (1987)



$LDA/CO_2/CH_2N_2$	JACS *108* 800 (1986)
$KN(SiMe_3)_2/CO_2/CH_2N_2$	JACS *102* 889 (1980)
 $CH_3/CO_2/MeI$	TL *27* 2767 (1987) (enantioselective)
$LDA/NCCO_2R'$	TL *24* 5425 (1983); *26* 2291 (1985); *28* 1051 (1987) JACS *109* 2850 (1987)
$(Li)NaN(SiMe_3)_2/NCCO_2Me$	JACS *107* 2730 (1985) TL *28* 3985 (1987)
$MeLi/NCCO_2R$ (on enol silane)	TL *26* 5433 (1985)
$NaOMe, OC(OMe)_2$	JACS *107* 7967 (1985)
$NaH/OC(OEt)_2$	JACS *69* 2677 (1947); *70* 2287 (1948); *75* 4287 (1953) Chem Ind 576 (1956) Org Syn Coll Vol *5* 198 (1973)
$NaNH_2/OC(OEt)_2$	JACS *66* 1768 (1944); *67* 2197 (1945)
$KO\text{-}t\text{-}Bu/OC(OEt)_2$	BSCF 543 (1959)
$NaO\text{-}t\text{-}Am, CS_2/MeI/MeOH, BF_3\cdot OEt_2, HgO$	Syn Commun *12* 829 (1982)



$ClCO_2R'$, DMAP	JOC *52* 5425 (1987)
$LDA/NCCO_2R'$	TL *27* 1221, 1225, 1229 (1986) (all lactones); *28* 1051, 1725 (1987)

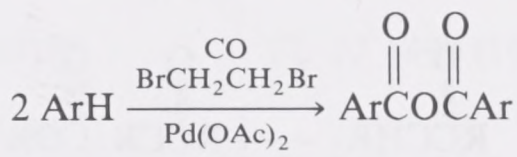


TL *28* 4901 (1987)

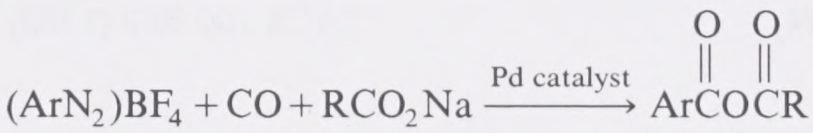
3. Lactones

See page 941, Section 8.

4. Acid Anhydrides



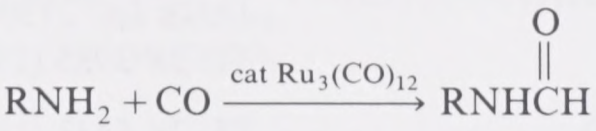
CC 132 (1982)



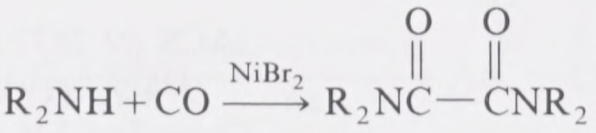
TL *21* 2877 (1980)

JOC *46* 4413 (1981)

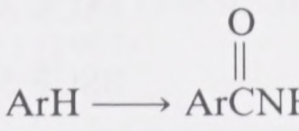
5. Amides



JOMC *309* 333 (1986)

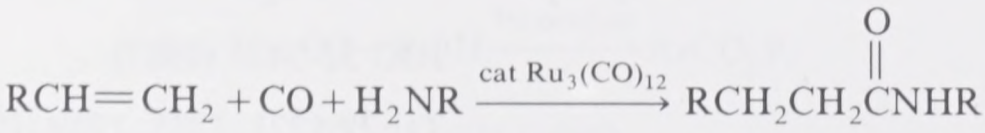


JOMC *236* C53 (1982)

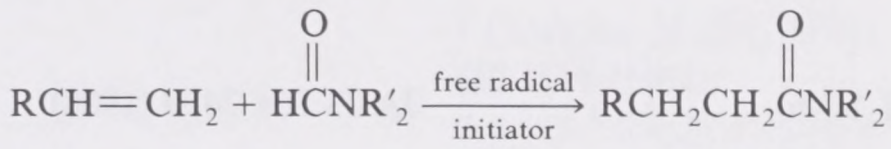


$ClCONH_2$, $AlCl_3$ — Ann *244* 47 (1888)
Houben-Weyl VIII (1952), p 380 (review)

$EtOCONH_2$, $AlCl_3$ — Syn 977 (1981)

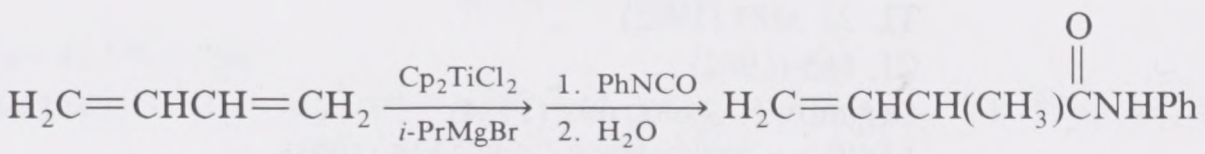


JOMC *309* 333 (1986)

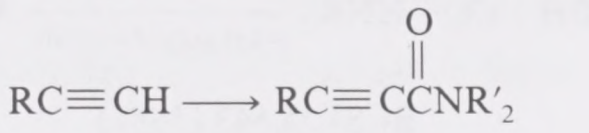


$R' = H, Me$

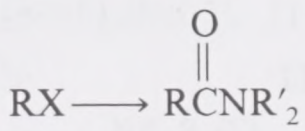
Angew *73* 621 (1961)
Chem Ind 362 (1962)
JOC *29* 1855 (1964); *30* 3361 (1965); *31* 3829 (1966)
Z Chem *4* 177 (1964)
Syn 99 (1970) (review)



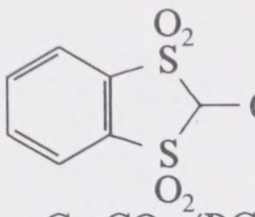
CC 342 (1981)
JOMC *224* 327 (1982)



$RLi/R'NCO/H_2O$	Ann 1844 (1981)
$ClCONMe_2$, cat $PdCl_2(PPh_3)_2$, cat CuI, Et_3N	Syn 777 (1977)



n-BuLi/$ClCONEt_2$ (R = aryl)	JACS *109* 3402 (1987)
$Mg/PhNCO/H_2O$ (R = 2° alkyl, 2° benzylic)	JOC *18* 441 (1953)
Mg/Cp_2TiCl_2, $PhNCO/H_2O$ (R = 1°, 2° alkyl in RX; R = 1° alkyl in $RCONR'_2$)	TL *28* 3815 (1987)
Mg, *t*-BuNCO, ultrasound/H_2O (R = aryl)	TL *27* 501 (1986)
$Ni(CO)_4$, HNR'_2 (R = vinylic)	JACS *91* 1233 (1969)
$Li[(CO)_3NiCONMe_2]$ (R = aryl, benzylic, allylic, vinylic)	JOC *36* 2721 (1971)
$LiCu(CONR'_2)_2$ (R = aryl, allylic)	JOC *44* 3734 (1979)
CO, HNR'_2, Pd catalyst (R = aryl, vinylic)	JOC *39* 3327 (1974); *43* 1684 (1978) (lactam) BCSJ *48* 2091 (1975) Heterocycles *6* 1711, 1841 (1977) (lactam) CC 741 (1982) (lactam) Chem Pharm Bull *32* 3840 (1984) (lactam) JACS *107* 4577 (1985)
CO, R'_3N, cat $PhPdI(PPh_3)_2$ (R = aryl, vinylic)	JOMC *231* C12 (1982)



JACS *106* 2469 (1984)

$Cs_2CO_3/BCl_3/HNR'_2$ (R = 1° alkyl)

$$RX + CO + HNR'_2 \xrightarrow{\text{Pd catalyst}} RC(=O)-C(=O)NR'_2$$

R = aryl, vinylic

JOMC *233* C64 (1982)
TL *23* 3383 (1982)
CL 865 (1982)
Organomet *3* 683, 692 (1984)
JACS *106* 1506 (1984); *107* 3235 (1985)
JOC *51* 415 (1986)

$$ArCH_2OH + CO + HNR_2 \xrightarrow[\text{ethyl polyphosphate}]{NaI,\ Co_2(CO)_8} ArCH_2C(=O)NR_2$$

BCSJ *55* 643 (1982)

$$ArO_3SCF_3 \xrightarrow[R_2NH,\ Ar_3P]{CO,\ \text{cat } Pd(OAc)_2} ArC(=O)NR_2$$

TL *27* 3931 (1986)

$$RCH{=}CR(OTf) \xrightarrow[\text{Pd catalyst}]{CO,\ R_2NH} RCH{=}CR(CONR_2)$$

TL *26* 1109 (1985); *28* 6117 (1987)

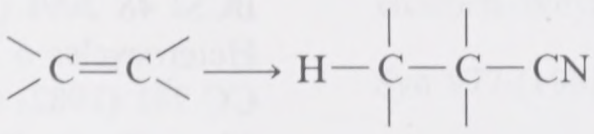
$$RCH_2CO_2R \longrightarrow RCH{=}C(OSiMe_3)R \xrightarrow[2.\ H_2O]{1.\ ArNCO} RCH(CONHAr)CO_2R$$

JOMC *164* 123 (1979)

6. Nitriles

$$ArH \xrightarrow[2.\ DMF]{1.\ ClSO_2NCO} ArCN$$

Org Syn *50* 52 (1970)



Review:

E. S. Brown in "Organic Syntheses via Metal Carbonyls," Eds. I. Wender and P. Pino, Wiley Interscience, New York (1977), Vol 2, p 655

HCN, cat $Co_2(CO)_8$ JACS *76* 5364 (1954)

HCN, Ni catalyst	J Catalysis *26* 254 (1972) CC 1098 (1981) Austral J Chem *35* 2041 (1982) Adv Catalysis *33* 1 (1985) (review)
HCN, Pd catalyst	CC 112 (1969) JACS *101* 6128 (1979) TL *23* 1621 (1982) Austral J Chem *35* 2041 (1982)
$Cp_2ZrHCl/RN{=}C$ (R = *t*-Bu, $SiMe_3$)/I_2	TL *28* 295 (1987)

$$RX + CN^- \longrightarrow RCN$$

R = 1°, 2° alkyl

Chem Rev *42* 189 (1948)
"The Chemistry of the Cyano Group," Ed. S. Patai, Interscience, New York (1970), p 67

$$R_3CX \longrightarrow R_3CCN$$

Me_3SiCN, $SnCl_4$	Angew Int *20* 1017 (1981) Tetr *39* 961 (1983)
t-BuLi/$(CN)_2$	JOC *52* 2674 (1987)

$$RCH{=}CHX \xrightarrow{\text{reagent(s)}} RCH{=}CHCN$$

X	Reagent(s)	
Cl, Br	KCN, $NiBr_2(PPh_3)_2$, Zn, PPh_3	CL 1565 (1982)
	$Co(CN)_4^{3-}$	JACS *104* 1560 (1982)
Br	$K_4Ni_2(CN)_6$, KCN	JACS *91* 1233 (1969)
	KCN, cat $Pd(PPh_3)_4$	TL 4429 (1977)
	$Co(CN)_5^{3-}$	JOC *50* 3934 (1985)
	CuCN	BSCF 720 (1973) JOC *43* 2839 (1978); *52* 2674 (1987)
	$NaCu(CN)_2$	JOC *34* 3626 (1969)
I	CuCN	JOMC *93* 415 (1975) TL *28* 6351 (1987)

$$RCH{=}CHSO_2Ar \xrightarrow[\text{crown ether}]{KCN} RC(CN){=}CH_2$$

JOC *46* 4817 (1981)

$$ArX \longrightarrow ArCN$$

Review: Chem Rev *42* 189 (1948)

Reagent(s)	X	
CuCN	Cl, Br, I	Org Syn Coll Vol *3* 212, 631 (1955) JACS *81* 3667 (1959) JOC *26* 2522, 2525 (1961); *34* 3626 (1969); *50* 2128 (1985); *51* 4169 (1986); *52* 3196 (1987) JCS 1097 (1964) Quart Rev *19* 95 (1965)

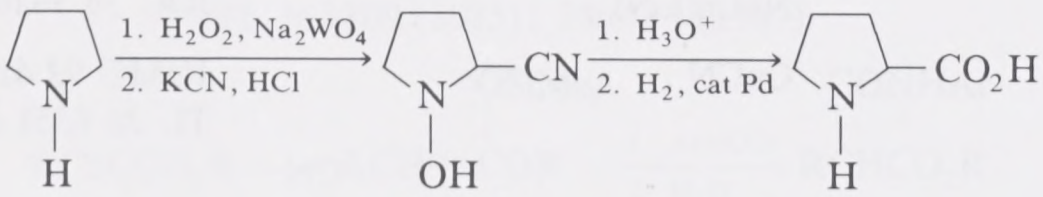
Reagent(s)	X	
CuCN-charcoal	Br	CC 877 (1986)
$NaCu(CN)_2$	I	JOC *34* 3626 (1969)
Me_3SiCN, cat $Pd(PPh_3)_4$	I	JOC *51* 4714 (1986)
NaCN, cat $Ni(PPh_3)_4$	Cl, Br, I	JOMC *54* C57 (1973)
(Na)KCN, cat $Ni(PPh_3)_4$ or $ArNiCl(PPh_3)_2$, phase transfer	Cl, Br	JOMC *173* 335 (1979)
KCN, cat $Pd(OAc)_2$, NaOEt	Br, I	BCSJ *48* 3298 (1975)
KCN, cat $Pd(PPh_3)_4$	I	CL 277 (1975)
NaCN-alumina, cat $Pd(PPh_3)_4$	Br, I	JOC *44* 4443 (1979)

$$RM \longrightarrow RC{\equiv}N$$

RM	Reagent(s)	
RLi (R = vinylic, alkynyl)	PhOCN	Syn 150 (1980)
$RC{\equiv}CLi$	ClCN	Rec Trav Chim *92* 667 (1973)
$RC{\equiv}CMgX$	ClCN	BSCF IV *17* 228 (1915)
$RCH{=}CHCu{\cdot}MgX_2$	ClCN, $ArSO_2CN$	Syn 784 (1977)
E-$RCH{=}CHAlMe(i\text{-}Bu)_2$	$(CN)_2$	JACS *90* 7139 (1968)

$$ArNH_2 \longrightarrow ArN_2^+ \xrightarrow{CuCN} ArCN$$

Org Syn Coll Vol *1* 514 (1941)

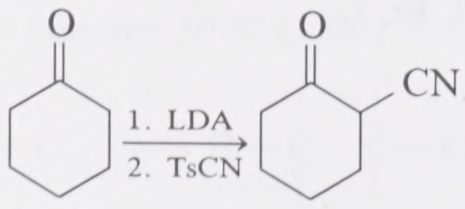


TL *28* 6469 (1987)

$$ROH \xrightarrow[\text{cat NaI}]{Me_3SiCl,\ NaCN} RCN$$

R = 1°, 2°, 3° alkyl

JOC *46* 2985 (1981)

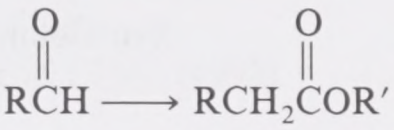


TL *22* 5011 (1981)

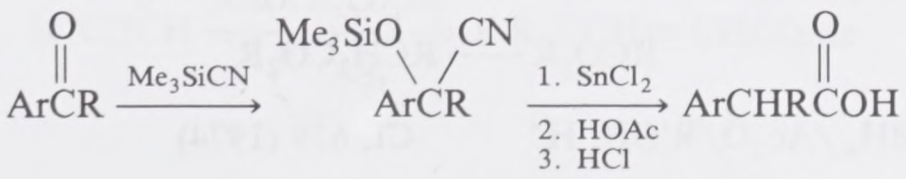
4. CARBONYL HOMOLOGATION AND DEGRADATION

See also page 941, Section 8.

1. Homologation

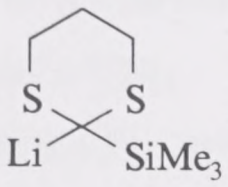


R	Reagents	
aryl	$NaC(NMe_2)[PO(OEt)_2]_2/H_3O^+$ ($R' = H$)	Angew Int *7* 391 (1968)
	n-$Bu_3SnCH(OEt)_2$, n-BuLi/H_2O or CH_3OH?	JOMC *212* C13 (1981)
	$MeSOCH_2SMe$, base/H^+, R′OH	TL 1383 (1972) BCSJ *52* 2013 (1979)
	$ArCONMeCH_2CN$, NaOH (phase transfer)/H_3O^+	Syn 1043 (1983)
	CBr_4, PPh_3/OH^-, cat $Pd(dppe)_2$, PEG-400 ($R' = H$)	JOC *51* 4354 (1986)
vinylic	CBr_4, PPh_3/OH^-, cat $Pd(dppe)_2$, PEG-400 ($R' = H$)	JOC *51* 4354 (1986)



Syn Commun *12* 763 (1982)

$$(RCHO)\ R_2C{=}O \longrightarrow R_2CH\overset{\overset{O}{\|}}{C}OR'$$


/H_2O, $HgCl_2$ ($R' = H$) — CC 526 (1972)

$NCCH_2Cl$, NaO-*t*-Am/HCl/Ac_2O, Et_3N, Δ/OH^-/H^+ ($R' = H$) — CC 988 (1974)

$NCCH_2Cl$, NaO-*t*-Am/$LiClO_4$/OH^-/H^+ ($R' = H$) — CC 988 (1974)

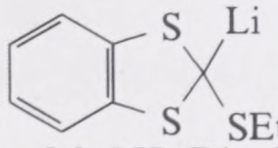
$PhNMeCH_2CN$, KH/H_3O^+ ($R' = H$) — JOC *48* 3566 (1983)

$(EtO)_2POCH(CN)O$-*t*-Bu/Ac_2O, $ZnCl_2$, Δ/ OH^- or $R'O^-$ — JACS *99* 182 (1977)

$Ph_3P{=}CF_2$ / $R'OH$-H_2SO_4 or $R'OH$-$Hg(OAc)_2$-$(CF_3CO)_2O$ — CL 651 (1980)

CBr_4, PPh_3/OH^-, cat $Pd(dppe)_2$, PEG-400 ($R' = H$) — JOC *51* 4354 (1986)

$$(RCHO)\ R_2C{=}O \longrightarrow R_2C(OH)CO_2R'$$


/$Hg(ClO_4)_2$, MeOH ($R' = Me$, ketones only) — Syn Commun *11* 209 (1981)

$(RS)_3CLi$/$HgCl_2$, H_2O ($R' = H$, aldehydes and ketones) — Angew Int *6* 442 (1967); Ber *105* 487 (1972); TL *22* 4009 (1981)

See also page 849, Section 1.

$$(RCHO)\ R_2C{=}O \longrightarrow R_2CH\overset{\overset{O}{\|}}{C}NR'_2$$

$Ph_3P{=}CF_2$ /$LiNR'_2$/H_2O (aldehydes only) — CL 935 (1980)

$(EtO)_2POCH(CN)O$-*t*-Bu/Ac_2O, $ZnCl_2$, Δ/R'_2NH (ketones only) — JACS *99* 182 (1977)

$$(RCHO)\ R_2C{=}O \longrightarrow R_2CHC{\equiv}N$$

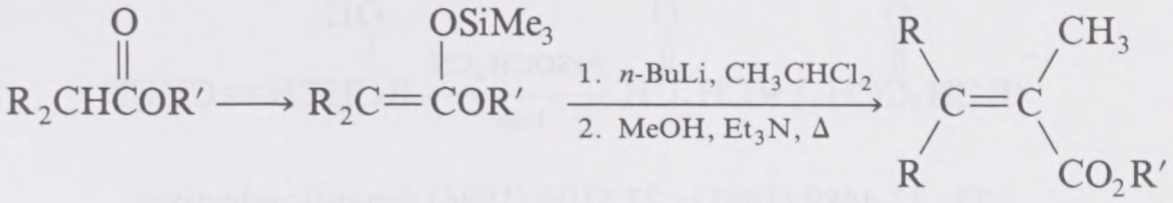
$TsCH_2NC$, KO-*t*-Bu (ketones only) — TL 1357 (1973)

2,4,6-$(i\text{-}Pr)_3C_6H_2SO_2NHNH_2$/KCN, Δ (aldehydes and ketones) — CC 280 (1977)

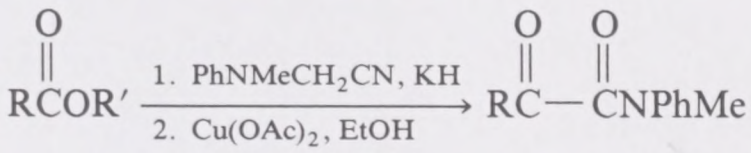
$$RCO_2R \longrightarrow RCH_2CO_2R'$$

MeSOCHNaSMe/$NaBH_4$/Ac_2O/$R'OH$, H^+ — CL 659 (1974)

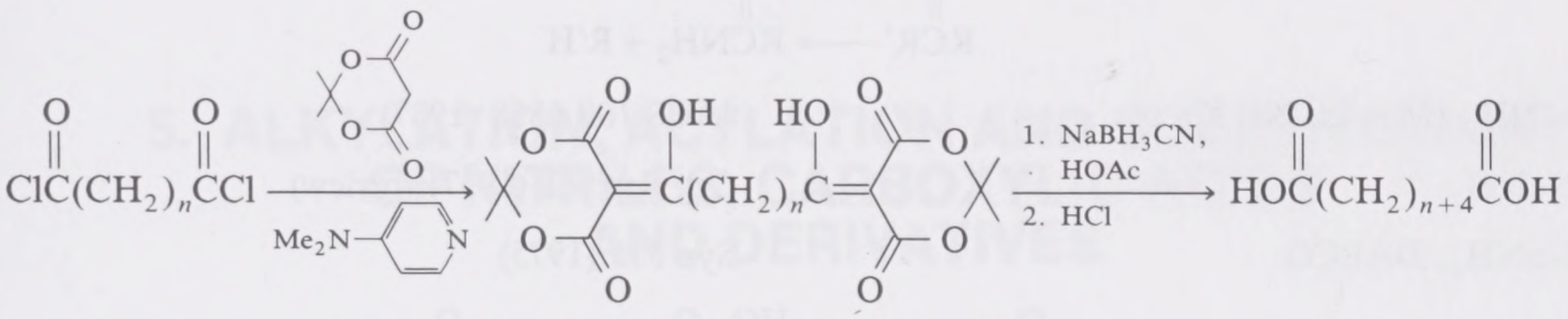
$LiCHBr_2$ /*n*- or *t*-BuLi/EtOH ($R' = Et$) — JACS *104* 321 (1982); *107* 1429 (1985)



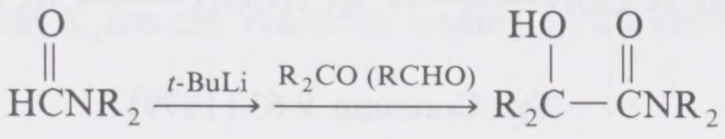
Syn 58 (1982)



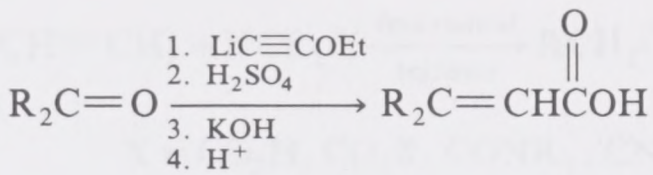
CL 859 (1983)



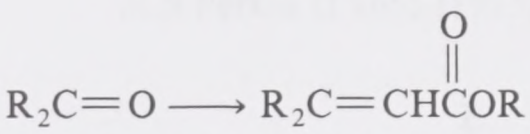
Syn Commun *12* 19 (1982)



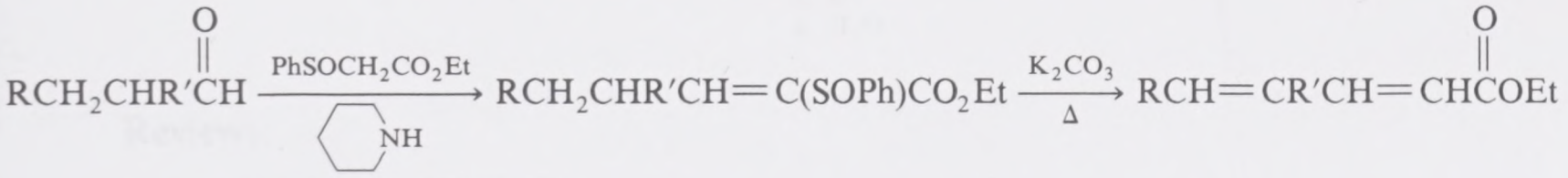
Angew Int *12* 836 (1973); *15* 293 (1976)
Can J Chem *52* 185 (1974)
CC 387 (1976)
JCS Perkin I 1881 (1977)



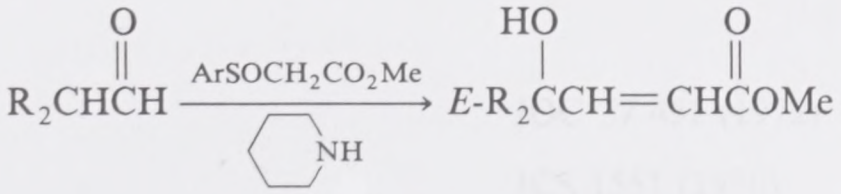
JACS *108* 2691 (1986)



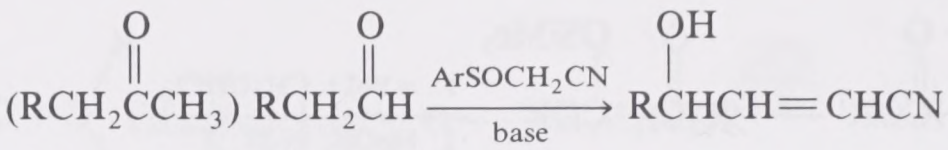
See page 173, Section 4.



CL 781 (1980)

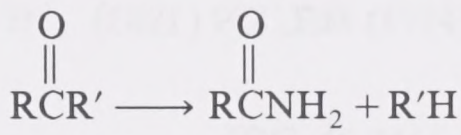


Syn 134 (1983)

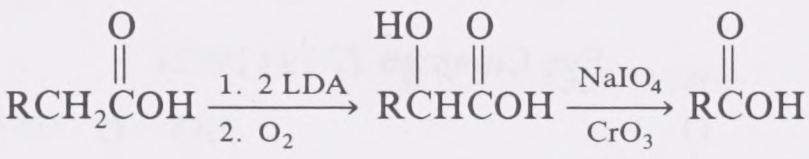


TL *22* 4489 (1981); *27* 5109 (1986) (enantioselective)
JACS *106* 7890 (1984)

2. Degradation



MNH_2 (M = Li, Na, K)	JACS *109* 6858 (1987)
$NaNH_2$	Org Rxs *9* 1 (1957) (review)
$NaNH_2$, DABCO	Syn 395 (1975)



Syn Commun *9* 63 (1979)

5. ALKYLATION, ACYLATION AND SUBSTITUTION OF NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

See also page 119, Section 8, for ene reactions leading to unsaturated carboxylic acids, esters and amides.

1. Carboxylic Acids

See also page 873, Section 2.

$$RCH{=}CH_2 + HCR_2X \xrightarrow[\text{initiator}]{\text{free radical}} RCH_2CH_2CR_2X$$

$$X = CO_2H,\ CO_2R,\ CONR_2,\ CN$$

Syn 99 (1970) (review)
JCS Perkin II 1655 (1973)

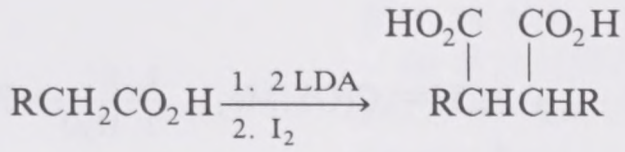
$$R_2CHCO_2H \xrightarrow[2.\ E^+\ 3.\ H_2O]{1.\ \text{base}} R_2\overset{\displaystyle E}{\overset{|}{C}}CO_2H$$

Reviews:

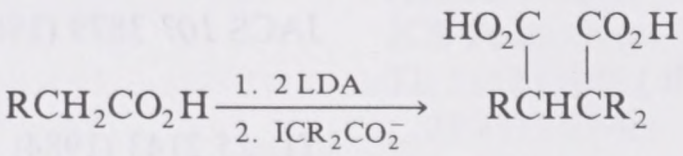
Syn 509 (1977); 521 (1982)
P. L. Creger, "Annual Reports in Medicinal Chemistry," Vol 12, Academic Press, New York (1977), Chpt 12

E^+	
D_2O	JOC *37* 451 (1972)
R′X	JCS 1551 (1950) JACS *78* 4942 (1956); *89* 2500 (1967); *92* 1397 (1970); *103* 5459 (1981); *104* 5523 (1982); *107* 7776 (1985); *109* 1186, 7816 (1987)

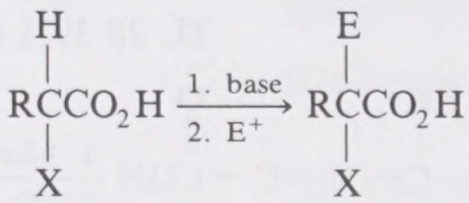
	JOC *26* 3696 (1961); *32* 2797 (1967); *35* 262 (1970); *37* 451 (1972); *45* 3236 (1980) (stereochemistry); *46* 1616 (1981); *47* 893 (1982); *50* 2719 (1985); *51* 1541 (1986); *52* 1309, 2549 (1987) Org Syn *50* 58 (1970) Syn 517 (1975); 710 (1980) Can J Chem *58* 716 (1980); *60* 1238 (1982) Tetr *36* 775 (1980) TL *27* 4545 (1986); *28* 2941 (1987) CC 656 (1987) (chiral base)
$PhCH_2SeCH_2Br$	JOC *51* 2981 (1986)
epoxide	JACS *89* 2500 (1967) Can J Chem *58* 716 (1980) JOC *52* 34 (1987)
H_2CO	JOC *37* 1256 (1972)
RCHO, R_2CO	JACS *74* 1730 (1952); *94* 2000 (1972); *102* 2841 (1980) Compt Rend C *270* 1471 (1970) BSCF 1848 (1970) Israel J Chem *8* 731 (1970) JOC *36* 1149 (1971); *40* 8 (1975); *46* 3359 (1981); *51* 1478 (1986); *52* 3143, 4124 (1987) CC 52 (1979); 98 (1986) Tetr *40* 2211 (1984) (enantioselective with chiral bases) TL *28* 2753, 4787 (1987)
HCO_2R	TL 699 (1970); 603 (1974) JOC *52* 4303 (1987)
RCO_2R	JACS *93* 6321 (1971); *106* 1811 (1984)
RCOCl	JOC *42* 1189 (1977) J Chem Res (S) 44 (1980)
EtO_2CCO_2Et	TL *22* 2459 (1981)
CO_2	Israel J Chem *8* 731 (1970) JOC *37* 451 (1972) Syn 587 (1982)
$RCH{=}CHX$ ($X = CO_2R$, CN; 1,4-addition)	JACS *93* 6321 (1971)
$RCH{=}CHNO_2$ (1,4-addition)	CL 1505 (1982)
O_2	Syn 647 (1971) (hydroxy acid) JOC *40* 3253 (1975) (hydroxy or hydroperoxy acid); *41* 370 (1976) (hydroperoxy acid)
MeSSMe	JACS *107* 8066 (1985)
RNCO, RNCS	JOC *45* 1106 (1980)

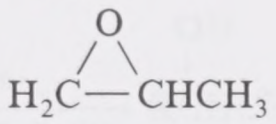
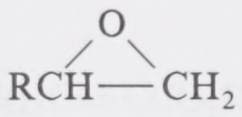
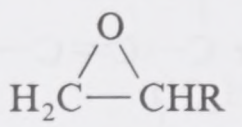


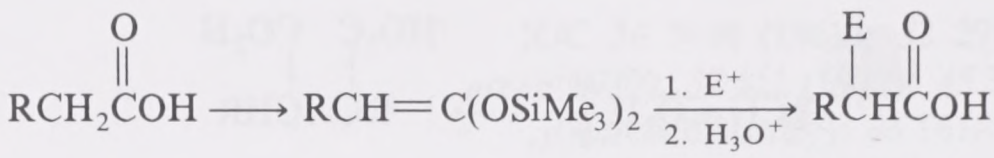
TL *25* 5969 (1984); *27* 127 (1986); *28* 4441 (1987)
JOC *52* 2549 (1987)



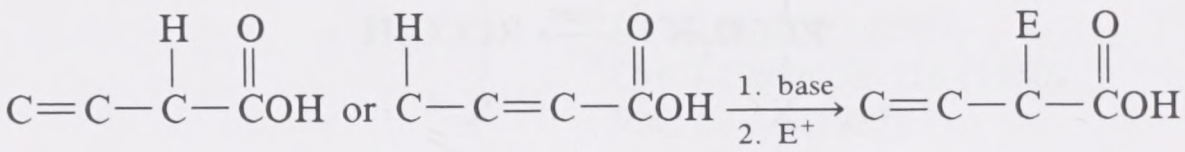
TL *25* 5969 (1984)



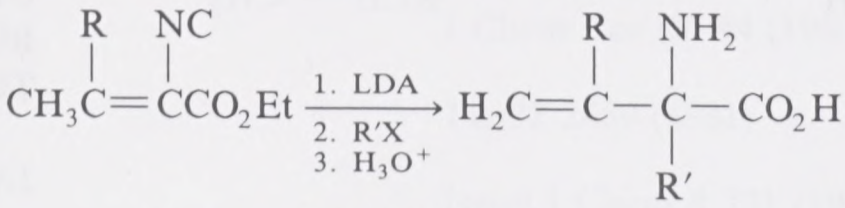
X	R	E^+	
Cl	Me	RX, RCOCl (decarboxylation), α,β-unsaturated esters (cyclopropanes)	Syn 284 (1982)
PhO	H	D_2O, RX	Syn 828 (1978)
		D_2O, RX, RCHO, R_2CO	JOC *43* 772 (1978)
			TL 2835 (1977)
PhO	PhO	D_2O, RX	Syn 828 (1978)
MeO	Me	R_2CO	Can J Chem *51* 981 (1973)
MeS	$CH_2CH{=}CH_2$	RX, RCHO	CL 351 (1982)
PhS	H		CL 385 (1974) BCSJ *50* 242 (1977) TL *26* 5623, 5627, 5631 (1985) JACS *108* 5352 (1986)
PhS	H, Me	$RCH{=}CRNO_2$ (1,4-addition)	CL 1505 (1982)
PhSe	H		CC 754 (1986) TL *28* 1147 (1987)
CO_2R	H	RCOCl	JOC *44* 310 (1979) Org Syn *61* 5 (1983)
PhCONH	H	D_2O, RX	TL 2205 (1976)
CN	H	RCOCl	Syn 308 (1983)



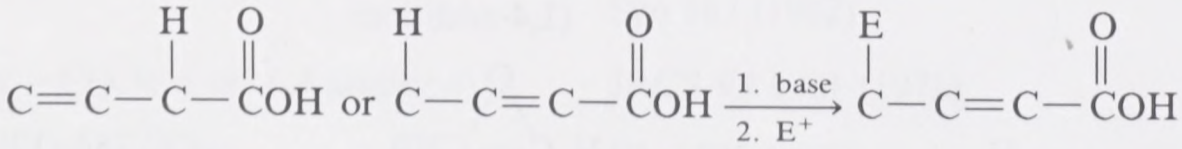
E^+	
RCHClSPh, $ZnBr_2$	TL *23* 5083 (1982)
$HC{\equiv}CCO_2Me$, $TiCl_4$ ($E = CH{=}CHCO_2Me$)	JACS *107* 3879 (1985)
RCHO, $TiCl_4$	TL *25* 2143 (1984)
$RCH{=}NR$, $TiCl_4$ (lactam formation)	TL *25* 2143 (1984)
$Pb(OAc)_4$ ($E = OAc$)	TL *28* 3971 (1987)



E^+	
H_2O or D_2O	JOC *36* 3290 (1971); *52* 4471 (1987) TL *26* 1939 (1985)
R′X	JCS 1551 (1950) JACS *93* 4330 (1971); *98* 4925 (1976) JOC *36* 3290 (1971); *42* 260 (1977); *46* 239 (1981); *52* 4471 (1987) Gazz Chim Ital *104* 625 (1974) Tetr *32* 1347 (1976) TL 335 (1979); *22* 1691 (1981)
RCHO, R_2CO	TL 1163 (1973); *22* 4913 (1981); *23* 4773 (1982); *28* 3853 (1987) JCS Perkin I 400 (1973) Tetr *32* 107 (1976) JOC *40* 8 (1975); *46* 239 (1981); *49* 4424 (1984) JCS Perkin I 1651 (1978) Syn 802 (1985)



Syn 646 (1981)



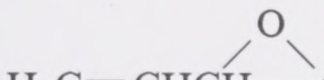
E^+	
R′X, CuI	JACS *98* 4925 (1976) Tetr *32* 1347 (1976) CC 500 (1977) JOC *46* 239 (1981) TL *22* 1691 (1981)

RCHO, R_2CO

JOC *29* 3161 (1964); *46* 2439 (1981); *49* 4424 (1984)
JACS *90* 3282 (1968)
Compt Rend C *270* 1471 (1970)
BSCF 1848 (1970)
Chem Ind 80 (1972)
Austral J Chem *25* 2393 (1973)
JCS Perkin I 400 (1973); 1651 (1978)
TL 1163 (1973); 3851 (1974); *22* 4913 (1981); *23* 4773 (1982); *28* 3853 (1987)
Gazz Chim Ital *103* 117 (1973)
Tetr *32* 107 (1976)
Syn 802 (1985)

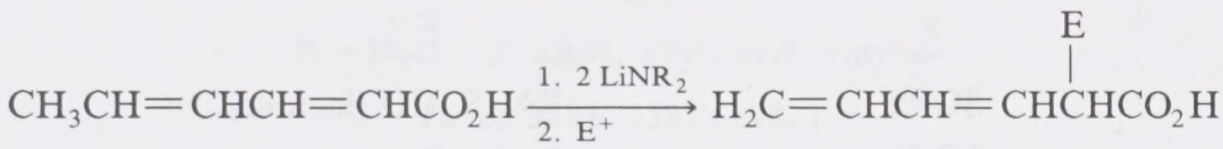
$H_2C{=}CHCOR$ (1,4-addition)

JCS Perkin I 1651 (1978)



$H_2C{=}CHCH{-}CH_2$, CuI (1,4-addition)

JOC *46* 239 (1981)



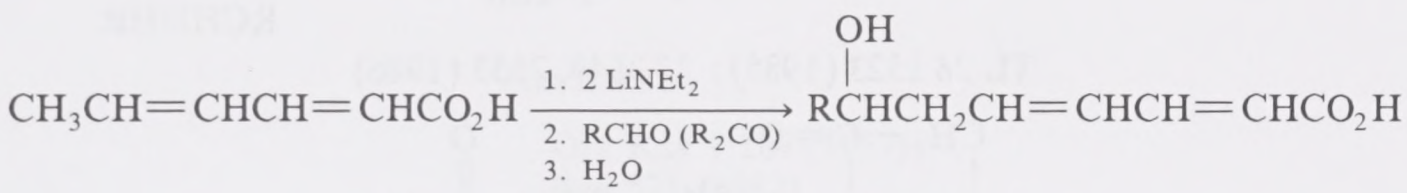
2. $\underline{E^+}$

RX

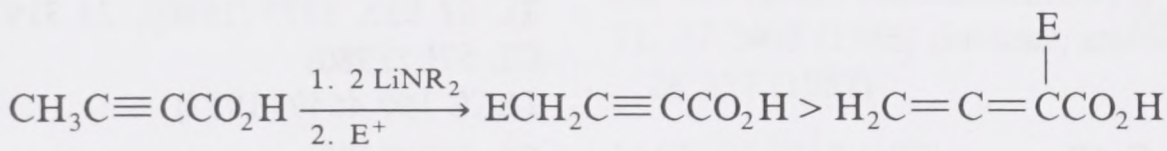
JOC *48* 3003 (1983)

RCHO, R_2CO

TL *26* 3625 (1985)



TL *26* 3625 (1985)



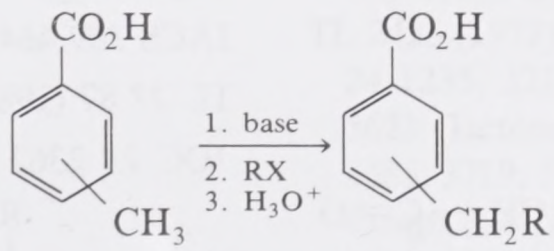
$\underline{E^+}$

R′X

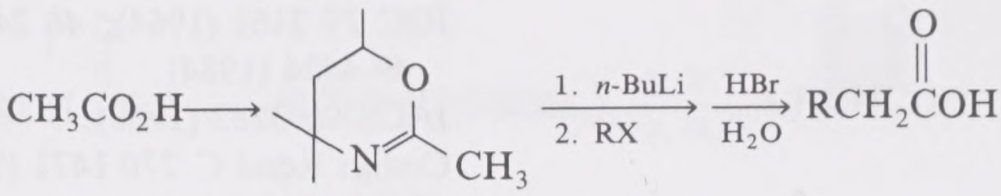
JOC *40* 269 (1975)
Tetr *32* 1347 (1976)

RCHO

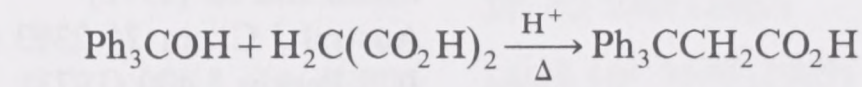
TL 3221 (1975)



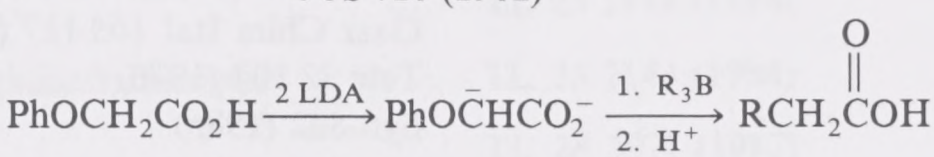
JACS *92* 1396 (1970)



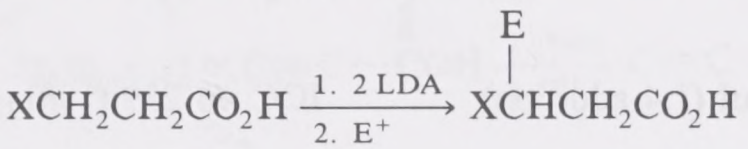
JACS *91* 5886 (1969)



JACS *49* 1735 (1927)
JCS 716 (1962)

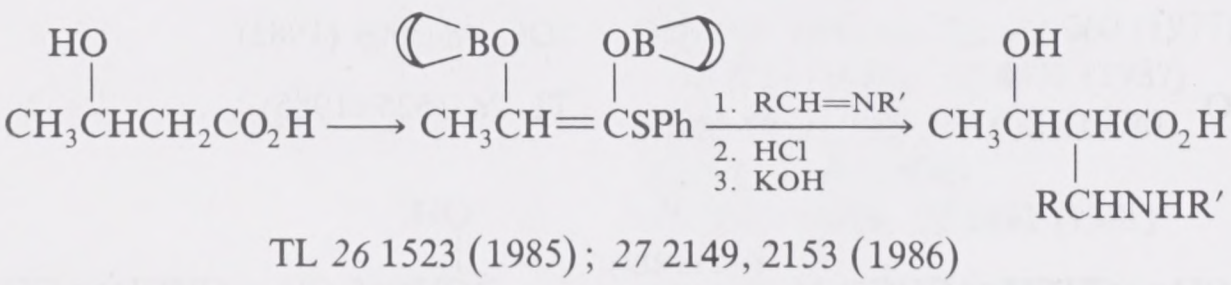


TL 2891 (1978)

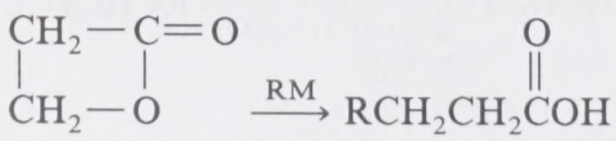


X	E^+
SOPh	RX, R_2CO (lactone)
SO_2Ph	R_2CO (lactone)

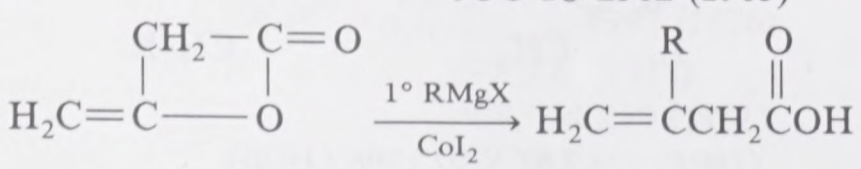
Syn Commun *6* 357 (1976)



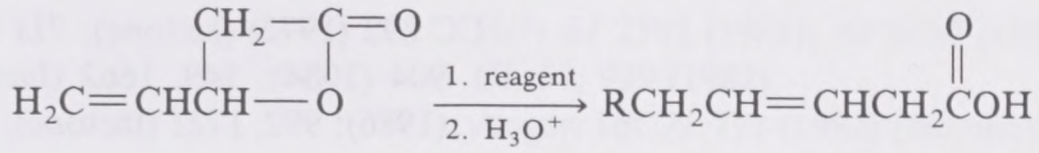
TL *26* 1523 (1985); *27* 2149, 2153 (1986)



RM	
RMgX, cat CuX	TL *21* 935, 3377 (1980); *23* 3193, 3587 (1982) CL 571 (1980) JACS *109* 4649 (1987)
RMgX, cat Li_2CuCl_4	CL 569 (1982) BCSJ *56* 345 (1983)
R_2CuLi	TL *21* 935, 2181 (1980) JACS *109* 4649 (1987)
$(RCuC{\equiv}CR')Li$	TL *21* 935 (1980)
R_2CuMgX	TL *21* 935, 2181, 3377 (1980) CL 1123 (1980)
$R_2Cu(CN)Li_2$	JACS *109* 4649 (1987)
$\mathbf{RC{\equiv}C}AlMe_2$	TL *27* 87 (1986)
RCdX	JOC *28* 2362 (1963)

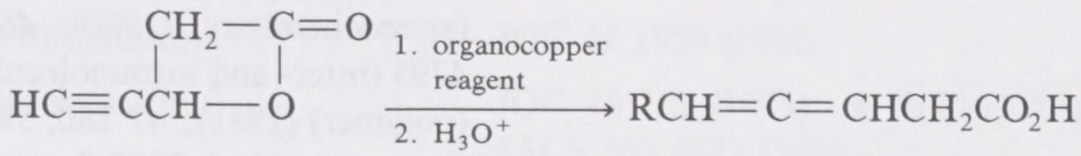


BCSJ *55* 3555 (1982)

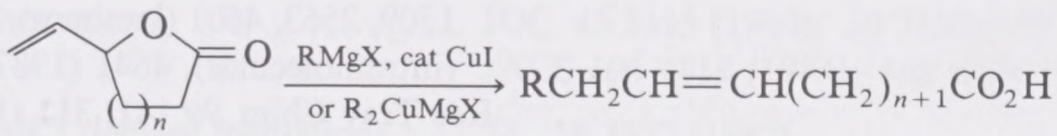


Reagent

R_2CuLi or R_2CuMgX or RMgX-cat CuI	TL *22* 1817 (1981) CL 1307 (1981); 71, 219, 1521 (1982)
LiI (R = I)	CL 71 (1982)



TL *22* 2375 (1981)

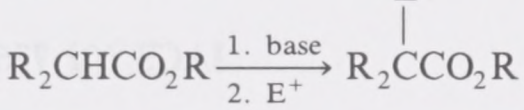


$n = 1, 2$

R = 1°, 2°, 3° alkyl; allyl; aryl; vinylic

TL *23* 3583, 3587 (1982)

2. Esters

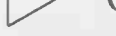


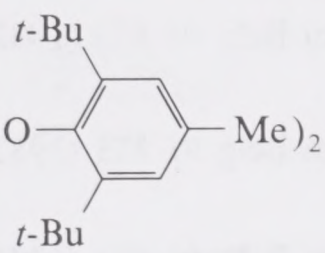
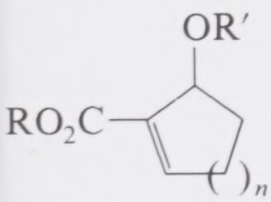
Reviews:

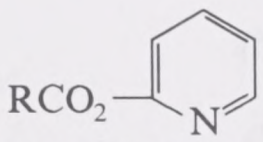
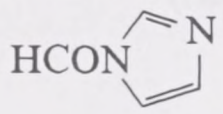
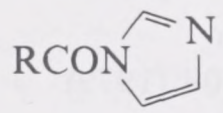
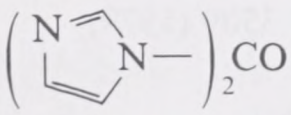
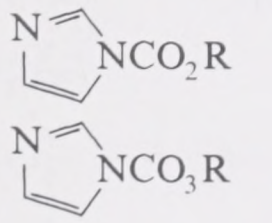
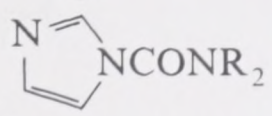
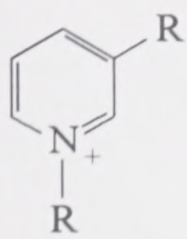
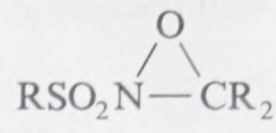
Org Rxs *9* 107 (1957)
Syn 521 (1982)

E^+

H_2O	CC 149 (1985) (stereochemistry) TL *27* 2405 (1986) (lactone, stereochemistry); *28* 517 (1987)
D_2O	JACS *93* 2318 (1971) CC 892 (1972) (lactone)
Me_2SO_4	JACS *109* 2426 (1987)
RX (X = halogen or sulfonate ester)	Organomet Chem Syn *1* 237 (1971) JACS *93* 2318 (1971); *102* 3620 (1980); *104* 1735 (1982); *107* 1435, 2512, 5570 (lactone) (1985); *108* 800, 2451 (lactone) (1986); *109* 6858 (1987) TL 2425 (1973); *21* 1137 (1980); *23* 5271 (1982); *24* 1235, 3213 (1983) (both chiral); *26* 397, 5623 (lactone) (1985); *27* 1781, 1785, 3247, 3685, 3719, 5335, 5769, 5951 (1986) (all lactones except 3685 and 5951); *28* 183, 1623 (lactone), 1685, 1933 (lactone), 2045, 2087, 2849 (chiral), 4629, 5075 (intramolecular), 5161 (intramolecular), 5205, 5659 (1987)

	CC 892 (1972) (lactone); 711 (1973); 616 (1980); 904 (1984); 149, 1662 (lactone) (1985); 288 (1986); 992, 1721 (lactone), 1786 (lactone) (1987) JCS Perkin I 694 (1977) Syn 112 (1977); 710 (1980); 305 (1982) J Polym Sci, Polym Chem Ed *17* 3499, 3509 (1979) JOC *44* 2165 (1979); *45* 891, 3236 (stereochemistry) (1980); *46* 3756 (polymer), 4795 (inter- and intramolecular), 5364 (polymer) (1981); *47* 180, 598 (1982); *50* 2128 (intramolecular), 2668 (lactone) (1985); *51* 4828 (lactone), 5492 (intramolecular) (1986); *52* 569, 1309, 2563, 4601 (lactones), 4633 (intramolecular), 4641 (1987) Rec Trav Chim *99* 141, 311 (1980) CL 1621 (1981); 81 (1986) Angew Int *20* 207, 574 (1981) Tetr *37* 3981 (1981); *40* 2211 (1984) Can J Chem *60* 2007 (1982) Org Prep Proc Int *15* 149 (1983) Ann 531 (1984)
$RC{\equiv}CCl$ (R = Cl, Ph, SPh)	TL *23* 2373 (1982) JACS *106* 3551 (1984)
ArX, hν	JACS *102* 7765 (1980)
RX (R = aryl, vinylic), Ni catalyst	JACS *99* 4833 (1977)
epoxide	J Polym Sci, Polym Chem Ed *17* 3509 (1979) JOC *51* 4840 (1986)
thiirane	J Polym Sci, Polym Chem Ed *17* 3509 (1979)
 COX (X = OR, NR_2, Ph) (cyclopropane opening)	Ber *114* 32 (1981)
RCHO, R_2CO	JACS *92* 3222 (1970); *95* 3050 (1973); *101* 2501 (1979); *105* 1667 (1983) (diastereoselectivity); *106* 3252 (1984); *107* 1379, 2138 (lactone), 5541 (1985); *108* 1019 (1986) Org Syn *53* 66 (1973); *63* 99 (1984) Syn 719 (1974); 112 (1977); 297 (1983) TL 1745 (1975); 3975 (1980); *23* 4285 (lactone), 5271 (1982); *24* 1311 (1983); *27* 2489, 3577, 4601, 4873, 6341, 6345 (1986); *28* 655, 1761, 1925, 3059, 3723 (intramolecular), 5661, 5921 (1987) JOC *45* 1066, 1726, 3549, 3846 (1980); *50* 3022 (1985) (enones); *51* 1402, 5492 (1986); *52* 2378 (lactone), 3541 (lactone) (1987) Tetr *37* 4087 (1981) Acta Chem Scand B *35* 273 (1981)

	Helv *64* 2592 (1981); *69* 1699 (1986) CL 57, 929 (1982) Angew Int *21* 777 (1982) (lactone); *24* 874 (1985) (diastereoselective) Syn Commun *12* 225 (1982) (silyl ester) CC 305, 878, 1199, 1237 (1986)
$(Me_2\overset{+}{N}{=}CH_2)X^-$	CC 305 (1986)
$RCH{=}NOCH_2Ph$ (lactam formation)	CL 369 (1984)
$RCH{=}NSPh$ (lactam formation)	JOC *51* 1929 (1986)
$RCH{=}NSiMe_3$ (lactam formation)	JOC *48* 289 (1983); *50* 5120 (1985) JACS *106* 4819 (1984) TL *27* 1695 (1986); *28* 5369 (1987)
$RCH{=}NAr$ (lactam formation)	JOC *45* 3413 (1980); *50* 5120 (1985) JACS *106* 4819 (1984); *108* 6054 (1986)
$RCH_2CH{=}NR$, Me_2AlCl (lactam formation)	TL *28* 3377 (1987)
$RCH{=}C{=}NR$ (lactam formation)	TL *28* 4347 (1987)
enal (1,4-addition)	J Polym Sci, Polym Chem Ed *17* 3509 (1979)
enone (1,2- or 1,4-addition)	JOC *41* 4044 (1976); *47* 3464 (1982); *50* 3022 (1985) J Polym Sci, Polym Chem Ed *17* 3509 (1979) CC 305 (1986) TL *27* 3927 (1986) (intramolecular)
enone,  (1,4-addition)	TL *28* 5723 (1987)
$RCH{=}CHNO_2$	Chimia *38* 255 (1984)
HCO_2Me	TL *27* 5397 (1986)
RCO_2R	Syn 715 (1983) TL *27* 5177 (1986); *28* 2017, 2753 (1987)
lactone	TL 4323 (1978); *27* 6345 (1986); *28* 5661 (1987) JACS *107* 1691 (1985); *109* 1564 (1987)
$RCH_2CH{=}CHCO_2R(NR_2)$ (1,4-addition)	See page 915, Section 6.
 ($n = 1, 2$; $R' = Ac, SiMe_3$; S_N2' substitution of OR′)	TL *28* 5521 (1987)
RCOCl	TL 2953 (1971); *28* 3551 (1987) (lactone) JOC *39* 3455 (1974); *46* 3756 (polymer), 4795 (inter- and intramolecular), 5364 (polymer) (1981); *51* 4813 (1986); *52* 4531, 4601 (lactones) (1987)

	Compt Rend *286* 401 (1978) J Chem Res (S) 44 (1980) JACS *102* 3620 (1980); *107* 5289 (1985); *108* 7686 (1986); *109* 7488 (1987) JCS Perkin I 2885 (1982) Syn Commun *13* 183 (1983) (silyl ester)
RCO_2CO_2R'	JOMC *127* C65 (1977) TL 3713 (1978) Tetr *37* 307 (1981) JOC *52* 4531 (1987)
	JOC *52* 4531 (1987)
RCOCN	TL *28* 4011 (1987)
RCN	TL *23* 1597 (1982)
	JOC *52* 4303 (1987)
	Bull Soc Chim Belg *91* 871 (1982) TL *27* 5281 (1986); *28* 2837 (1987) JACS *109* 4717 (1987) CC 1228 (1987)
	Bull Soc Chim Belg *91* 871 (1982)
	Bull Soc Chim Belg *91* 871 (1982)
	Bull Soc Chim Belg *91* 871 (1982)
	Bull Soc Chim Belg *91* 871 (1982)
$ClCO_2R$	JOC *39* 2114 (1974); *46* 3151 (1981) J Polym Sci, Polym Chem Ed *17* 3509 (1979) JACS *102* 3620 (1980) JCS Perkin I 2885 (1982)
CO_2	TL 3001 (1971)
$NCCO_2R$	TL *27* 1221, 1225, 1229 (1986) (all lactones); *28* 1051 (1987)
p-$MeOC_6H_4N{=}C{=}X$ (X = O, S)	TL *28* 3593 (1987)
 (1,4-dihydropyridine)	TL *28* 4457 (1987)
O_2 (hyroxy ester)	TL 1731 (1975) JOC *52* 3323 (1987)
$MoO_5 \cdot py \cdot HMPA$ (E = OH)	JOC *52* 3346 (1987) TL *28* 221 (1987)
 (chiral) (E = OH)	JOC *51* 2402 (1986)

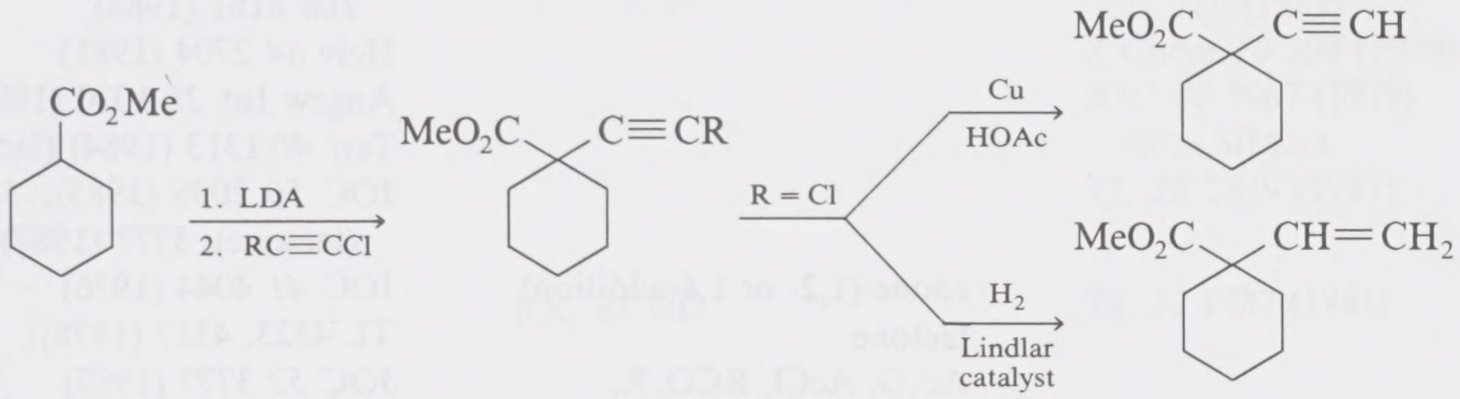
RSSR (R = Me, Ph)	JACS *95* 6840 (1973); *98* 4887 (1976) TL 2429 (1973) JOC *39* 2114 (1974)
PhSeX (X = Cl, Br)	JACS *95* 5813 (1973) JOC *39* 2114 (1974); *52* 2563 (1987) Tetr *34* 1049 (1978)
PhSeSePh	JOC *52* 2563, 2639 (1987)
$Ph_2MeSiCl$	JACS *103* 2418 (1981) Syn Commun *13* 833 (1983)

$$RCH_2CO_2R \xrightarrow[2.\ \text{reagent}]{1.\ \text{LDA}} RO_2CCHCHCO_2R \quad (R\ R)$$

I_2	Syn 396 (1975) TL *28* 4441 (1987)
$CuBr_2$ or $(n\text{-}C_4H_9CO_2)_2Cu$	JACS *93* 4605 (1971)
Cl_3CCCl_3 or $BrCMe_2CMe_2Br$	JOC *35* 2085 (1970)

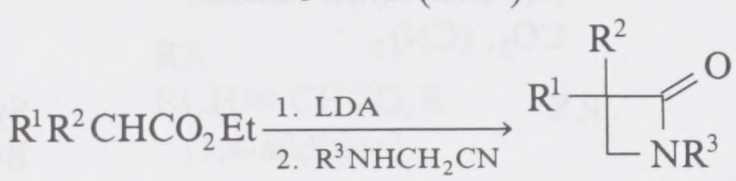
$$CH_3CO_2R \xrightarrow[2.\ t\text{-}BuMe_2SiCH_2CHO\ \ 3.\ BF_3\cdot OEt_2]{1.\ \text{LDA}} H_2C{=}CHCH_2CO_2R$$

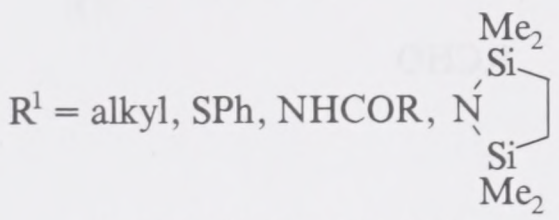
JACS *103* 6251 (1981)



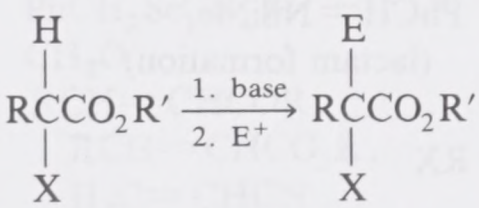
R = Cl, Ph, SPh

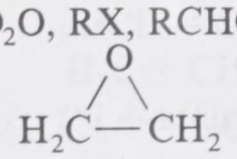
TL *23* 2373 (1982)

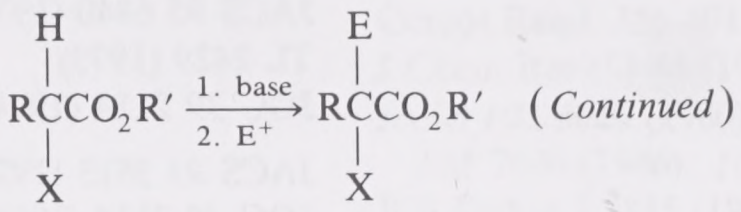




JACS *107* 1698 (1985)

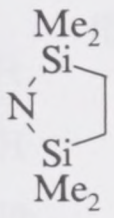


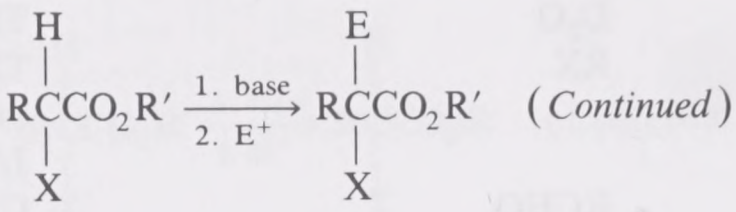
X	E^+	
F	R_2CO	Syn 322 (1983)
OH	D_2O, RX, RCHO, R_2CO, 	JOC *42* 2948 (1977)



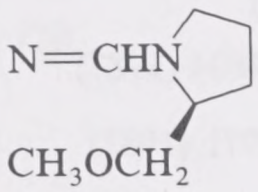
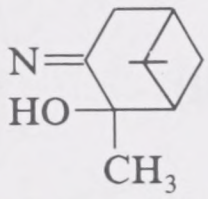
(*Continued*)

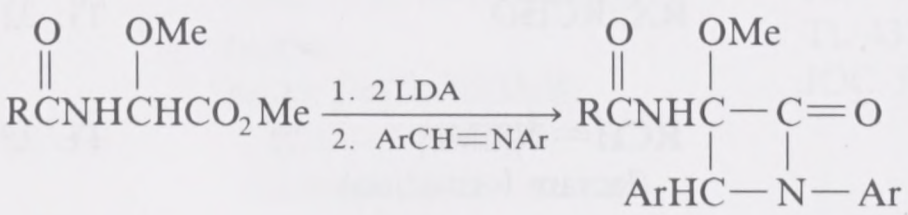
X	E^+	
OR	RX	CC 951 (1971) Helv *64* 2704 (1981); *65* 385 (1982) TL *22* 4221 (1981); *28* 221 (1987) Angew Int *20* 1030 (1981); *21* 449 (1982) Ann 1930 (1983) Tetr *40* 1313 (1984) (lactone) JOC *51* 3746 (1986); *52* 3777 (1987)
	ArX (heterocyclic)	TL *27* 6059 (1986)
	RCHO, R_2CO	TL 1477 (1975); 2835 (1977); *24* 5869 (1983) JACS *103* 4972 (1981); *106* 8161 (1984) Helv *64* 2704 (1981) Angew Int *20* 1030 (1981) Tetr *40* 1313 (1984) (lactone) JOC *50* 2095 (1985); *52* 3176 (lactone), 3777 (1987)
	enone (1,2- or 1,4-addition)	JOC *41* 4044 (1976)
	lactone	TL 4323, 4327 (1978)
	Ac_2O, AcCl, RCO_2R, $H_2C{=}CHCO_2R$ (1,4-addition), CO_2, $(CN)_2$	JOC *52* 3777 (1987)
SR	RX	Syn Commun *3* 265 (1973) BCSJ *50* 242 (1977) (lactone) TL *24* 3391 (1983)
	RCHO	TL *24* 523 (1983) JOC *48* 2705 (1983); *52* 4631 (1987) (lactone) CC 717 (1985)
	enone (1,2- or 1,4-addition)	JOC *41* 4044 (1976)
	$PhCH{=}NSiMe_3$ (lactam formation)	JACS *106* 4819 (1984)
SePh	RX	JACS *95* 6137 (1973) TL *27* 3297 (1986)
	RCHO	JACS *103* 4114 (1981)
NO_2	RX	BCSJ *43* 2277 (1970); *46* 337 (1973)
$PhCH_2OCONH$	RCHO, R_2CO	JOC *44* 3967 (1979)

RCONR	D_2O	TL 2205 (1976)
	RX	TL 2205 (1976); *28* 2243 (1987) Pol J Chem *53* 2397 (1979) JACS *109* 4649, 6537 (1987)
	RCHO	CC 1738 (1987)
	RCHO, R_2CO, RCOCl	JOC *46* 2809 (1981)
	RCOCl, $(RCO)_2O$	CC 753 (1978)
	RCOCl	CC 1283 (1987)
RO_2CNR	RCHO	JOC *52* 2881, 4804 (1987)
HCONH	RX	Angew Int *20* 971 (1981)
NMe_2	RCHO	TL 1477 (1975)
NR_2	RX	Helv *64* 2704 (1981) CC 1329 (1987)
	RCHO, R_2CO	CC 1329 (1987)
	D^+, RX, RCHO, R_2CO, $C_6H_6 \cdot Cr(CO)_3$ (E = Ph), PhSSPh	JACS *105* 5390 (1983)
$N(SiMe_3)_2$	RX	Angew Int *7* 809 (1968) Z Chem *10* 392 (1970)
	RCHO, R_2CO	Angew Int *7* 809 (1968); *21* 210 (1982) Z Chem *10* 393 (1970) JOC *44* 3967 (1979) (R′ = $SiMe_3$) TL *28* 2849 (1987)
	RX, RCHO	TL *22* 1787 (1981)
	$RCH{=}NSiMe_3$ (lactam formation)	TL *28* 5369 (1987)
N=C:	RX	Angew Int *10* 331 (1971)
	$RCH{=}CHCO_2R$ (1,4-addition)	Ann 1571 (1973)
N=CHR	RX	JOC *41* 3491 (1976) TL 1455 (1977); *23* 4255, 4259 (1982); *27* 4435 (1986) BCSJ *55* 961 (1982) (enantioselective) Syn 789 (1983)
	$PhCH_2SeCH_2Br$	JOC *51* 2981 (1986)
	CH_2O	Syn 445 (1981)
	$RCH{=}CHCOR$, $RCH{=}CHCO_2R$, $H_2C{=}CHCN$ (all 1,4-addition)	JOC *41* 3491 (1976) TL 1455 (1977)
$N{=}CHNMe_2$	RX, epoxide (lactone), $ArCH{=}C(CO_2R)_2$*, $ArCH{=}CHNO_2$*, $H_2C{=}CHCO_2R$* (*1,4-addition)	JOC *42* 2639 (1977)

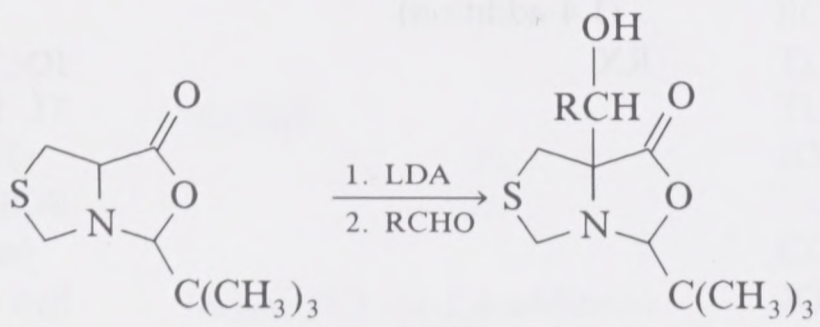


(*Continued*)

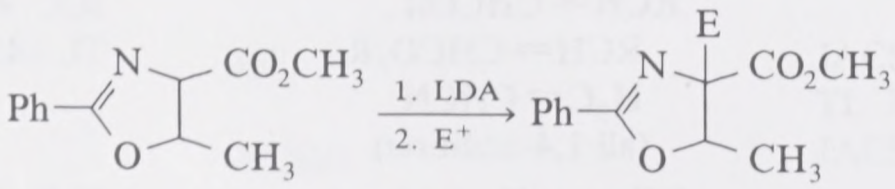
X	E^+	
	$PhCH_2SeCH_2Br$	JOC *51* 2981 (1986)
	RX	Ann 1668 (1983) (chiral)
	RX	TL *24* 3721 (1983) (chiral)
$N{=}C(Me)C(OH)(Me)Ph$	RCHO	CL 279 (1981) (chiral)
$N{=}CR_2$	RX	CC 136 (1976) TL *23* 2863, 4255 (1982); *27* 3839 (1986) (chiral); *28* 3801 (1987)
	$PhCH_2SeCH_2Br$	JOC *51* 2981 (1986)
	$H_2C{=}CRCH_2O_2CX$ (X = Me, OEt), cat PdL_2 ($E = H_2C{=}CRCH_2$)	TL *27* 23, 4573 (1986)
	RCHO	CL 145 (1982)
$N{=}C(SR)_2$	RX	Angew Int *14* 426 (1975)



Syn 407 (1982)

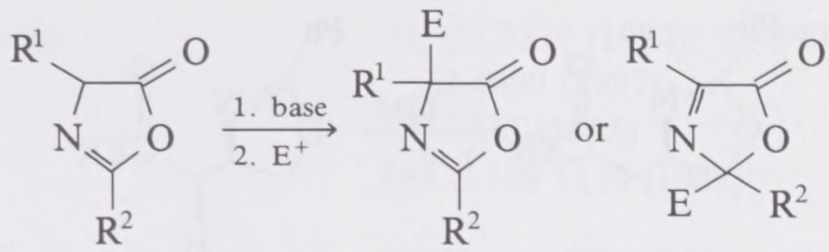


TL *24* 3315 (1983)



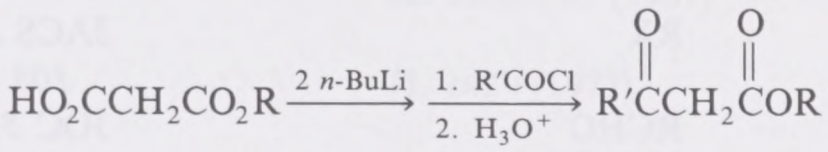
$E^+ = D^+$, RX, RCHO, R_2CO

TL *24* 3311 (1983)
JOC *52* 3326 (1987)

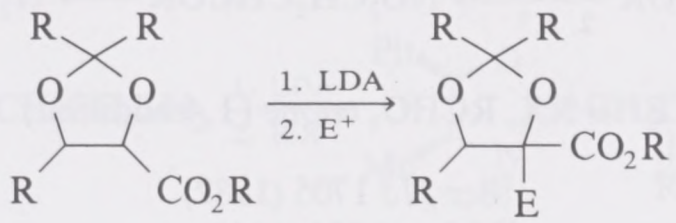


$E^+ = RX$, RCOCl, Michael acceptors

Ber *102* 883 (1969); *113* 3706 (1980)
Angew Int *10* 653 (1971)

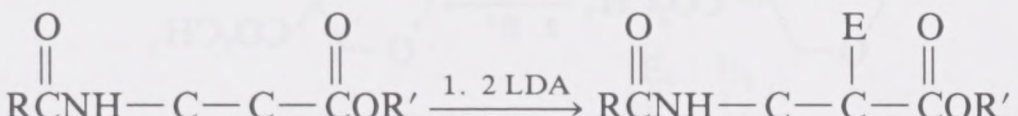


JOC *44* 310 (1979)
Org Syn *61* 5 (1983)

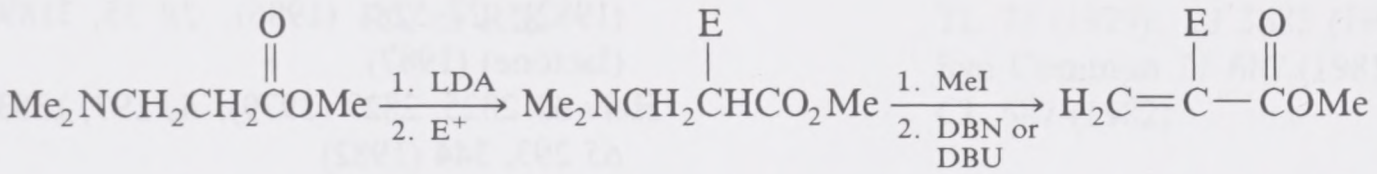


$E^+ = RX, R_2CO$

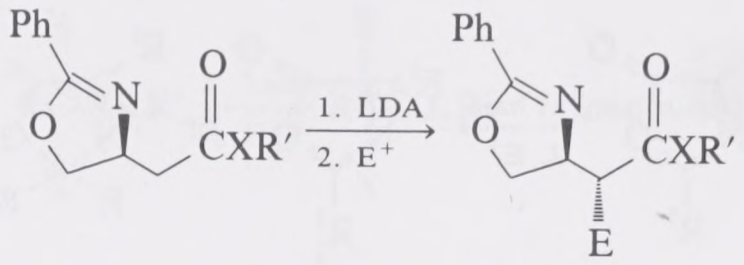
Ber *116* 3413 (1983)



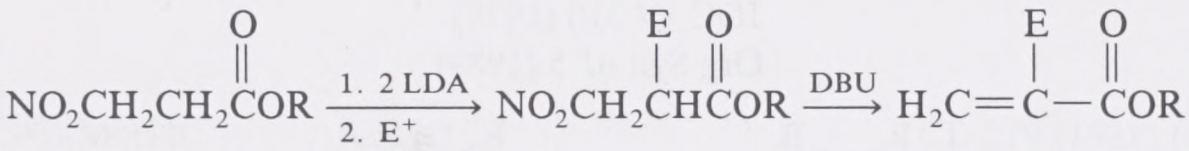
R	E^+	
H	RX	Angew Int *20* 971 (1981)
Ph	RX	TL *24* 2733 (1983) (lactone); *28* 3103 (1987) JACS *108* 4943 (1986) (lactone)
	RCHO	TL *28* 3103 (1987)
$PhCH_2O$	RX R_2CO	TL *24* 2733 (1983) (lactone) JACS *105* 1659 (1983) (lactone)



E^+	
RX	TL 3423 (1978) JOC *46* 4536 (1981) Syn Commun *11* 591 (1981)
RCHO	CC 1112 (1983) JOC *49* 3784 (1984); *50* 157 (1985); *52* 5452 (1987)
$PhCH{=}NSiMe_3$ (lactam formation)	JACS *106* 4819 (1984)

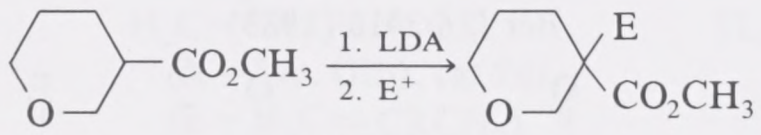


X	E^+	
O	RX	TL *24* 2733 (1983)
S	RX	JACS *107* 1435 (1985); *108* 4943 (1986)
	RCHO	JOC *51* 3742 (1986)



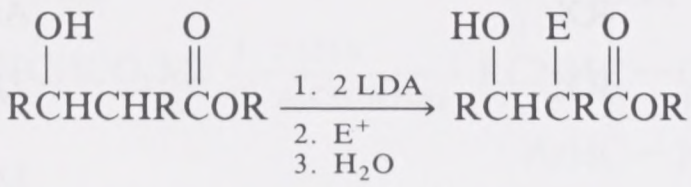
E^+ = RX, RCHO, enone (1,4-addition)

Ber *115* 1705 (1982)
Helv *65* 385 (1982)



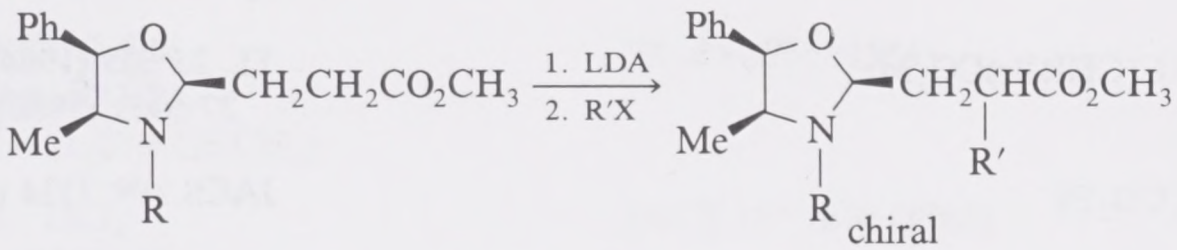
E^+ = MeI, I_2, O_2, $(RS)_2$, PhSeBr

Can J Chem *64* 1781, 1788 (1986)

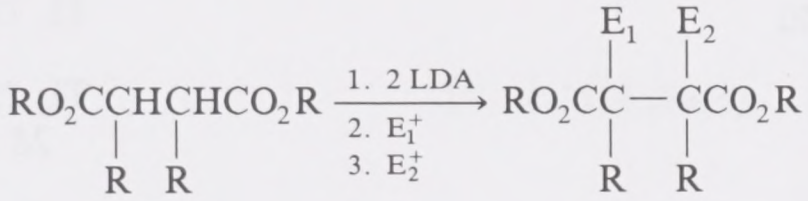


E^+	
RX	TL 2429 (1973); *22* 425 (1981); *23* 3055, 4991 (1982); *27* 5281 (1986); *28* 35, 3189, 5033 (lactone) (1987) Helv *62* 2825, 2829 (1979); *63* 197, 1383 (1980); *65* 293, 344 (1982) JOC *46* 4319 (1981); *48* 1114 (1983); *49* 2168 (1984) (lactone); *52* 1780 (1987) Ber *114* 2786, 2802 (1981) Ann 939, 2114 (1983) Org Syn *63* 109 (1984) JACS *107* 5292 (1985); *108* 2105 (1986) CC 1368 (1987)
RCHO ($ZnCl_2$)	JOC *46* 4319 (1981); *49* 2168 (1984) (lactone)
R_2CO	Helv *63* 197 (1980)
$R^2CH{=}CR^1NO_2$	Helv *63* 2005 (1980)

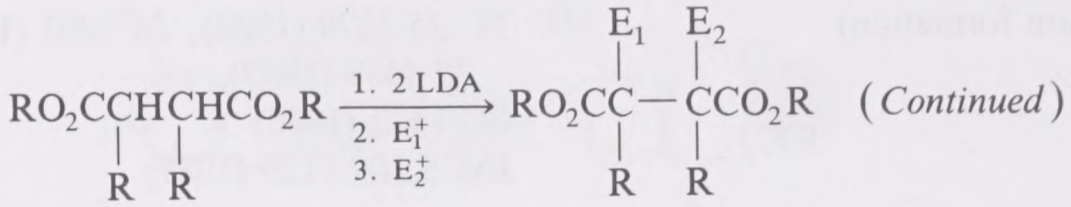
RCH=NAr (lactam formation)	TL *25* 3779 (1984); *26* 3903 (1985); *28* 4489 (1987) CC 1433 (1985) JACS *109* 1129 (1987)
$RCH{=}NSiMe_3$ (lactam formation)	JACS *106* 4819 (1984) TL *26* 937, 5493 (1985) CL 1927 (1984); 651 (1985)
$RCH{=}NCO_2R$	TL *28* 69, 83 (1987)
$(MeS)_2$	TL 2429 (1973)
I_2 (epoxide formed)	TL 4575 (1977) Helv *63* 197 (1980)



Syn Commun *17* 241 (1987)

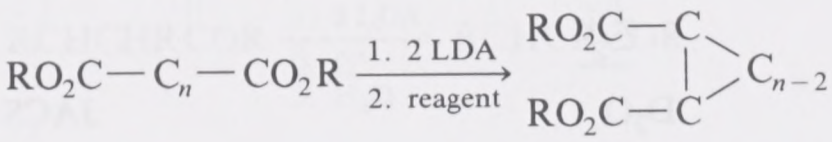


E_1^+	E_2^+	
D_2O	D_2O	JACS *100* 7753 (1978)
Me_3SiCl	Me_3SiCl	Syn Commun *11* 687 (1981) (O silylation)
RX	RX or R′X	TL 73 (1979); *23* 3683 (1982) Syn Commun *11* 687 (1981) CL 687 (1982)
RCHO, R_2CO	HCl	CL 687 (1982)
RCHO	RCHO	TL 73 (1979) JOC *47* 4731 (1982)
$X{-}C_n{-}X$ (n=1–5)		TL 1815 (1979); *27* 5951 (1986); *28* 589 (1987) Syn 389 (1980) Syn Commun *14* 227 (1984) JOC *49* 1412 (1984); *50* 5727 (1985) JACS *107* 3343 (1985) (chiral)

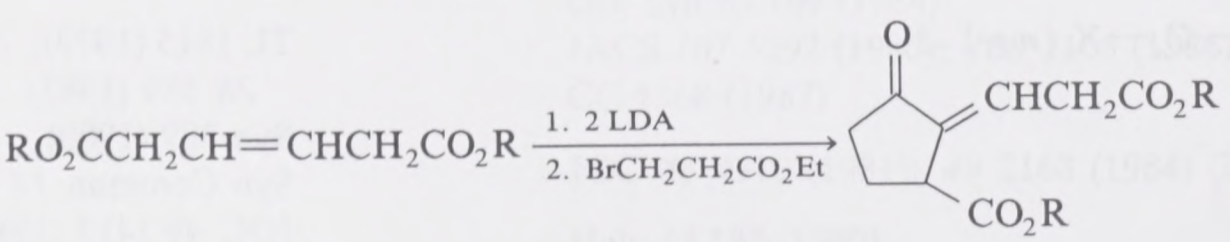


(*Continued*)

E_1^+	E_2^+	
		TL *28* 351 (1987)
$BrCH_2CH_2COCH_3$		JOC *50* 5727 (1985)
$Br-C_n-CO_2Et$ ($n = 2, 3$)		TL *22* 1755 (1981) JOC *47* 4731 (1982); *51* 5450 (1986) Syn Commun *14* 227 (1984)
$RCH=C(CHRBr)CO_2Me$		TL *25* 669 (1984); *27* 5951 (1986)
$RC\equiv CCO_2Ph$		JACS *109* 7534 (1987)
o-$BrCH_2ArCO_2Me$		TL *23* 1031 (1982) JOC *49* 2785 (1984)
o-$EtO_2CC_6H_4CO_2Et$		TL 73 (1979); *23* 1031 (1982)
$H_2C=CHCO_2Ar$		TL *27* 5951 (1986); *28* 5241 (1987)
$TsOCH=CHCOC(CH_3)_3$		TL *27* 5951 (1986)

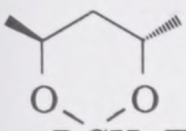
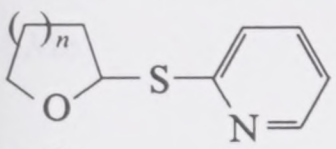
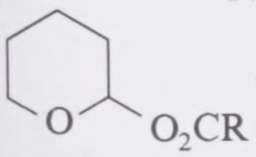
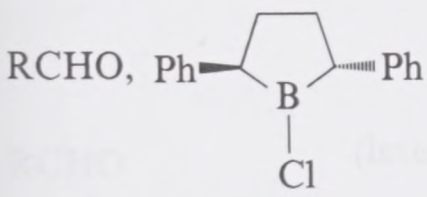


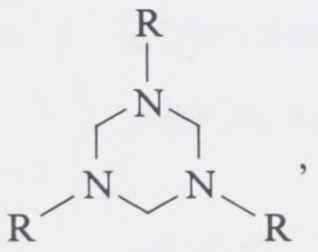
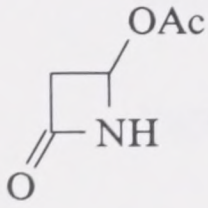
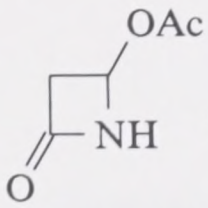
Reagent	n	
I_2	2, 5	Syn Commun *14* 227 (1984) TL *28* 1831 (1987)
$Cu(OTf)_2$	3, 6	Chem Pharm Bull *28* 262 (1980)
$CuCl_2$ or $CuBr_2$	3–6	JOC *48* 1125 (1983); *52* 3462 (1987)



TL *25* 671 (1984)

$$R_2CHCO_2R \xrightarrow[2.\ ClSiMe_3]{1.\ LiNR_2} R_2C{=}C(OSiMe_3)COR \xrightarrow{E^+} R_2C(E')CO_2R$$

E^+	
NO_2-Ar-H, $[(Et_2N)_3S]Me_3SiF_2/Br_2$ or DDQ ($E' = NO_2-Ar$)	JACS *107* 5473 (1985)
$R_2C{=}CHCH_2X$ (X = Cl, Br), high pressure	TL *25* 1075 (1984)
R_3CCl, $ZnCl_2$	TL 1455 (1978) Tetr *37* 319 (1981)
CH_3OCH_2Cl, $ZnBr_2$	CC 305 (1986)
Cl_2CHOCH_3, $ZnCl_2$ ($E' = CHO$, $MeOCHCR_2CO_2R$)	Syn 723 (1982)
$H_2C{=}CHCH_2OCO_2Me$, cat $Pd_2(DBA)_3 \cdot HCCl_3$, cat dppe ($E' = H_2C{=}CHCH_2$)	TL *25* 4783 (1984)
$HC{\equiv}CCO_2H$, $TiCl_4$ ($E' = CH{=}CHCO_2H$)	JACS *107* 3879 (1985)
$RCH(OMe)ONR_2$, $TiCl_4$ or $Zn(OTf)_2$ ($E' = RCHOMe$)	JACS *107* 2569 (1985)
 RCH, $TiCl_4$	TL *26* 2535 (1985)
$R_2C(OR)_2$, $TiCl_4$	TL *28* 1313 (1987) (intramolecular)
	JACS *107* 4289 (1985)
 , Me_3SiOTf	TL *28* 1035 (1987) (intramolecular)
RCHO or R_2CO, high pressure	TL *25* 1075 (1984)
RCHO, $BF_3 \cdot OEt_2$	JACS *105* 1667 (1983) JOC *51* 3027 (1986) (diastereoselection) TL *28* 5615 (1987)
RCHO, 	TL *27* 4721 (1986) (enantioselective)
RCHO, $MgBr_2$	JOC *52* 888 (1987)
RCHO, $SnCl_4$	TL *25* 5973 (1984) JOC *51* 3027 (1986) (diastereoselection)
RCHO, $TiCl_4$	TL 4029 (1979); *25* 4655 (1984) CL 531 (1983) JACS *106* 5305 (1984); *107* 5812 (1985) (enantioselective)

	Angew Int *24* 874 (1985) (diastereoselective) JOC *51* 5032 (1986); *52* 2754 (1987) (enantioselective) Helv *69* 1699 (1986) (diastereoselective)
RCHO, $TiCl_4$, R_3P	TL *27* 1735 (1986)
RCHO, Rh catalyst	TL *28* 793 (1987)
RCHO; cat $SmCl_3$, $CeCl_3$, $LaCl_3$ or $Eu(fod)_3$	TL *28* 5513 (1987)
R_2CO, $TiCl_4$ or $FeCl_3$ or $AlCl_3$	Syn Commun *13* 449 (1983)
$PhSCH_2Cl$, $ZnBr_2$	TL 993 (1979) CC 305 (1986)
PhSCHClR, $TiCl_4$ or $ZnBr_2$	TL 2179 (1979); *23* 2399 (1982) CC 1472 (1987)
	CC 305 (1986)
$PhSCH_2CH_2Cl$, $ZnBr_2$	TL *24* 1315 (1983)
	TL *24* 913 (1983)
cat CF_3SO_3H ($E' = CH_2NHR$)	
 , cat Me_3SiOTf	TL *28* 507 (1987)
 , ZnI_2	CL 1343 (1985)
$(Me_3Si)_2NCH_2OCH_3$, cat Me_3SiOTf [$E' = CH_2N(SiMe_3)_2$]	CC 883 (1984)
R_2NCH_2OR, $ZnCl_2$ ($E' = CH_2NR_2$)	BCSJ *56* 645 (1983)
$Me_2NCH(OMe)_2$, $ZnCl_2$ (3-dimethylamino-2,4-dialkylpentanedioic esters)	Syn 787 (1983)
$HC(OMe)_3$, $TiCl_4$ [$E' = CH(OMe)_2$]	TL *26* 4129 (1985) (chiral)
RCH=NR′, cat Me_3SiOTf (E′ = CHRNHR′)	CL 1371 (1985) CC 119 (1985) TL *28* 4331, 4335 (1987)
$RCH{=}NSiMe_3$, ZnI_2 ($E' = CHRNHSiMe_3$)	CC 539 (1985)
RCH=NR′, $TiCl_4/H_2O$ (E′ = CHRNHR′)	TL 3643 (1977); *21* 2077, 2081 (1980); *28* 227 (1987) Syn 545 (1981)

$RCH{=}NOCH_2Ph$, cat Me_3SiOTf ($E' = CHRNHOCH_2Ph$)	TL *24* 4707 (1983)
$t\text{-}BuO_2CN{=}NCO_2\text{-}t\text{-}Bu$, $TiCl_4$, [$Ti(O\text{-}i\text{-}Pr)_4$] [$E' = N(CO_2\text{-}t\text{-}Bu)NHCO_2\text{-}t\text{-}Bu$]	JACS *108* 6394 (1986) Helv *69* 1923 (1986)
$R^1CH{=}\overset{+}{N}(O^-)R^2$ ($E' = CHR^1NR^2OSiR_3$)	CL 1787 (1982) TL *28* 1431 (1987)
nitro-olefins, $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$ (γ-keto esters)	CL 1043 (1980) JACS *106* 2149 (1984)
enone, $TiCl_4$ (1,4-addition)	JACS *107* 2797 (1985) (stereoselection) JOC *51* 279 (1986); *52* 2754 (1987) (enantioselective)
2-acyl-2-alkenoate ester (1,4-addition)	JACS *102* 4262 (1980)
$Pb(OAc)_4$ ($E' = OAc$)	Helv *68* 216 (1985)

$$R_2CHCO_2R \longrightarrow R_2C{=}\underset{\displaystyle OSiMe_3}{C}COR \xrightarrow[2.\ \Delta]{1.\ MeLi,\ PhCHCl_2} R_2C{=}\underset{\displaystyle Ph}{C}CO_2R$$

Syn Commun *12* 401 (1982)

$$RCHCO_2R \longrightarrow RC{=}\underset{\displaystyle OSiR_3}{C}COR \xrightarrow{E^+} RCXCO_2R$$

X	E^+	
OR	RCHO or R_2CO, $ZnCl_2$	CC 20 (1985)
SMe	RCHO, Lewis acid	TL *26* 6509 (1985)

$$RCH_2COH \longrightarrow \text{(oxazoline, } CH_2R\text{)} \xrightarrow[2.\ E^+]{1.\ n\text{-}BuLi} \xrightarrow[H_2SO_4]{EtOH} RCHCOEt \quad (E)$$

E^+	
RX	JACS *92* 6644 (1970); *96* 6508 (1974) JOC *39* 2778, 2787 (1974); *46* 3097 (1981) Angew Int *15* 270 (1976) Pure Appl Chem *51* 1255 (1979) (asymmetric induction) TL *28* 5509 (1987)
RCHO	JACS *103* 4278 (1981) (B azaenolate)

$$RX + CuCH_2CO_2Et \longrightarrow RCH_2CO_2Et$$

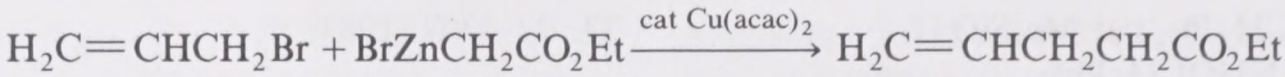
R = allylic, benzylic

TL 1163 (1972)

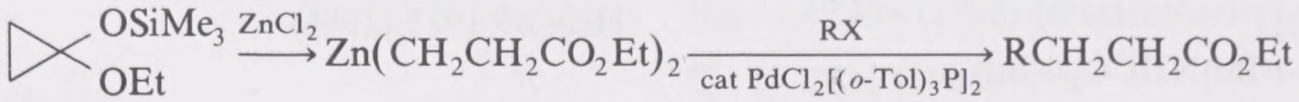
$$RX + BrZnCH_2CO_2\text{-}t\text{-}Bu \longrightarrow RCH_2CO_2\text{-}t\text{-}Bu$$

R = allylic or α-halo ester

Syn Commun *13* 523 (1983)

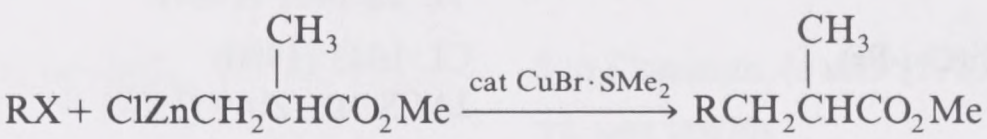


TL *24* 2749 (1983)



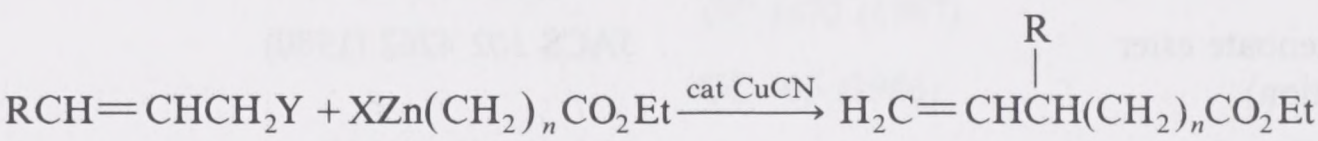
R = aryl, vinylic, acyl

TL *27* 83 (1986)



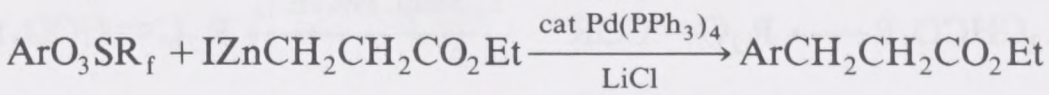
R = allylic, aryl, vinylic, acyl

TL *28* 337 (1987)

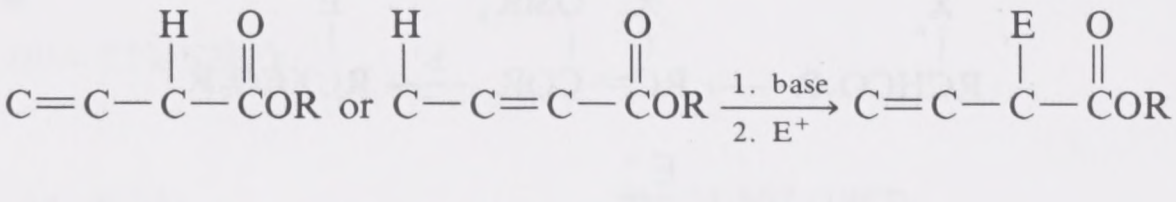


Y = Cl, Br, OTs; n = 2–4

JOC *52* 4418 (1987)



TL *28* 2387 (1987)



$\underline{E^+}$	
H_2O or D_2O (See also page 110, Section 2.2)	TL 4249 (1972); *25* 1333, 5177 (*Z* alkene), 5181 (*Z* alkene) (1984); *28* 5075 (1987) BCSJ *51* 2970 (1978) JACS *102* 3964 (1980); *107* 1293 (1985); *108* 2776 (1986); *109* 6389, 8117 (1987) J Med Chem *23* 525 (1980) Helv *64* 1023 (1981) (stereochemistry) JOC *47* 163 (1982) (stereochemistry) Syn 129 (1982)
R′X	Agric Biol Chem *24* 685 (1960); *26* 705 (1962); *36* 793 (1972) JACS *94* 1790 (1972); *96* 5662 (1974); *107* 1285, 7184 (1985) TL 4249 (1972); 2433 (1973); 4135, 4171 (1975); 4485 (1977); *21* 2509 (1980); *22* 1691 (1981); *28* 6253 (1987) JOC *39* 2323 (1974); *44* 300 (1979); *47* 163 (1982); *49* 3278 (1984); *51* 123, 561 (1986); *52* 353, 4471, 4517 (1987) Syn Commun *7* 483 (1977) CC 799 (1980); 502 (1982); 1717 (1986) Syn 129 (1982)

RCHO, R_2CO	TL 4249 (1972); 4135 (1975) JOC *41* 4065 (1976); *45* 1181 (1980); *47* 163 (1982); *52* 3956 (1987) JACS *108* 3755 (1986)
$PhCH{=}NSiMe_3$ (lactam formation)	JACS *106* 4819 (1984)
O_2, $SnCl_2$ (E = OH)	TL 4215 (1976)
$(PhCO_2)_2$ (E = $PhCO_2$)	TL 4215 (1976)
$PhSSO_2Ph$ (E = SPh)	JOC *51* 4594 (1986)
$MeSSO_3Me$ (E = SMe)	TL 4215 (1976)

$$RCH_2CH{=}CHCO_2R \xrightarrow[\substack{2.\ Me_3SiCl \\ 3.\ HCl}]{1.\ LDA} RCH{=}CHCH_2CO_2R$$

JACS *109* 7063 (1987)

$$R_3SnCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCO_2Et + RCHO \xrightarrow[\text{or } n\text{-}Bu_4NF]{\text{Lewis acid}} H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\underset{\underset{\displaystyle RCHOH}{|}}{C}HCO_2Et$$

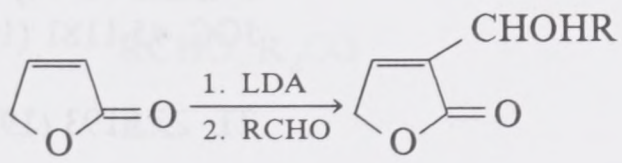
CC 561 (1987)

$$RY{-}\overset{\overset{\displaystyle H}{|}}{C}{-}C{=}C{-}\overset{\overset{\displaystyle O}{\|}}{C}OR \xrightarrow[2.\ R'X]{1.\ base} RY{-}C{=}C{-}\overset{\overset{\displaystyle R'}{|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}OR$$

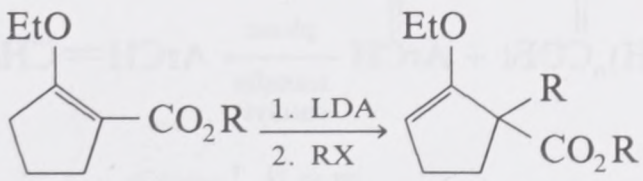
Y

O Syn Commun *7* 189 (1977)

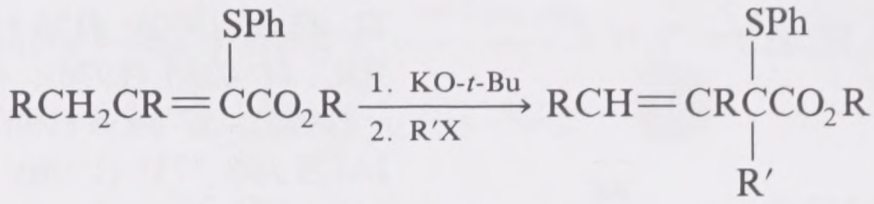
S TL 405 (1975); *24* 3391 (1983)



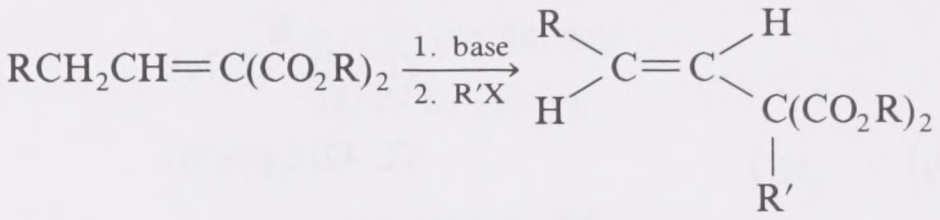
TL *28* 985 (1987)



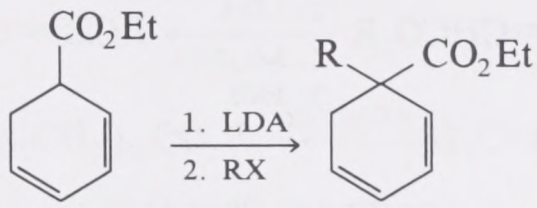
JOC *52* 5745 (1987)



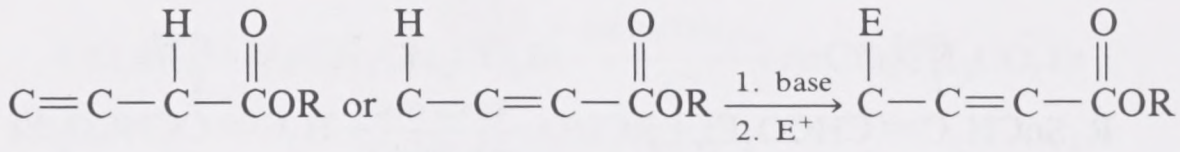
TL *24* 2113, 3391 (1983)



JACS *62* 314 (1940)
CL 1909 (1982)
JOC *51* 4944 (1986)



JACS *109* 6187 (1987)



$\underline{E^+}$

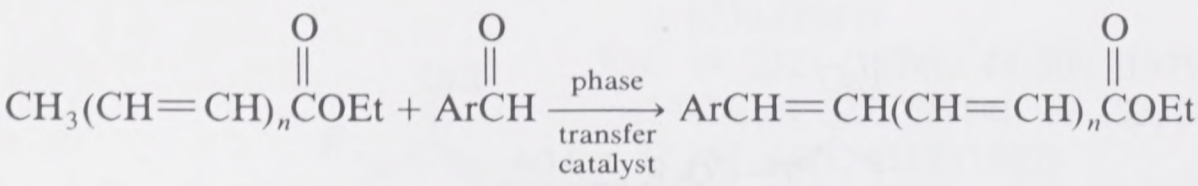
H_2O BCSJ *51* 2970 (1978)
JOC *50* 3526 (1985)

$R'X$ JACS *94* 1790 (1972); *96* 5662 (1974); *98* 1204 (1976); *107* 7184 (1985)
JOC *39* 669 (1974)

RCHO, R_2CO JACS *74* 5529 (1952); *77* 4111 (1955)
J Vitaminol (Osaka) *4* 178, 190 (1958) [CA *53* 5329b,d (1959)]
Helv *45* 528 (1962)
Can J Chem *46* 3115 (1968)
TL 1507 (1972); 4135 (1975); *23* 4773 (1982); *28* 5249 (1987)
Ber *106* 2643 (1973); *110* 1594 (1977)
Syn 343 (1974)
JOC *45* 1181 (1980)

$CdCl_2$/RCHO TL *27* 5193 (1986)

PhSeCl JOC *51* 5243 (1986)



$n = 0, 1$

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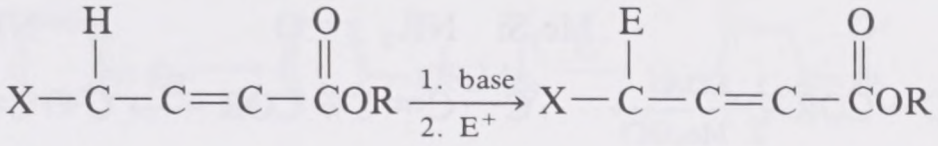
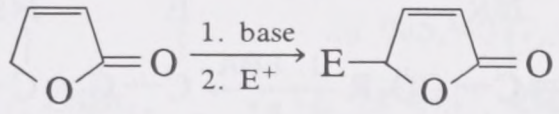
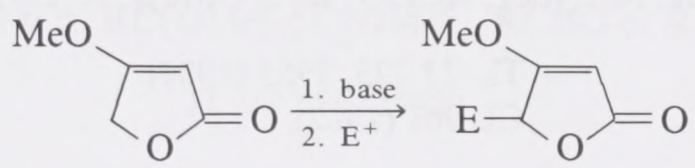


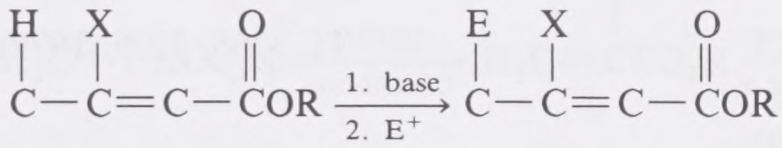
X	E^+	
Br	RCHO	TL 1507 (1972)
$PhSO_2$	R′X	BSCF 743, 746 (1973)
$Ph_3\overset{+}{P}$	RCHO, base (2,4-alkadienoate ester)	JOC *39* 821 (1974)



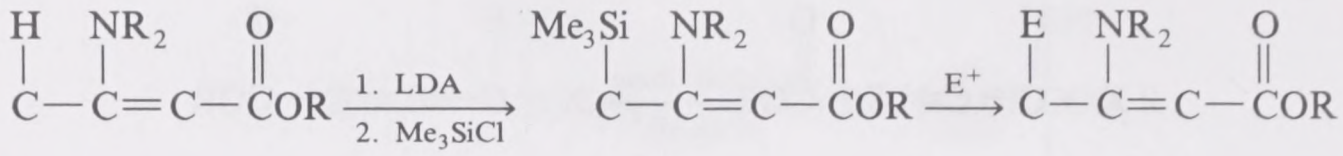
E^+	
D_2O	TL 1627 (1979)
R′X	CC 81 (1979)
RCHO, R_2CO	JOC *39* 669 (1974) JCS Perkin I 70 (1979) CC 81 (1979) TL 1627 (1979); *28* 985 (1987) (lactone)
Michael acceptors (RCH=CHCOR, $RCH{=}CHCO_2R$, $H_2C{=}CHCN$)	TL 3129 (1977)



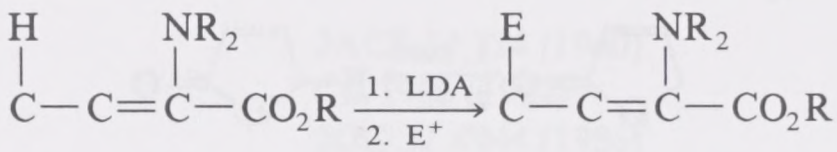
E^+	
D_2O, NBS, RCHO	TL 1627 (1979)
$BF_3 \cdot OEt_2 + RCH(OMe)_2$, $R(OMe)_3$ or $C(OMe)_4$	TL *23* 5229 (1982)



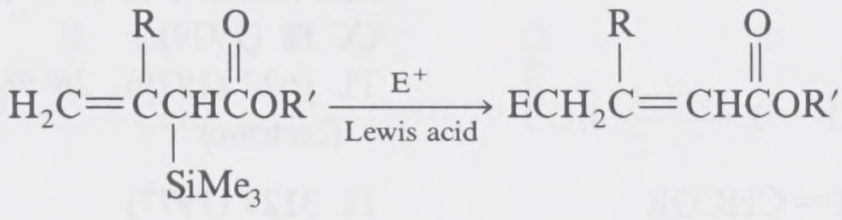
X	E^+	
OR	RCHO, R_2CO	JOC *45* 1181 (1980)
NR_2	RX	TL 39 (1973); 3963 (1974) Syn 401 (1976)
	RCHO, R_2CO	JOC *45* 1181 (1980) JACS *104* 357 (1982); *107* 1777 (1985); *108* 3112 (1986) TL *27* 6173 (1986) ($ZnCl_2$ added)
	RCOCl	JOC *52* 708 (1987)
	Me_3SiCl	TL *23* 3011 (1982)



E^+	
$RCHO, R_2CO, HC(OMe)_3$	TL *23* 3011 (1982)
$RCOCl$	TL *23* 3011 (1982); *28* 5423 (1987)

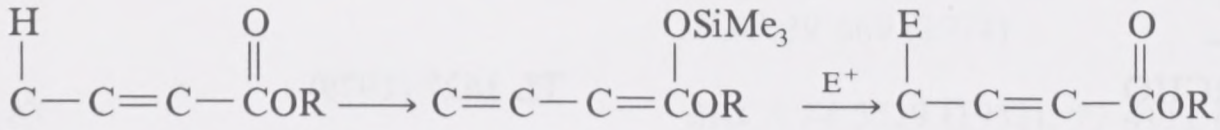


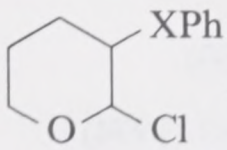
E^+	
RX	Syn 58 (1983)
$RCHO, R_2CO$	Syn 61 (1983)
$RCHO, ZnCl_2$	JACS *109* 1587 (1987)

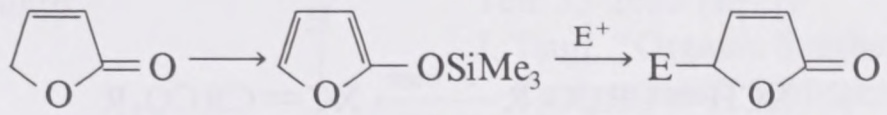


$E^+ = RX$ (R = allylic, benzylic), $RCHO$, $R_2C(OMe)_2$, R_2CO, $RCOCl$, $PhSCHClR$

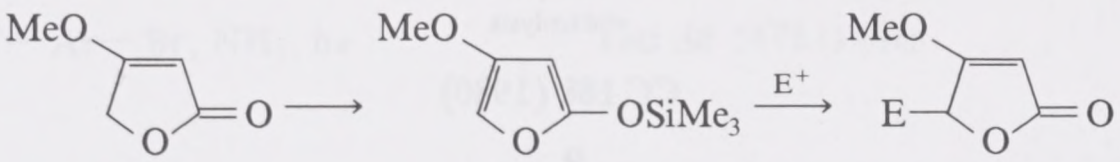
TL *23* 723, 2953 (1982)
CL 961 (1982)



E^+	
$PhSCl$, $PhSCHClR$, $RCOCl$, RBr (R = allylic, benzylic), $MeOCH_2Cl$, $MeCH(OEt)_2$, or $(MeO)_3CH$; $ZnBr_2$	TL 3205, 3209 (1979)
 , $ZnBr_2$ (X = S, Se)	TL *24* 5911 (1983)
$(MeO)_3CH, ZnBr_2$	TL *26* 397 (1985)
$RCOCl, ZnBr_2$	JOC *52* 708 (1987)
$RCH{=}NR, TiCl_4$	TL *28* 613 (1987) (5,6-dihydro-2-pyridones or 5-amino-2-alkenoates)
nitro-olefins, $ZnBr_2$	CL 1043 (1980)

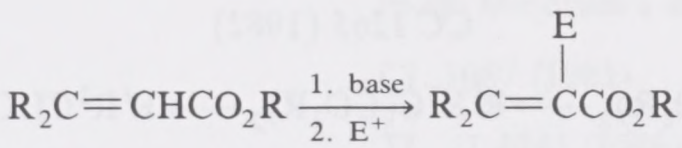


E^+	
allylic halide, AgO_2CCF_3	TL *28* 949 (1987)
$RCH(OMe)_2$ or $R_2C(OMe)_2$, $SnCl_4$	TL *22* 4269 (1981)
RCHO, cat *n*-Bu_4NF-silica	Heterocycles *19* 2327 (1982)
RCHO or R_2CO, $SnCl_4$	TL *21* 4611 (1980); *22* 4269 (1981); *28* 985, 4037, 4041 (1987)
RCHO or R_2CO; $BF_3 \cdot OEt_2$, $ZnCl_2$, $ZnBr_2$, CsF, *n*-Bu_4NF, $(Ph_3C)ClO_4$, or R_3SiOTf (R = Me, Et)	TL *28* 4037, 4041 (1987)
$HC(OR)_3$, cat $SnCl_4$	BCSJ *52* 1953 (1979)
$RC(OR)_3$, cat Lewis acid	BCSJ *52* 1953 (1979)
$RCHCl(OAc)$, cat $SnCl_4$	BCSJ *52* 1953 (1979)
$Pb(OAc)_4$ (E = OAc)	BCSJ *53* 1061 (1980)

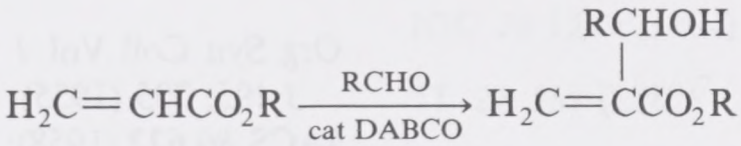


$E^+ = ZnBr_2$ or $TiCl_4$ plus $RCH(OMe)_2$, $RC(OMe)_3$, $C(OMe)_4$, RCHO or R_2CO; Br_2; $Pb(OAc)_4$ (E = OAc)

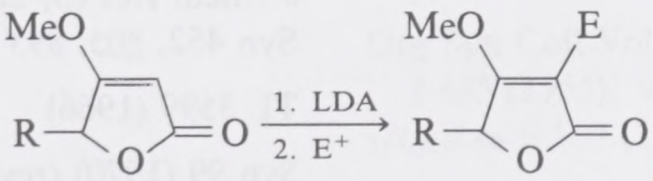
TL *23* 353 (1982)



See page 185, Section 1.

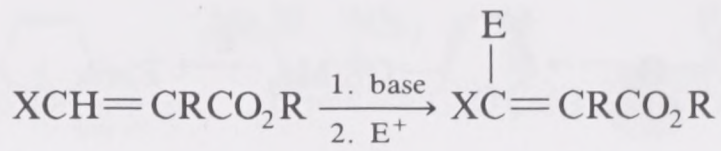


Angew Int *22* 795, 796 (1983)
JCS Perkin I 2293 (1983)
Helv *67* 413 (1984)
JOC *50* 3849 (1985)
TL *27* 5007 (1986)



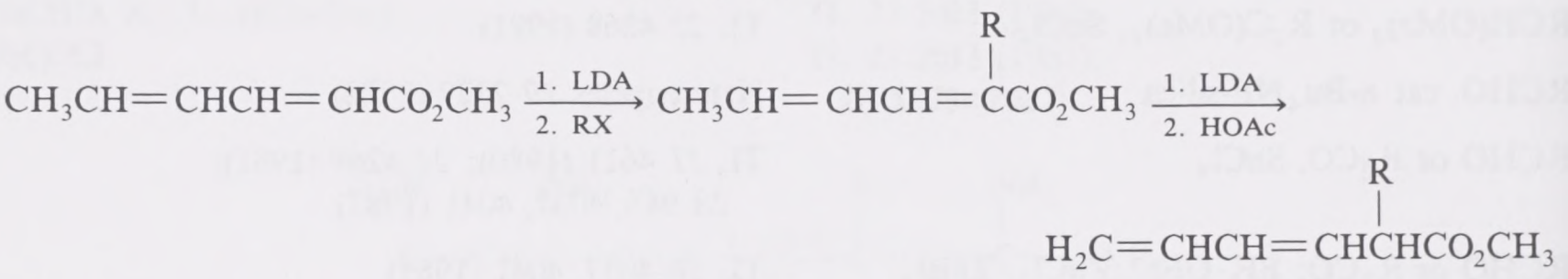
E^+ = MeOD, MeI, RCHO, $(RCO)_2O$, RCO_2R, RSSR, $(RCO_2)_2$

Angew Int *21* 637 (1982)
TL *23* 581, 585, 1793 (1982)

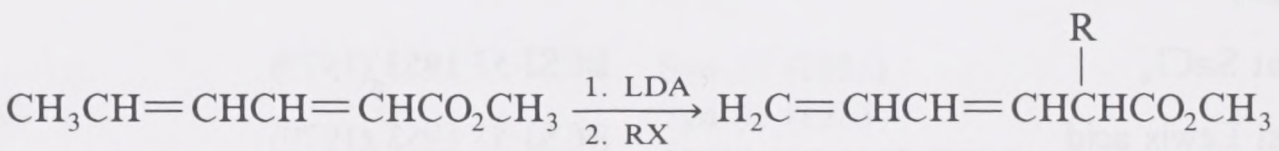


X = Ph, OR, SR, NR_2, CO_2R

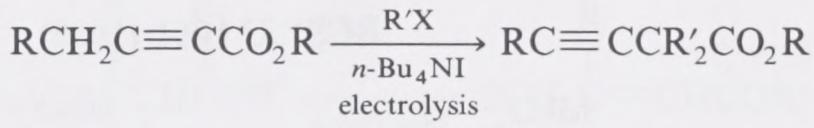
See page 185, Section 1.



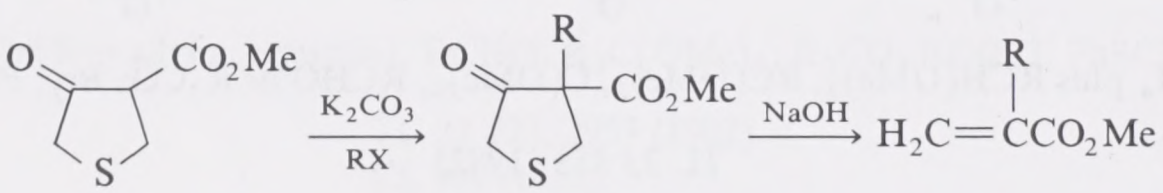
TL *24* 261 (1983)



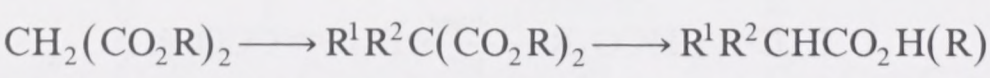
JOC *48* 3003 (1983)



CC 188 (1980)



CC 1265 (1982)



Review: Org Rxs *9* 107 (1957)

Alkylation:

base/R′X	Org Syn Coll Vol *1* 250 (1941); *2* 474 (1943); *3* 495, 705 (1955); *4* 288 (1963) JACS *80* 622 (1958); *106* 1051 (1984) (intramolecular); *109* 7477 (1987) JCS B 67 (1968) (intramolecular) JOC *43* 4682 (1978); *46* 3127 (1981) (intramolecular); *47* 3769 (1982) CC 522 (1979) Rec Trav Chim *99* 96 (1980) J Chem Res (S) 283 (1980) Syn 452, 805, 893 (1982)
BF_3/R′Cl	TL 3599 (1966)
alkene, free radical initiator	Syn 99 (1970) (review)

Allylation:

$H_2C{=}CHCH_2X$ (X = OAc, O_2SPh), cat $NiCl_2L_2$	JOMC *250* C21 (1983)

via π-allyl Pd compounds	Tetr *33* 2615 (1977) J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) (review) Acct Chem Res *13* 385 (1980) Pure Appl Chem *54* 189 (1982) (chiral) R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985) (review) JOC *52* 5430 (1987)
via π-allyl Mo compounds	JACS *104* 5543 (1982); *105* 3343 (1983); *109* 1469 (1987) Organomet *2* 1687 (1983)
via π-allyl W compounds	JACS *105* 7757 (1983); *109* 2176 (1987)
Arylation:	
ArH, $(NH_4)_2Ce(NO_3)_6$	TL *27* 2763 (1986)
$ArPb(OAc)_3$	TL *21* 965 (1980) Austral J Chem *37* 1245 (1984)
KO-*t*-Bu/Ar_2IX (X = Cl, Br, I)	JOC *52* 4115 (1987) (Meldrum's acid)
KO-*t*-Bu/ NC—Ar—Br, NH_3, hν	Tetr *38* 3479 (1982)
Acylation:	
RCOCl, $MgCl_2$, 2 Et_3N	JOC *50* 2622 (1987)
base, RCOCl	Syn 451 (1982) Syn Commun *12* 19 (1982) (both Meldrum's acid)
base/$RCOPO(OEt)_2$	CL 1087 (1981)
ArI, CO, Pd catalyst	TL *27* 4745 (1986)
Decarboxylation:	
~ 500°C	JOC *29* 1249 (1964)
Δ, CuCl, chiral alkaloid (enantioselective)	TL *28* 539 (1987)
hydrolysis/Δ, Cu_2O	Syn 1029 (1986)
DABCO, Me_2S, Celite, Δ	JACS *109* 3010 (1987)
$(Me_4N)OAc$, DMSO	JACS *98* 6188 (1976)
$(Me_4N)OAc$, HMPA	JACS *98* 630 (1976); *100* 3426 (1978)
$OH^-/H^+/\Delta$	Org Syn Coll Vol *2* 416, 474 (1943); *3* 495 (1955); *4* 630 (1963) Org Rxs *9* 107 (1957) (review)
B_2O_3, 170–190°C	Syn Commun *9* 609 (1979)
water, salts, dipolar aprotic solvent	Syn 805 (1982) (review)

H_2O, DMSO	TL 1091, 1095 (1974) JOC *43* 138 (1978)
LiCl, H_2O, DMSO	JOC *43* 138 (1978)
NaCl, H_2O, DMSO	TL 957 (1973); 1091 (1974); *28* 171 (1987) JOC *43* 138 (1978); *52* 3205 (1987)
NaCN, LiI, H_2O, DMF	JACS *100* 3426 (1978); *107* 2033 (1985)
KCN or NaCN, DMSO, (H_2O)	TL 215 (1967) Tetr *26* 5437 (1970) JOC *43* 138 (1978) JACS *107* 1421 (1985)
Me_3SiI	Syn Commun *9* 233 (1979)

$$NCCH_2CO_2R \longrightarrow \underset{\displaystyle R}{\overset{\displaystyle |}{NCCHCO_2R}} \longrightarrow RCH_2CN$$

Alkylation:

base/RX	Org Rxs *9* 107 (1957) (review)
diol, $EtO_2CN{=}NCO_2Et$, PPh_3 (dialkylation)	TL 2455 (1976)

Decarbalkoxylation:

H_2O, DMSO	TL 1095 (1974)
water, salts, DMSO	Syn 893 (1982) (review)
H_2O, NaCl, DMSO, Δ	Syn 893 (1982) (review)

TL 957 (1973); *27* 3353 (1986)

$$RCH{=}CH_2 + XCH_2CO_2Et \longrightarrow RCH_2CH_2CHXCO_2Et$$

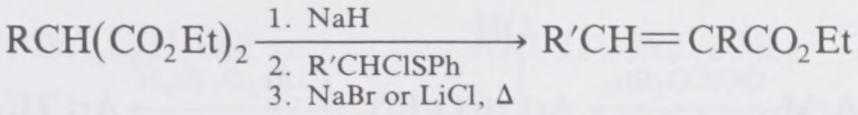
X	Reagent(s)	
CO_2Et	$Mn(OAc)_3 \cdot 2\ H_2O$	CC 693 (1973)
CO_2Et, CN	CuO, Cu_2O, NiO_2, PbO_2, MnO_2, AgO or Ag_2O	Syn 454 (1977)

$$RCH_2CH{=}CH_2 + H_2C(CO_2Et)_2 \xrightarrow[\text{cat } Cu(OAc)_2]{Mn(OAc)_3 \cdot 2\ H_2O} RCH{=}CHCH_2CH(CO_2Et)_2$$

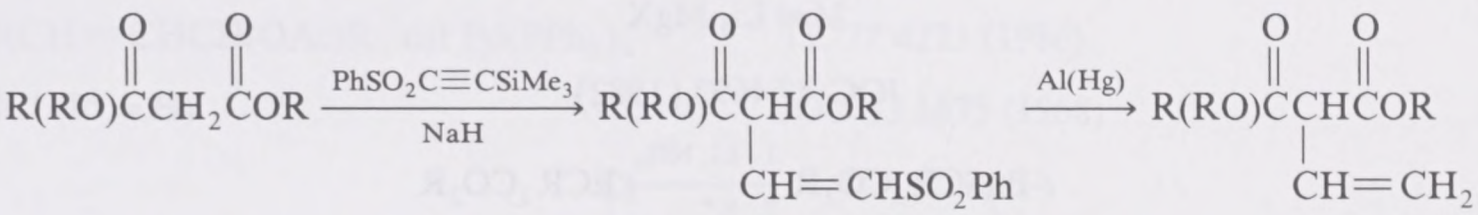
CC 693 (1973)

$$R^1(R^1O)C\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}CH_2\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}OR^2 + H_2C{=}CHR^3 \xrightarrow{PdCl_2} \begin{cases} \xrightarrow{H_2} R^1(R^1O)C\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}CH\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}OR^2 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad R^3CHCH_3 \\ \xrightarrow{25^\circ C} R^1(R^1O)C\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}CH\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}OR^2 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad R^3C{=}CH_2 \end{cases}$$

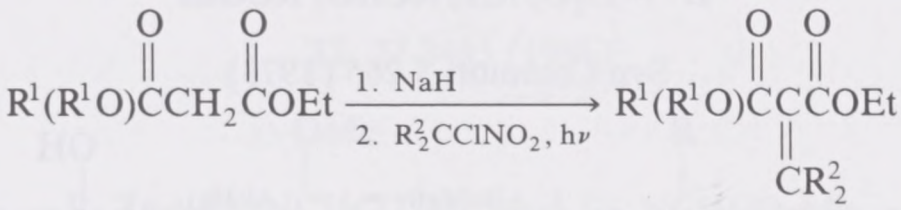
JACS *99* 7093 (1977)



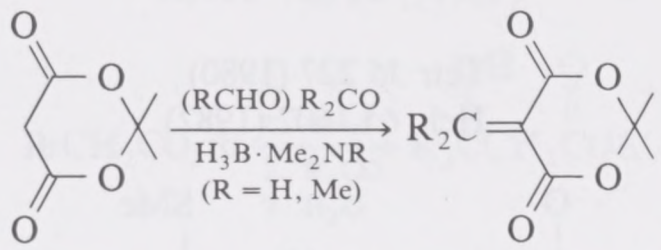
Syn 131 (1982)



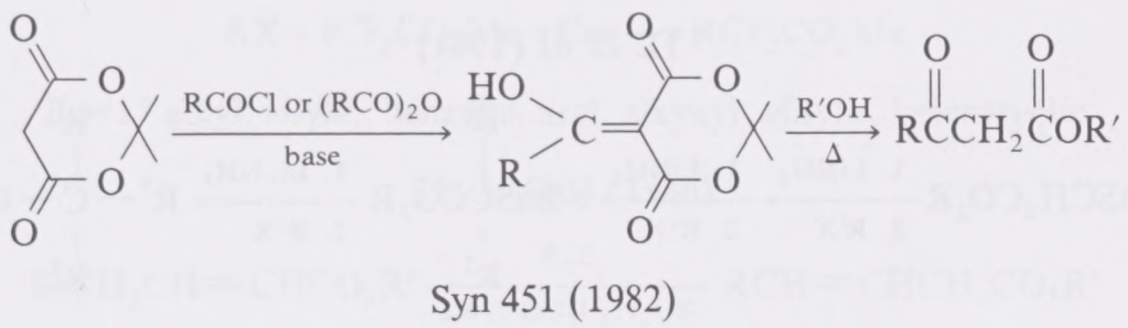
JOC *47* 4713 (1982)



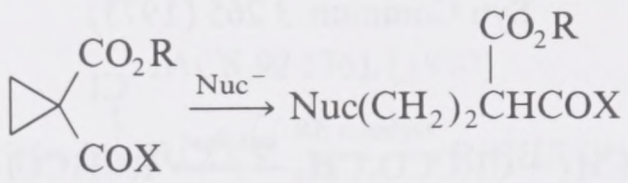
Syn 62 (1981)



TL *24* 4951 (1983)



Syn 451 (1982)

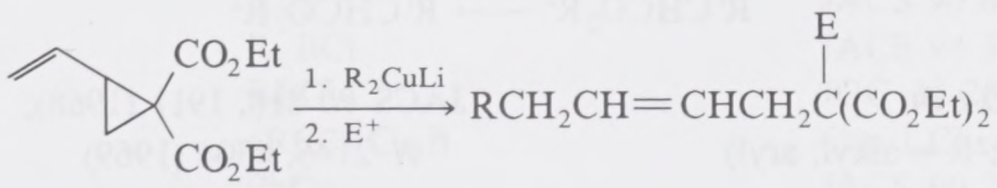


X = R, OR

Review: Acct Chem Res *12* 66 (1979)

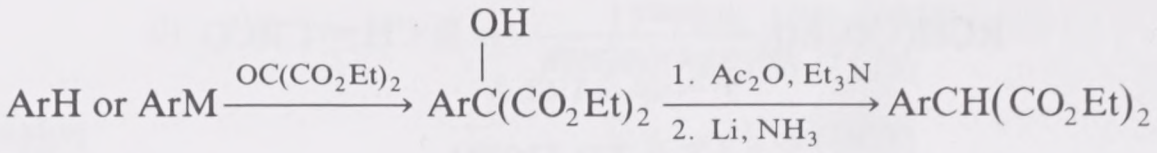
Nuc$^-$

R_2CuLi	JACS *94* 4014 (1972) TL 997 (1972); 529 (1975); 3857 (1976) Can J Chem *60* 825 (1982)
Et_2AlCN (Nuc = CN)	Can J Chem *60* 825 (1982)



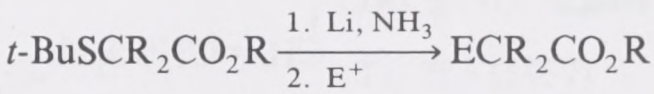
E^+

H_2O	TL 997 (1972)
R′X	JOC *38* 2100 (1973)



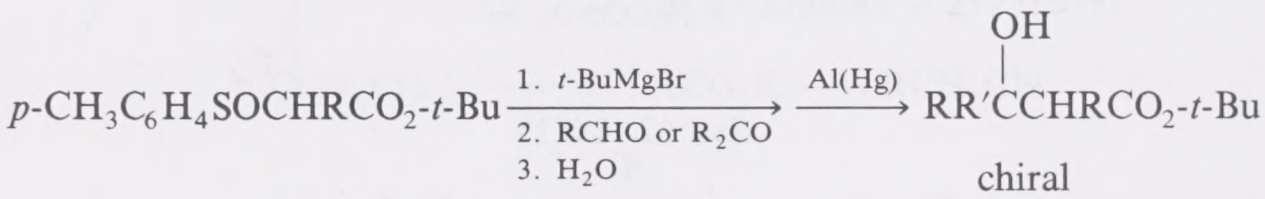
$M = Li, MgX$

JOC *47* 4692 (1982)

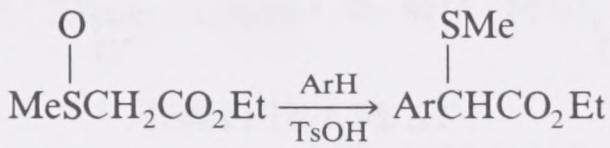


$E^+ = H_2O, RX, RCHO, RCOCl$

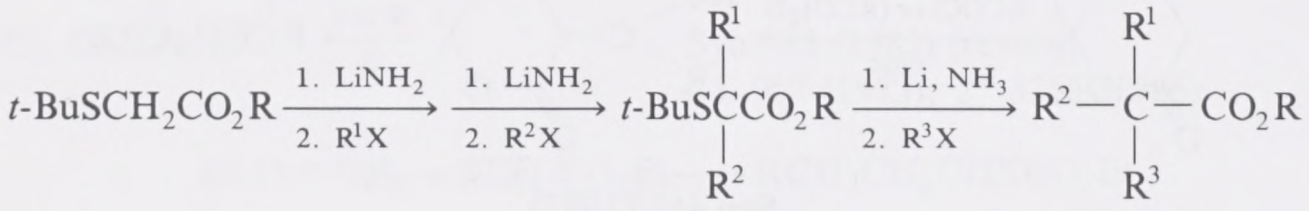
Syn Commun *3* 265 (1973)



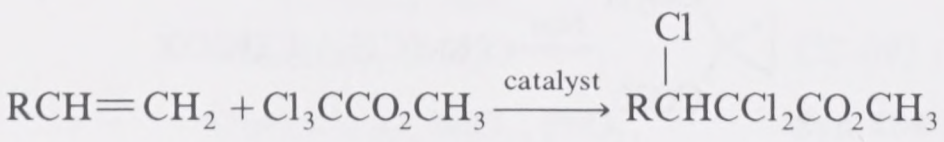
Tetr *36* 227 (1980)
Helv *65* 1602 (1982)



TL *22* 81 (1981)



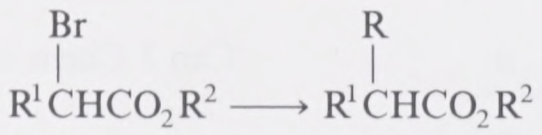
Syn Commun *3* 265 (1973)

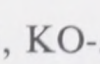
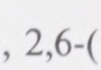


Review: Syn 145 (1977)

Catalyst

$RuCl_2(PPh_3)_3$	JOC *41* 396 (1976)
CuCl	JOC *29* 2104 (1964)



R_3B or RB  , KO-*t*-Bu (R^1 = H, Br, alkyl; R = alkyl, aryl)	JACS *90* 818, 1911 (1968); *91* 2146, 4304 (1969)
R_3B or RB  , 2,6-(*t*-Bu)$_2$C$_6$H$_3$OK	JACS *91* 6855 (1969) (R^1 = H, Br; R = alkyl) Organomet Chem Syn *1* 95 (1970) (R^1 = CN, R = alkyl)

$RCH{=}CHB\langle\rangle$, 2,6-$(t\text{-Bu})_2C_6H_3OK$	JOC *51* 3398 (1986)
Zn/ArX, Ni or Pd catalyst ($R = Ar$, $R^1 = H$)	JOMC *132* C17 (1977); *177* 273 (1979)
$Zn/RCH{=}CHCH(OAc)R$, cat $Pd(PPh_3)_4$	TL *27* 4223 (1986)
$PhCdCl$ ($R^1 = H$)	JOC *33* 1675 (1968)

$$RMgBr + R'NHCH(Cl)CO_2Me \longrightarrow R'NHCH(R)CO_2Me$$

TL *27* 2435 (1986)

$$R_2Zn + Et_2NCH(OMe)CO_2Me \longrightarrow Et_2NCH(R)CO_2Me$$

JOMC *256* 193 (1983)

$$BrCH_2CO_2R' \xrightarrow[2.\ R_2CO\ \ 3.\ H_2O]{1.\ \text{metal}} R_2CCH_2C(OH)(O)R'$$

See page 553, Section 2.1.

$$RX + ICF_2CO_2Me + Cu \longrightarrow RCF_2CO_2Me$$

R = 1° alkyl, allylic, benzylic, aryl, alkynyl, vinylic, heterocyclic

TL *27* 6103 (1986)

$$BrCH_2CH{=}CHCO_2R' \xrightarrow[2,6\text{-}(t\text{-Bu})_2C_6H_3OK]{R_3B} RCH{=}CHCH_2CO_2R'$$

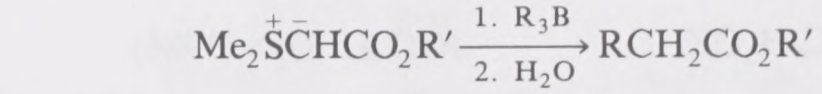
JACS *92* 1761 (1970)

$$R'H + N_2CRCO_2R \xrightarrow{\text{Rh catalyst}} R'CHRCO_2R$$

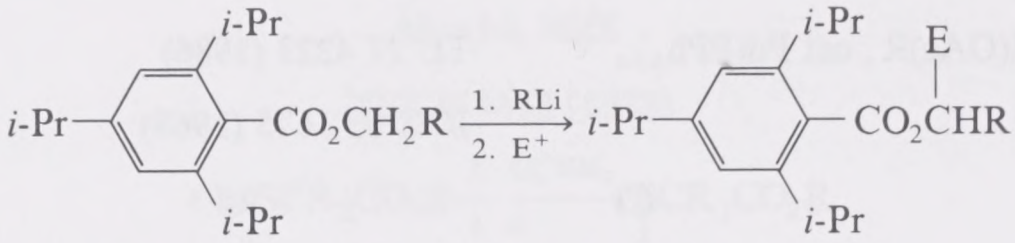
CC 688 (1981)
TL *23* 4321 (1982)

$$N_2CHCO_2R' \xrightarrow{\text{organometallic}} \xrightarrow{E^+} RCH(E)C(O)R'$$

E^+	Organometallic	
H_2O	R_3B	JACS *90* 6891 (1968)
	R_2BCl	JACS *94* 3662 (1972)
	$RBCl_2$	JOC *38* 2574 (1973)
	$(RC{\equiv}C)_3B$	Can J Chem *50* 1105 (1972)
	PhCu	JACS *90* 2186 (1968)
		CC 515 (1969)
D_2O	R_3B	JACS *91* 6195 (1969)
NCS, NBS	R_3B	Can J Chem *50* 2387 (1972)

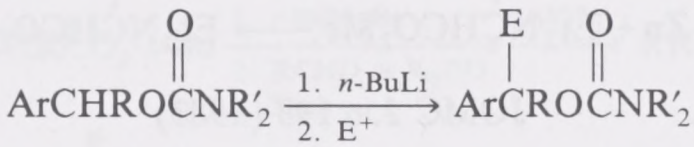


JACS *89* 6804 (1967)



$E^+ = RX, RCHO, R_2CO, Me_3SiCl, n\text{-}Bu_3SnCl$

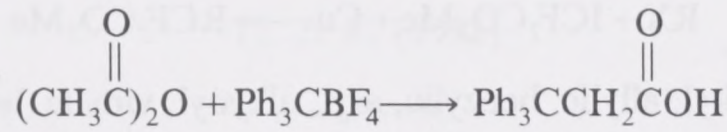
JACS *99* 5213 (1977)
JOC *43* 4255 (1978); *46* 2363 (1981)
Chem Rev *78* 275 (1978) (review)



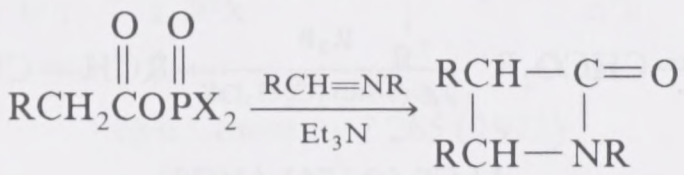
$E^+ = RX, RCHO, R_2CO, (MeO)_2CO, Me_3SiCl$

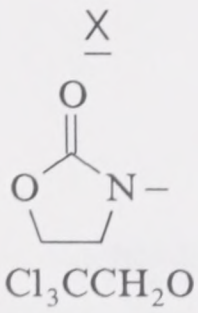
Syn 1045 (1982)

3. Anhydrides



JOC *35* 278 (1970)

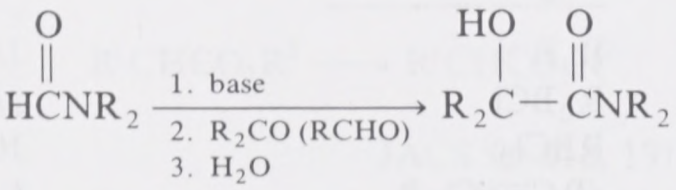




Syn 63 (1982)

Syn 1053 (1982)

4. Amides



Angew Int *12* 836 (1973); *15* 293 (1976); *20* 795 (1981)
Can J Chem *52* 185 (1974)
CC 387 (1976)
JCS Perkin I 1881 (1977)
Chem Rev *78* 275 (1978) (review)

$$Ph_3COH + CH_2(CONH_2)_2 \xrightarrow{H^+} Ph_3CCH(CONH_2)_2$$

JCS 716 (1962)

$$NCCH_2CONR_2 \xrightarrow[2.\ RX]{1.\ base} NC\overset{\displaystyle R}{\overset{|}{C}}HCONR_2$$

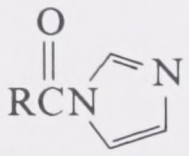
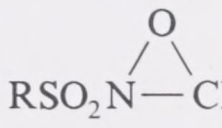
chiral chiral

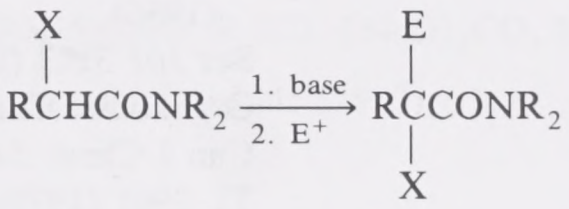
TL *27* 2463 (1986)

$$R_2CHCONR_2 \xrightarrow[2.\ E^+]{1.\ base} R_2\overset{\displaystyle E}{\overset{|}{C}}CONR_2$$

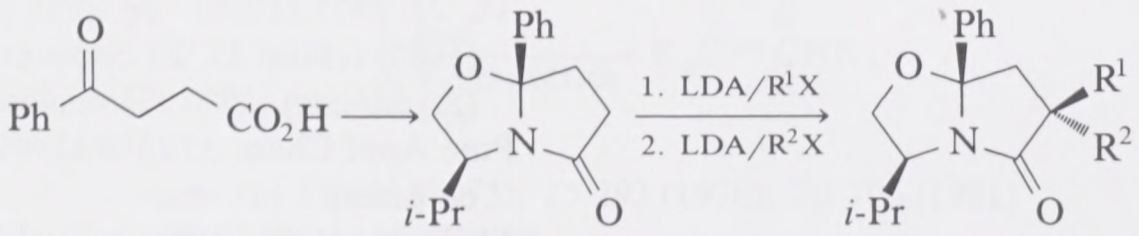
Review: Syn 509 (1977) (polyalkali metal amides)

$\underline{E^+}$	
RX	JOC *26* 3696 (1961); *31* 982, 989, 3873 (1966); *39* 2475 (1974); *42* 1688 (1977); *51* 1541, 1936 (lactam), 3140 (lactam), 4080 (intramolecular) (1986) Ber *101* 3113 (1968) Organomet Chem Syn *1* 237 (1971) Can J Chem *54* 1098 (1976) TL 3961 (1978); *21* 4233 (1980); *25* 857 (1984) (chiral); *28* 651 (chiral), 2041, 6389 (1987) JOMC *177* 5 (1979) (chiral) Pure Appl Chem *53* 1109 (1981) (chiral) JACS *107* 3915, 7776 (chiral lactam) (1985); *108* 306 (1986) (chiral lactam); *109* 4405 (1987) (lactam) CC 992 (1987)
ArX, hν	JOC *45* 1239 (1980) JACS *107* 435 (1985) (intramolecular)
ArBr, $LiNR_2$	JOC *52* 2110 (1987)
epoxide	JOC *37* 1907 (1972); *42* 1688 (1977); *46* 2831 (1981) Ber *105* 1621 (1972) Can J Chem *55* 266 (1977) JACS *107* 7776 (1985) (chiral lactam)
RCHO, R_2CO	Ber *101* 3113 (1968) JOC *39* 2475 (1974); *42* 1688 (1977); *45* 1068 (1980); *50* 3019 (1985) (enones) Can J Chem *55* 266 (1977) Syn 954 (1979); 247 (1980) TL *21* 3975 (1980); *24* 3883 (1983); *26* 5807 (1985) (chiral Li, Zr enolates); *28* 651 (Zr enolate), 2037 (Ti enolate), 6137 (1987) Pure Appl Chem *53* 1109 (1981) (chiral Li, B, Zr enolates) JACS *103* 2876 (1981) (chiral Li, Zr enolates); *105* 1667 (1983) (diastereoselectivity) Angew Int *22* 788 (1983) CC 992 (1987)

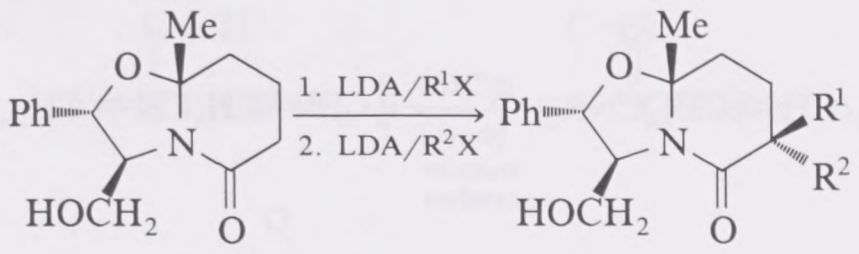
enones (1,4-addition)	JOC *50* 3019 (1985)
RCOCl	TL *25* 6015 (1984)
ROCOCl	TL *28* 4901 (1987)
diketene	TL *28* 4901 (1987)
	CC 1447 (1986)
RCO_2CO_2Et	Syn 954 (1979)
 (chiral) (E = OH)	JOC *51* 2402 (1986)
MeSSMe	JOC *42* 3236 (1977)
PhSeSePh	JACS *108* 306 (1986) (chiral lactam)



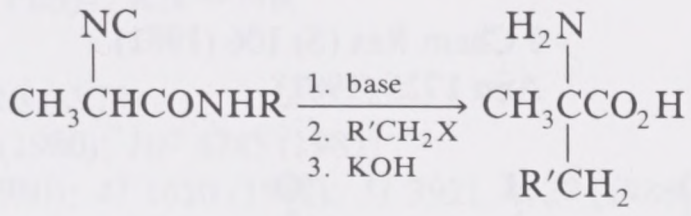
X	E^+	
F	RX	TL *27* 6103 (1986)
Cl	RCHO	JACS *108* 4598 (1986) (chiral)
RO	RX	TL *26* 1343 (1985) (chiral); *27* 2731 (1986) (chiral)
	RCHO	JACS *106* 8161 (1984)
R_3SiO	RX	TL *27* 2731 (1986)
RCONR	RX	JOC *52* 4044 (1987)
	RCHO	TL *27* 6361 (1986)
ArCH=N	RX, RCHO, RCOCl, $ClCO_2R$	Helv *51* 1905 (1968) JACS *95* 4324 (1971) CC 1138 (1972) TL 375 (1972)
$Ar_2C=N$	RX, $ClCO_2R$	Helv *64* 1145 (1981)
$(MeS)_2C=N$	RX	TL *27* 3403 (1986)



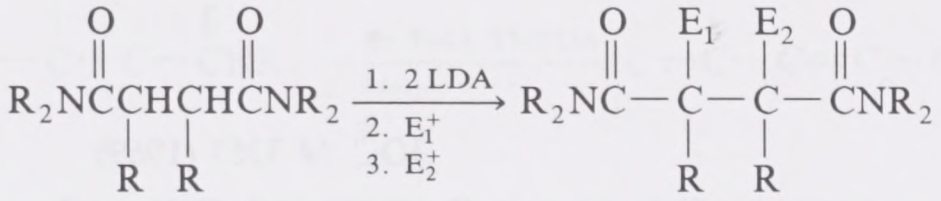
JACS *106* 1146 (1984)
TL *26* 2047 (1985)
JOC *51* 1541 (1986)



JOC *51* 1936 (1986)

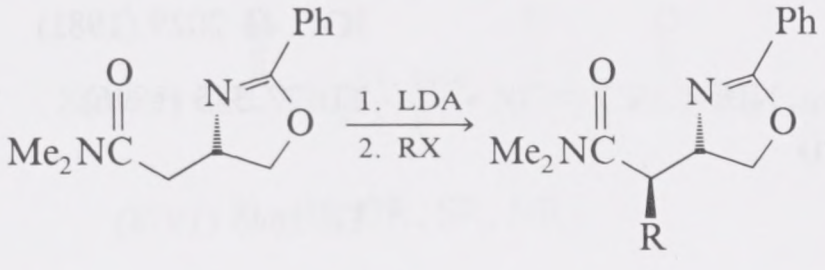


Ann 439 (1981)

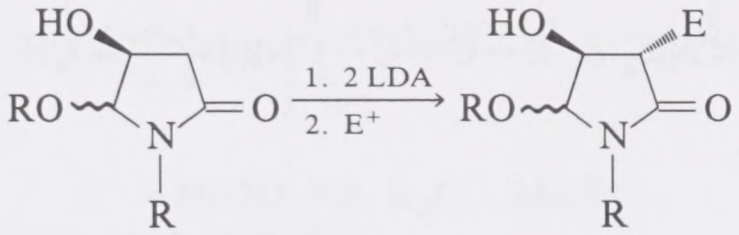


$E^+ = D_2O$, RX, RCHO, $Br(CH_2)_4Br$, $Br(CH_2)_3CO_2Et$, RCO_2Et, *o*-$C_6H_4(CO_2Et)_2$, $(PhS)_2$, $(PhSe)_2$

TL *23* 3971, 3975 (1982)

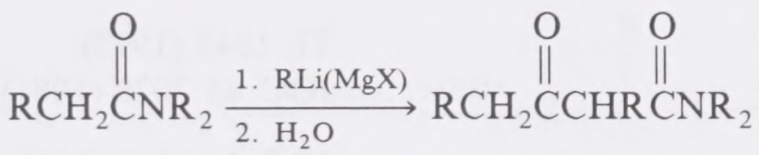


TL *24* 2733 (1983)
JACS *108* 4943 (1986)

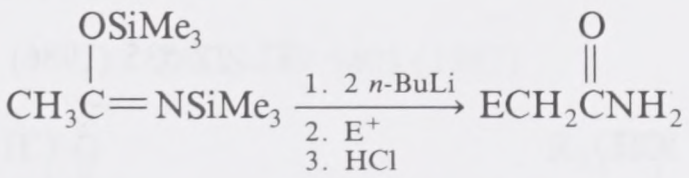


$E^+ = RX, R_2CO$

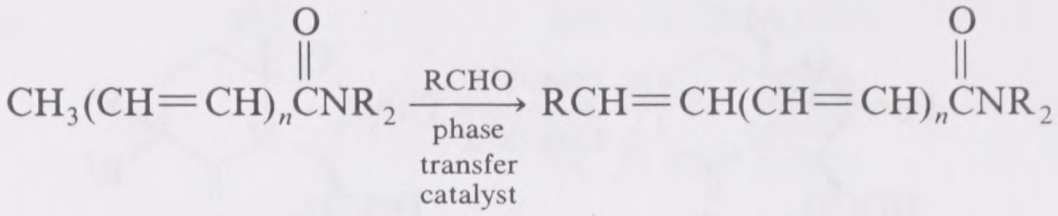
TL *28* 1581 (1987)



Tetr *38* 557 (1982)

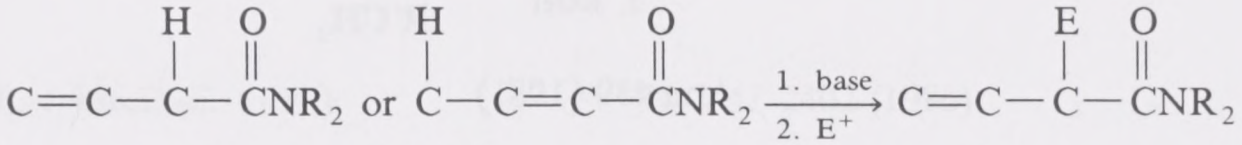


E^+	
RCHO, R_2CO	TL *21* 3227 (1980)
RCO_2R	JACS *107* 7760 (1985)

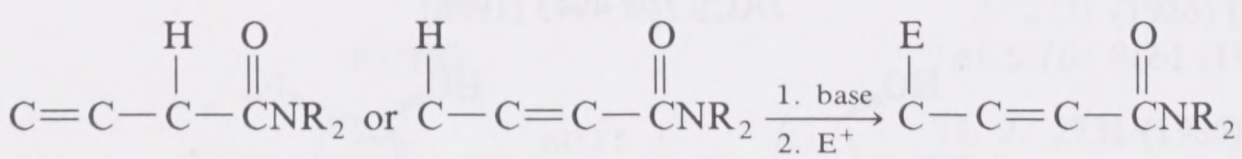


$n = 0$–2

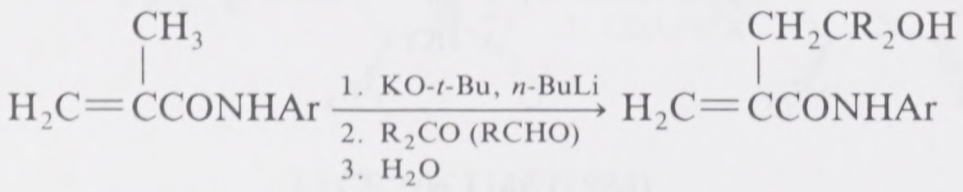
J Chem Res (S) 106 (1981)
Ann 1725 (1981)



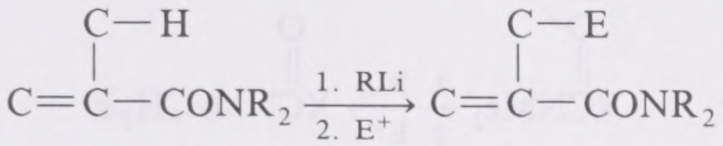
E^+	
H_2O	JOC *34* 3263 (1969)
R′X	JOC *34* 3263 (1969); *46* 2029 (1981) TL 1645 (1978); *27* 531 (1986)
RCHO, R_2CO	TL 1645 (1978) JOC *46* 2029 (1981)
Me_3SiCl/Δ/RCHO, *n*-Bu_4NF or $TiCl_4$ (E = RCHOH)	TL *27* 535 (1986)
$PhCO_2Me$	TL 1645 (1978)
PhSeBr	TL 1645 (1978)

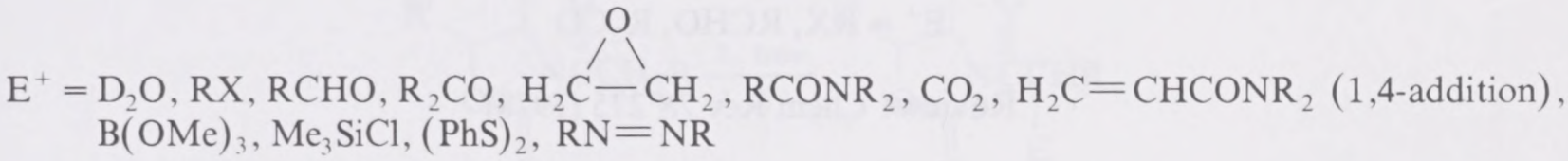


E^+	
H_2O	JOC *50* 3526 (1985)
R′X	JOC *34* 3263 (1969) TL 2057 (1975)
R′X, CuI	TL 1645 (1978) JOC *46* 2029 (1981)
RCHO, R_2CO	JOC *34* 3263 (1969); *46* 2029 (1981)
CO_2	JOC *34* 3263 (1969)
Me_3SiCl, Δ	TL *27* 535 (1986)

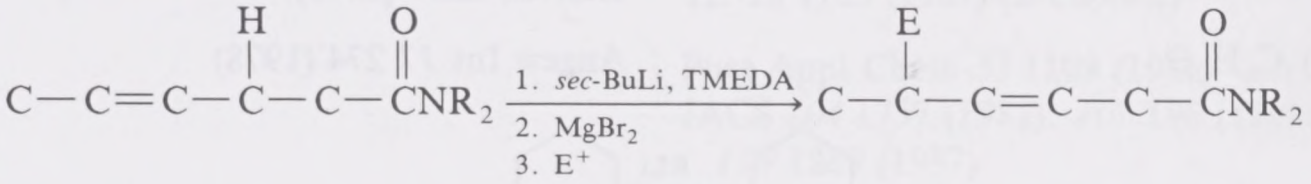


CL 1567 (1980)



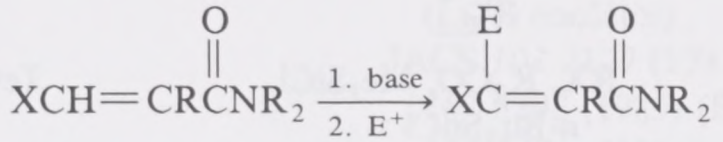


Angew Int *13* 468 (1974)
JACS *102* 4550 (1980); *107* 4745 (1985)
JOC *45* 4257 (1980); *47* 1610 (1982); *51* 3921, 4627 (1986); *52* 218 (1987)



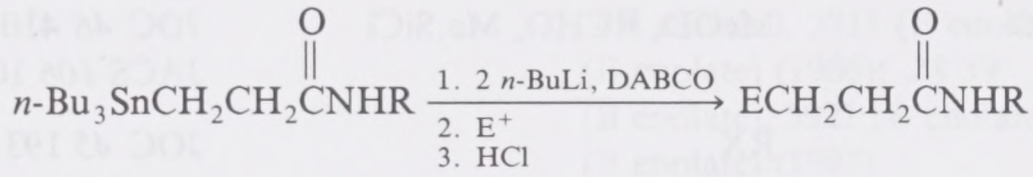
$E^+ = D_2O$, RX, H_2CO, R_2CO, Me_3SiCl, Ph_3SnCl

JACS *105* 6350 (1983); *109* 5403 (1987)



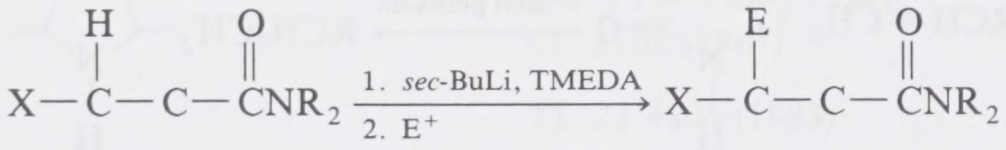
X = H, OR, SR, NR_2

See page 185, Section 1.



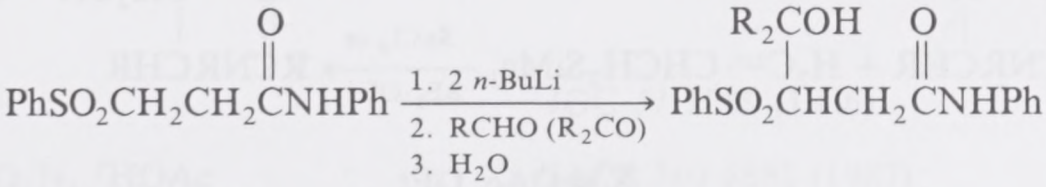
$E^+ = MeOD$, RX, R_2CO, Me_3SiCl

TL *23* 1463 (1982)
JACS *105* 7182 (1983)

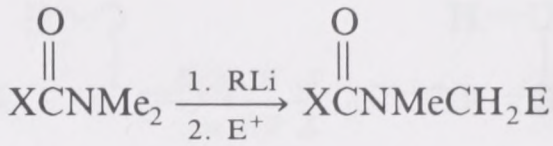


X = Ph, SPh, C≡C ; $E^+ = D_2O$, RX, R_2CO, Me_3SiCl, Ph_3SnCl, PhSSPh

JACS *109* 5403 (1987)



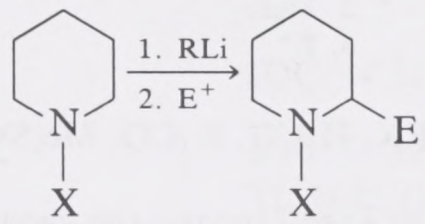
CL 1359 (1984)



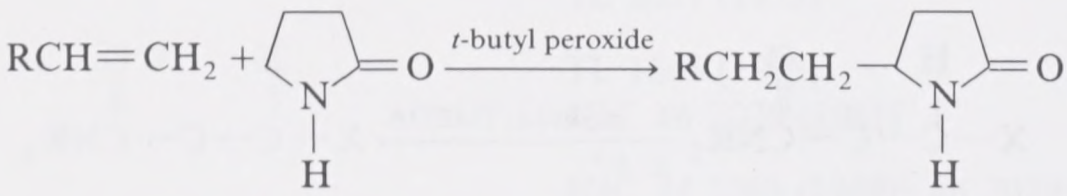
$E^+ = RX, RCHO, R_2CO$

Review: Chem Rev *78* 275 (1978)

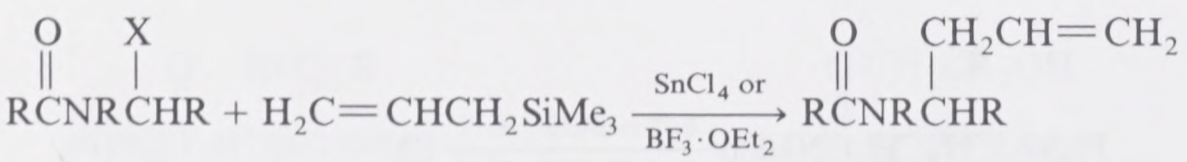
X		
2,4,6-$(i\text{-Pr})_3C_6H_2$		TL 1839 (1977) Helv *61* 512 (1978)
R_2N		Helv *61* 2239 (1978)
2,4,6-$(t\text{-Bu})_3C_6H_2O$		Angew Int *17* 274 (1978)



X	E^+	
Me_3CCO	RX, R_2CO, Me_3SiCl, $n\text{-}Bu_3SnCl$	Tetr *39* 1963 (1983)
Et_3CCO	MeOD, 1° RI, RCHO, R_2CO	JOC *46* 4316 (1981) JACS *106* 1010 (1984)
Ph_3CCO	RX, RCHO, R_2CO	Helv *64* 1337 (1981)
2,4,6-$(i\text{-Pr})_3C_6H_2CO$	MeOD, RCHO, Me_3SiCl	JOC *46* 4108 (1981) JACS *106* 1010 (1984)
MeOCO	RX	JOC *45* 193 (1980) (allylic anion)
$PO(NMe_2)_2$	RX, RCHO, R_2CO, epoxide, $ArH\cdot Cr(CO)_3$, I_2, Me_3SiCl, $n\text{-}Bu_3SnCl$	Helv *64* 643 (1981) Tetr *39* 1963 (1983)



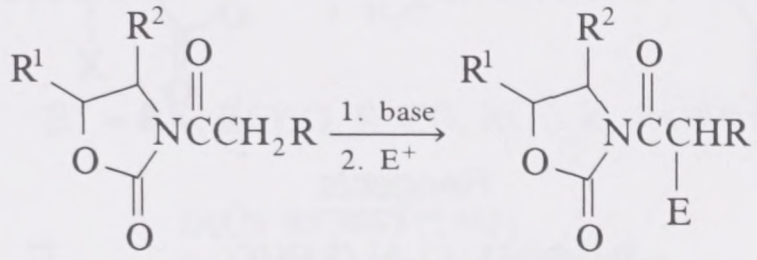
Bull Acad Sci USSR, Div Chem Sci 1745 (1964)
Proc Acad Sci USSR, Chem Sec *158* 1069 (1964)



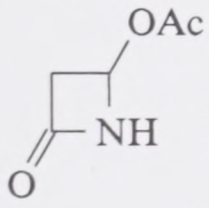
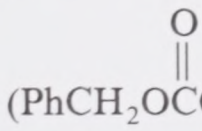
X = OAc, OEt

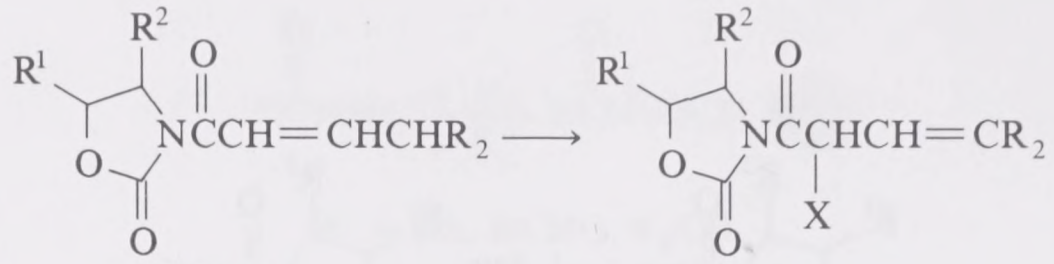
CC 134 (1982)

5. Imides

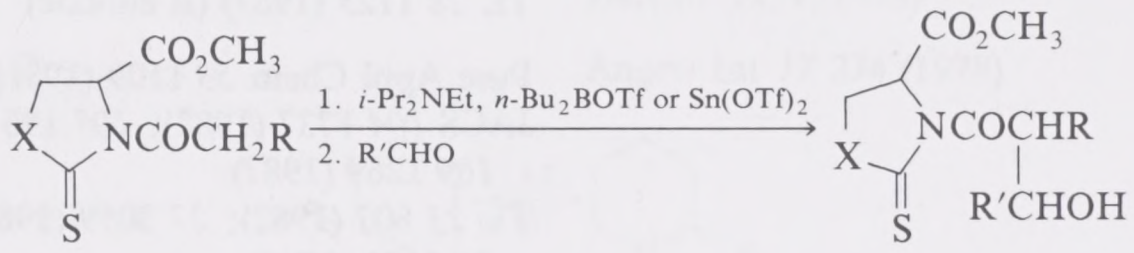


chiral chiral

E^+	
NBS	TL *28* 1123 (1987) (B enolate)
RX	Pure Appl Chem *53* 1109 (1981) JACS *104* 1737 (1982); *107* 196 (1985); *109* 1269 (1987) TL *23* 807 (1982); *27* 3059 (1986); *28* 3651 (1987) JOC *52* 3168 (intramolecular), 3759 (1987)
RCHO	Pure Appl Chem *53* 1109 (1981) (Li, B enolates) JACS *103* 2127 (1981) (B enolate); *107* 5292 (1985) (B enolate); *108* 2476, 4595 (Li, B, Sn, Zn enolates), 6757 (Sn enolate) (1986); *109* 7151 (1987) (Sn enolate) TL *23* 807 (1982) (Li, B enolates); *24* 3395 (1983) (B enolate); *27* 897 (Ti enolate), 3311 (B enolate), 5683 (B enolate) (1986); *28* 39 (B enolate), 5921 (B enolate), 6001 (B enolate) (1987) CC 1237 (1986) (B enolate) JOC *51* 4322 (1986) (B enolate); *52* 5588 (1987) (B enolate)
RCHO, ZnI_2	JACS *108* 4675 (1986) (Si enolate)
RCOCl	JACS *106* 1154 (1984) CC 1102 (1987)
$(RCO)_2O$	TL *24* 4805 (1983)
 , $ZnBr_2$	JACS *108* 4675 (1986)
	JOC *51* 3700 (1986)
2,4,6-(*i*-Pr)$_3$C$_6$H$_2$SO$_2$N$_3$/HOAc	JACS *109* 6881 (1987)
$RO_2CN{=}NCO_2R$	JACS *108* 6395, 6397 (1986)



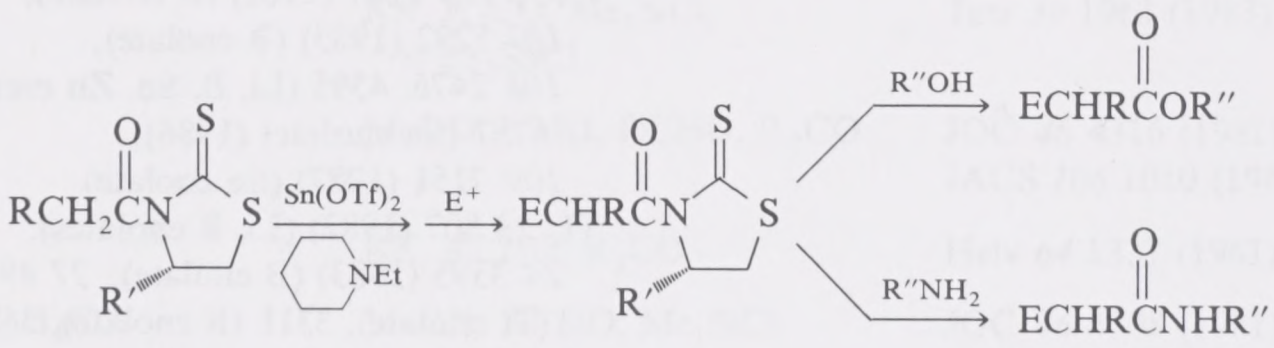
X	Reagents	
RCHOH	*n*-Bu_2BOTf, Et_3N/RCHO	TL *27* 4957, 4961 (1986)
OH	$NaN(SiMe_3)_2$ / PhHC(O)NSO_2Ph	JACS *107* 4346 (1985)



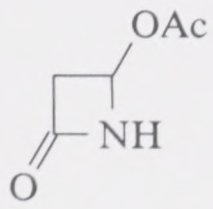
chiral chiral

X = O, S

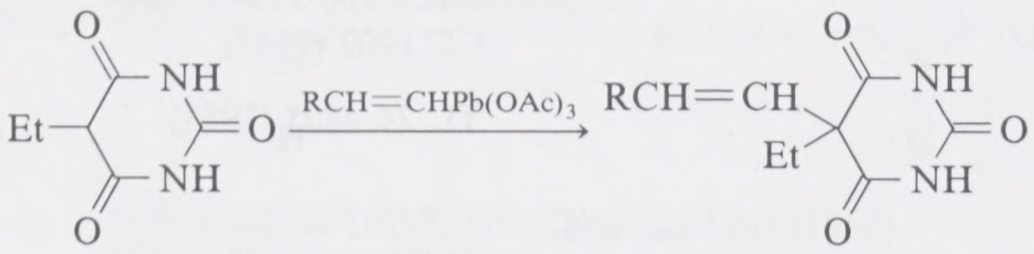
JOC *52* 2201 (1987)



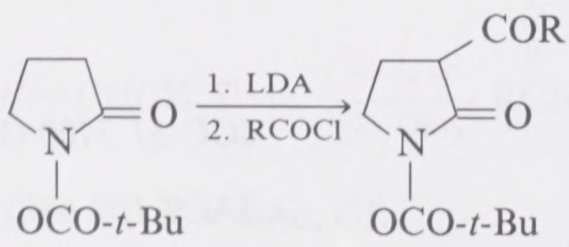
E^+	
RCHO	CL 1903 (1982); 297 (chiral), 1799 (chiral) (1983)



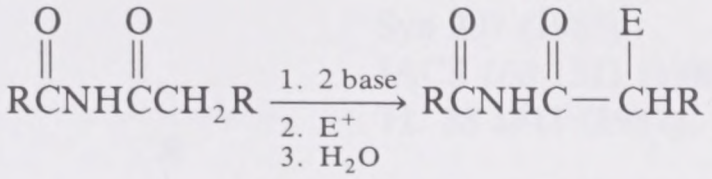
JACS *108* 4673 (1986) (chiral)



CC 965 (1984)

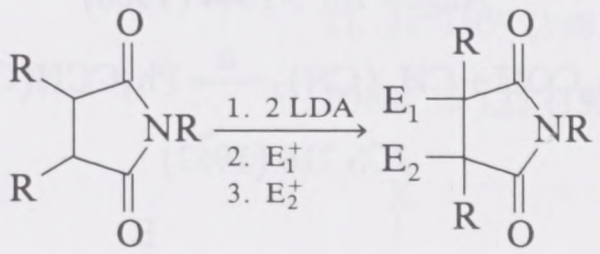


TL *27* 2691 (1986)

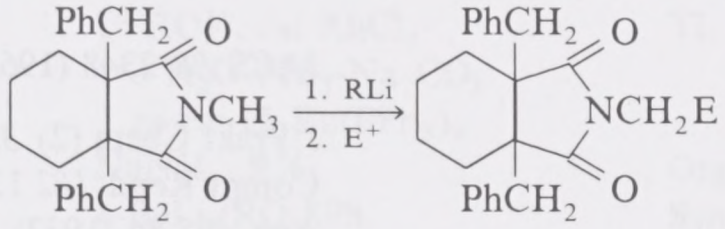


$E^+ = RX, RCHO, R_2CO, RCO_2R, PhSSPh$

JACS *83* 3468 (1961)
Can J Chem *46* 2561 (1968)
JOC *51* 495 (1986)

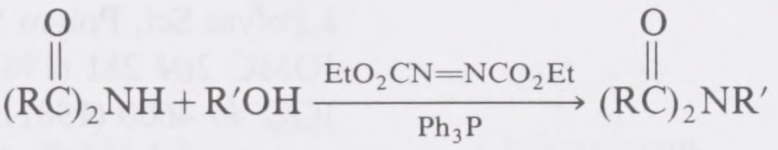


E_1^+	E_2^+	
RX	RX	JOC *47* 68 (1982)
$X—C_n—X$ ($X = Br, OTs$; $n = 3–5$)		JOC *47* 68, 4731 (1982)



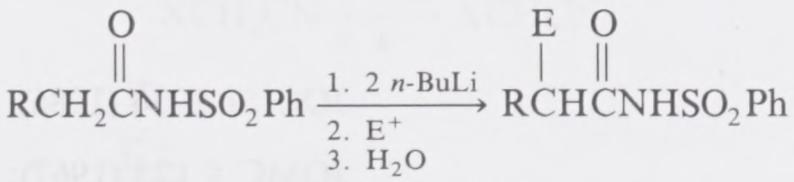
$E^+ = RX, RCHO, R_2CO, RCO_2Me, Me_3SiCl$

Helv *60* 1459 (1977)



JACS *94* 679 (1972)
JOC *52* 5127 (1987)

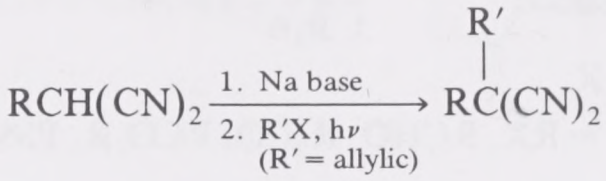
For further alkylations of imides see page 397, Section 3.



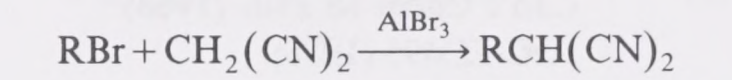
$E^+ = RX$, $RCH{=}CHCO_2R$ (1,4-addition), I_2 (dimerization)

TL *27* 131 (1986)

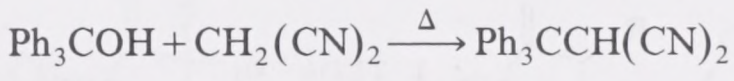
6. Nitriles



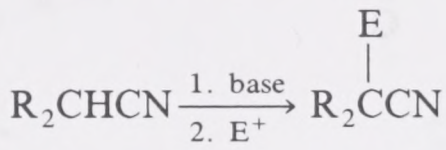
Austral J Chem *36* 527 (1983)



Angew Int *5* 1044 (1966)

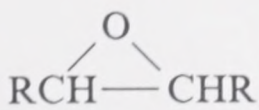


JCS 716 (1962)



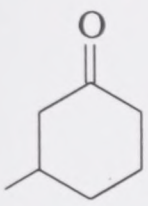
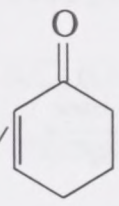
Reviews:

Chem Rev *12* 135 (1933); *20* 451 (1937)
Org Rxs *9* 107 (1957); *31* 1 (1984)

$\underline{E^+}$	
D_2O	JACS *88* 2348 (1966)
RX	J Prakt Chem (2) *39* 233 (1889) Compt Rend *182* 1226 (1926) Ann *495* 84 (1932); *652* 99 (1962) JACS *67* 2152 (1945); *88* 2348 (1966) BSCF 1881 (1965) Tetr *24* 175 (1968); *31* 153 (1975); *36* 775 (1980) TL 707 (1974); *27* 3685 (1986); *28* 4329 (1987) J Polym Sci, Polym Sci Ed *17* 3499 (1979) JOMC *204* 281 (1981) JOC *46* 4600 (1981); *51* 3007, 4080 (intramolecular) (1986); *52* 4142 (1987) Syn 305 (1982) Can J Chem *61* 2006 (1983) CC 279 (1986); 1342 (1987)
ArX	JOC *48* 4397 (1983); *50* 1334 (1985); *51* 5157 (1986); *52* 1333, 2619 (1987)
	JOC *51* 2230 (1986)
RCHO, R_2CO	JOMC *9* 125 (1967); *57* C36 (1973) Ber *101* 3113 (1968) JOC *33* 3402 (1968) Gazz Chim Ital *103* 117 (1973) Coll Czech Chem Commun *46* 1682 (1981)

	Syn 297 (1983) JACS *108* 1311 (1986) TL *28* 1611 (1987)
RCO_2R	JACS *67* 2152 (1945); *79* 725, 728 (1975) TL *24* 2059 (1983); *28* 4641, 4645 (1987) (both intramolecular)
RCO_2CO_2Et	TL 1585 (1979)
CO_2	JOC *31* 3873 (1966)
RCN	JOMC *9* 125 (1967) TL *24* 3509 (1983)
Me_3SiCl	JOMC *9* 125 (1967)

$$ArCH_2CN \longrightarrow Ar\overset{\overset{\displaystyle X}{|}}{C}HCN$$

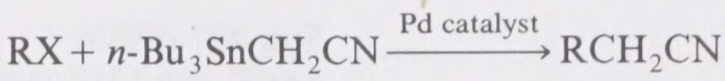
X	Reagents	
R	Na, ROH	TL 1509 (1966) Chem Pharm Bull *15* 1811 (1967); *18* 550 (1970) JOC *36* 2948 (1971)
	1° ROH, cat $RhCl_3 \cdot 3\ H_2O\text{-}PPh_3\text{-}Na_2CO_3$ or cat $H_2Ru(PPh_3)_4$	TL *22* 4107 (1981)
	$NaNH_2$, RX	Org Syn Coll Vol *3* 219 (1955)
	n-BuLi/RO_3SPh	Syn Commun *13* 35 (1983)
COR	Na, RCO_2R	JOC *36* 2948 (1971)
	*n*-BuLi/ 	Tetr *37* 1927 (1981)

$$PhCH_2CN \xrightarrow[2.\ BrCMe_2CMe_2Br]{1.\ KNH_2} Ph\overset{\overset{\displaystyle NC}{|}}{C}H\overset{\overset{\displaystyle CN}{|}}{C}HPh$$

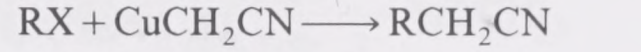
JOC *35* 2085 (1970)

$$XCH_2CN \xrightarrow[2.\ E^+]{1.\ base} X\overset{\overset{\displaystyle E}{|}}{C}HCN$$

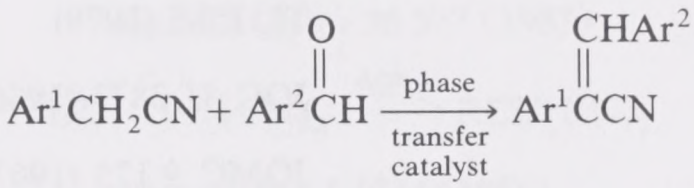
X	E^+	
R_2N	RX	TL *28* 547 (1987)
	R_2CO	JOC *52* 2427 (1987)
t-BuS	RX	Syn Commun *3* 265 (1973)



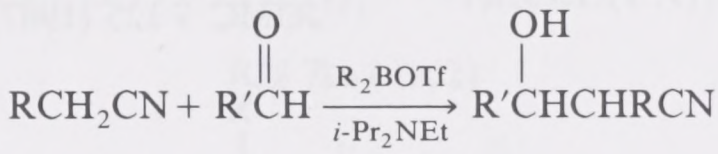
CL 1511 (1984) (RX = aryl bromide)
JACS *109* 7223 (1987) (RX = heterocyclic iodide)



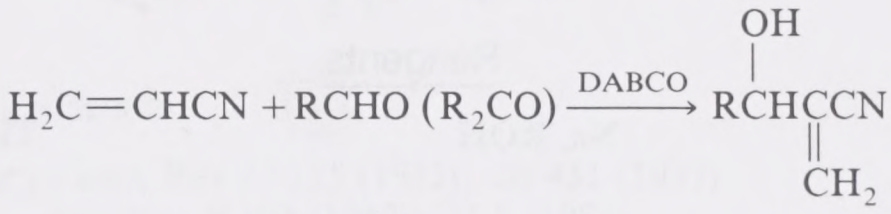
TL 487 (1972)



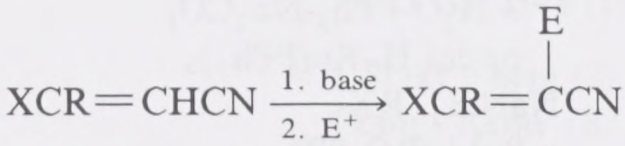
Syn 913 (1981)



CL 1401 (1982)

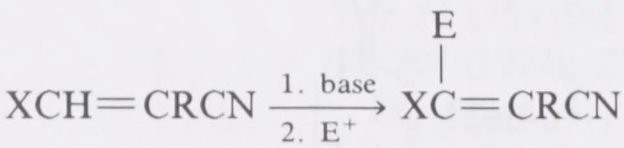


TL *27* 4307, 5007 (1986)
Syn Commun *17* 587 (1987)



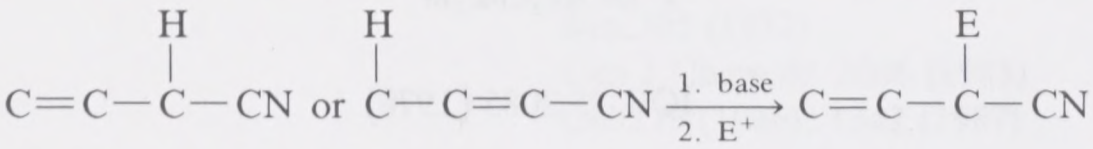
X = Ar, OR, NR_2, SR

See page 185, Section 1.

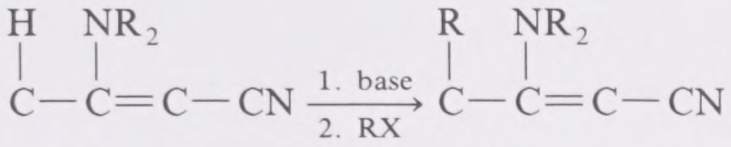


X = OR, NR_2

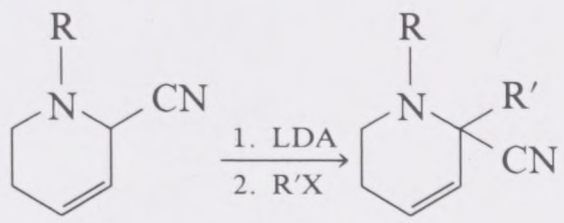
See page 185, Section 1.



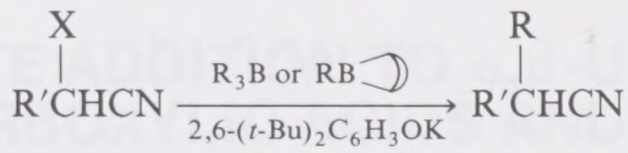
$\underline{E^+}$	
RX	BSCF 951 (1965) JOC *36* 877 (1971); *40* 1162 (1975); *44* 300 (1979) TL 1377 (1974); 4647 (1975) Tetr *31* 153 (1975)
$RCH{=}CHCO_2R$ (1,4-addition)	CL 1085 (1986) TL *28* 1785 (1987)
$H_2C{=}CHCN$ (1,4-addition)	JACS *65* 18 (1943)



TL 3963 (1974)

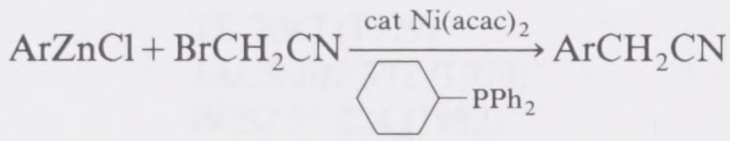


TL *28* 6179 (1987)

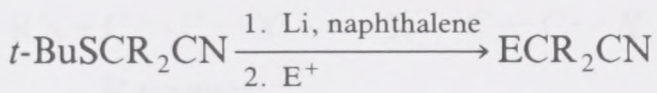


X = Cl, Br; R′ = H, Cl, alkyl, CO_2R; R = alkyl, vinylic

JACS *91* 6854 (1969); *92* 5790 (1970)
Organomet Chem Syn *1* 95 (1970)
JOC *46* 229 (1981); *51* 3398 (1986) (R = vinylic)
TL *23* 2077 (1982)

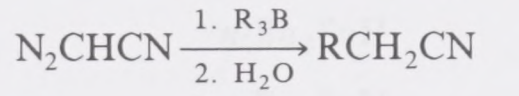


Syn 40 (1987)

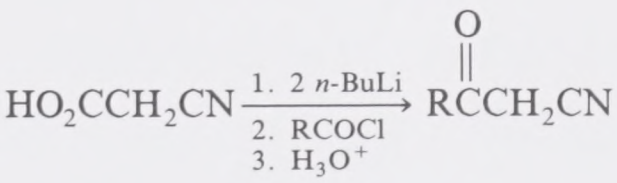


$E^+ = H_2O$, RX, RCHO, R_2CO, RCOCl, HCO_2R

Syn Commun *3* 265 (1973)

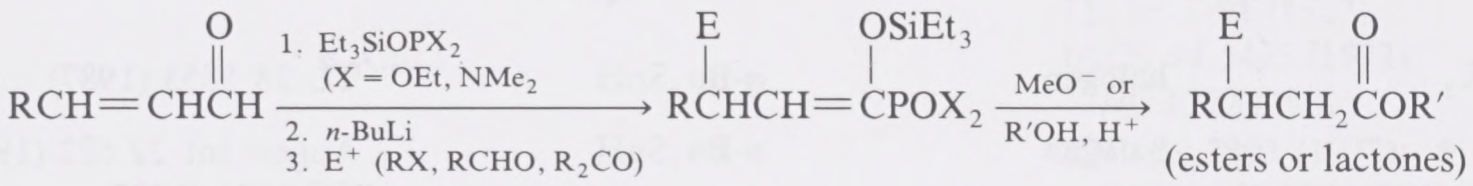


JACS *90* 6891 (1968)

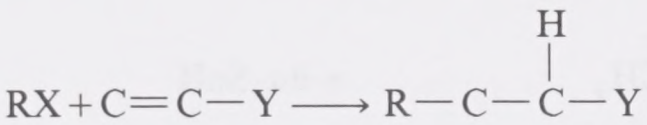


Syn 308 (1983)

6. CONJUGATE ADDITION TO α,β-UNSATURATED NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES



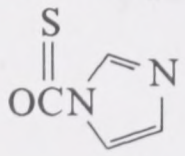
TL 2047 (1979)
JACS *101* 371 (1979)
BCSJ *55* 224 (1982)



Reviews:

Angew Int *24* 553 (1985)
Chimia *39* 203 (1985)

Y	X	Reagent	
CO_2H	halogen	*n*-Bu_3SnH	CC 944 (1983)
CO_2R	halogen	*n*-Bu_3SnH	JOC *47* 3348 (1982); *48* 1782 (1983) (intramolecular); *50* 546 (1985) (intramolecular) TL *27* 5071 (1986) (intramolecular, R = vinylic); *28* 5853 (1987) JACS *108* 3102 (1986) (intramolecular); *109* 4976 (1987) (intramolecular) Angew Int *25* 450 (1986) CC 1006, 1438 (intramolecular) (1987) Ann 231 (1987)

Y	X	Reagent	
		Ph_3SnH	CC 944 (1983)
		cat $Pd(PPh_3)_4$	TL *28* 3179 (1987) (R = Ar)
	SePh	*n*-Bu_3SnH	JOC *47* 3348 (1982) TL *28* 5853 (1987)
		Ph_3SnH	CC 944 (1983)
CO_2R, CN	halogen	*n*-Bu_3SnH	Angew Int *23* 69 (1984) Israel J Chem *26* 387 (1985) JOC *52* 3659 (1987)
		cat *n*-Bu_3SnCl, $NaBH_4$, hν	Angew Int *23* 69 (1984) JOC *51* 3726 (1986)
		vitamin B_{12}, reductant	Pure Appl Chem *55* 1791 (1983)
	NO_2	*n*-Bu_3SnH	CL 635 (1985)
	$\begin{matrix} S \\ \| \\ OCSCH_3 \end{matrix}$	cat *n*-Bu_3SnCl, $NaBH_4$, hν	Angew Int *23* 69 (1984)
$CONR_2$	halogen	*n*-Bu_3SnH	TL *28* 5853 (1987)
CN	halogen	*n*-Bu_3SnH	Angew Int *22* 622 (1983) CC 1006 (1987) Org Syn *65* 236 (1987)
		vitamin B_{12}, reductant	Chimia *39* 211 (1985)
	NO_2	*n*-Bu_3SnH	JACS *107* 4332 (1985)
	$\begin{matrix} S \\ \| \\ OCSCH_3 \end{matrix}$	*n*-Bu_3SnH	Angew Int *23* 69 (1984)
		*n*-Bu_3SnH	Angew Int *23* 69 (1984) TL *28* 4645 (1987)
OAc	halogen	*n*-Bu_3SnH	JOC *52* 3659 (1987)

$$RNO_2 + H_2C{=}CHX \xrightarrow[2.\ n\text{-}Bu_3SnH,\ AIBN]{1.\ base} RCH_2CH_2X$$

R = 2° alkyl, 1° allylic or benzylic

X = CN, CO_2R, SOPh, SO_2Ph, CHO, COR

JOC *50* 3692 (1985); *52* 1601 (1987) (KF-alumina as base, no reduction)

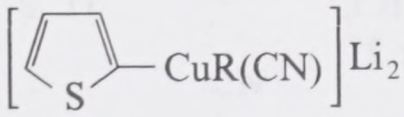
$$I{-}C_n{-}C{\equiv}C{-}CO_2R \xrightarrow{n\text{-BuLi}} RO_2C{-}C{-}C{\equiv}C{-}C_n$$

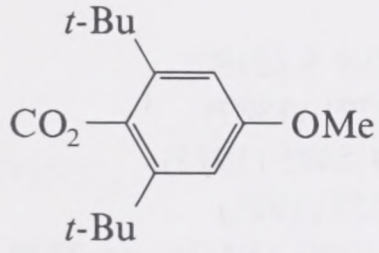
$n = 3, 4$

JOC *49* 1144 (1984)

$$R'CH{=}CHX \xrightarrow[2.\ H_2O \text{ or } H_3O^+]{1.\ RM} R'\underset{\displaystyle R}{\underset{|}{C}}HCH_2X$$

Reviews: Org Rxs *10* 179 (1959) (Michael addition); *19* 1 (1972) (organocopper reagents)

X	RM	
CO_2H	RLi or RMgX	JOC *52* 5729 (1987) (α-silyl acids)
	RMgX	JACS *75* 6342 (1953)
	$RCu \cdot BF_3$	JACS *100* 3240 (1978); JOC *47* 119 (1982)
CO_2R'	RMgX	BCSJ *39* 910 (1966); Org Syn Coll Vol *5* 762 (1973)
	RMgX, cat CuX	JOC *27* 2706 (1962); *42* 3209 (1977); *45* 4117 (1980); BCSJ *39* 910 (1966); Syn Commun *9* 325 (1979); CC 1472 (1987)
	RMgBr, cat $CuBr \cdot SMe_2$, Me_3SiCl, HMPA	TL *27* 4025 (1986)
	R_2CuMgX	JOMC *199* 9 (1980); TL *28* 3791 (1987)
	R_2CuLi	JACS *94* 5495 (1972); *103* 1222 (1981); JOC *38* 3893 (1973); *46* 3874 (1981); *51* 3376, 5041 (1986); *52* 3541 (lactone), 4603 (lactone) (1987); CC 907 (1973); Acta Chem Scand B *31* 667 (1977); *34* 113 (1980); Syn Commun *9* 325 (1979); Tetr *37* 3981 (1981); TL *27* 2519 (1986) (lactone); *28* 949, 3791 (1987) (both lactones)
	$(py)_2CuLi$, LiI	Tetr *38* 1509 (1982)
	R_2CuLi, Me_3SiCl	TL *27* 1047 (1986); JOC *51* 5041 (1986)
	(RCuAr)Li	Acta Chem Scand B *31* 667 (1977); *32* 483 (1978); Tetr *34* 3023 (1978)
	(**py**CuPh)Li, LiI	Tetr *38* 1509 (1982)
	$[(\mathbf{H_2C{=}CR})CuC{\equiv}C(CH_2)_2CH_3]^-$	TL *28* 3551 (1987)
	RLi, $CuC{\equiv}CSiMe_3$, Me_3SiCl	TL *28* 5719 (1987)
	(RCuCN)Li	TL *22* 2985 (1981)
	$(R_2CuCN)Li_2$	TL *24* 127 (1983)
	$[(H_2C{=}CH)_2CuCN]Li_2$	JACS *109* 7495 (1987)
		JOMC *285* 437 (1985)
	$RCu \cdot BF_3$	JACS *100* 3240 (1978); *109* 5820 (1987); Helv *64* 2808 (1981); JOC *47* 119 (1982)

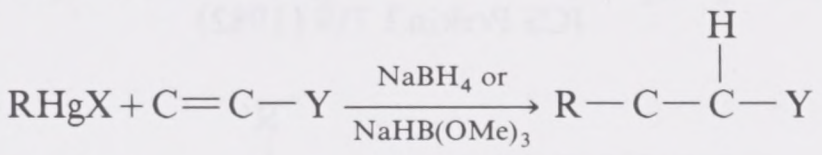
X	RM	
		CC 904 (1984); 464, 1572 (1987) TL *27* 943 (1986)
	RLi, *n*-$Bu_3P \cdot CuI$	TL *27* 4713 (1986)
	$RCu \cdot n\text{-}Bu_3P \cdot BF_3$	TL *24* 4971 (1983); *27* 1139 (1986) Helv *68* 212 (1985)
	R_2CuLi, $BF_3 \cdot OEt_2$	Tetr *37* 3981 (1981) JACS *104* 1774 (1982); *109* 5820 (1987) CC 1572 (1987)
	R_3CuLi_2, $BF_3 \cdot OEt_2$	CC 1572 (1987)
	$RCu[P(OMe)_3]_3$	JOC *45* 4117 (1980)
	$[(PhMe_2Si)_2CuCN]Li_2$	CC 1472 (1987) (lactones)
	$H_2C{=}CHCH_2SiMe_3$, $TiCl_4$	JOC *51* 1745 (1986)
	RLi or $LiCH_2CO_2R'$	JOC *51* 1637 (1986)
CO_2R', $CONR'_2$, CN	$H_2C{=}CHCH_2SiMe_3$, cat *n*-Bu_4NF	JOC *51* 1745, 1753 (intramolecular) (1986) CC 1472 (1987) (lactone)
CO_2R', CN	$(H_2C{=}CHCH_2)_2CuLi$	JOC *51* 1745 (1986)
CONHR	RMgBr, cat CuCN	JOC *51* 3921 (1986)
	$[Ph_2Cu(CN)_2]Li_2$	JOC *51* 3921 (1986)
$CONR'_2$	RLi	JOC *22* 1013 (1957) TL *21* 1881 (1980)
	RMgX	BSCF I 1087 (1934) JACS *77* 4413 (1955) JOC *22* 1013 (1957) TL 3251 (1971)
	R_2CuLi, Me_3SiCl	TL *27* 1047 (1986)
	$[(PhMe_2Si)_2CuCN]Li_2$	CC 1472 (1987) (lactam)
$CSNR'_2$	RLi or RMgX	JACS *100* 5221 (1978)
$CONHCOCH_3$	R_2CuLi, Me_3SiCl	TL *27* 1047 (1986)
CONRCOR	RMgCl, 0.5 $CuBr \cdot SMe_2$/HCl, MeOH/KOH (R = 1° or 2° alkyl, aryl, vinylic)	TL *27* 369 (1986)
CN	$(R_3BMe)Li$, CuBr	TL 255 (1976)
	Me_2CuLi, Me_3SiCl (product is $R'CHMeCH_2COMe$)	TL *27* 1047 (1986)

COCN

$H_2C{=}CR'CH_2SiMe_3$, $TiCl_4/R'OH$ (R = $H_2C{=}CRCH_2$; X = CO_2R' in product) — TL *21* 4487 (1980)

$H_2C{=}C{=}CHSiMe_3$, $TiCl_4/R'OH$ (R = $HC{\equiv}CCH_2$; X = CO_2R' in product) — TL *21* 4487 (1980)

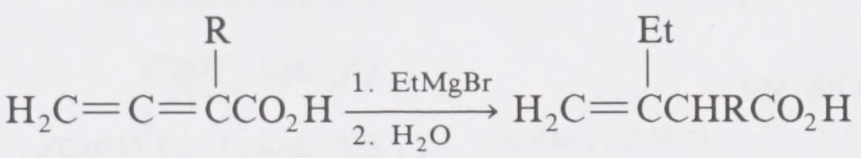
$RSiMe_3$, $TiCl_4$ (R = allylic, allenic, propargylic, alkynyl) — JOC *51* 1199 (1986)



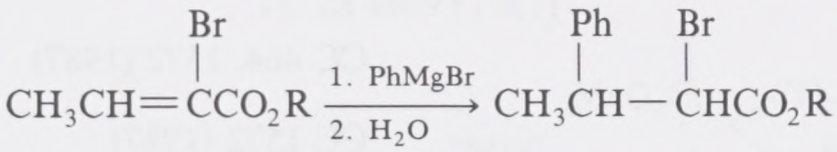
Y = CO_2R, CO_2COR, CN

R = 1°, 2°, 3° alkyl; benzyl; MeO—C—C—; MeO—C—C—C; C=C—C(OMe)—C—; HCO—C—C—; $RCOCHRCH_2$; RCONR—C—C—

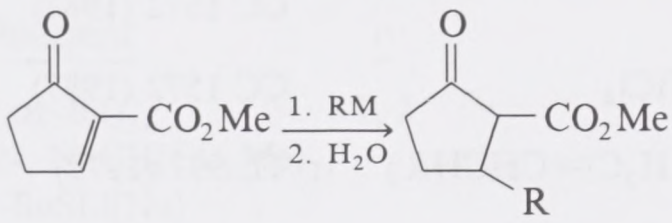
Ber *110* 2588 (1977); *112* 3759 (1979); *113* 1192, 2787 (1980); *114* 1572 (1981); *115* 2526 (1982); *117* 859, 2132, 3160, 3175 (1984); *118* 1289, 1345, 1616 (1985); *119* 1291 (1986)
TL *21* 1829, 3569 (1980); *22* 2155 (1981); *23* 931, 2765 (1982); *24* 11, 15, 2051, 3221 (1983); *25* 2743 (1984); *27* 4841 (1986)
Angew Int *20* 965 (1981); *21* 130 (1982); *24* 553 (1985) (review); *26* 479 (1987)
JOC *47* 3348 (1982); *49* 1313 (1984)
Syn 735 (1982)
Organomet *1* 675 (1985)
Tetr *41* 4025 (1985)



JACS *74* 2559 (1952)



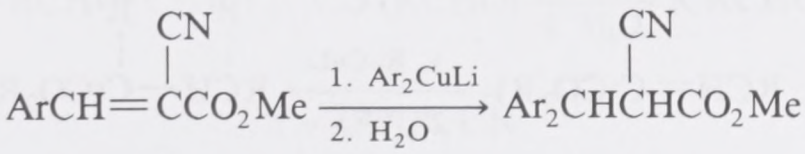
JOC *35* 666 (1970)



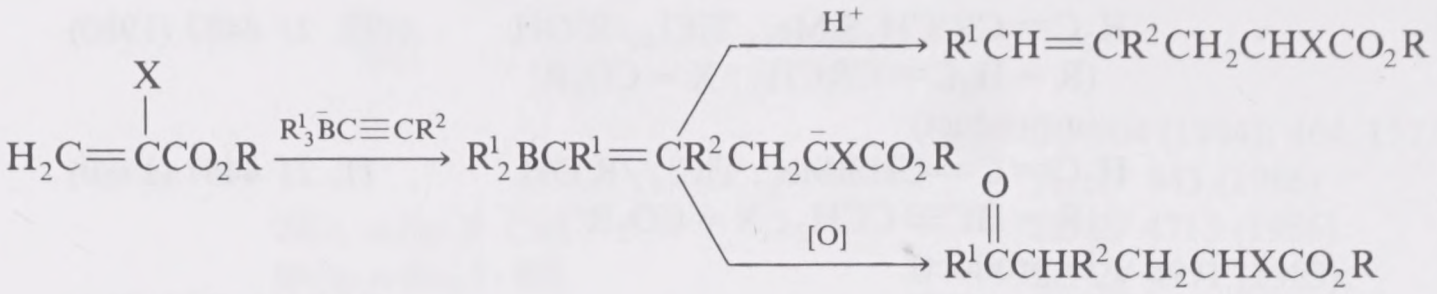
RM

$Et_2AlC{\equiv}CR$ — TL *27* 2885 (1986)

Me_2CuLi — JACS *109* 6199 (1987)

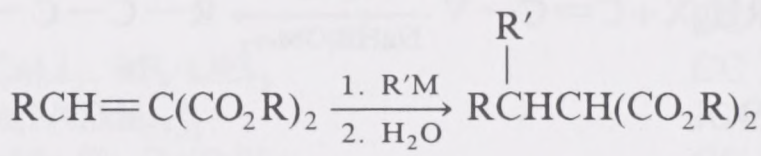


TL *27* 5319 (1986)

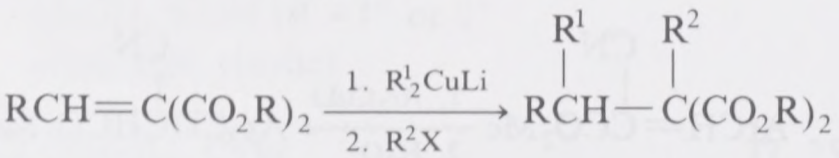


X = COMe, CO_2Et

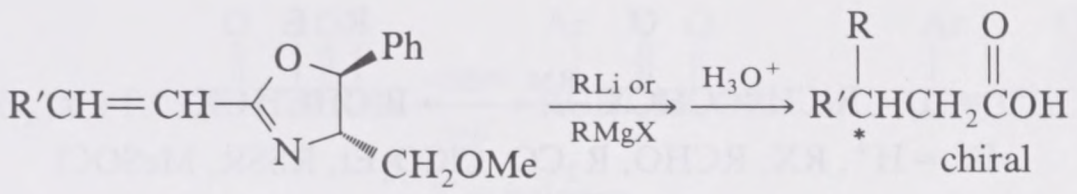
JCS Perkin I 719 (1982)



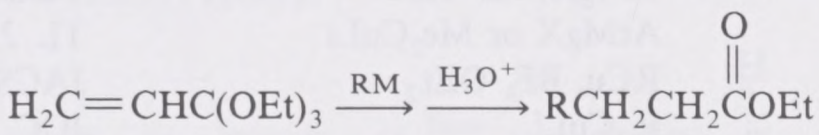
R′M	
R′Li	CC 464 (1987)
R′MgX	CC 464, 1572 (1987)
ArMgX	TL *27* 2235 (1986)
$RC{\equiv}CMgX$	BSCF 2542 (1964)
R′MgX, cat CuCl	Org Syn *50* 38 (1970) TL *23* 75 (1982)
R′Cu	CC 464 (1987)
R′Cu, $BF_3{\cdot}OEt_2$	CC 464, 1572 (1987)
R'_2CuLi	CC 464, 1572 (1987)
R'_2CuLi, $BF_3{\cdot}OEt_2$	CC 464, 1572 (1987)
R'_3CuLi_2, $BF_3{\cdot}OEt_2$	CC 1572 (1987)
(ArCuCN)Li	TL *27* 2235 (1986)
$LiAlR'_4$	CC 1572 (1987)
$H_2C{=}CHCH_2Sn(n\text{-}Bu)_3$, $TiCl_4$	CC 1572 (1987)
$RCH{=}CHCH_2ZnBr$ ($R' = H_2C{=}CHCHR$)	TL 997 (1972)
R′NLi | $RC{=}CRCO_2R$ (chiral)	CC 1345 (1987) (enantioselective)



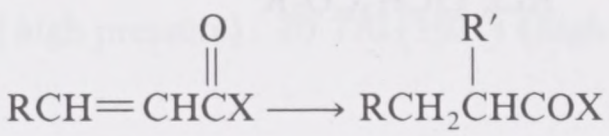
JOC *38* 2100 (1973)



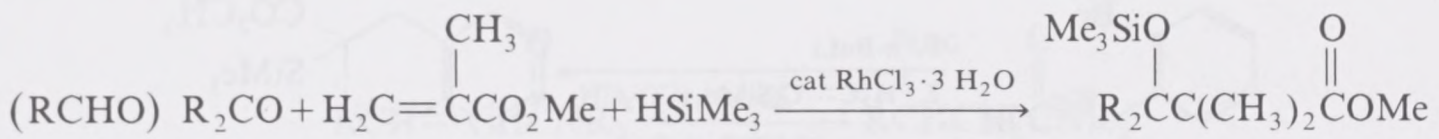
JOC *44* 2247, 2250 (1979); *46* 3874 (1981)



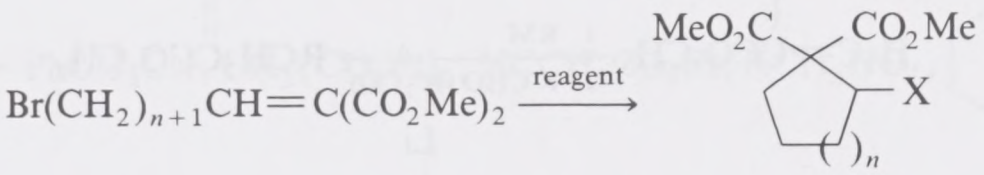
RM		
RMgX, cat CuBr		BSCF II 305 (1979)
E-RCMe=CCHAlMe$_2$, cat Pd(PPh$_3$)$_4$, ZnCl$_2$		JOC *50* 3406 (1985)
PhZnCl, cat Pd(PPh$_3$)$_4$, ZnCl$_2$		JOC *50* 3406 (1985)



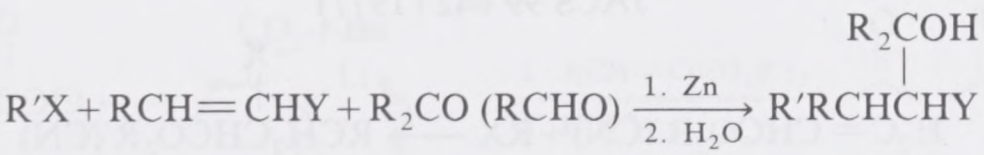
X	Reagents	
OR	LiHB(*sec*-Bu)$_3$/R′X	JOC *40* 2846 (1975)
	i-Bu$_2$AlH, cat MeCu/MeLi/R′X	JOC *52* 439 (1987)
NR$_2$	LiHB(*sec*-Bu)$_3$/R′X	TL *27* 4717 (1986)



TL *28* 4809 (1987)

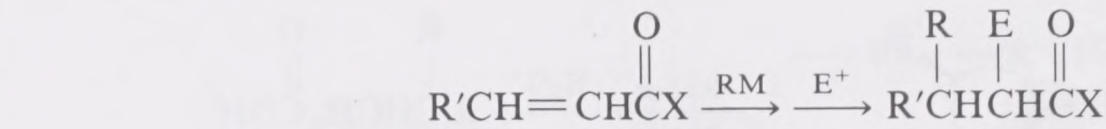


X	Reagent	n	
H, CN, CH(CO$_2$Me)$_2$ or *t*-BuS	LiHB(*sec*-Bu)$_3$, KCN, NaCH(CO$_2$Me)$_2$, or *t*-BuSLi(Na)	1, 2	JOC *47* 362 (1982)
H	electrolysis	0, 1, 2	TL *23* 1339 (1982)



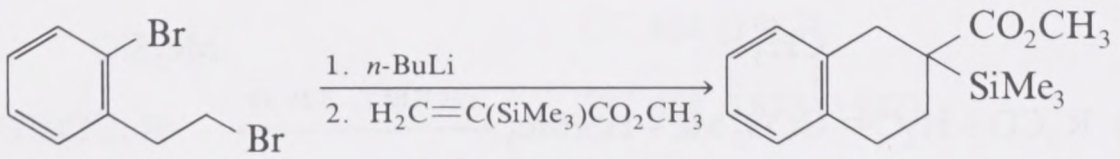
Y = CO$_2$R, CN

JACS *100* 4314 (1978)

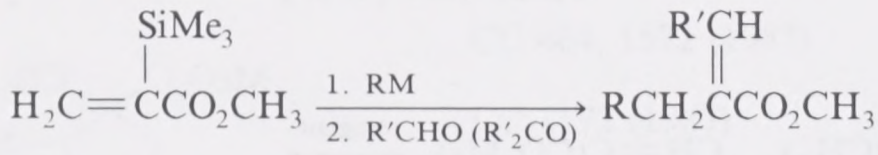


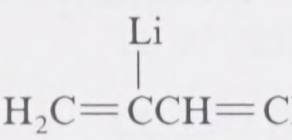
$E^+ = H^+$, RX, RCHO, R_2CO, $ClCO_2Et$, RSSR, MeSOCl

X	RM	
OR′	RMgX, cat CuX	CL 1159 (1981)
	ArMgX or Me_2CuLi	TL *23* 3287 (1982)
	RCu, $BF_3 \cdot OEt_2$	JACS *109* 5820 (1987)
	R_2CuLi	JOC *51* 3376 (1986) (intramolecular acylation to 2-carboalkoxycycloalkanone)
		TL *28* 3791 (1987)
	$[(PhMe_2Si)_2CuCN]Li_2$	CC 1472 (1987) (lactone)
	Me_3SnLi	TL *27* 5417 (1986)
	RLi, $LiCH_2CO_2R$	JOC *51* 1637 (1986)
NHPh	RLi	TL *21* 1881 (1980)
NR_2	RLi, RMgX or $(RS)_2CHLi$	TL *21* 4823 (1980)
	$ArC(SR)_2Li$	TL *21* 4827 (1980)
	RMgX	CL 913 (1981)
	R_2CuLi, Me_3SiCl	TL *27* 1047 (1986)
$NMeNMe_2$	RLi	Syn Commun *10* 837 (1980)

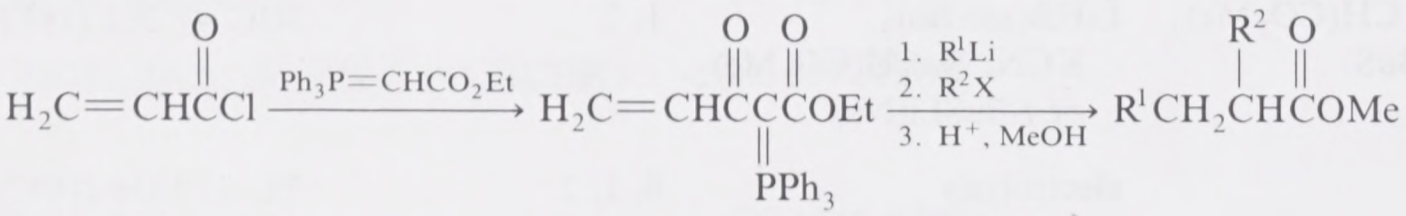


TL *22* 3707 (1981)

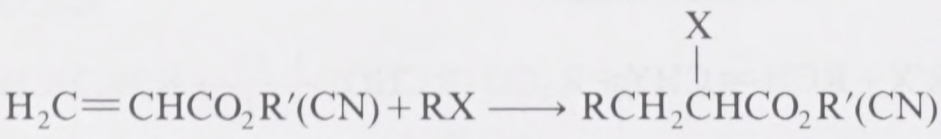


RM = PhMgBr (cat CuCl),  , MeSCHLiSOMe

CL 1993 (1984)

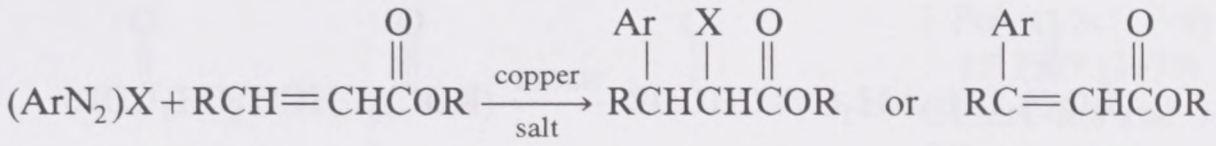


JACS *99* 642 (1977)



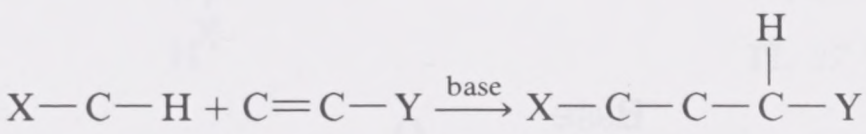
X = halogen

various initiators	Syn 145 (1977) (review)
CuCl, hν	TL *21* 4457 (1980)



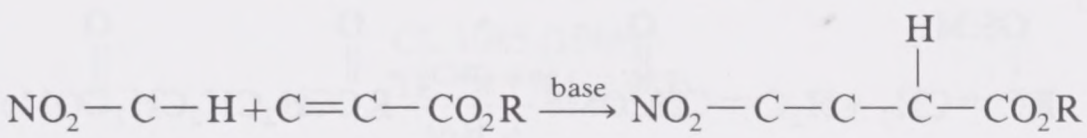
X = halogen

Org Rxs *11* 189 (1960); *24* 225 (1976) (both reviews)
JOC *52* 2997 (1987)

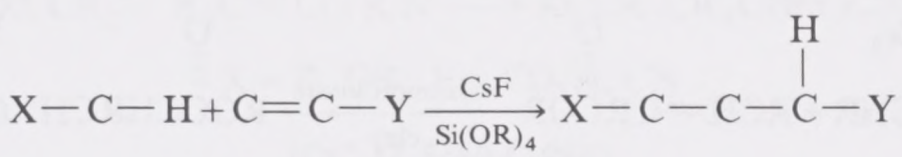


X = COR, CO_2R, $CONR_2$, CN; Y = CO_2R, $CONR_2$, CN

Org Rx *10* 179 (1959) (review)

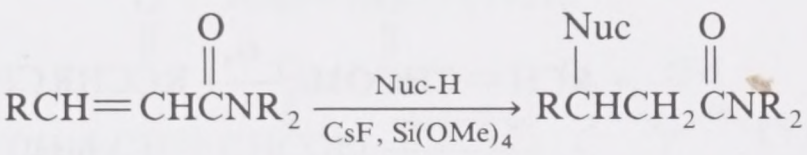


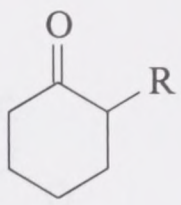
Angew *19* 1013 (1980) (high pressure); *20* 770 (1981) (high pressure, F^- catalyzed)



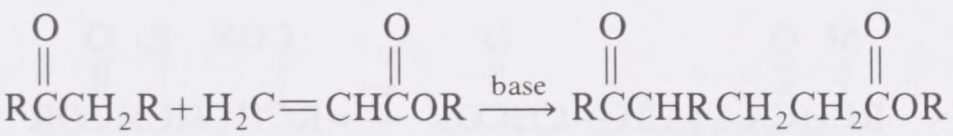
X = COR, CN; Y = CO_2R, CN

CC 122 (1981)
Tetr *39* 117, 999 (1983)

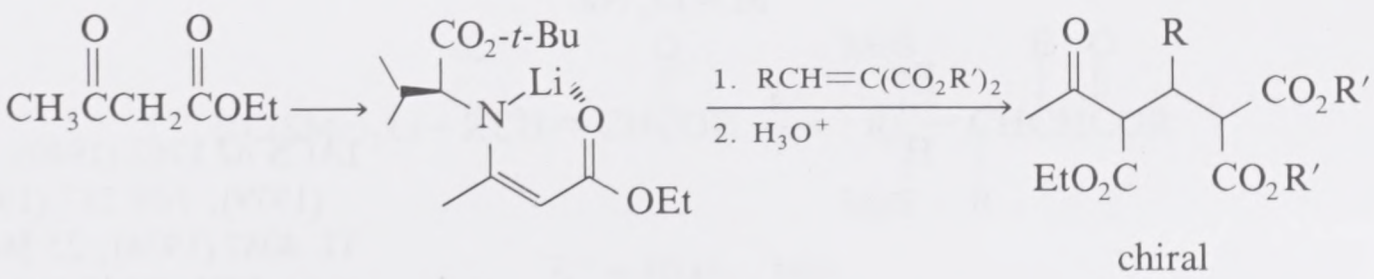


Nuc-H = $PhCH_2CN$, $CH_2(CO_2Et)_2$, $NCCH_2CO_2Et$, RCH_2NO_2, 

TL *23* 5531 (1982)
Tetr *39* 999 (1983)

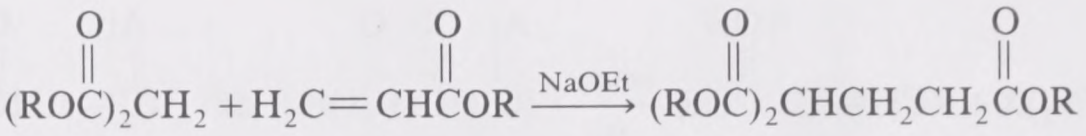


BSCF 823 (1962)

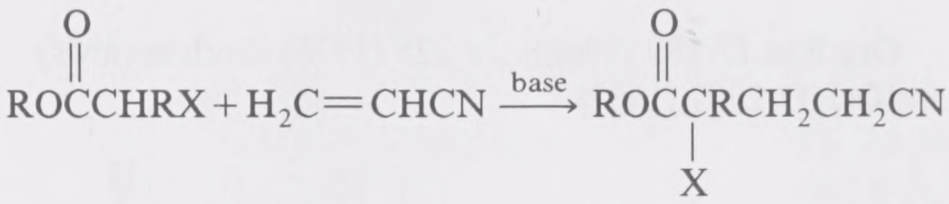


chiral

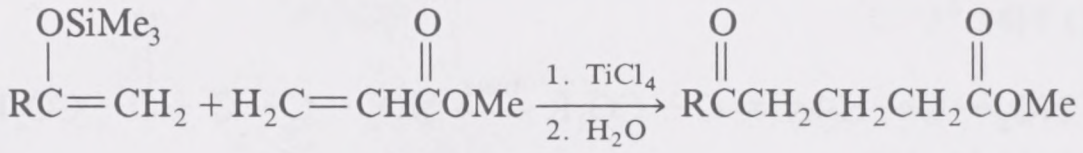
TL *27* 4611 (1986)



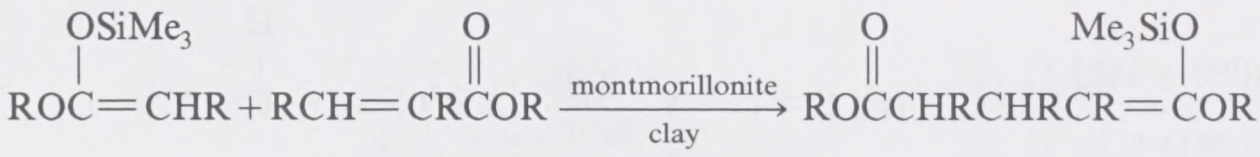
Org Syn Coll Vol *4* 630 (1963)



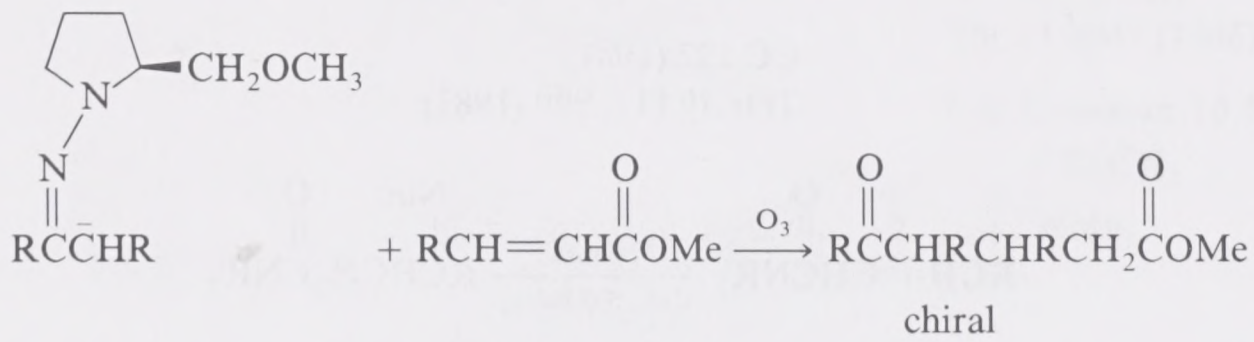
X	Base	
CO_2R	NaOEt	JACS *67* 2044 (1945)
CN	KOH	Org Syn Coll Vol *4* 776 (1963)



BCSJ *49* 779 (1976)

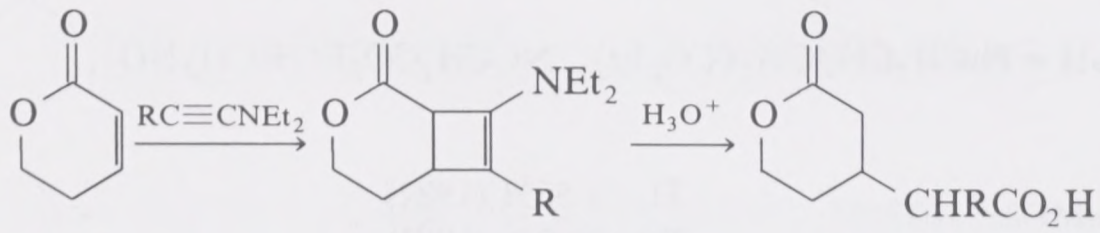


CC 1203 (1987)

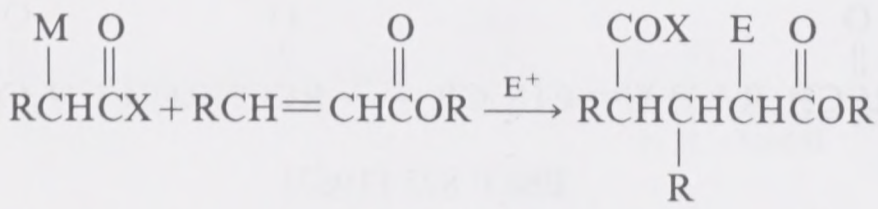


chiral

TL *24* 4967 (1983); *27* 3491 (1986)



TL *23* 1821 (1982)



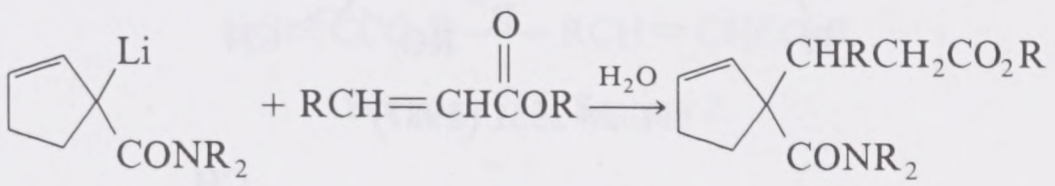
M = Li, Na

X	E^+	
OR	H^+	JACS *62* 1763 (1940); *101* 1544 (1979); *109* 287 (1987) TL 4087 (1974); *25* 5661 (1984); *26* 5025 (1985) (chiral); *27* 3551 (1986) (chiral catalysis)

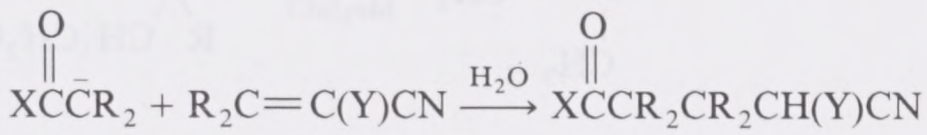
J Polym Sci, Polym Chem Ed *17* 3509 (1979)
Gazz Chim Ital *109* 95 (1979)
CC 869 (1983)
Syn 715 (1983)
CL 375 (1984)

I_2 JACS *101* 1544 (1979)
$R'X$ TL *26* 1723 (1985)

NR_2 H^+ TL *27* 959 (1986)

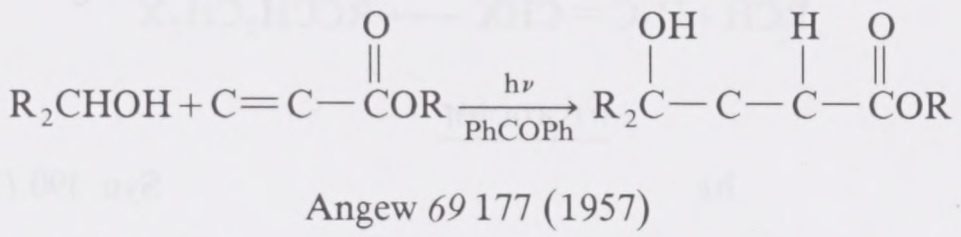


CL 1085 (1986)
TL *28* 1785 (1987)

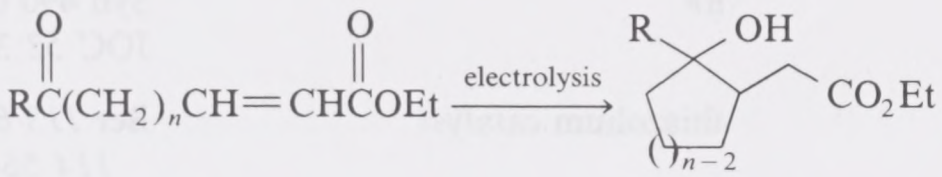


$X = R, OR; Y = CO_2R, CN$

JOC *51* 5480 (1986)

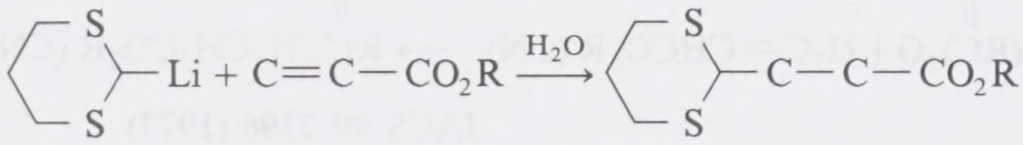


Angew *69* 177 (1957)



$n = 3, 4$

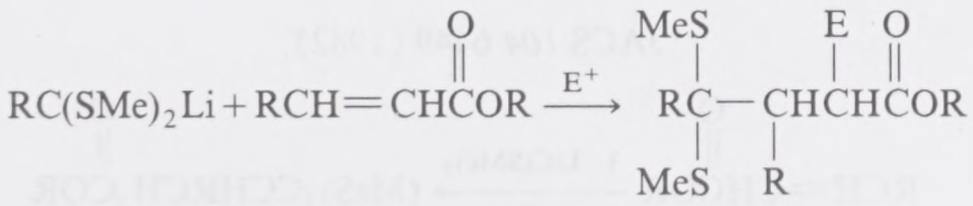
JOC *50* 2202 (1985)



R

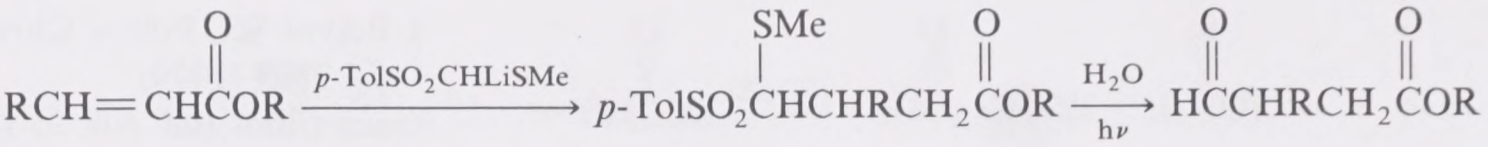
H JOC *49* 2682 (1984)

Ar JOC *51* 1637 (1986)

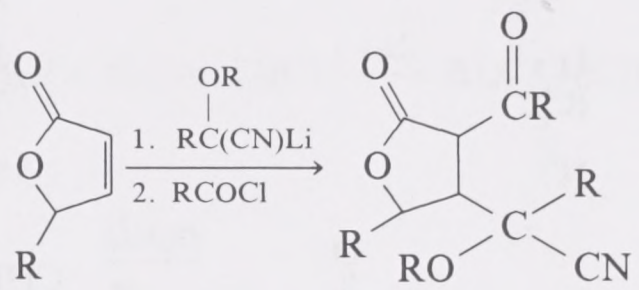


$E^+ = HOAc, MeI$

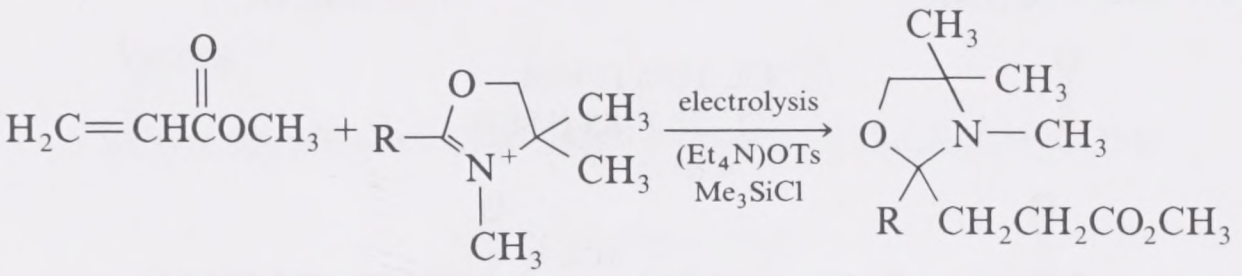
TL *26* 3031 (1985)



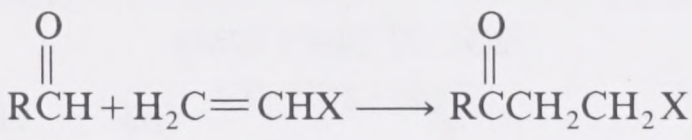
JOC *51* 508 (1986)



TL *28* 3551 (1987)

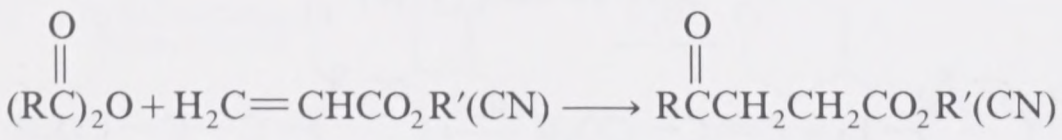


TL *28* 4411 (1987)



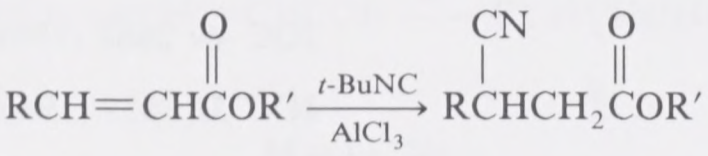
X	Promoter	
CO_2H	hν	Syn 490 (1980)
CO_2R	hν	Syn 490 (1980) JOC *52* 3323 (1987)
CO_2R' or CN	thiazolium catalyst	Ber *113* 690 (1980); *114* 564 (1981) Syn 129, 626 (1981)

See also page 792, Section 2.

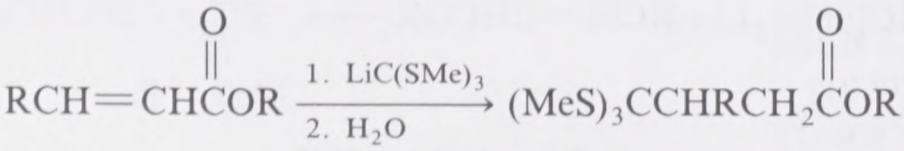


electrolysis — JACS *99* 7396 (1977)

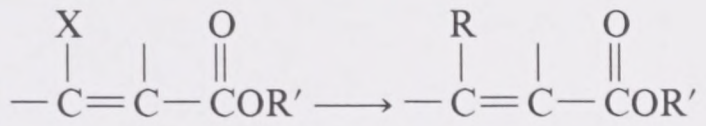
vitamin B_{12}, electrolysis, hν — JACS *105* 7200 (1983)



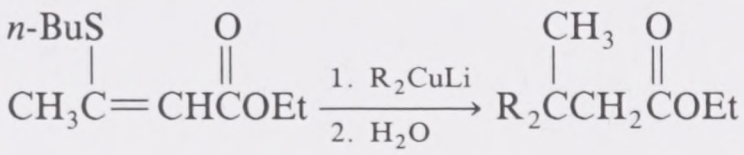
JACS *104* 6449 (1982)



TL *28* 1147 (1987)



See page 198, Section 12; page 201, Section 13; and page 206, Section 4.



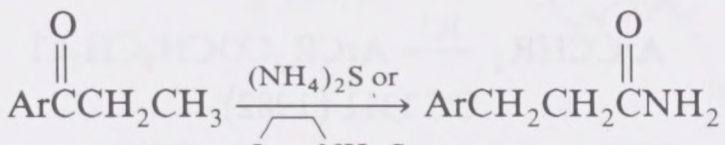
CC 907 (1973)

See page 215, Section 2.

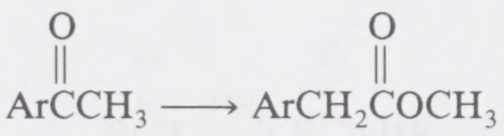
7. REARRANGEMENTS

1. Willgerodt and Related Reactions

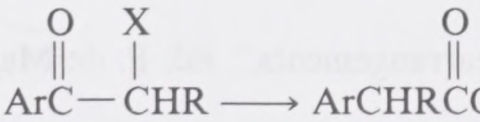
Review: Angew Int *23* 413 (1984)



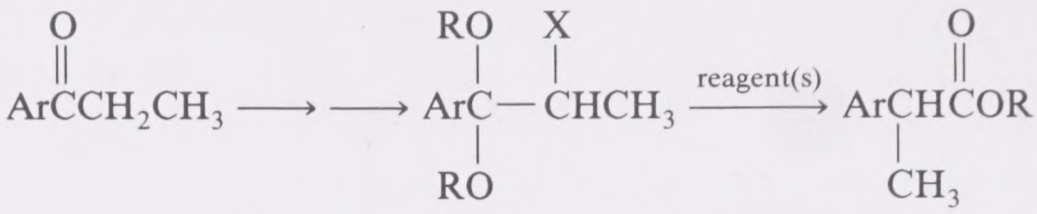
JACS *64* 3051 (1942); *68* 2029 (1946)
Org Rxs *3* 83 (1946)
Angew Int *3* 19 (1964)
Newer Methods Prep Org Chem *3* 1 (1964)



$BF_3 \cdot OEt_2$, $Pb(OAc)_4$, CH_3OH	Syn 126 (1981)
$Tl(NO_3)_3$, CH_3OH	JACS *93* 4919 (1971) JCS Perkin I 235 (1982) JOC *51* 1607 (1986)
$Pb(OAc)_4$, $HC(OMe)_3$, $HClO_4$	Syn 456 (1982)
$AgNO_3$, I_2, CH_3OH	JCS Perkin I 235 (1982)

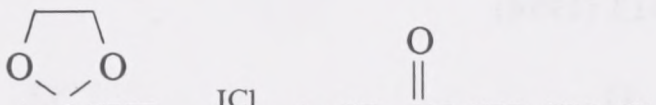


X	Reagents	
Cl, Br	$Tl(NO_3)_3 \cdot 3\ H_2O$, $HC(OR')_3$	Syn 444 (1983)
Br	Ag^+, R'OH	TL *23* 1385 (1982)

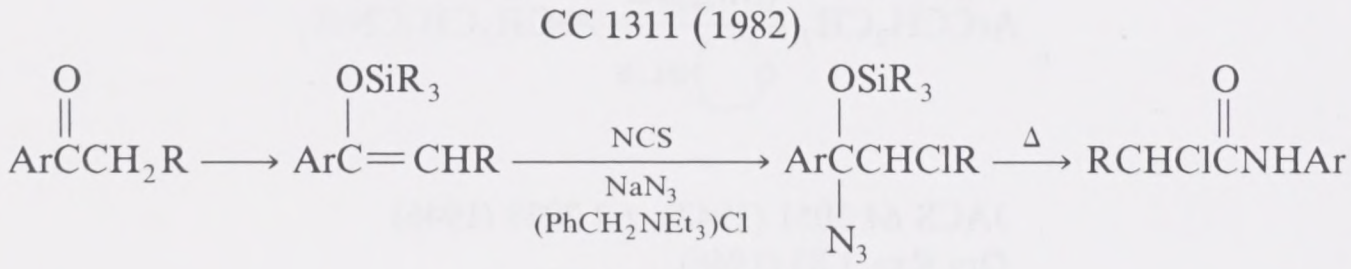


Review: Angew Int *23* 413 (1984)

X	Reagent(s)	R	
Cl	$ZnCl_2$	Me	JOC *52* 10 (1987)
Cl, Br	ZnX_2 (X = Cl, Br), $SnCl_2$, $CoCl_2$, Hg_2Cl_2, $PdCl_2$ or Cu_2Br_2	Me, Et	JOC *48* 4658 (1983)
Br	Δ, ROH	Me, $-C_n-$ ($n = 2, 3$)	Syn 505 (1985)
	$AgBF_4$, H_2O	H	JOC *52* 3018 (1987) (chiral)
I	RCO_3H	Me	JCS Perkin I 1483 (1983)
RSO_2	$CaCO_3$, H_2O, CH_3OH	Me	TL *22* 4305 (1981); *23* 5427 (1982)



CC 1311 (1982)

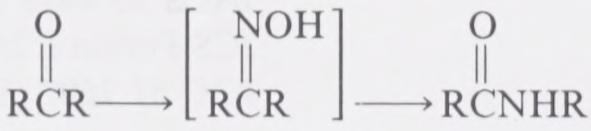


CC 1727 (1987)

2. Baeyer–Villager

See page 841, Section 14.

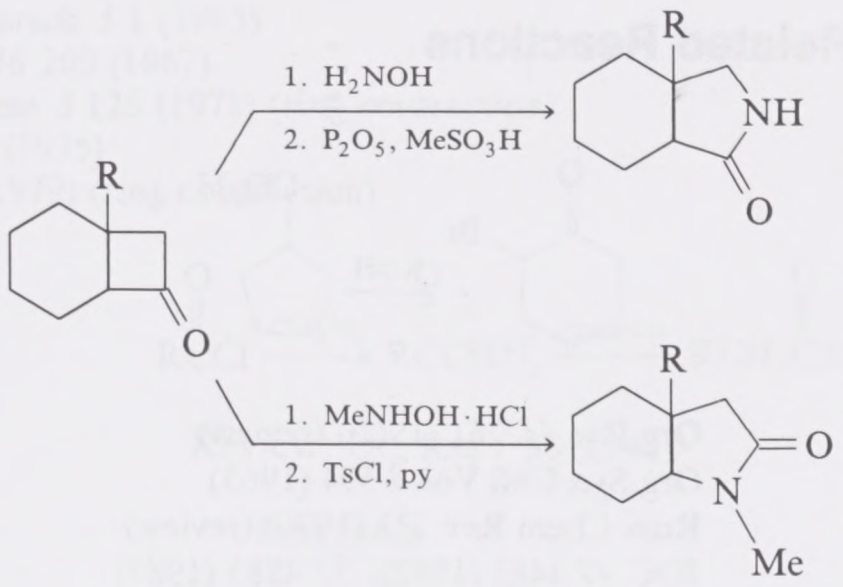
3. Beckmann



Reviews:

Chem Rev *12* 215 (1933); *35* 335 (1944)
Org Syn Coll Vol *2* 76 (1943)
Org Rxs *11* 1 (1960)
P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, p 483
C. G. McCarty, "Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 408–439
R. T. Conley and S. Ghosh, "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, J. Wiley, New York (1971), pp 203–250
Tetr *37* 1283 (1981)

H_2NOSO_3H	JACS *67* 1941 (1945)
H_2NOSO_3H, HCO_2H, Δ	Syn 537 (1979) Org Syn *63* 188 (1984)
H_2NOH/P_2O_5, $MeSO_3H$	JOC *38* 4071 (1973); *47* 3876 (1982)
H_2NOH/H_3PO_4, Ac_2O	JOC *38* 4073 (1973)
H_2NOH/TsCl, py, cat DMAP	JACS *106* 6414 (1984)
H_2NOH/TsCl, py/Et_3N, Δ	JACS *106* 6702 (1984)



JOC *47* 3876, 3881 (1982)

4. Schmidt

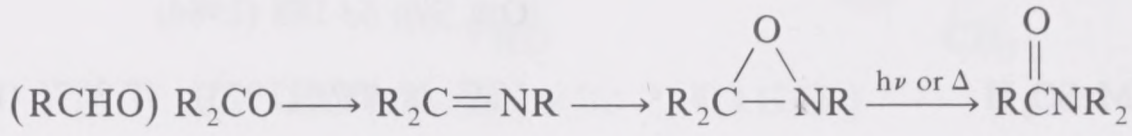
$$RC(=O)R \xrightarrow{HN_3} RC(=O)NHR$$

JACS *67* 1941 (1945)
Org Rxs *3* 307 (1946)
P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, pp 507–527
D. V. Banthorpe, "Chemistry of the Azido Group," Ed. S. Patai, Interscience, New York (1971), p 397
Russ Chem Rev *40* 835 (1971)
Tetr *37* 1283 (1981)

5. Curtius

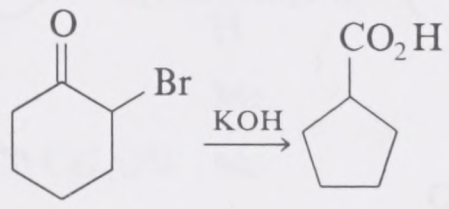
See page 431, Section 1.

6. Oxaziridine → Amide

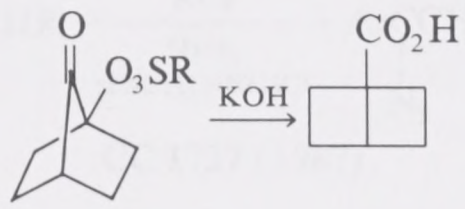


JACS *79* 5739 (1957)
Adv Heterocyclic Chem *24* 63 (1979) (review)
TL *28* 2595 (1987)

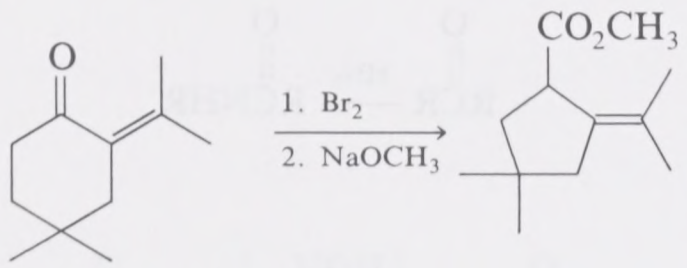
7. Favorski and Related Reactions



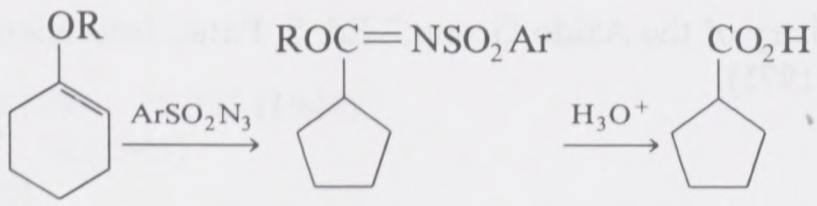
Org Rxs *11* 261 (1960) (review)
Org Syn Coll Vol *4* 594 (1963)
Russ Chem Rev 732 (1970) (review)
JOC *47* 4485 (1982); *52* 4885 (1987)
JACS *109* 7230 (1987)



Tetr *42* 1621 (1986)

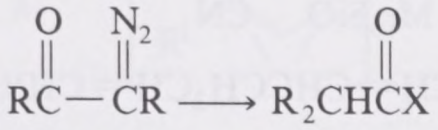


JOC *46* 5434 (1981)



R	
Me	TL 3111 (1973)
Me_3Si	Helv *56* 1826 (1973) JOC *47* 5042 (1982)

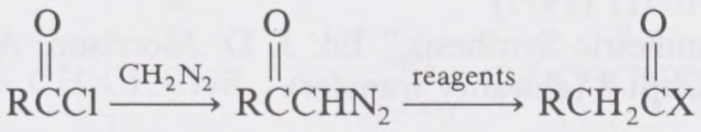
8. Arndt–Eistert and Wolff



$$X = OH, OR, NR_2$$

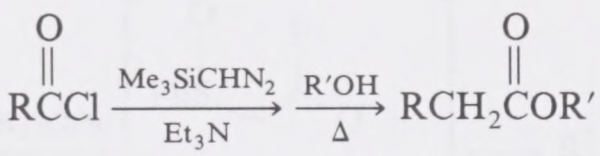
Reviews:

Newer Methods Prep Org Chem *1* 513 (1948); *3* 451 (1964)
Angew *72* 535 (1960)
Fortschr Chem Forsch *5* 1 (1965)
Russ Chem Rev *36* 260 (1967)
Adv Alicyclic Chem *3* 125 (1971) (ring contraction)
Angew Int *14* 32 (1975)
JACS *101* 7675 (1979) (ring contraction)

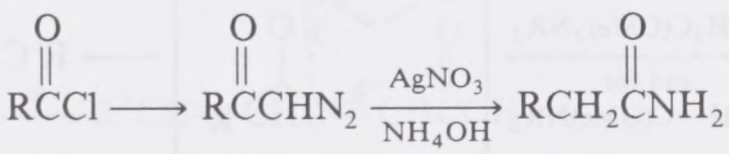


Review: Org Rxs *1* 38 (1942)

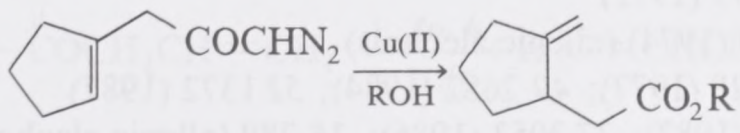
X	Reagents	
OH	$h\nu$, H_2O	Ber *91* 430 (1958)
	Ag_2O or $h\nu$, H_2O	Org Rxs *1* 38 (1942)
	Ag_2O, Na_2CO_3, $Na_2S_2O_3$, H_2O	TL 2667 (1979)
OR	$h\nu$, ROH	JACS *107* 5732 (1985); *109* 4626 (1987)
	AgO_2CPh, Et_3N, ROH (R = Me, Et)	Org Syn *50* 77 (1970); TL 2667 (1979); JACS *109* 5432 (1987)
NH_2	$h\nu/NH_4OH$	JACS *106* 6437 (1984)



TL *21* 4461 (1980)

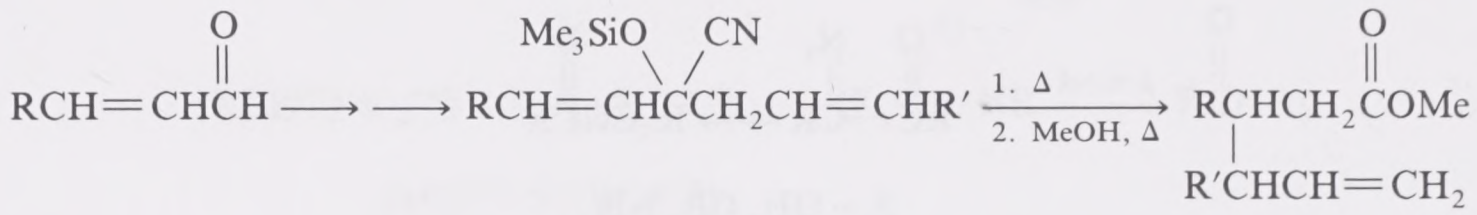


JOC *5* 606 (1940)



JACS *106* 3995, 4001 (1984)

9. Cope

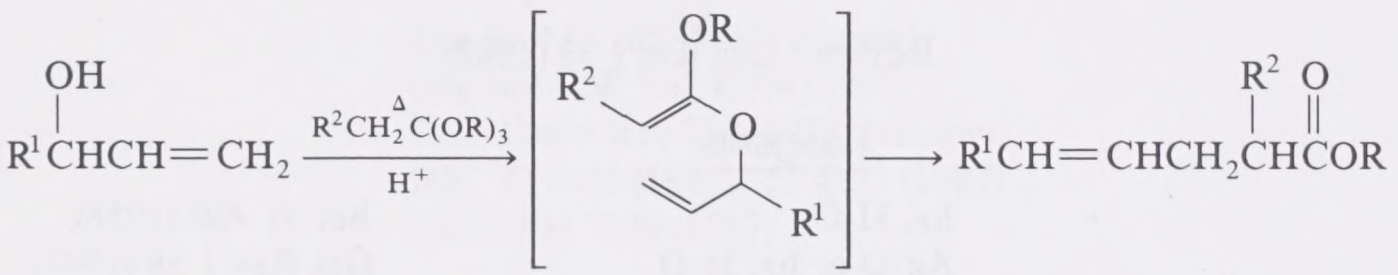


TL *21* 2125 (1980); *22* 1179 (1981)
JACS *106* 718 (1984)

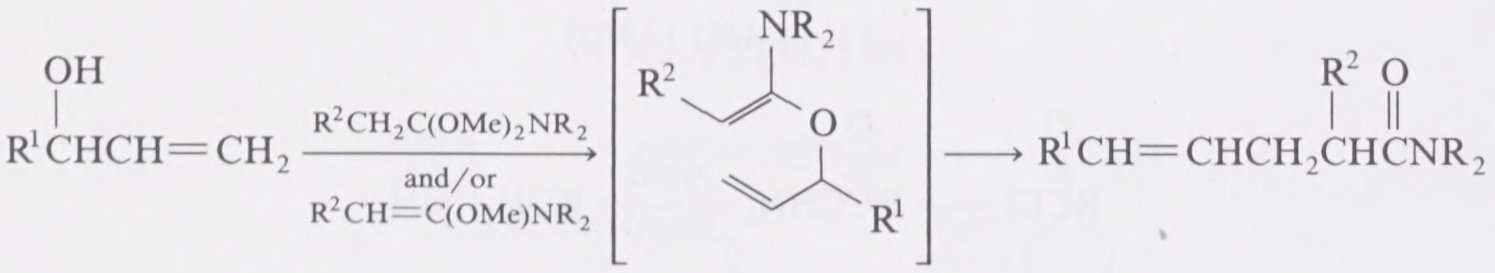
10. Claisen

Reviews:

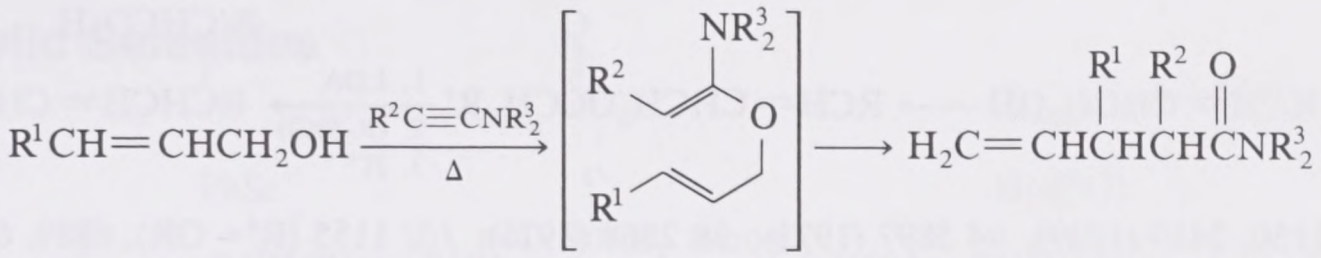
Syn 589 (1977)
Acct Chem Res *10* 227 (1977)
R. K. Hill, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 8 (chirality transfer)



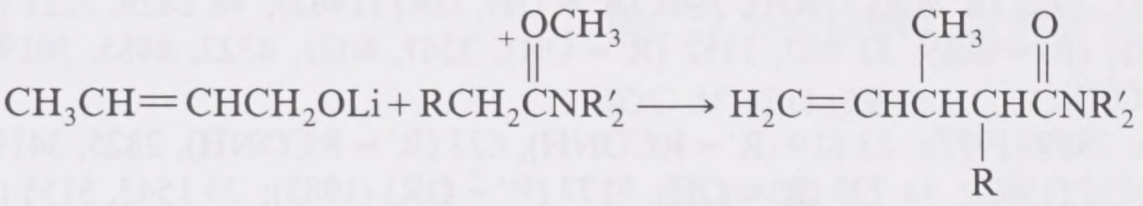
JACS *92* 741 (1970); *98* 1583 (1976); *100* 8272 (1978); *101* 3066 (1979); *102* 6891 (1980); *103* 2419, 5259 (1981); *108* 1039, 4603 (1986); *109* 3025 (1987)
CC 1512, 1513 (1970); 858 (1979); 123 (1982)
TL 1281 (1973); 691 (1975); 2543 (1977); 2575 (1978) (allenic alcohol); 3057 (1979); *21* 1285, 4335 (1980); *23* 947, 3531 (1982); *28* 2597 (1987)
JOC *39* 3315 (1974); *41* 3497 (1976); *43* 3435 (1978); *44* 3374 (1979); *45* 891, 2080 (1980); *46* 1485, 3896 (1981); *47* 337, 620, 2420 (1982); *48* 1829 (1983); *51* 3402, 5429 (1986); *52* 1201, 3541 (1987)
BSCF 2040 (1974) (allenic alcohols)
CL 1721 (1981); 1113 (1982)
JCS Perkin I 2909 (1982)
Syn Commun *12* 395 (1982)
Org Syn *64* 175 (1985)



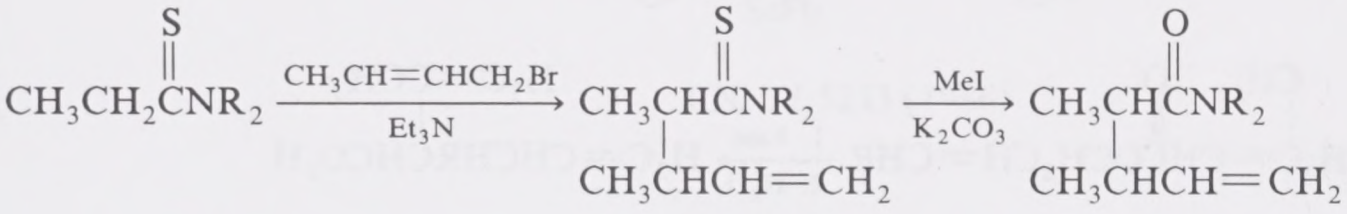
Helv *47* 2425 (1964); *52* 1030 (1969); *62* 1922 (1979)
Ber *104* 3679 (1971)
BSCF 2040 (1974) (allenic alcohols)
JOC *42* 3828 (1977); *49* 2682 (1984); *52* 1372 (1987)
TL *23* 109 (1982); *27* 3053 (1986); *28* 789 (allenic alcohol), 2041 (1987)
Angew Int *24* 700 (1985) (allenic alcohol)
CC 1759 (1986)



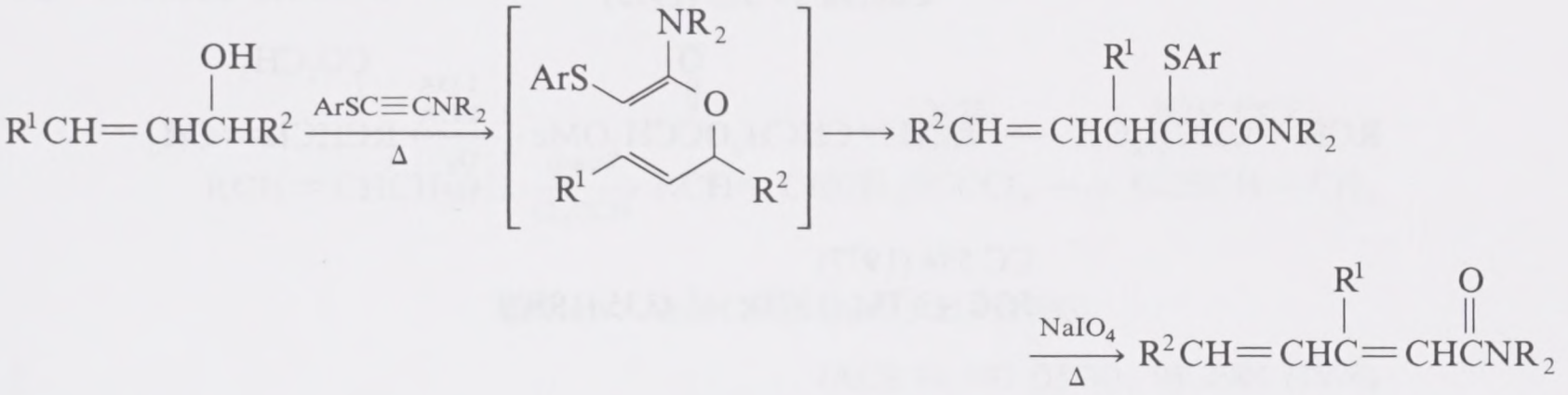
TL 6425 (1966)
Compt Rend C *268* 1446 (1969) (allenic alcohol)
JOC *44* 882 (1979); *46* 3896 (1981)



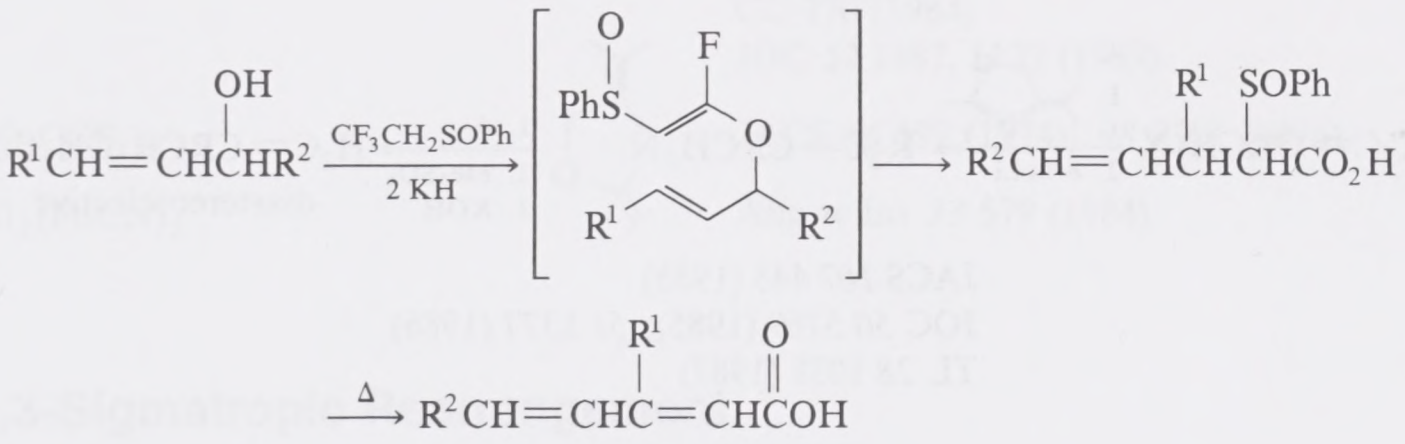
JOC *50* 5909 (1985)
JACS *109* 6716 (1987)



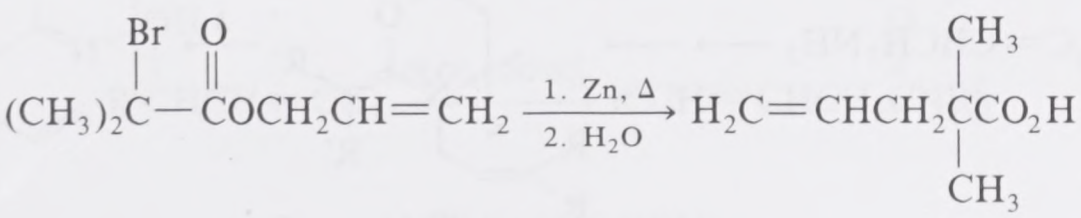
JACS *109* 6716 (1987)



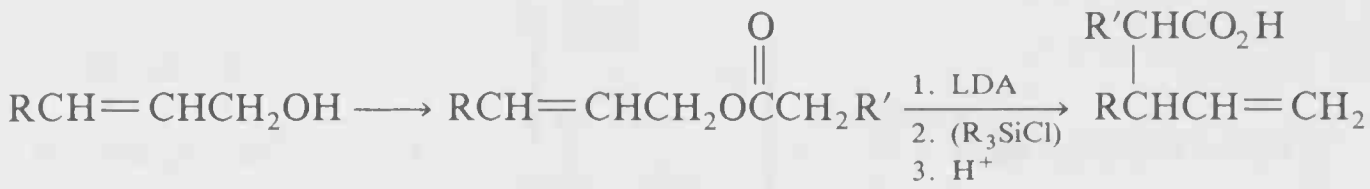
TL *22* 4097 (1981)



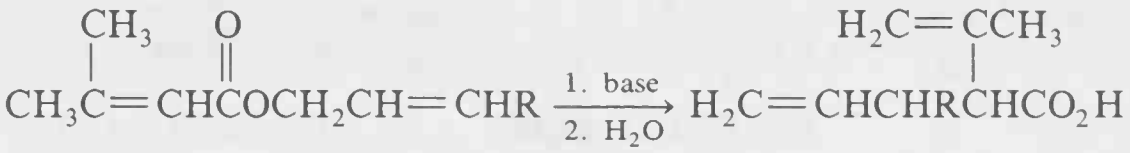
CL 1289 (1981)



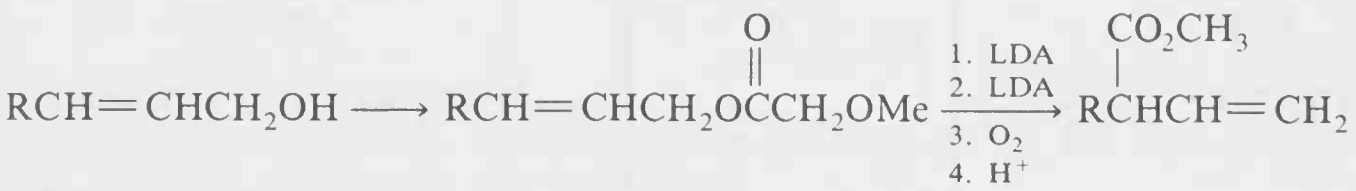
CC 117 (1973)



JACS *71* 1150, 2439 (1949); *94* 5897 (1972); *98* 2868 (1976); *102* 1155 (R′ = OR), 6889, 6891 (1980); *103* 3205 (1981); *104* 1124, 4030 (1982); *106* 3668, 5002 (1984); *107* 1448, 3271, 3279, 3285 (1985); *108* 2105, 2662 (1986)
Syn Commun *2* 27 (1972)
JOC *39* 3315 (1974); *41* 986 (1976); *43* 784 (1978) (R′ = OR); *45* 48, 4259 (1980); *46* 479, 3896 (1981); *47* 337, 3933 (R′ = RCONH), 3941 (R′ = OH, OR) (1982); *48* 1829, 5221 (R′ = OR) (1983); *50* 1128 (1985) (R′ = OR); *51* 503, 1152 (R′ = OR), 3247, 4023, 4322, 4485, 5019 (1986); *52* 3889 (1987) (R′ = OR)
TL 3975 (1975); 2839 (1977); *23* 619 (R′ = RCONH), 623 (R′ = RCONH), 2825, 3419 (R′ = OH, PhS), 3799, 4309, 5455 (1982); *24* 729 (R′ = OH), 5177 (R′ = OR) (1983); *25* 1543, 5155 (R′ = OH) (1984); *27* 3345 (1986); *28* 1035, 1439, 1925, 3031, 4143 (R′ = OR), 4147 (R′ = OR), 4629 (1987)
CL 1721 (1981)
BCSJ *55* 3555 (1982)
CC 1220 (1987)

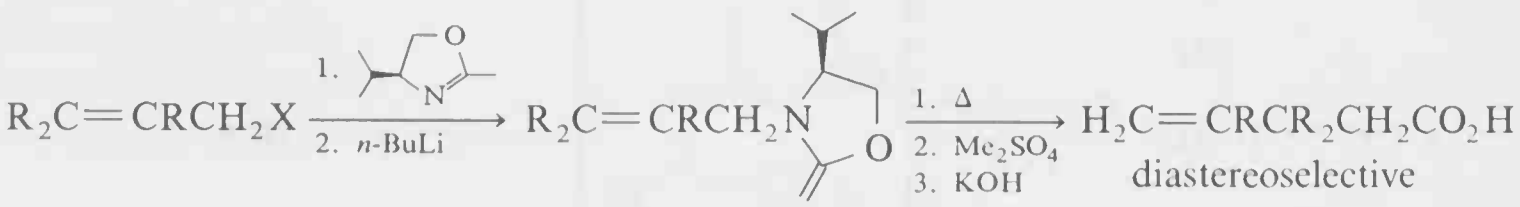


JOC *40* 3309 (1975)
Chimia *29* 528 (1975)

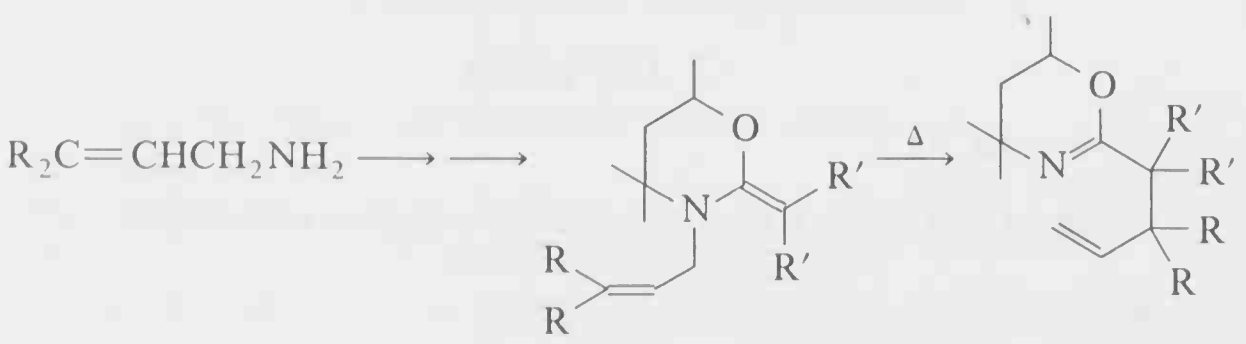


CC 594 (1977)
JOC *43* 784 (1978); *45* 4135 (1980)

11. Aza-Claisen

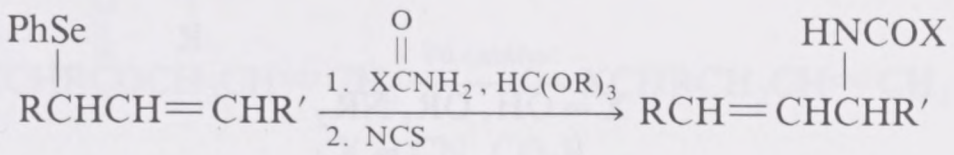


JACS *107* 443 (1985)
JOC *50* 5769 (1985); *51* 1377 (1986)
TL *28* 1031 (1987)

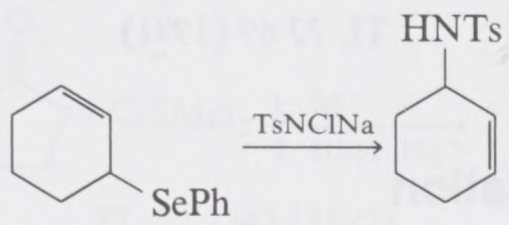


JOC *39* 421 (1974)

12. Allylic Selenides

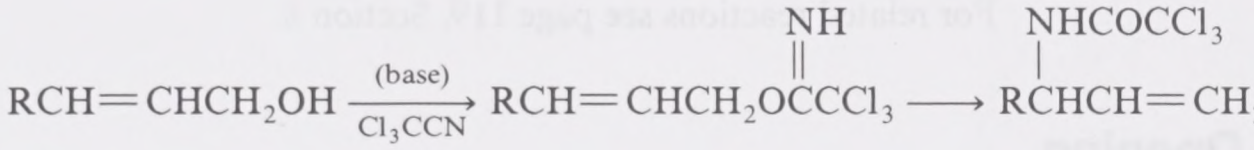


X	
OR	JOC *51* 5243 (1986); *52* 3759 (1987)
CH(OMe)Ph	JOC *51* 5243 (1986)



JOC *51* 5243 (1986)

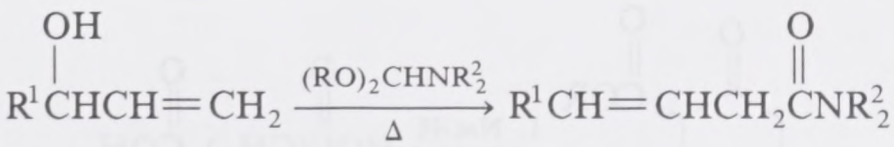
13. Imidic Esters



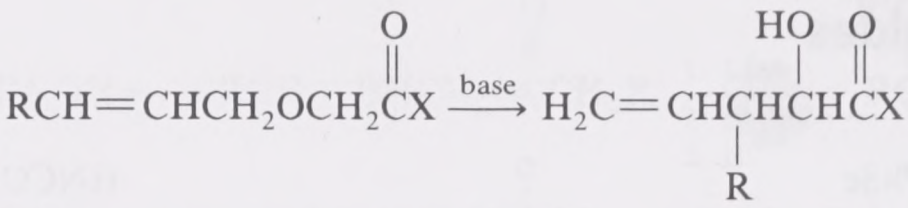
Review: Acct Chem Res *13* 218 (1980)

Δ	JACS *96* 597 (1974); *98* 2901 (1976) BCSJ *49* 3247 (1976) Org Syn *58* 4 (1978) CC 770 (1984) JOC *52* 1487, 5127 (1987)
cat $Hg(O_2CCF_3)_2$	JACS *96* 597 (1974); *98* 2901 (1976)
cat $PdCl_2(PhCN)_2$	Angew Int *23* 579 (1984)

14. 2,3-Sigmatropic Rearrangement

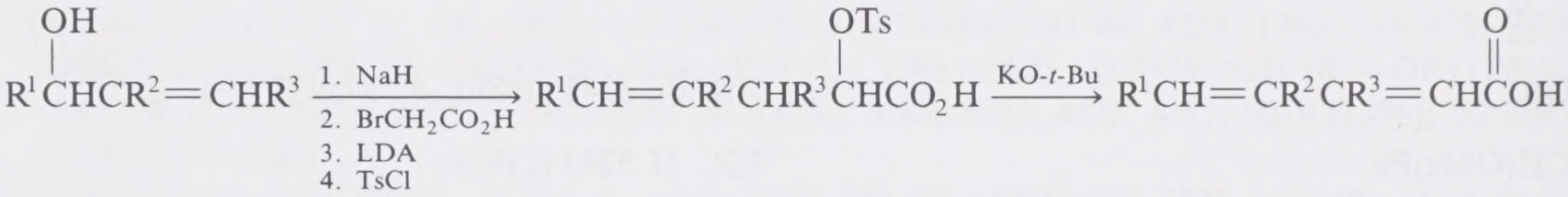


JACS *96* 5563 (1974)
JOC *42* 3828 (1977)



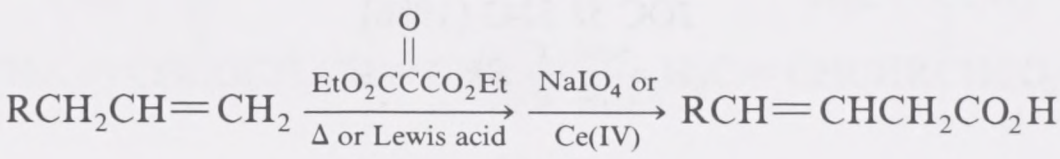
$X = OH, OR, NR_2$

See page 521, Section 5.



TL *22* 69 (1981)

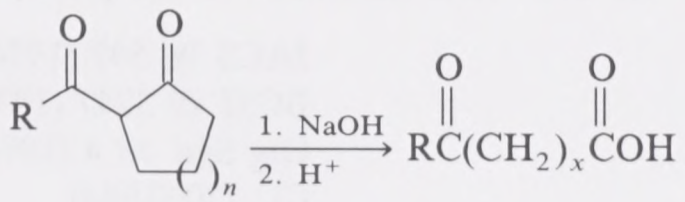
15. Ene Reaction—Oxidation



JACS *102* 2473 (1980); *106* 1092, 3797 (1984)
JOC *45* 1228 (1980); *47* 4201 (1982)

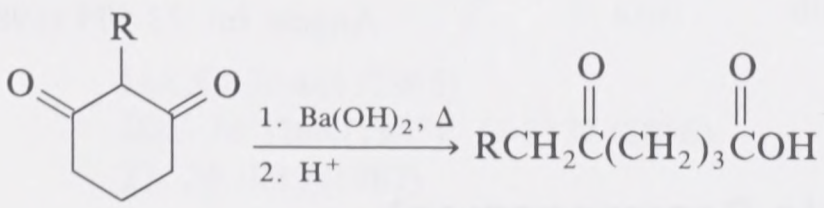
For related reactions see page 119, Section 8.

16. Ring Opening

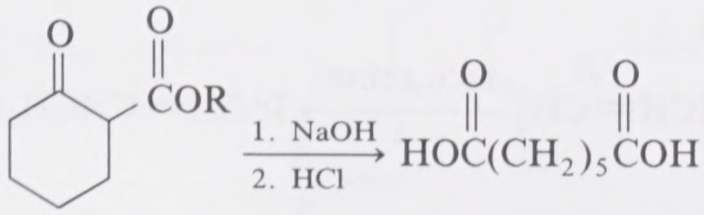


$n = 1, 2;\ x = 4, 5$

JACS *70* 4023 (1948); *75* 5030 (1953)

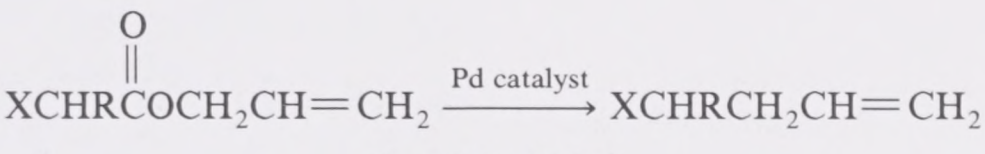


Ber *85* 1061 (1952)



Org Syn Coll Vol *2* 531 (1943)

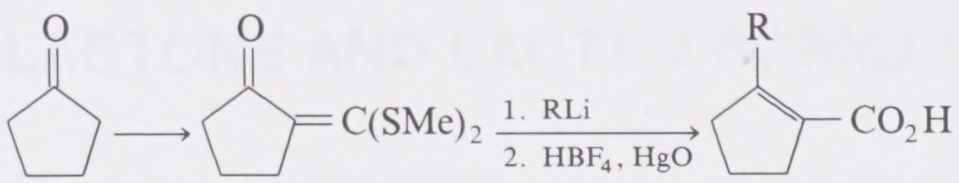
17. Decarboxylation—Allylation



$X = CN, CO_2R$

JOC *52* 2988 (1987)

18. Other Reactions



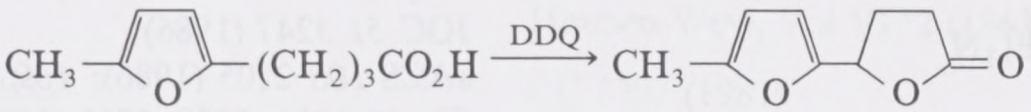
TL *23* 3747 (1982)

8. LACTONE AND LACTAM FORMATION

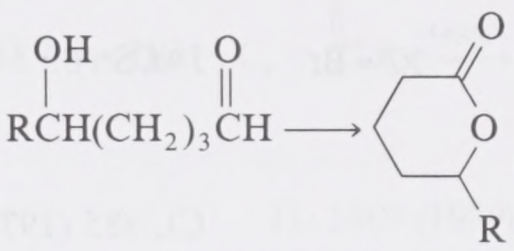
See also page 836, Section 12.

Reviews:

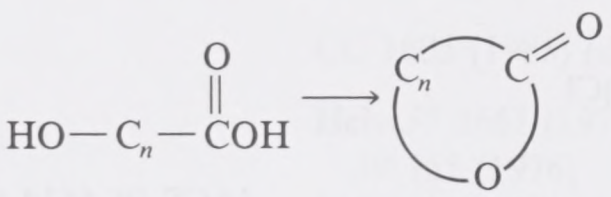
Syn 67 (1975) (α-methylene lactones)
Tetr *33* 683, 3041 (1977)
Angew Int *16* 585 (1977)
Org Prep Proc Int *13* 59 (1981) (saturated γ-lactones)



TL *28* 5175 (1987)



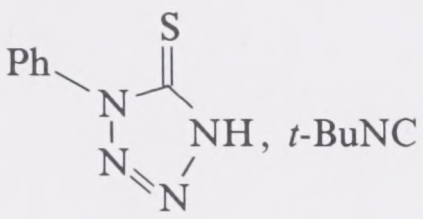
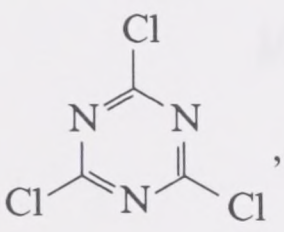
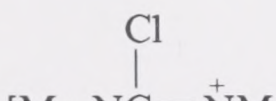
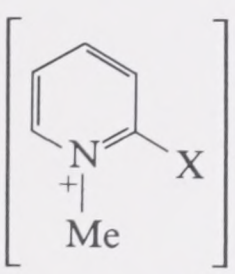
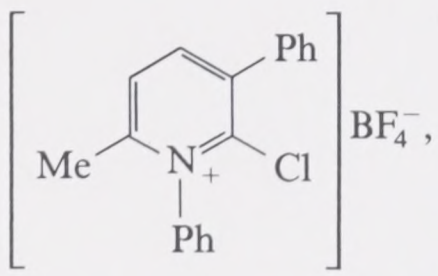
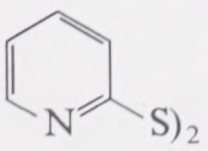
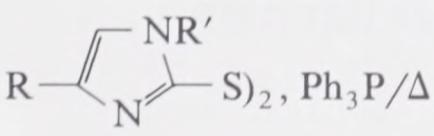
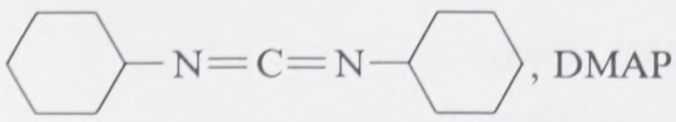
See page 844, Section 15.

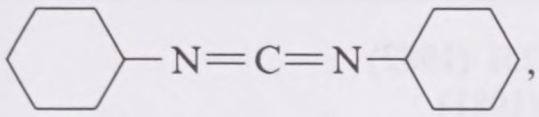


Reviews:

Houben-Weyl, Vol VI/2 (1963), p 511
Tetr *33* 683, 3041 (1977)
Angew Int *18* 707 (1979)

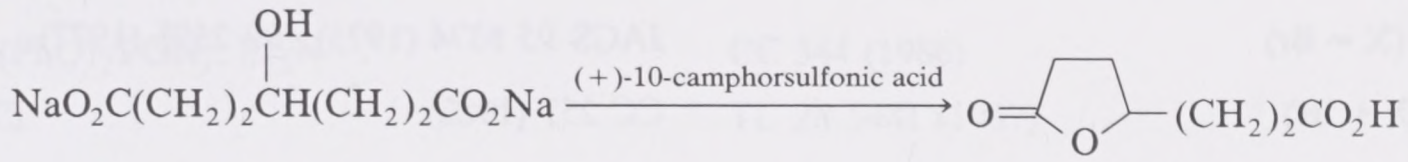
cat TsOH, Δ	Helv *17* 1283 (1934); *18* 1087 (1935)
TsOH, microemulsion, Δ	JOC *46* 2594 (1981)
n-Bu_2SnO	JACS *102* 7578 (1980); *105* 7130 (1983)
n-Bu_2SnO – *n*-Bu_2SnCl_2	TL *27* 4501 (1986)
2,6-$Cl_2C_6H_3COCl$, Et_3N/DMAP, Δ	TL *28* 2409 (1987)

$2,4,6\text{-}Cl_3C_6H_2COCl$, Et_3N/DMAP, Δ		BCSJ *52* 1989 (1979) TL *25* 2163 (1984); *28* 4569 (1987)
$Me_2NCH(OCH_2CMe_3)_2$		Angew Int *16* 876 (1977)
$EtO_2CN{=}NCO_2Et$, Ph_3P		TL 2455 (1976); 2371 (1978); *25* 2163 (1984) Syn 1 (1981) (review) JOC *51* 4840 (1986) JACS *109* 6176 (1987)
		Angew Int *20* 771 (1981)
 , Et_3N		TL *21* 1893 (1980); *27* 2369 (1986)
 $[Me_2NC{=}\overset{+}{N}Me_2]Cl^-$, collidine ($n$ = 11, 12, 14)		CL 1891 (1982)
 I^-, Et_3N	X = Cl	CL 49 (1976); 441, 763, 959 (1977) Angew Int *20* 286 (1981) JOC *51* 3247 (1986) JACS *108* 2105 (1986); *109* 8117 (1987) TL *28* 3031, 5759, 5763 (1987) CC 1220 (1987)
	X = Br	JACS *109* 5437 (1987)
 BF_4^-,		CL 885 (1978)
pyridine base, $(PhCH_2NEt_3)Cl$		
 , Ph_3P		JACS *96* 5614 (1974); *97* 653, 654, 2287 (1975); *98* 222 (1976); *103* 3213 (1981); *104* 1774 (1982); *108* 6800 (1986) TL 3405 (1976); *21* 2791 (1980); *27* 1815 (1986); *28* 4993 (1987)
		TL 3409 (1976) JACS *100* 4621 (1978); *101* 7131 (1979); *106* 2735 (1984)
 , DMAP		JACS *108* 2776 (1986)



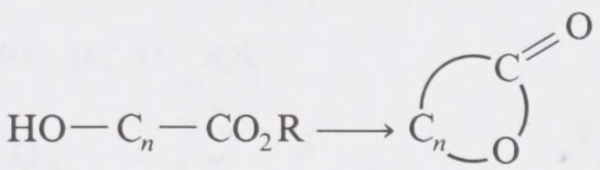
JOC *50* 2394 (1985)

DMAP, DMAP·HCl

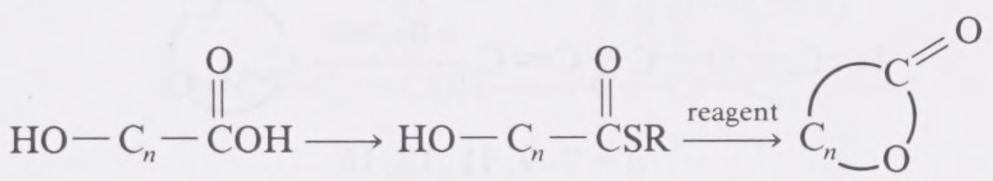


chiral

JACS *107* 6404 (1985)
TL *27* 5381 (1986)

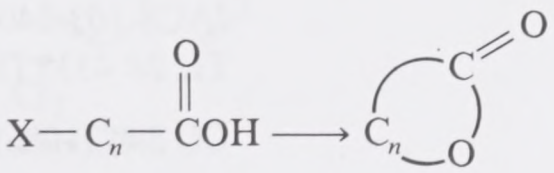


Lipase P	TL *28* 805 (1987)
porcine pancreatic lipase	TL *28* 805, 3861, 5367 (1987)
imidazole	JACS *109* 2208 (1987)
$EtO_2CN{=}NCO_2Et$, Ph_3P	JACS *99* 646 (1977)
KH	JACS *108* 2662 (1986)
n-BuLi (R = $CH_2SO_2CH_3$)	CL 455 (1982) JACS *106* 2954 (1984)
H^+	Houben-Weyl, Vol VI/2 (1963), p 511
$ZnCl_2$, molecular sieves	CC 1797 (1987)



Reagent

KO-*t*-Bu	TL 1469 (1979) JOC *45* 1535 (1980); *46* 3209 (1981) CC 251 (1982)
CuO_2CCF_3	CC 1805 (1985) (dimerization)
AgX	Helv *57* 2661 (1974); *58* 2036 (1975); *59* 755 (1976) JACS *99* 6756 (1977); *109* 6205 (1987) Org Syn *63* 192 (1984)
HgX_2	JACS *97* 3513, 3515 (1975); *98* 7874 (1976)



$KHCO_3$, (polymer-PBu_3)OMs, H_2O, toluene (X = OMs)	JACS *104* 2064 (1982)
K_2CO_3 (X = Br, I)	Ber *80* 129 (1947)

Cs_2CO_3 (X = Br, I) — CC 286 (1979); 251 (1982); JACS *103* 5183 (1981)

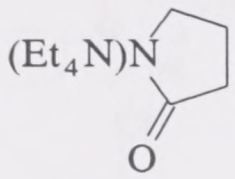
Cs_2CO_3 (X = OMs) — CC 668 (1982)

NaOH (X = Br) — JACS *95* 8374 (1973); *99* 2591 (1977)

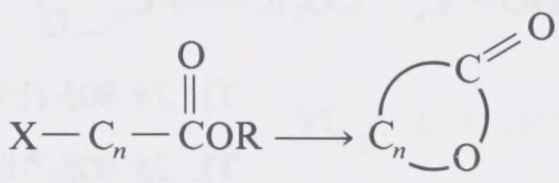
KOH (X = Br) — CC 251 (1982)

KOH, microemulsion (X = Br) — JOC *46* 2594 (1981)

KOH, *n*-Bu_4NBr (phase transfer) (X = Br) — JOC *48* 1533 (1983)



(X = Br) — JOC *51* 546 (1986)

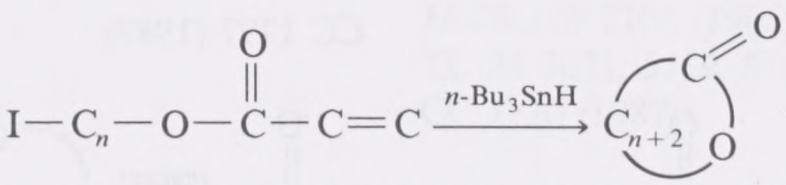


X = halogen

Δ ($n = 3$) — JOC *50* 2128 (1985) (phthalide)

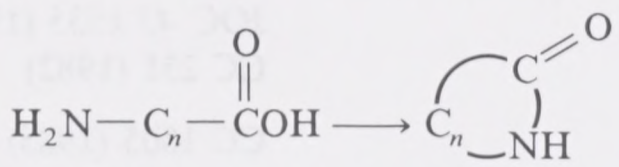
Δ, silica gel ($n = 3$) — CL 1909 (1982); JOC *51* 4944 (1986)

TsOH, $Hg(OAc)_2$ or $AgClO_4$ ($n = 3$) — Heterocycles *12* 699 (1979)



n = 7–9, 11, 12, 16

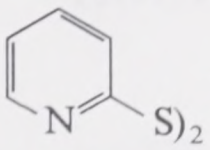
JACS *109* 4976 (1987)



alumina or silica gel ($n = 3$–5) — TL *21* 2443 (1980)

n-Bu_2SnO ($n = 3$–5) — JACS *102* 7578 (1980); *105* 7130 (1983)

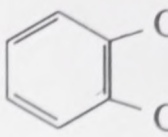
o-$NO_2C_6H_4SCN$, *n*-Bu_3P ($n = 3$–5) — JOC *44* 2945 (1979)



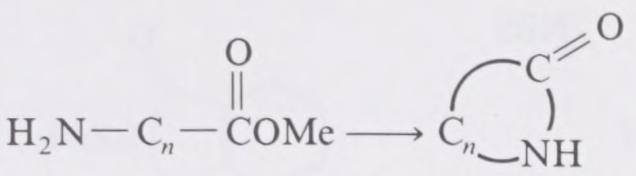
, Ph_3P ($n = 2$) — JACS *103* 2406 (1981); TL *28* 4335 (1987)

$(PhO)_2PON_3$, Et_3N ($n = 7$) — CC 344 (1986)

$(Me_3Si)_2NH$, Δ ($n = 3$–5) — Syn 614 (1978)

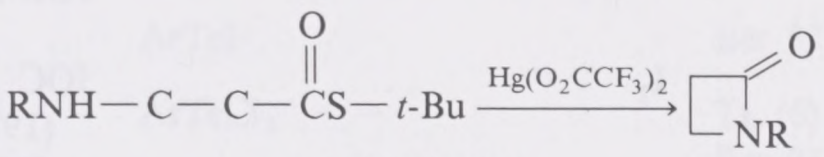


, py ($n = 3, 5$) — JOC *43* 4393 (1978)

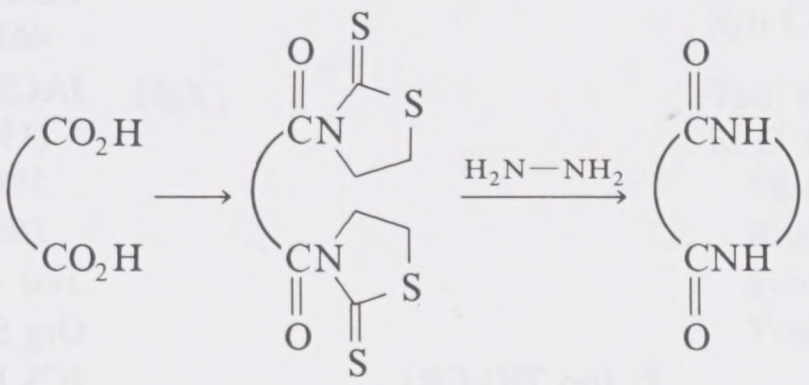


$NaOH/(PhO)_2PON_3$, Et_3N CC 344 (1986)

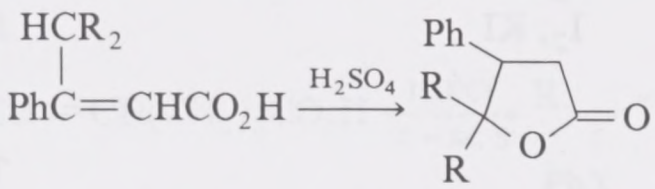
t-BuMgCl TL *28* 5481 (1987)



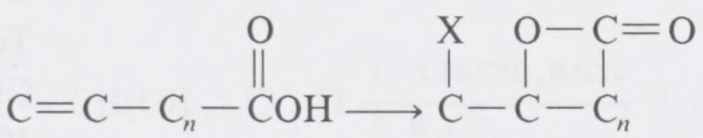
CL 915 (1986)



CL 159 (1980)

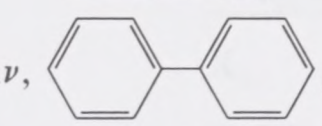
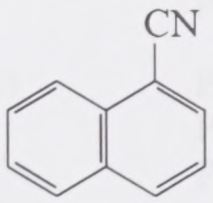


Acta Chem Scand B *36* 371 (1982)

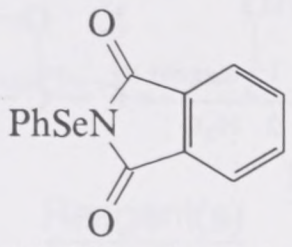


Reviews:

Russ Chem Rev *40* 272 (1971) (X = halogen)
Chem Soc Rev *8* 171 (1979) (X = halogen)
Tetr *37* 4097 (1981) (X = SePh)
P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 6

X	Reagent(s)	
H	$h\nu$, 	JACS *109* 7547 (1987)
		
Cl	Cl_2	Tetr *4* 393 (1958)
	TsNClNa	JOC *46* 3552 (1981)
Br	Br_2	Tetr *4* 393 (1958)
		Tl 2595 (1971)
	Br_2 (on TlO_2CR)	TL 335 (1979)
	Br_2, TlO_2CCMe_3	CC 1045 (1987)

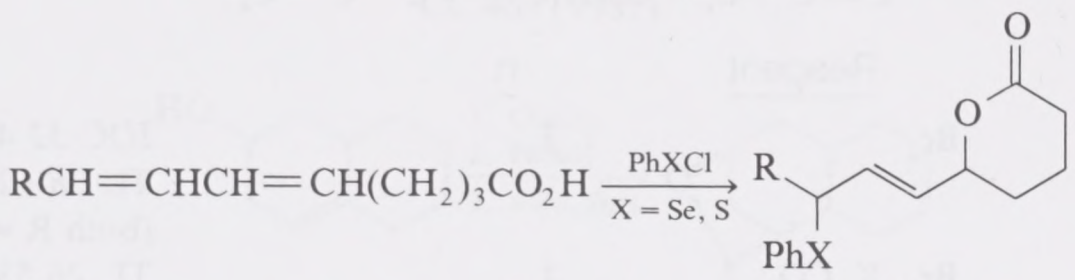
	NBS	TL 3983 (1967); 1005 (1977) (chiral); *21* 2733 (1980); *27* 6079 (1986); *28* 2801 (1987) Tetr *30* 819 (1974); *35* 2337, 2345 (1979) CL 1109 (1977) (chiral) JOC *52* 1372 (1987)
I	I_2	JOC *38* 800 (1973); *44* 1625 (1979); *51* 2505, 4840 (1986); *52* 3346 (1987) TL 2543 (1977); 335 (1979); *22* 4611 (1981); *27* 6079 (1987) JACS *100* 3950 (1978); *102* 2118 (1980); *103* 4114 (1981); *105* 5819 (1983); *108* 5559 (1986); *109* 6844 (1987) Tetr *40* 2317 (1984) Org Syn *64* 175 (1985)
	I_2 (on TlO_2CR)	JCS Perkin I 1864 (1974)
	I_2, TlOAc	Austral J Chem *32* 2793 (1979)
	I_2, KI	JACS *76* 2315 (1954); *91* 5675 (1969); *92* 397 (1970); *106* 7854 (1984); *109* 6389 (1987) TL 1777 (1972); 2543 (1977); *27* 3297, 5467 (1986) CC 472 (1972) Tetr *30* 819 (1974) CL 351 (1982) JOC *51* 4600, 4944 (1986); *52* 4399 (1987)
OTs	PhI(OH)OTs	TL *27* 4557 (1986)
MeS	$(MeSSMe_2)BF_4$, *i*-Pr_2NEt	TL *26* 6159 (1985)
PhS	PhSCl, R_3N	CC 293 (1977) JACS *101* 3884 (1979) TL *28* 523 (1987)
ArSe	PhSeCl	CC 484 (1977) JACS *99* 3185 (1977); *101* 3884 (1979); *103* 4114 (1981); *106* 6060 (1984) TL 4801 (1979); *24* 4769 (1983) Tetr *36* 1399 (1980); *37* 4097 (1981) (review); *40* 2317 (1984) JOC *51* 3023 (1986)
	ArSeX (X = Cl, Br)	Ber *93* 317 (1960)
	PhSeOTf	CL 849 (1987)



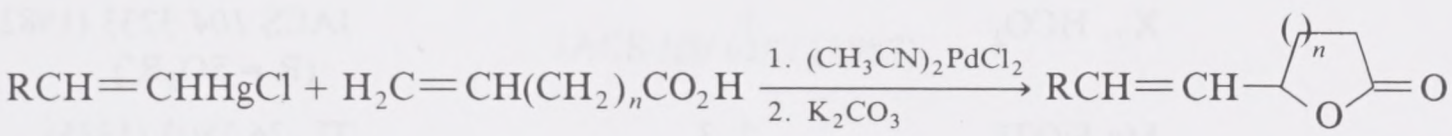
Tetr *40* 2317 (1984)

$(PhSe)_2$, electrolysis — TL *28* 6511 (1987)

ArTe	ArTeI	Ber *93* 317 (1960)
$ArTeCl_2$	$ArTeCl_3$	TL (6) 11 (1959) Ber *93* 317 (1960) Tetr *18* 521 (1962) Syn Commun *13* 889 (1983)
HgX	HgX_2	Tetr *40* 2317 (1984) R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 5 (review)

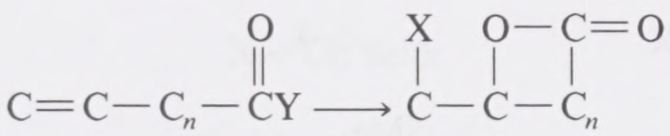


TL *27* 5919 (1986)

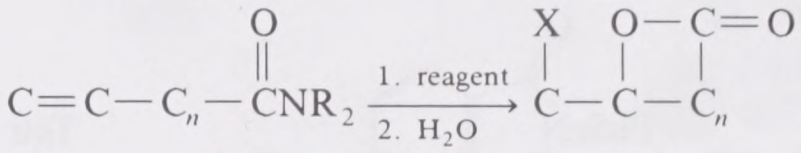


$n = 1, 2$

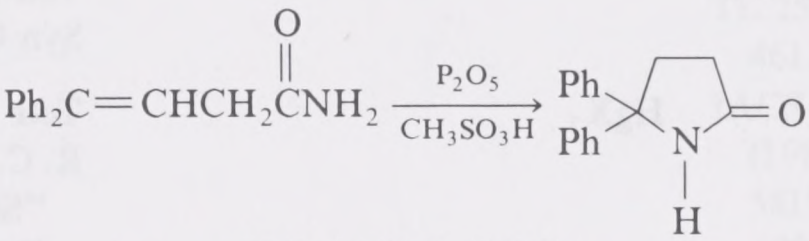
TL *28* 4977 (1987)



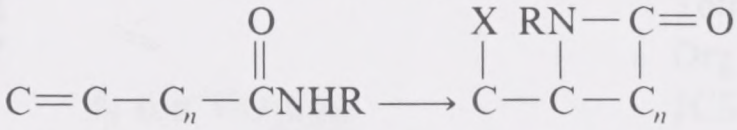
X	Y	Reagent	
Cl, Br, I	OCH_3	X_2	JOC *45* 839 (1980)
PhS	OCH_3	PhSCl	JOC *45* 839 (1980)
PhSe	$OSiMe_2(t\text{-Bu})$	PhSeCl	JACS *107* 1448 (1985)
	OCH_3	PhSeCl	JOC *45* 839 (1980)
		PhSeOTf	CC 849 (1987)
HgX	OR	HgX_2	R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 6 (review)



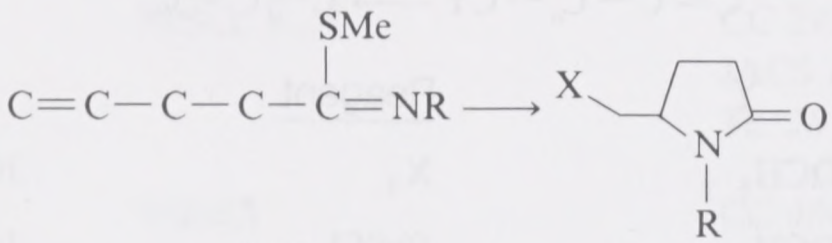
X	Reagent	
Cl	NCS	JACS *106* 1079 (1984)
Br	NBS	JACS *106* 1079 (1984)
I	I_2	TL 1625 (1977) JACS *106* 1079 (1984); *109* 6716 (1987) CC 156 (1986)



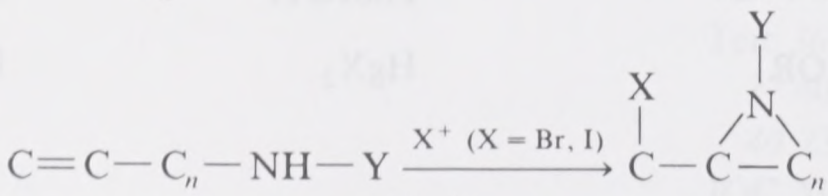
JOC *50* 2220 (1985)



X	Reagent	n	
Br	Br_2	1	JOC *52* 4471 (1987) TL *28* 6257 (1987) (both R = OCO_2CH_2Ph)
	Br_2, K_2CO_3	1	TL *26* 5385 (1985) (R = O_2CR')
Br, I	X_2, HCO_3^-	1	JACS *104* 3233 (1982) (R = SO_2R')
I	Me_3SiOTf, Et_3N/I_2	2, 3	TL *26* 1803 (1985)
PhS	PhSCl/base	0 (β-lactam formation)	JACS *105* 7345 (1983)
PhSe	PhSeX	2, 3	JOC *51* 1724 (1986); *52* 2018 (1987)



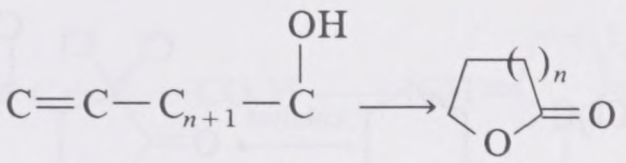
X	Reagent	
Br	$BrClO_4(collidine)_2$	Heterocycles *26* 359 (1987)
I	I_2	CC 1627 (1987)



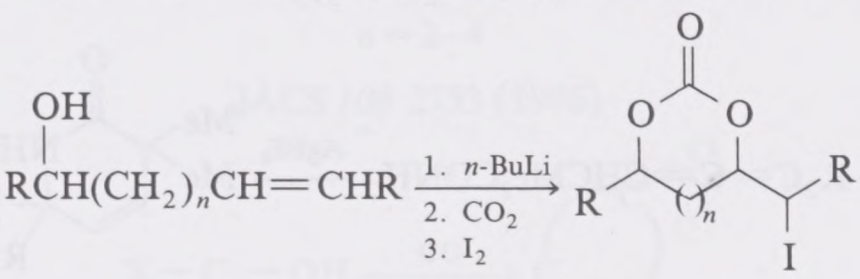
$n = 3, 4$

Y = CO_2Me, p-$MeC_6H_4SO_2$

Heterocycles *23* 192 (1985)

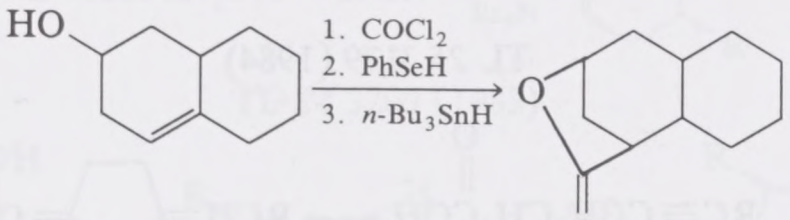


n	Reagent(s)	
1, 2	$(n\text{-}C_{16}H_{33}NMe_3)MnO_4$	TL *27* 4079 (1986)
1, 2	$(bipyH_2)CrOCl_5$	CL 551 (1985)
1, 2	CrO_3, HOAc, Ac_2O	TL *26* 127 (1985)

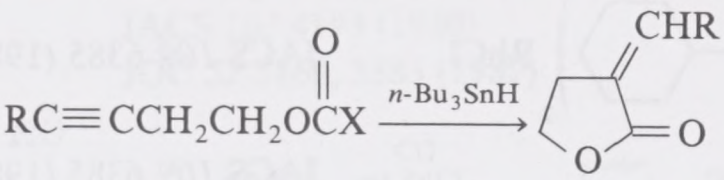


$n = 0, 1$

CC 465 (1981)

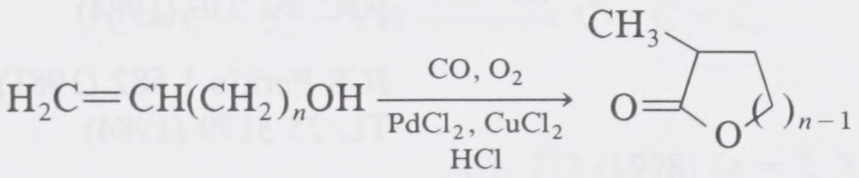


JACS *109* 6187 (1987)



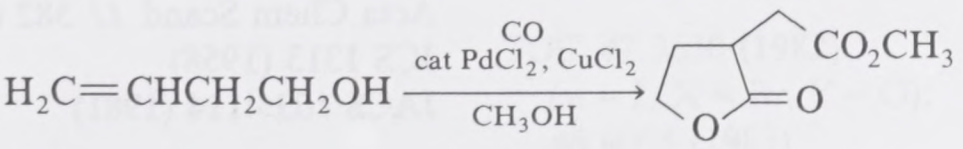
X = Cl, SePh

TL *27* 641 (1986)

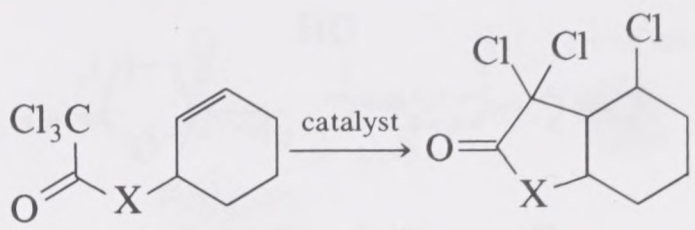


$n = 2, 3$

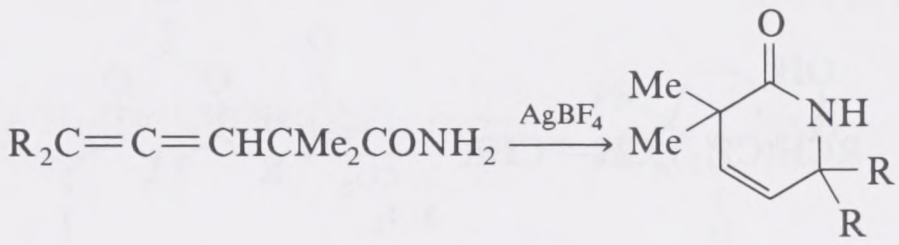
CC 511 (1985)



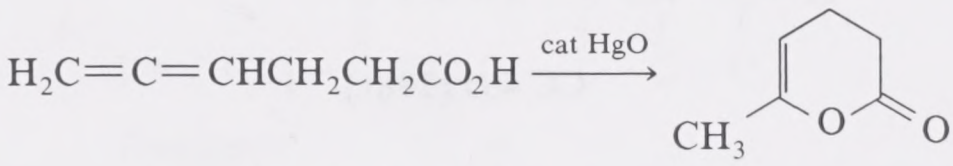
TL *26* 3207 (1985); *28* 325 (1987)



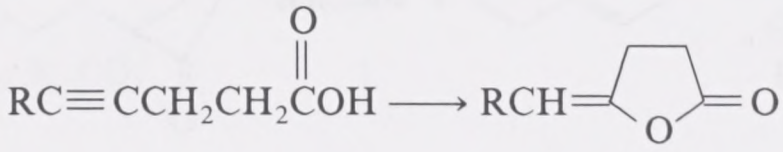
X	Catalyst	
O	CuCl	TL *24* 2395 (1983) Heterocycles *22* 1779 (1984)
NR	$CuCl$ or $RuCl_2(PPh_3)_3$	CC 652 (1984); 518 (1985)

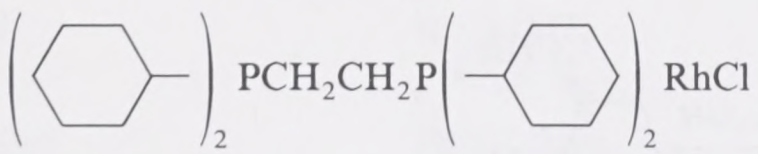


TL *27* 5089 (1986)

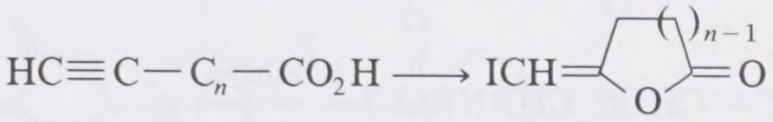


TL *25* 3179 (1984)

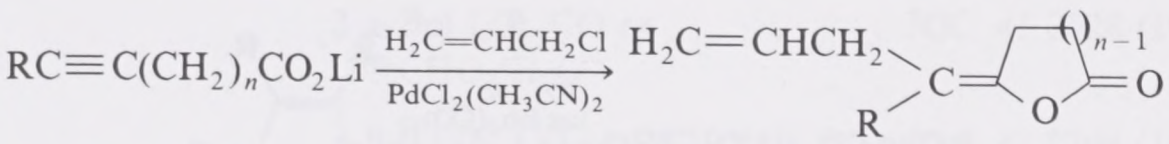


Catalyst	
	JACS *109* 6385 (1987)
$Pd(PPh_3)_4$	JACS *109* 6385 (1987)
$PdCl_2(PhCN)_2$	TL *25* 5323 (1984)
Ag_2CO_3	TL *28* 6448 (1987)
$AgNO_3$	JCS 3962 (1958) JOC *49* 736 (1984)
HgO	JCS Perkin I 582 (1981) TL *25* 3179 (1984)
$Hg(OAc)_2$	JOC *43* 560 (1978) JACS *103* 5459 (1981)
$Hg(O_2CCF_3)_2$	JACS *103* 4114 (1981); *108* 5589 (1986) JOC *50* 2331 (1985)
HCO_3^-	Acta Chem Scand *11* 582 (1957) JCS 1313 (1958) JACS *103* 4114 (1981)

For intermolecular reactions see page 830, Section 5.

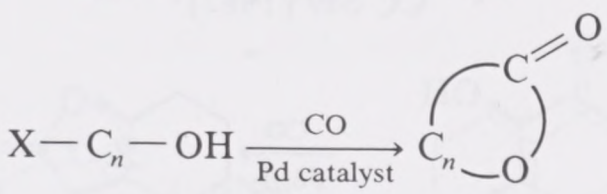


Reagent(s)	n	
I_2	3	JOC *50* 2331 (1985)
NIS, $NaHCO_3$	2	JACS *108* 5589 (1986)

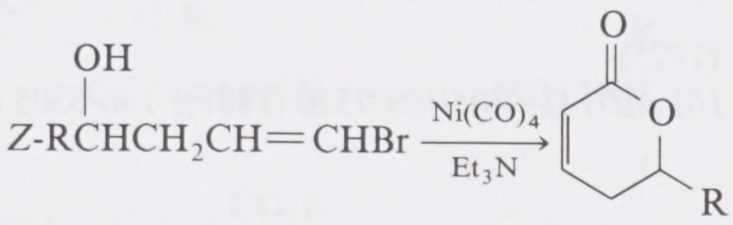


$n = 2$–4

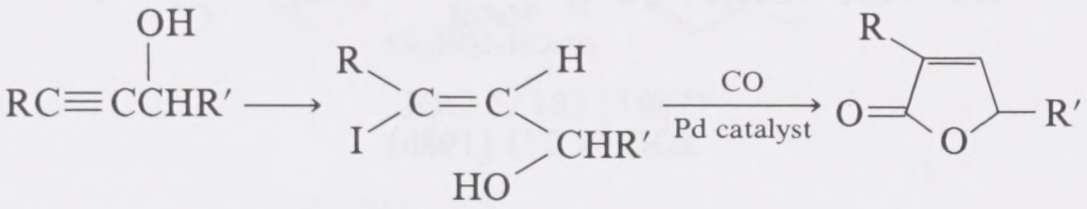
JACS *108* 2753 (1986)



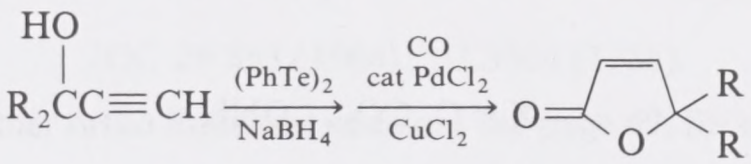
JACS *102* 4193 (1980)



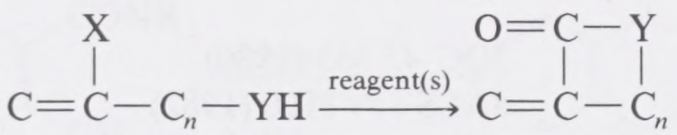
TL *24* 3209 (1983)



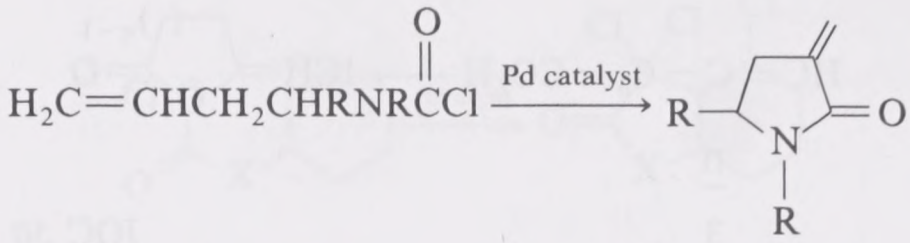
TL 133 (1979); *28* 723 (1987)
JACS *102* 4193 (1980)
JOC *52* 3860, 3883 (1987)



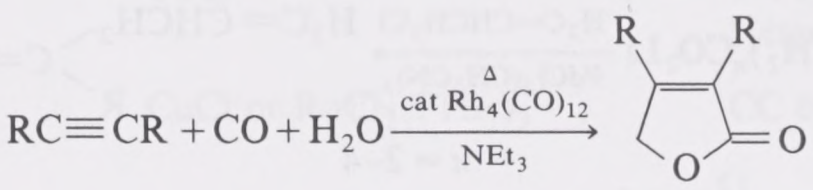
JOC *52* 4859 (1981)



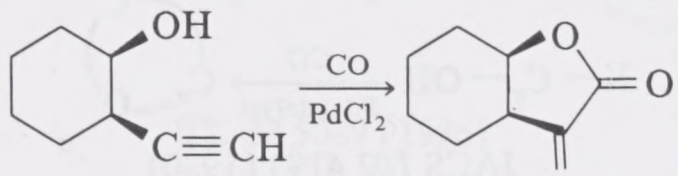
Reagent(s)	
$Ni(CO)_4$, KOAc	CL 773 (1978) ($n = 2$, X = Br, Y = O)
$Ni(CO)_4$ or $Ni(CO)_2(PPh_3)_2$	JOC *46* 1723 (1981) ($n = 2, 3$; X = Br; Y = O)
$Ni(CO)_2PPh_3$	JACS *104* 6879 (1982) ($n = 2$; X = Br; Y = O)
CO, Pd catalyst	JOC *47* 3630 (1982) ($n = 2$, X = Br, Y = O); *48* 4058 (1983) ($n = 2$–4; X = Br, I; Y = O, NH)



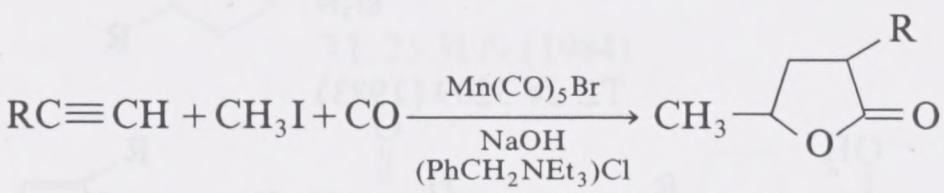
TL *27* 6339 (1986)



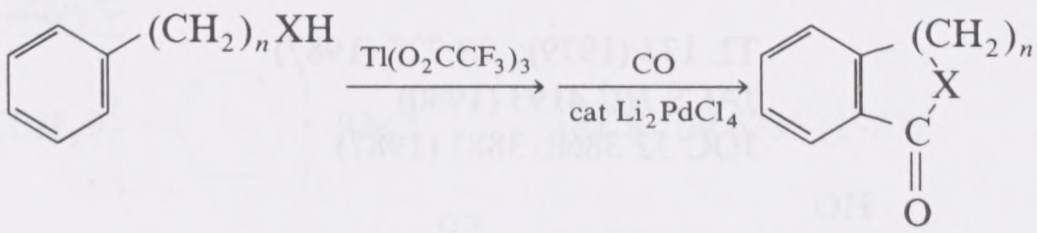
CC 649 (1987)



TL 51 (1975)
JACS *101* 4107 (1979); *103* 7520 (1981); *106* 5505 (1984)



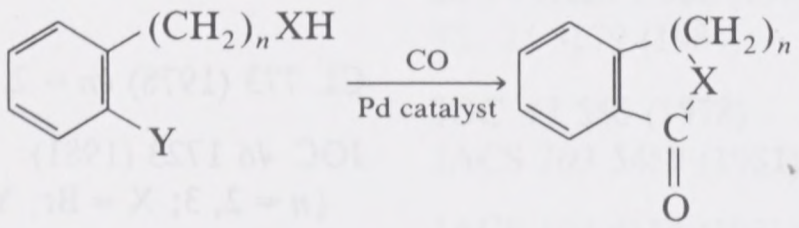
JOC *51* 273 (1986)



X = O, CO_2, CONH

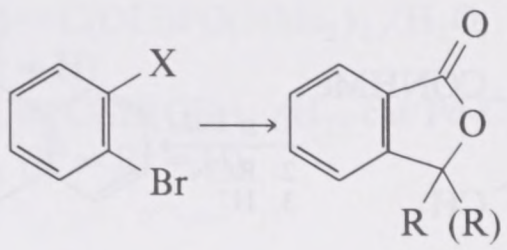
n = 0–2

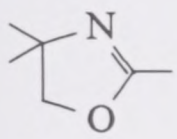
JOC *45* 363 (1980)
JACS *104* 1900 (1982)

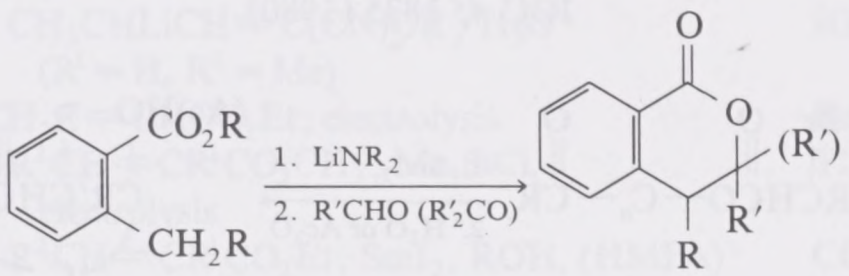


X = O, NR; Y = Br, I; *n* = 1–3

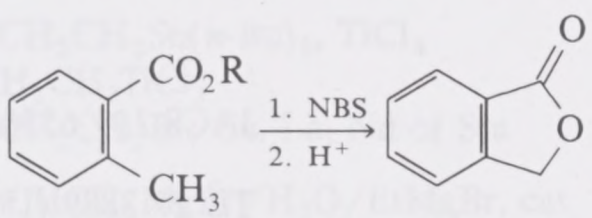
Heterocycles *6* 1711, 1841 (1977); *12* 921 (1979); *16* 1491 (1981)
JOC *43* 1684 (1978)
JACS *102* 4193 (1980)
CC 841 (1986)



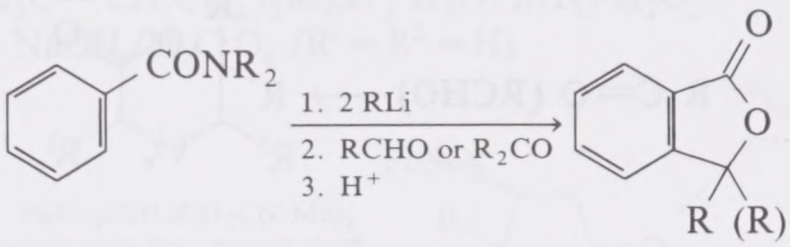
X	Reagents	
CO_2H	2 *n*-BuLi/R_2CO or RCHO/H_3O^+	JOC *41* 2628 (1976)
CO_2-*i*-Pr	*n*-BuLi/R_2CO or RCHO/H_3O^+	JOC *41* 2704 (1976)
	Mg/R_2CO or RCHO/H_3O^+	JOC *39* 2787 (1974)



CC 764 (1983) (chiral); 520 (1987)

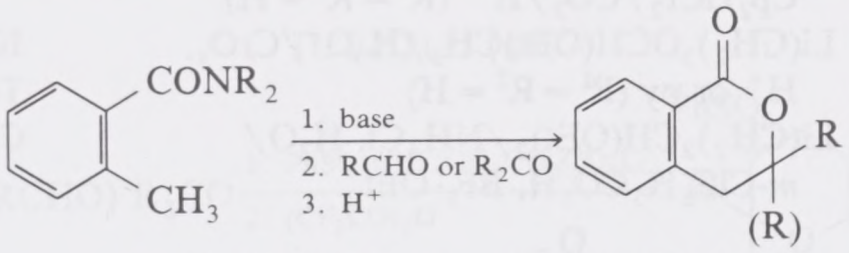


JOC *52* 183 (1987)

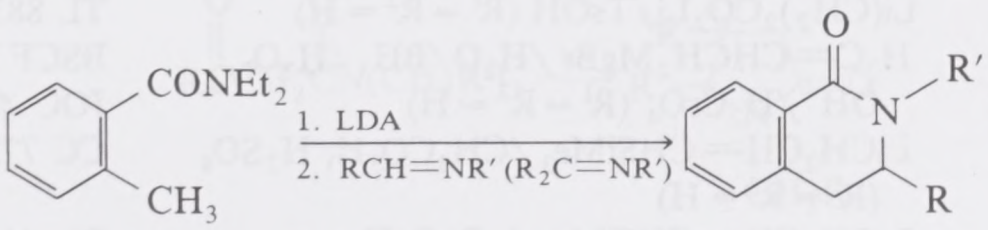


JOC *29* 853 (1964); *51* 3566 (1986)

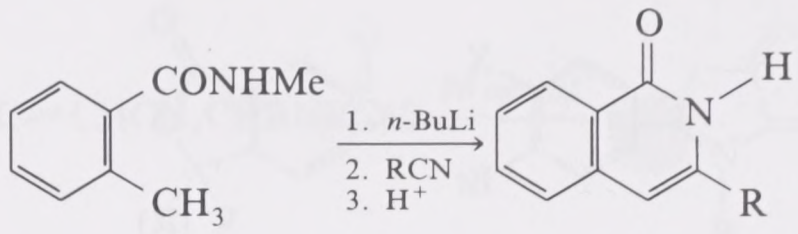
For other ortho lithiation reactions see page 49, Section 2.1.



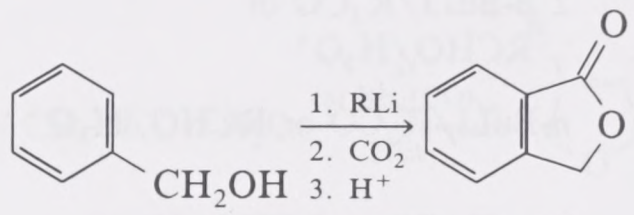
JOC *29* 3514 (1964); *51* 3566 (1986)
J Heterocyclic Chem *6* 83 (1969)
TL 633 (1970)



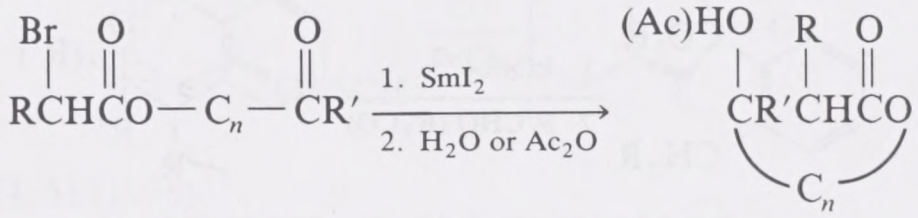
Heterocycles *23* 825 (1985)
JOC *52* 5378 (1987)



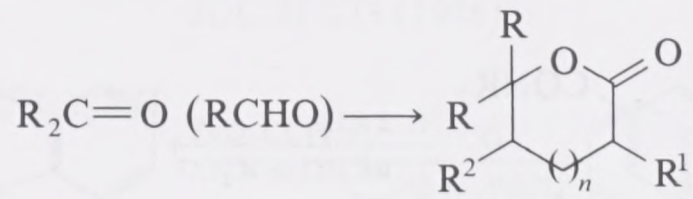
JOC *47* 3787 (1982)

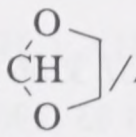


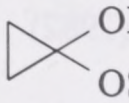
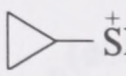
JOC *45* 1835 (1980)

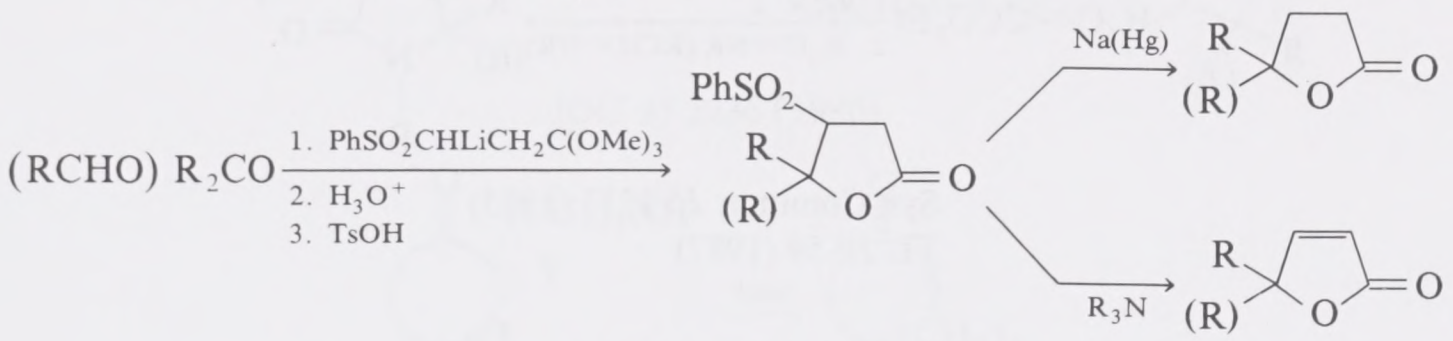


n		
2		JACS *109* 6556 (1987)
8–14		TL *27* 3889 (1986)

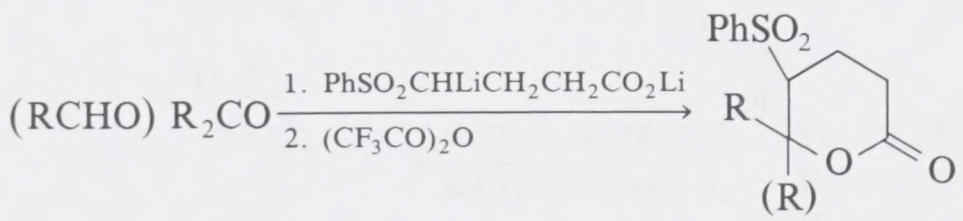


n	Reagents	
O	$H_2C{=}CHMgBr/H_2O/EtMgBr$, cat $Cp_2TiCl_2/CO_2/H^+$ ($R^1 = R^2 = H$)	JOMC *160* C8 (1978)
	$Li(CH_2)_3OCH(OEt)CH_3/H_3O^+/CrO_3$, H^+ or py ($R^1 = R^2 = H$)	JOC *37* 1947 (1972) TL 4651 (1976)
	$Li(CH_2)_2CH(OEt)_2/NH_4Cl$, H_2O/ *m*-$ClC_6H_5CO_3H$, $BF_3 \cdot OEt_2$	CC 1534 (1987)
	$BrMg(CH_2)_2$  $/Ac_2O/NaOH/H_3O^+/$ H_2CrO_4 ($R^1 = R^2 = H$)	Syn Commun *7* 27 (1977)
	$Li(CH_2)_2CO_2Li/TsOH$ ($R^1 = R^2 = H$)	TL 883 (1978)
	$H_2C{=}CHCH_2MgBr/H_2O/BH_3/H_2O_2$, OH^-/H_2CrO_4 ($R^1 = R^2 = H$)	BSCF 3377 (1973) JOC *42* 1623 (1977)
	$LiCH_2CH{=}CHSiMe_3/CH_3CO_3H$, H_2SO_4 ($R^1 = R^2 = H$)	CC 772 (1977)
	$LiCH_2CH{=}CHSiMe_3$ /*t*-BuO_2H, cat $VO(acac)_2$/MeOH, $BF_3 \cdot OEt_2/CrO_3$, H_2SO_4 ($R^1 = R^2 = H$)	TL *21* 11 (1980) JACS *102* 5004 (1980)

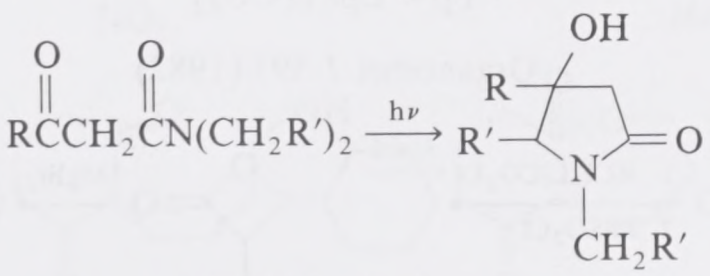
$LiCH_2CH{=}C(OLi)PO(NMe_2)_2/H_2O$ ($R^1 = R^2 = H$)	TL 47 (1976)
Li or $NaC{\equiv}CCH(OEt)_2/H_2$, cat Pd-C/ H_2CrO_4 ($R^1 = R^2 = H$)	JOC *22* 570 (1957) JACS *86* 485 (1964)
 , $TiCl_4$/TsOH ($R^1 = R^2 = H$)	JACS *99* 7360 (1977); *108* 3745 (1986)
 $/H^+$/NaOH, H_2O_2 or NaOBr or HOCl ($R^1 = R^2 = H$)	TL 887 (1972); 923 (1973) JACS *93* 3773 (1971); *94* 4777 (1972); *95* 5321 (1973)
$CH_3CHLiCH{=}C(CN)NMe_2/H_3O^+$ ($R^1 = H$, $R^2 = Me$)	TL *21* 1205 (1980)
$CH_3CHLiCH{=}C(CN)OR/H_3O^+$ ($R^1 = H$, $R^2 = Me$)	JOC *45* 395 (1980)
$H_2C{=}CHCO_2Et$, electrolysis	Rec Trav Chim *93* 47 (1974)
$R^2CH{=}CR^1CO_2CH_3$, Me_3SiCl, electrolysis	TL *21* 5029 (1980)
$R^2CH{=}CR^1CO_2Et$, SmI_2, ROH, (HMPA)	CC 624 (1986); 920 (1987) (intramolecular) TL *27* 5763 (1986)
$MeO_2CCH_2CH_2Sn(n\text{-}Bu)_3$, $TiCl_4$	JOC *50* 5907 (1985)
$RO_2CCH_2CH_2TiCl_3$	JACS *108* 3745 (1986)
$MeO_2CCH_2CH_2Br$; Ce, La, Nd or Sm	CC 475 (1986)
1 $H_2C{=}CHCH_2MgBr/H_2O$/EtMgBr, cat $Cp_2TiCl_2/CO_2/H^+$ ($R^1 = R^2 = H$)	JOMC *160* C8 (1978)
$H_2C{=}CH(CH_2)_2MgBr/H_2O/BH_3/H_2O_2$, $NaOH/H_2CrO_4$ ($R^1 = R^2 = H$)	BSCF 3377 (1973)



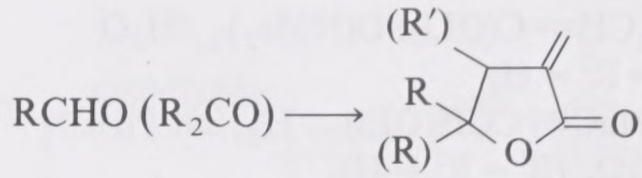
TL *28* 2135 (1987)



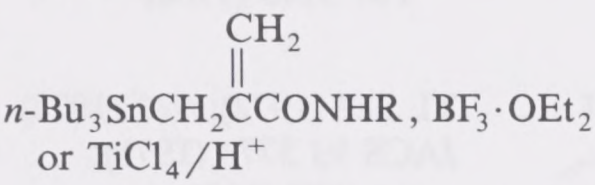
TL *28* 4243 (1987)



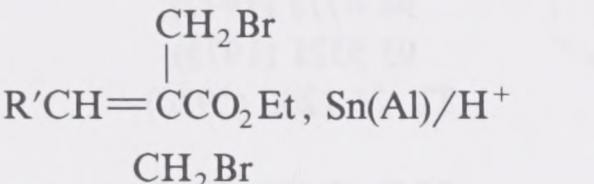
CC 743 (1974)
JOC *43* 1005 (1978)



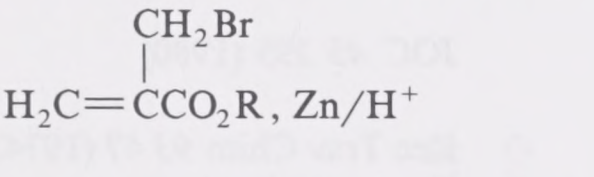
$H_2C{=}CBrSiMe_3$, $TiCl_4/CO$, cat $Ni(CO)_2(PPh_3)_2$ — JACS *104* 6879 (1982)



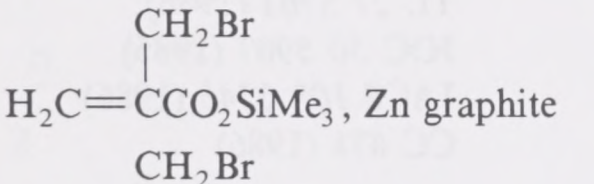
JOC *51* 1856 (1986)



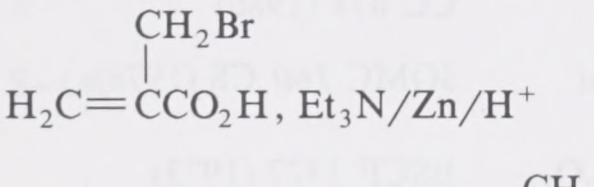
CL 541 (1986)



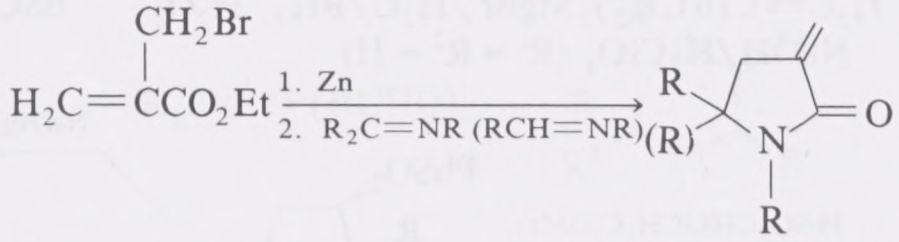
Angew *9* 457 (1970)
J Med Chem *17* 672 (1974); *18* 812 (1975); *19* 309 (1976); *23* 1031 (1980); *25* 650 (1985)
J Pharm Sci *70* 84 (1981)
TL *26* 5693 (1985)



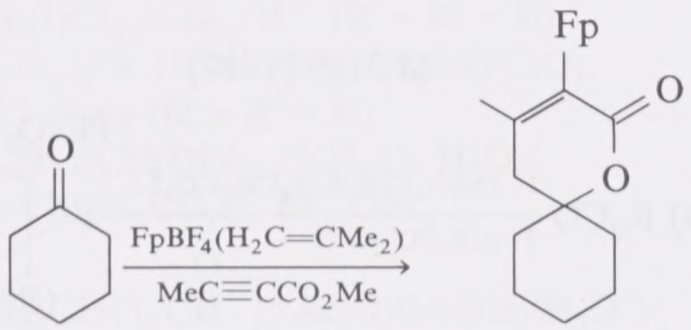
JOC *48* 4108 (1983)



TL *26* 5693 (1985)

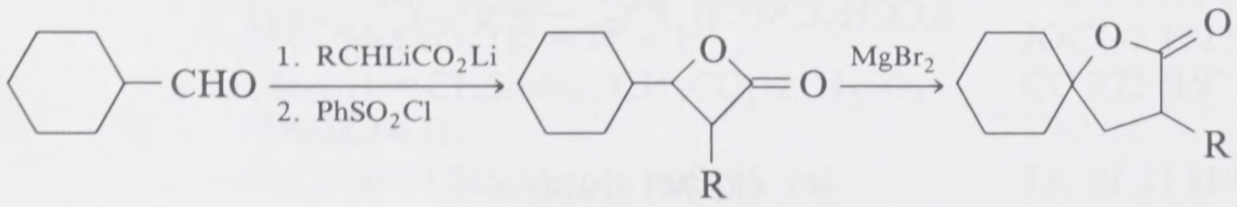


Syn Commun *15* 1233 (1985)
TL *28* 59 (1987)

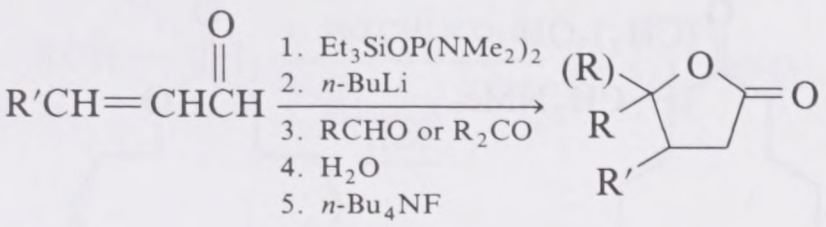


$Fp = CpFe(CO)_2$

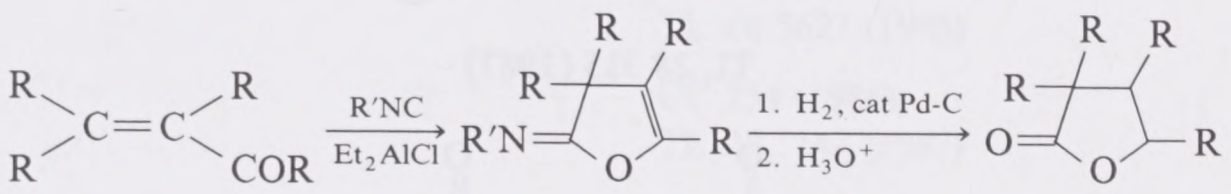
Organomet *1* 397 (1982)



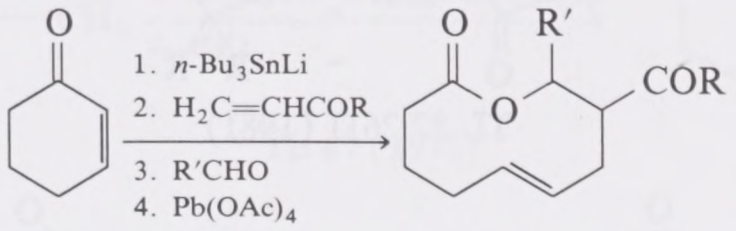
TL *28* 4787 (1987)

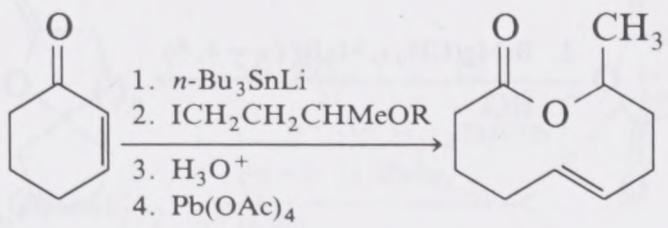


JACS *101* 371 (1979)

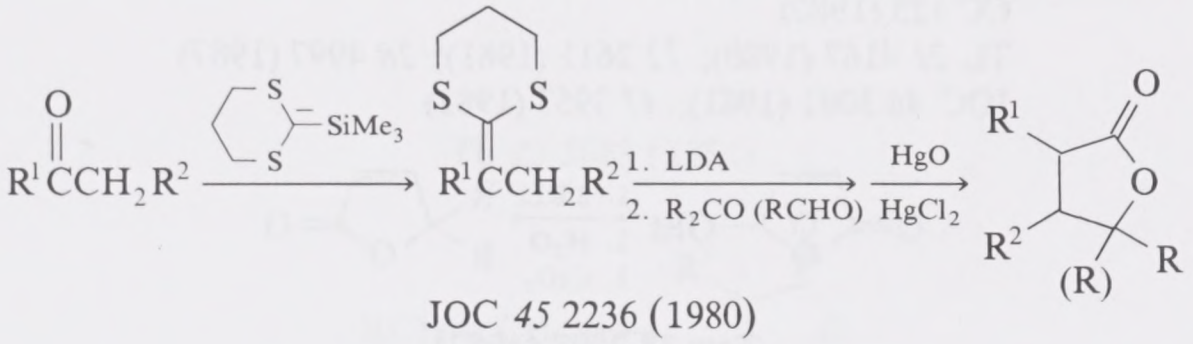


JOC *47* 741 (1982)

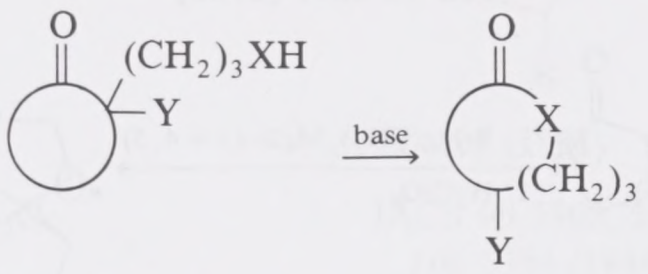




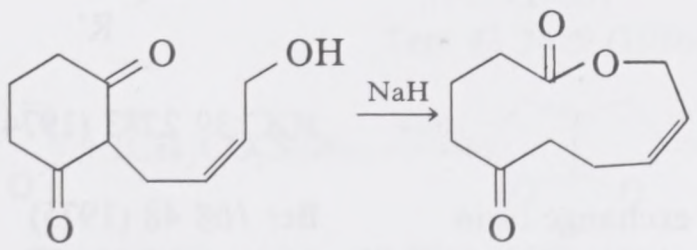
TL *28* 5071 (1987)



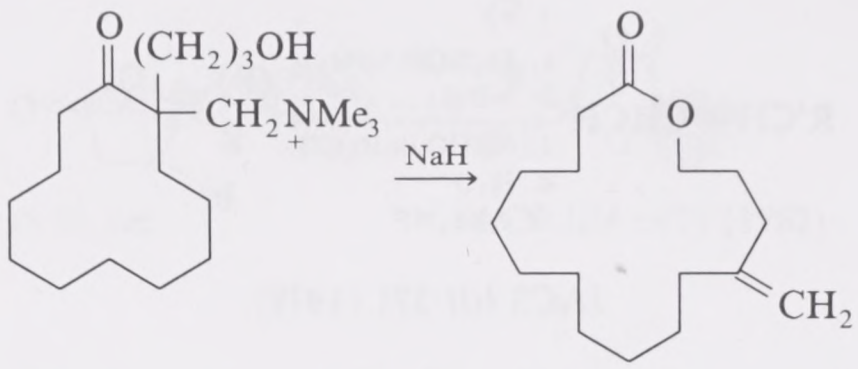
JOC *45* 2236 (1980)



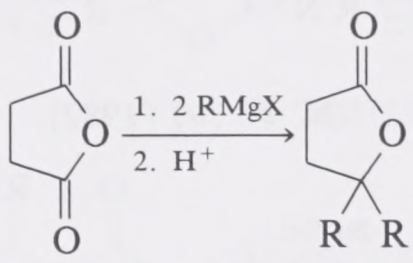
X	Y	
O	NO_2	TL *23* 3521 (1982) Helv *67* 1713 (1984)
	CN	Helv *68* 2115 (1985)
NH	NO_2	Helv *68* 484 (1985)



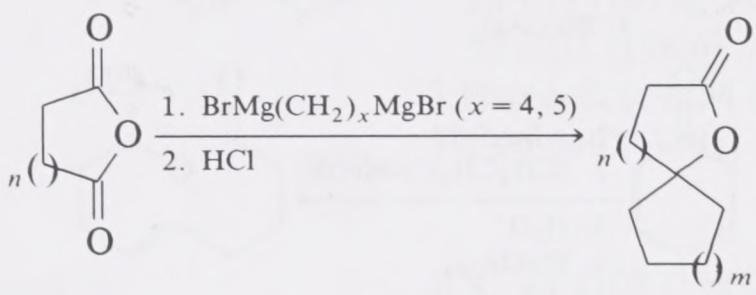
Syn 110 (1976)
JOC *52* 5296 (1987)



TL *28* 315 (1987)

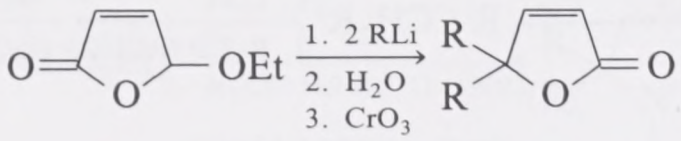


TL *22* 2611 (1981)

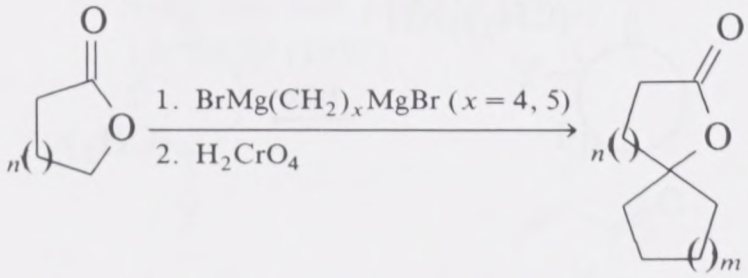


$n = 1, 2$; $m = 1, 2$

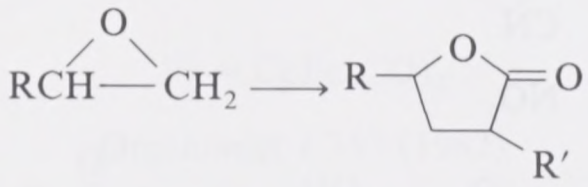
CC 125 (1980)
TL *21* 4167 (1980); *22* 2611 (1981); *28* 4997 (1987)
JOC *46* 3091 (1981); *47* 3953 (1982)



Tetr *38* 2897 (1982)



$n = 0$–3; $m = 1, 2$
JOC *45* 1828 (1980)

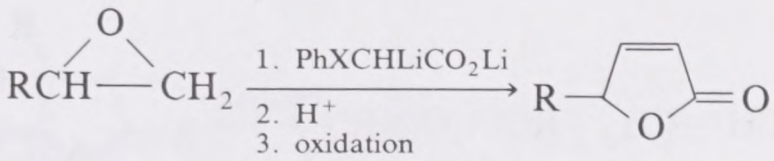




JOC *39* 2783 (1974)

$R'CHLiNCONMe_2$/acid ion exchange resin — Ber *108* 48 (1975)

See also the reaction of epoxides with alpha metallated carboxylic acids and derivatives under page 867, Section 5.



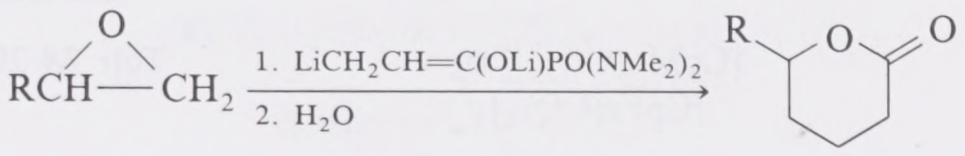
X

S

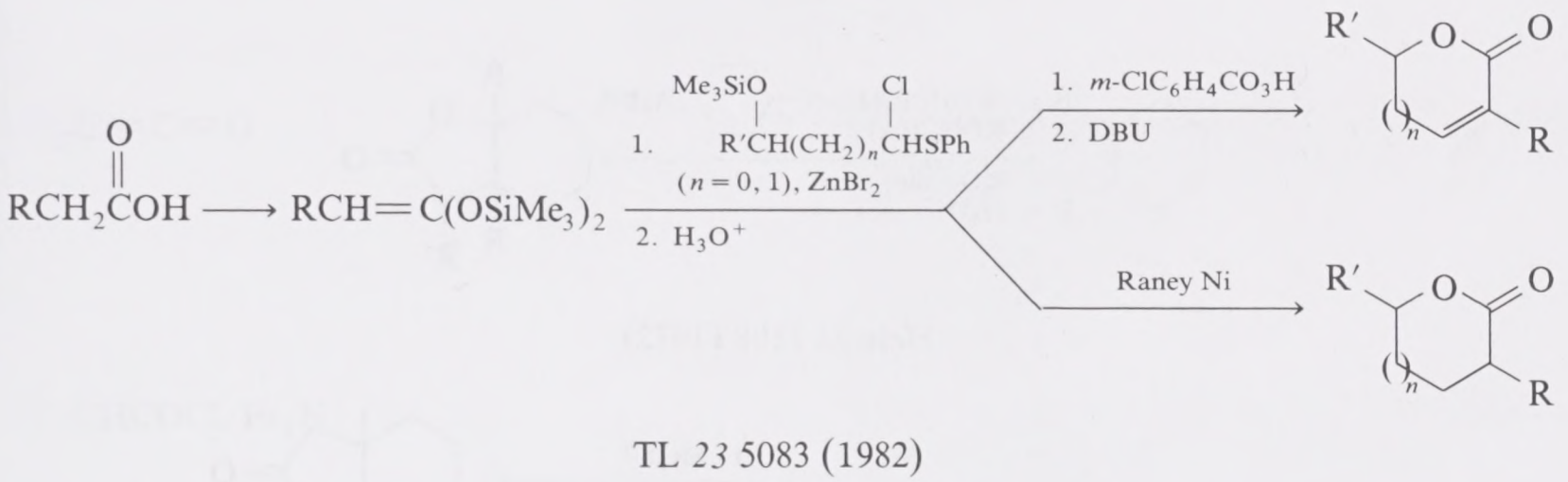
CL 385 (1974)
BCSJ *50* 242 (1977)
TL *26* 5627 (1985)

Se

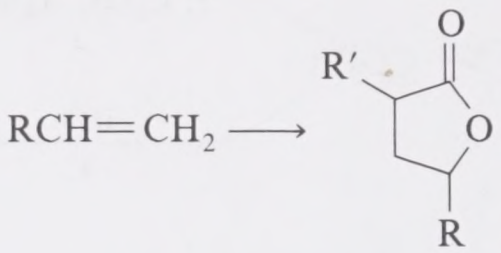
CC 754 (1986)
TL *28* 1147 (1987)



TL 47 (1976)



TL *23* 5083 (1982)

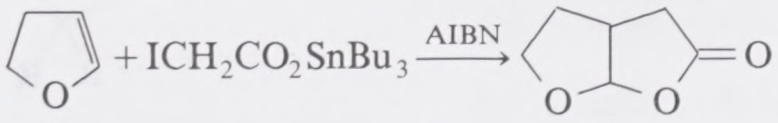


$R'CHBrCO_2H$, $(PhCO_2)_2$

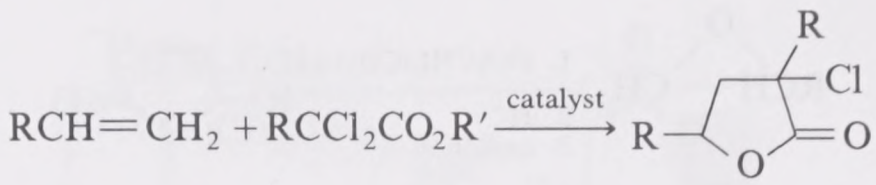
CL 415 (1981)

$R'CH_2CO_2H$, $Mn(OAc)_3 \cdot 2\ H_2O$

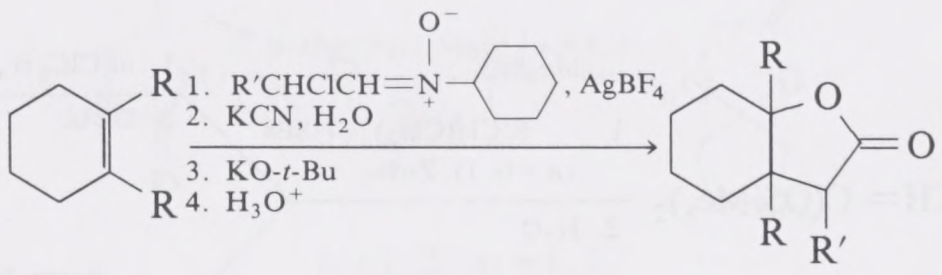
JACS *90* 5903, 5905 (1968); *96* 7977 (1974); *106* 5384 (1984) (intramolecular)
BCSJ *49* 1041 (1976)
Org Syn *61* 22 (1983)
TL *26* 3761 (intramolecular), 4921 ($R' = CN, CO_2Et$) (1985)
JOC *50* 10, 1026 ($R' = CO_2H$, spiro lactones), 3143 (1985)
Tetr *42* 3429 (1986) (mechanism)



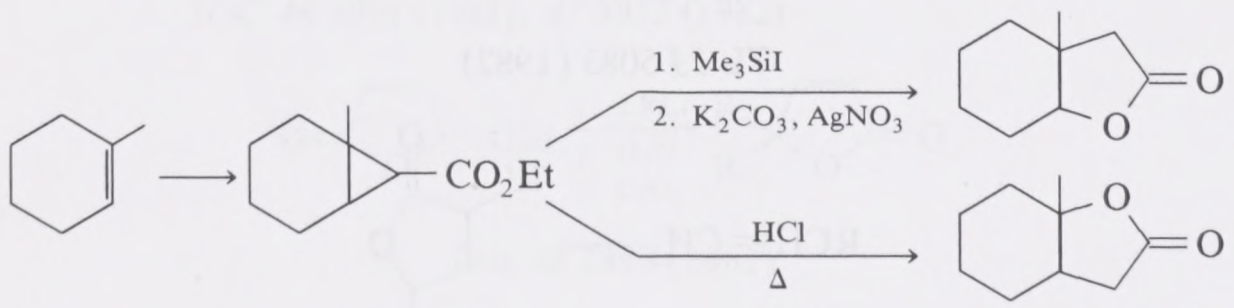
TL *25* 3939 (1984); *27* 3715, 5927 (1986)
Tetr *41* 4039 (1985)



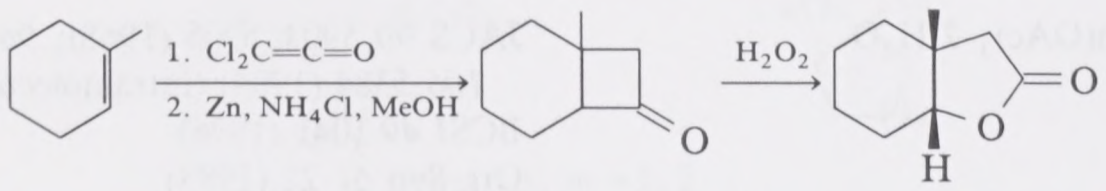
R′	Catalyst	
H	$RuCl_2(PPh_3)_3$	CC 363 (1978)
H, alkyl	$RuCl_2(PPh_3)_3$	JOC *51* 5501 (1986) (intramolecular)
H, alkyl	$FeCl_2[P(OEt)_3]_3$	JOC *51* 5501 (1986) (intramolecular)
Me	$[CpMo(CO)_3]_2$ or $[CpFe(CO)_2]_2$	Tetr *28* 29 (1972)
$SiMe_3$	$RuCl_2(PPh_3)_3$	CC 1011 (1979)



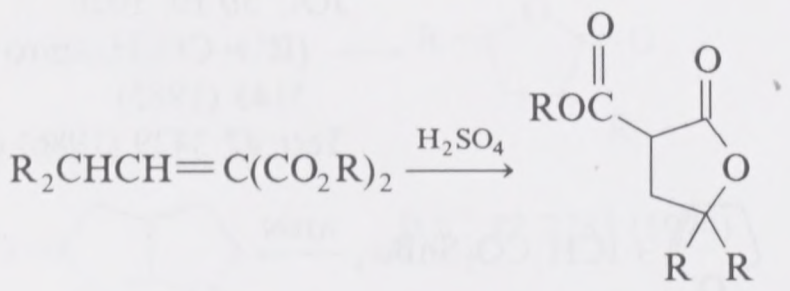
Helv *55* 2198 (1972)



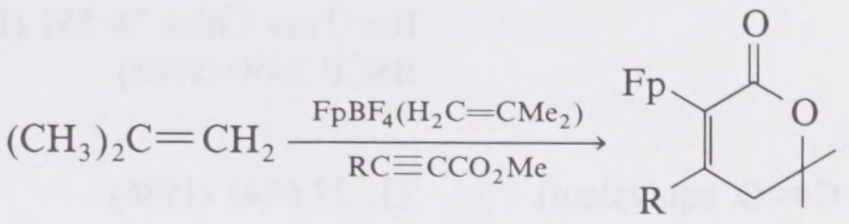
TL *22* 4891 (1981)



JOC *47* 3871 (1982)



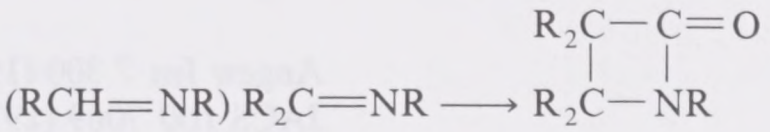
Syn Commun *11* 35 (1981)



R = H, Me

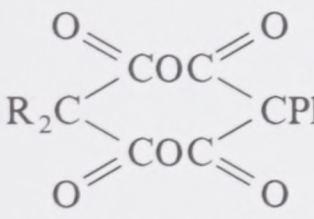
Fp = $CpFe(CO)_2$

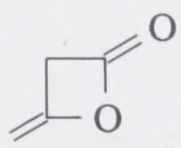
Organomet *1* 397 (1982)

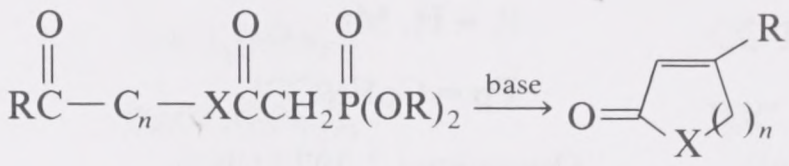


Reviews:

Org Rxs *9* 388 (1957)
Syn 327 (1973)
Chem Soc Rev *5* 181 (1976)
Tetr *34* 1731 (1978)

$R_2C{=}C{=}O$	Ann *356* 51 (1907); *401* 292 (1913); 760 (1977) Ber *50* 1035 (1917); *90* 2460 (1957) JACS *73* 3172 (1951) Tetr *24* 1011 (1968) CC 302 (1977) Syn 989 (1982)
$R_2CHCOCl$, Et_3N	JACS *73* 1204, 4367 (1951); *109* 1798 (1987) Tetr *23* 4769 (1967); *36* 3427 (1980) BSCF 2450 (1968) JOC *34* 2846 (1969); *38* 3437 (1973); *39* 115, 312, 2877 (1974); *41* 1112 (1976) TL 2633, 3135 (1974) Heterocycles *12* 405 (1979) Syn 933 (1980); 989 (1982)
R_2CHCO_2H, CBr_4, PPh_3	Syn 689 (1976)
R_2CHCO_2H, $ClPO(OR)_2$, Et_3N	Syn Commun *6* 435 (1976) Heterocycles *12* 405 (1979)
R_2CHCO_2H, Cl_2PONMe_2, Et_3N	TL *28* 1945 (1987)
	Helv *6* 291, 304 (1923)
$RCOC(N_2)R$, hν	Ber *89* 2759 (1956) Tetr *23* 957 (1967) BSCF 2450 (1968)
$RCOCHN_2$, Ag_2O	Ber *90* 2460 (1957)
RCH_2CO_2R, LDA	See page 873, Section 2.

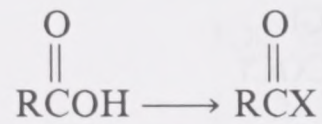
$RC{\equiv}COEt$, Δ	Rec Trav Chim *78* 551 (1959) BSCF 2450 (1968)
 ($CH_3COCH{=}C{=}O$ equivalent)	TL *27* 6241 (1986)

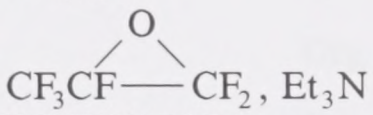
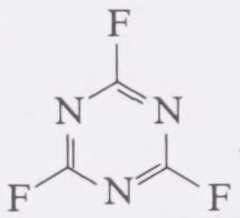
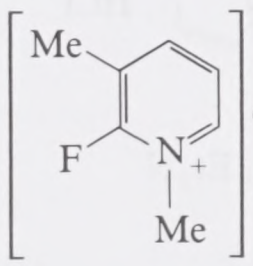


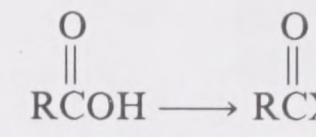
X	
O	Angew Int *7* 300 (1968) JACS *100* 7069 (1978) JOC *44* 4010, 4011 (1979) TL *28* 2717 (1987)
NH	CC 445 (1970)

9. INTERCONVERSION OF NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

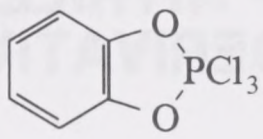
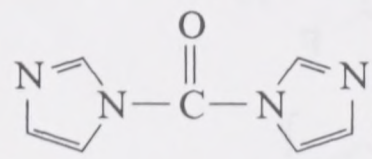
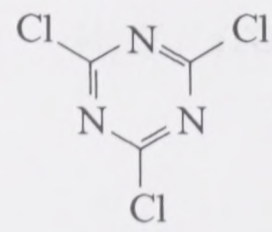
1. Carboxylic Acids to Acid Halides



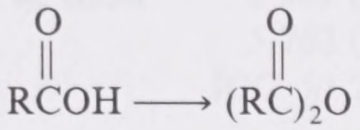
X	Reagent(s)	
F, Cl, Br, I	$Me_2C{=}CXNMe_2$	CC 1180 (1979)
F	SeF_4, py	JACS *96* 925 (1974)
		CL 483 (1977)
	$FClCHCF_2NEt_2$	J Gen Chem USSR *29* 2125 (1959)
	 , py	Syn 487 (1973)
		CL 303 (1976)
Cl	$SOCl_2$	Org Syn Coll Vol *1* 12, 147 (1941); *3* 169, 490, 547, 555, 712 (1955); *4* 154, 263, 339, 715, 739 (1963)
		JOC *50* 2719 (1985)
	$SOCl_2$, DMF	Helv *42* 1653 (1959)

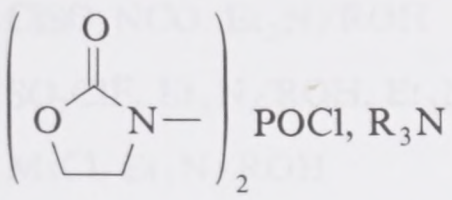
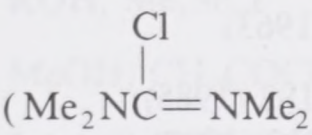
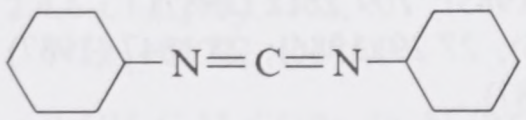


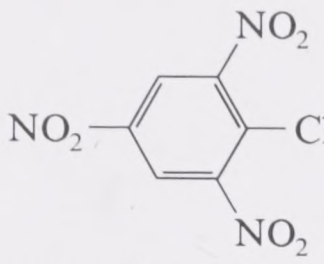
(*Continued*)

X	Reagent(s)	
	$SOCl_2$, py	JACS *75* 2347 (1953) JCS 491 (1963) Can J Chem *46* 2549 (1968)
	$SOCl_2$, py (on KO_2CR)	JACS *85* 643 (1963)
	PCl_3	Org Syn Coll Vol *2* 156 (1943)
	PCl_5	Org Syn Coll Vol *1* 394 (1941) JACS *67* 2239 (1945)
		Ber *96* 1387 (1963) Z Chem *22* 126 (1982) (review)
	CCl_4, Ph_3P	JACS *88* 3440 (1966)
	CCl_4, polymer-PPh_2	CC 622 (1975)
	polymer-PPh_2Cl_2	JACS *96* 6469 (1974)
	PhCOCl	JACS *60* 1325 (1938)
	ClCOCOCl	JACS *42* 599 (1920), *69* 2568 (1947) JCS 3490 (1953) Can J Chem *33* 1515 (1955) JOC *29* 843 (1964)
	OH^-/ClCOCOCl	JACS *42* 599 (1920); *70* 2427 (1948); *87* 3958 (1965) Helv *37* 45 (1954) Can J Chem *33* 1515 (1955) TL 3379 (1977)
	Cl_2CHOMe	Syn 163 (1975) Org Syn *61* 1 (1983)
	XCH_2CCl_2OEt (X = H, Cl)	Rec Trav Chim *76* 969 (1957)
		Ann *694* 78 (1966)
	 , Et_3N	TL 3037 (1979)
Br	PBr_3	JCS 1406 (1934)
	PBr_5	JACS *42* 599 (1920)
	Ph_3PBr_2	Ann *693* 132 (1966) Syn 684 (1982)
	BrCOCOBr	JACS *42* 599 (1920)

2. Carboxylic Acids to Acid Anhydrides



Ac_2O	JACS *63* 699 (1941); *72* 3294 (1950) Org Syn Coll Vol *1* 91, 410 (1941); *3* 449 (1955); *4* 630, 790 (1963)
$H_2C{=}C{=}O$	Org Syn Coll Vol *3* 164 (1955)
$H_2C{=}C(OAc)CH_3$, cat H_2SO_4	Ind Eng Chem *41* 2920 (1949)
RCOCl, 4-vinylpyridine copolymer	TL *27* 4933 (1986)
CH_3COCl	Org Syn Coll Vol *2* 560 (1943)
$COCl_2$, Et_3N	Helv *47* 162 (1964) Org Syn Coll Vol *5* 822 (1973)
ClCOCOCl	JACS *42* 599 (1920)
NaOH/ClCOCOCl	JACS *42* 599 (1920); *76* 5803 (1954)
$ClCO_2Et$, $Et_3N/(Et_3NH)O_2CR$	JOC *28* 1905 (1963)
TsCl, py	JACS *77* 6214 (1955)
$SOCl_2$, py	JACS *70* 2964 (1948) JCS 741 (1952); 2117 (1953)
$SOCl_2$, 4-vinylpyridine copolymer	TL *27* 4937 (1986)
$ClSO_2NCO$, Et_3N	Syn 506 (1982)
$POCl_3$	Org Syn Coll Vol *2* 560 (1943)
$(PhO)_2POCl$, Et_3N	Syn 218 (1981)
$(PhO)(PhNH)POCl$, R_3N	Syn 218 (1981)
	Syn 616 (1981)
Cl_2, $(Me_2N)_3P/Et_3N$	BSCF 3034 (1971)
$(Me_2N)_3P$, CCl_4	BSCF 3034 (1971)
	BCSJ *56* 3529 (1983)
	J lipid Res *7* 174 (1966) JOC *50* 2323 (1985)
polymer-$CH_2N{=}C{=}N$-*i*-Pr	TL 3281 (1972)
$PhCOCH{=}CHCOPh$, *n*-Bu_3P	JOC *29* 1385 (1964)



BCSJ *54* 1470 (1981)

$HC{\equiv}COMe$

JCS 1860 (1954)

$HC{\equiv}COEt$

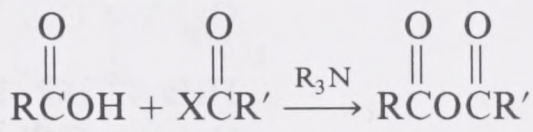
JOC *33* 3808 (1968)

$Me_3SiC{\equiv}COEt$

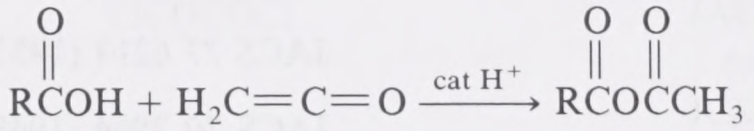
TL *25* 6027 (1984); *27* 3689 (1986); *28* 3971 (1987)
JOC *51* 4150 (1986)
CC 1474 (1987)



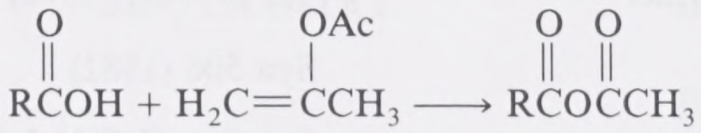
Ber *95* 2073 (1962)



Org Syn *26* 1 (1946)
JCS 2117 (1979)
CL 145 (1979)
TL *28* 4711 (1987)



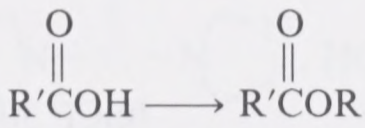
JACS *54* 3427 (1932)



Ind Eng Chem *41* 2920 (1949)

3. Carboxylic Acids to Esters

See also page 941, Section 8.



Review: Tetr *36* 2409 (1980)

alkene, H_2SO_4

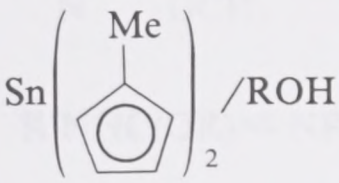
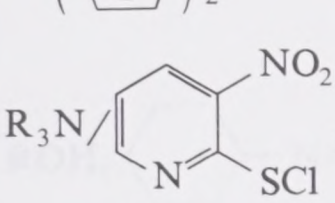
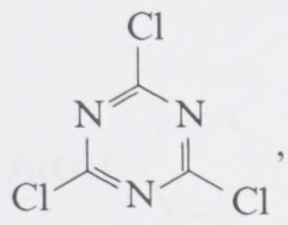
Org Syn Coll Vol *4* 261, 417 (1963)

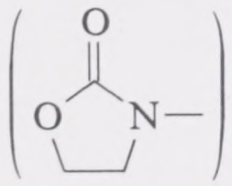
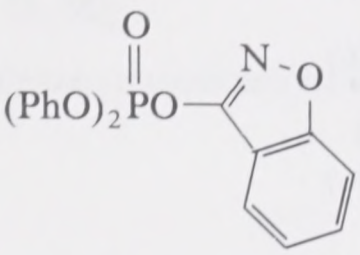
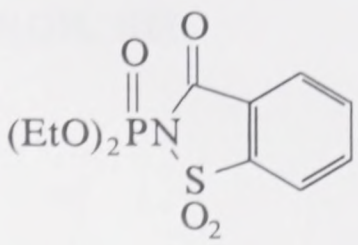
ROH, lipase (enantioselective)

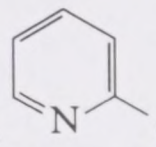
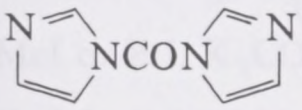
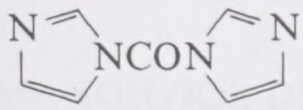
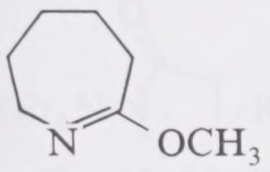
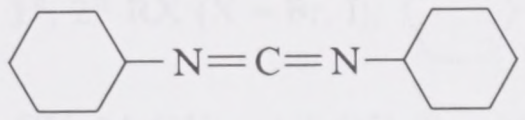
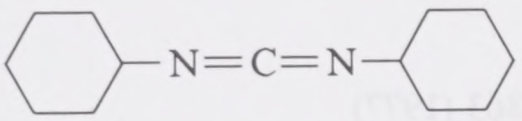
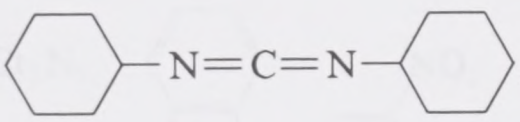
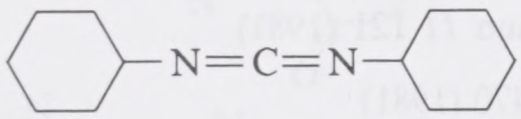
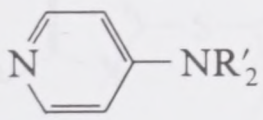
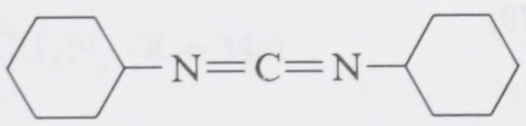
Proc Natl Acad Sci USA *82* 3192 (1985)
JACS *107* 7072 (1985); *109* 2812 (1987)
TL *26* 1857 (1985); *27* 29 (1986); *28* 1647 (1987)
JOC *52* 3477 (1987)

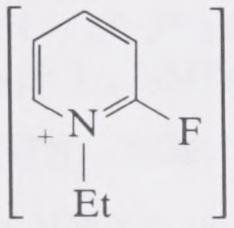
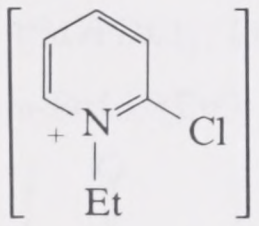
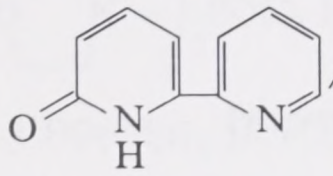
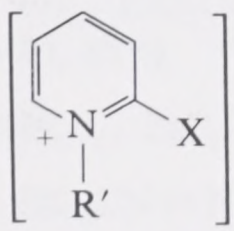
ROH, HCl

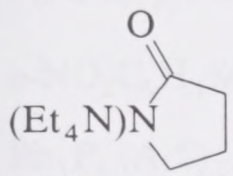
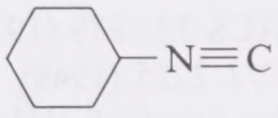
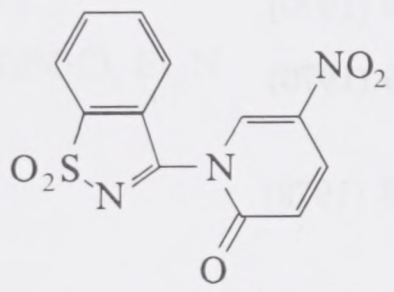
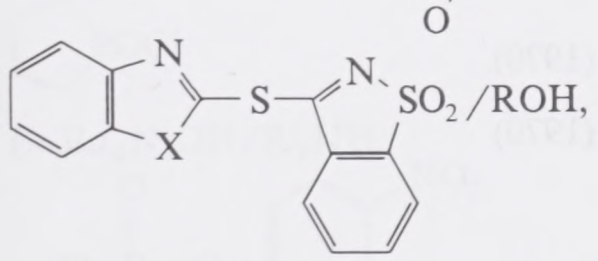
Org Syn Coll Vol *1* 237, 451 (1941); *2* 261, 276, 292 (1943)
JOC *52* 4689 (1987)

ROH, H_2SO_4	Org Syn Coll Vol *1* 241, 254 (1941); *2* 264, 365, 414 (1943); *3* 381 (1955); *4* 329, 532, 635 (1963); *5* 762 (1973) JOC *50* 2128 (1985)
100% H_2SO_4/ROH	JACS *63* 2431 (1941)
ROH, TsOH	Org Syn Coll Vol *3* 610 (1955)
ROH, graphite bisulfate	JACS *96* 8113 (1974)
ArOH, $B(OH)_3$, H_2SO_4	TL 3455 (1971)
ROH, $BF_3 \cdot OEt_2$	TL 4011 (1970) Syn 628 (1972) JACS *108* 468 (1986)
ROH, $BF_3 \cdot 2$ MeOH (R′ = H)	Org Prep Proc Int *14* 177 (1982)
ROH, $AlCl_3$-polymer	TL 1823 (1973)
ROH, cat R'_2SnCl_2 (R′ = Me, Ph)	TL *28* 3713 (1987)
 /ROH	CL 683 (1983)
	CL 979 (1978)
	TL 3029, 3037 (1979)
NaOH/*n*-$BuSO_3Cl/\Delta$ (R = *n*-Bu)	JACS *69* 1046 (1947)
$ClSO_2NCO$, Et_3N/ROH	Syn 506 (1982)
SO_2ClF, Et_3N/ROH, Et_3N	Syn 790 (1981)
MsCl, Et_3N/ROH	TL *23* 3799 (1982) Syn Commun *12* 727 (1982)
TsCl, py/ROH	JACS *77* 6214 (1955)
ROH, Me_3SiCl	BCSJ *54* 1267 (1981)
MeOH, CH_3COCl (R = Me)	JACS *108* 1039 (1986)
2,4,6-$Cl_3C_6H_2COCl$, NEt_3/ROH, DMAP	BCSJ *52* 1989 (1979) JACS *108* 4645 (1986)
o-$BrCH_2C_6H_4COBr$, Et_3N/ROH, Δ	CL 145 (1979)
o-$BrCH_2C_6H_4COBr$, $Et_3N/AgBF_4$, ROH	TL *28* 4711 (1987)
RO_2CCl, py/ROH	TL *28* 1665 (1987)

RO_2CCl, Et_3N/cat DMAP	TL *24* 3365 (1983) JOC *50* 560 (1985)
ROH, $H_2C{=}C(CH_3)COCOCl$, Et_3N or py, (cat DMAP)	TL *28* 1661, 1665 (1987)
$(CF_3CO)_2O$/ROH	Chem Rev *55* 787 (1955) TL 1285 (1964) Tetr *21* 3531 (1965) JOC *30* 927 (1965) Can J Chem *59* 2617 (1981)
$(CF_3CO)_2O$, NaF/ROH	Can J Chem *59* 2617 (1981)
ROH, PPh_3, CCl_4 (on KO_2CR')	JOC *50* 4991 (1985)
ROH (R = 2°, 3° alkyl), *n*-$Bu_3P{\cdot}I_2$, HMPA	Austral J Chem *35* 517 (1982)
$Ph_3P(OTf)_2$/ROH	TL 277 (1975)
py/Me_2NPOCl_2 or $PhOPOCl_2$/ROH	TL 4461 (1978)
$PhOPOCl_2$, DMF/ROH/py	Syn Commun *12* 681 (1982)
n-BuLi/$(EtO)_2POCl$/ROH	JOC *52* 3937 (1987)
 POCl, Et_3N/ROH	Syn 547 (1980)
$Cl_3CPO(OEt)_2$ (R = Et)	Tetr *38* 1457 (1982)
$ROP(OEt)_2$, $EtO_2CN{=}NCO_2Et$ (R = Et, allyl)	BCSJ *40* 2380 (1967)
$ROP(NEt_2)_2$, $EtO_2CN{=}NCO_2Et$	BCSJ *44* 3427 (1971)
ROH, $EtO_2CN{=}NCO_2Et$, Ph_3P	BCSJ *40* 2380 (1967); *44* 3427 (1971) TL 1619 (1973); *27* 5813 (1986) (on pyranose hemiacetals) Syn 1 (1981) (review) JOC *52* 3468, 3784 (1987) JACS *109* 3017 (1987)
ROH, $EtO_2CN{=}NCO_2Et$, PPh_3/NaO_2CPh	JOC *52* 4235 (1987)
ROH, $EtO_2CN{=}NCO_2Et$, polymer-PPh_2	JOC *48* 3598 (1983)
ROH,  , Et_3N	JOC *50* 760 (1985)
 , Et_3N/ROH	CL 123 (1985)

$[(RO)_3\overset{+}{P}CH_3]BF_4^-$ (on $R'CO_2H$ or $R'CO_2Na$)	JOC *49* 4877 (1984)
P_2O_5/ArOH (R = Ar)	Chem Ind 2102 (1964)
ArOH, polyphosphate ester, DMF (R = Ar)	Syn 429 (1979)
ROH,  $O)_2CO$, cat DMAP	CC 473 (1985)
 , ROH, Δ or NaOR	Angew Int *1* 351 (1962)
 /*t*-BuOH, DBU (R = *t*-Bu)	Syn 833 (1982)
 (R = Me)	Syn Commun *12* 453 (1982)
$R'NHC(OR)=NR'$ ($R' = i$-Pr, c-C_6H_{11})	Syn 561 (1979)
ROH, 	Tetr *21* 3531 (1965) Ber *100* 16 (1967) Tetr *37* 233 (1981) (review) Chem Rev *81* 589 (1981) (review)
ArOH, 	Compt Rend *256* 1804 (1963) Tetr *21* 3531 (1965)
ROH,  , TsOH	Acta Chem Scand B *33* 410 (1979)
ROH,  ,  [$R'_2 = Me_2, (CH_2)_5$]	TL 4475 (1978); *28* 4019 (1987) Angew Int *17* 522 (1978) Syn Commun *9* 539 (1979) BCSJ *54* 631 (1981) CC 1132 (1982) Org Syn *63* 183 (1984) JACS *108* 3112 (1986)
 , DMAP, DMAP·HCl/ROH	JOC *50* 2394 (1985)
ROH, $(EtN=C=C(CH_2)_3NMe_2)\cdot HCl$, DMAP	JOC *47* 1962 (1982)

$(R_3O)BF_4$ (R = Me, Et), *i*-Pr_2NEt	TL 4741 (1971) JOC *44* 1149 (1979)
Me_3SOH (R = Me)	JOC *44* 638 (1979)
K_2CO_3/R_3SX or $RSPh_2X$ (X = BF_4, ClO_4) (phase transfer)	Syn 926 (1980)
Me_3SeOH (R = Me)	TL 1787 (1979)
Me_4NOH/Δ (R = Me)	JACS *61* 1290 (1939)
$(R_3NCH_2Ar)OH$, Δ (R = CH_2Ar)	Syn 727 (1974) Austral J Chem *28* 2065 (1975)
ROH, $[Me_2NC(Cl)=\overset{+}{N}Me_2]Cl^-$, py	CL 1891 (1982)
ROH,  BF_4^-, CsF	CL 391 (1980)
 BF_4^-,	CL 563 (1980)
 /ROH, CsF	
ROH,  Y^-, *n*-Bu_3N	BCSJ *50* 1863 (1977)
(R′ = Me, Et; X = Cl, Br; Y = I, BF_4)	
2,4,6-$(NO_2)_3C_6H_2F$, Et_3N/ROH	BCSJ *51* 1866 (1978)
ROH, 2,4,6-$(NO_2)_3C_6H_2Cl$, DMAP	Syn Commun *11* 121 (1981)
ROH, 2,4,6-$(NO_2)_3C_6H_2Cl$, py	BCSJ *54* 1470 (1981)
NaOH or K_2CO_3/Me_2SO_4 (R = Me)	TL 757 (1972)
Et_2SO_4, DBN (R = Et)	Syn Commun *6* 89 (1976)
MeI, KOH, HMPA, EtOH (R = Me)	TL 4063 (1972)
MeI, KOH, DMSO (R = Me)	Tetr *31* 2169 (1979)
MeI, CaO, DMSO (R = Me)	Syn 262 (1972)
MeI, Cs_2CO_3, DMF (R = Me)	JOC *46* 4321 (1981)
EtI, anion exchange resin (R = Et)	JOC *44* 2425 (1979)

RX, $NaHCO_3$, DMF (R = 1°, 2° alkyl)	Syn 961 (1979)
RX, $NaHCO_3$, $[(n\text{-}C_8H_{17})_3NCH_3]Cl$, CH_2Cl_2 (R = 1° alkyl, benzyl)	Syn 957 (1979)
$CsCO_3$ or $Cs(HCO_3)_2$/RX, DMF (R = 1°, 2°, 3° alkyl; benzylic; X = halogen or sulfonate ester)	Helv *56* 1476 (1973) JOC *42* 1286 (1977); *46* 4321 (1981); *52* 3777, 4230 (1987) Syn Commun *13* 553 (1983) CL 1555 (1984) TL *26* 5257 (1985); *28* 1873 (1987)
1°, 2° RI; K_2CO_3 or KOH; acetone	JOC *44* 2425 (1979)
MeI or EtI, K_2CO_3	JOC *50* 2668 (1985)
K_2CO_3 or NaOH/1°, 2° RX, HMPA	TL 689 (1973) JOC *39* 1968 (1974)
Me_4NOH/RX, DMF	Syn Commun *2* 215 (1972)
 /RX, DMF (R = 1°, 2° alkyl; benzylic; allylic)	JOC *51* 546 (1986)
1°, 2° RX; DBU (X = Br, I)	BCSJ *51* 2401 (1978) Org Prep Proc Int *12* 225 (1980)
Cu_2O; 1°, 2° RX (X = Br, I); 	Syn Commun *2* 1 (1972)
$(MeO)_3CH$, MeOH, cat TsOH (R = Me)	JOC *50* 2607 (1985)
$(RO)_2CHNMe_2$	Angew *75* 296 (1963) (2 publications) Helv *48* 1746 (1965) Ann 821 (1974) Tetr *35* 1675 (1979) Syn 135 (1983)
ROH, Et_3N, 	CL 1161 (1980)
 /ROH, Et_3N (X = O, S)	Syn 933 (1982)
CH_2N_2 (R = Me)	Org Syn Coll Vol *2* 165 (1943) JACS *76* 4481 (1954) Ber *89* 933 (1956) Org Syn *41* 16 (1961) J Chem Ed *47* 710 (1970)

CH_2N_2 (R = Me) (*continued*) TL 1397 (1973)
JOC *47* 578, 1962 (1982);
50 2323, 2607 (1985)

$$HOC(CH_2)_nCOH \xrightarrow[2.\ CH_2N_2]{1.\ \text{alumina}} CH_3OC(CH_2)_nCOH$$

JACS *107* 1365 (1985)

$$RCOH + HC{\equiv}CR' \longrightarrow RCOCH{=}CHR'$$

See page 830, Section 5.

4. Carboxylic Acids to Amides

Reviews:

Syn 453 (1972); 549 (1974) (both peptide coupling)

$$RCOH + HNR'_2 \longrightarrow RCNR'_2$$

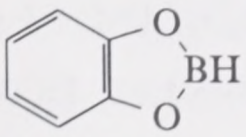
Δ JACS *53* 1879 (1931); *59* 401 (1937);
71 2215 (1949)
Org Syn Coll Vol *1* 3, 83, 111 (1941);
3 590 (1955)
JOC *8* 473 (1943)

$NaBH_4$ JOC *40* 3453 (1975)
Syn 766 (1978)

$BH_3 \cdot Me_3N$ Syn 1013 (1983)

$BH_3 \cdot n\text{-}Bu_3N$ Tetr *26* 1539 (1970)

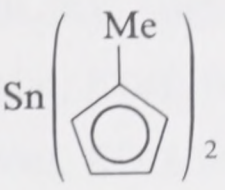
$HB(OR)_2$ (R = *i*-Pr, *t*-Am) Tetr *26* 1539 (1970)



JOC *43* 4393 (1978)

$ClB(OMe)_2$ Tetr *26* 1539 (1970)

BX_3 (X = n-C_8H_{17}, OMe) Tetr *26* 1539 (1970)

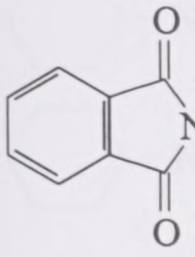
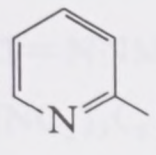
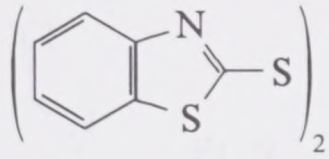
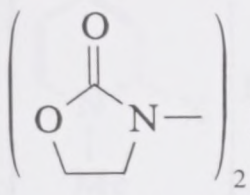
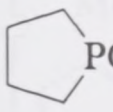
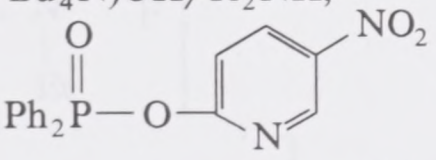
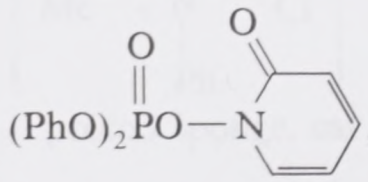


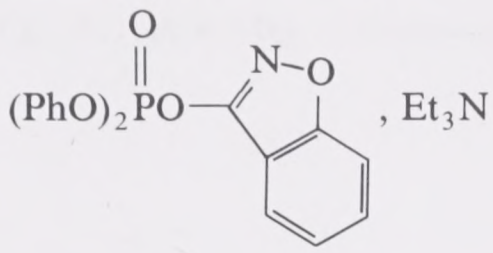
CL 683 (1983)

$TiCl_4$ Can J Chem *48* 983 (1970)

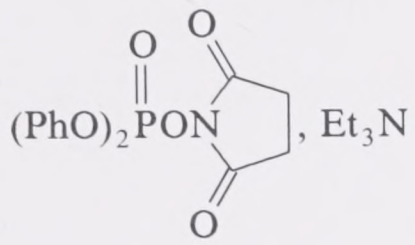
$MeSO_2Cl$, $(n\text{-}Bu_4N)HSO_4$, H_2O, CCl_4 CL 443 (1981) (β-lactams)

TsCl, py JACS *77* 6214 (1955)

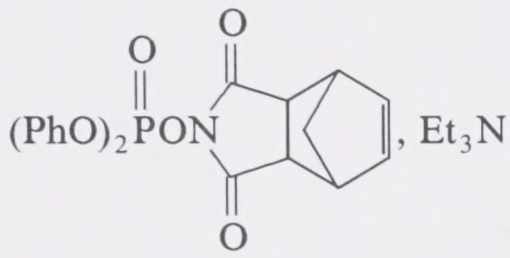
SO_2ClF, Et_3N (1° amines)	Syn 661 (1980)
$ClSO_2NCO$, Et_3N	Syn 506 (1982)
 $NSePh$, n-Bu_3P	JOC *46* 1215 (1981)
P_2I_4	CL 449 (1983)
Ph_3P, CCl_4 or $BrCCl_3$	JOC *36* 1305 (1971)
R_3P, CX_4 (R = n-Bu, Ph, NR_2; X = Cl, Br)	TL 3595 (1971)
$P(NMe_2)_3$, $COCl_2$	Ber *116* 2037 (1983)
$P(NMe_2)_3$, CCl_4	BSCF 3034 (1971)
o-$NO_2C_6H_4SCN$, n-Bu_3P	JOC *44* 2945 (1979)
Ph_3P, $(ArS)_2$, metal reagents	BCSJ *44* 1373 (1971)
Ph_3P,  $S)_2$	TL 1901 (1970)
Ph_3P,  , Et_3N	Syn 287 (1981)
$Ph_3P(OTf)_2$	TL 277 (1975)
 POCl, Et_3N	Syn 547 (1980); 413 (1984) JACS *107* 1421, 4342 (1985)
(PhO)(PhNH)POCl, Et_3N	Syn 288 (1982) TL *28* 4875 (1987)
Ph_2POCl	Syn 385 (1980)
	TL *25* 4825 (1984)
(n-Bu_4N)OH/R'_2NH, 	CL 1367 (1981)
KOH, n-Bu_4NX (X = HSO_4, Br)/ (o-$NO_2C_6H_4O)_2POPh$, R'_2NH	CL 285 (1981)
 , Et_3N	CC 719 (1986)


, Et_3N

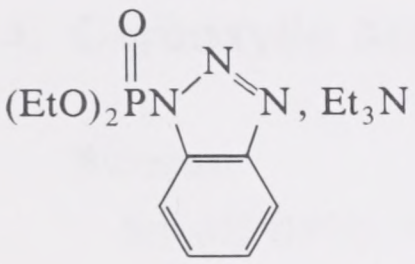
JOC *50* 760 (1985)


, Et_3N

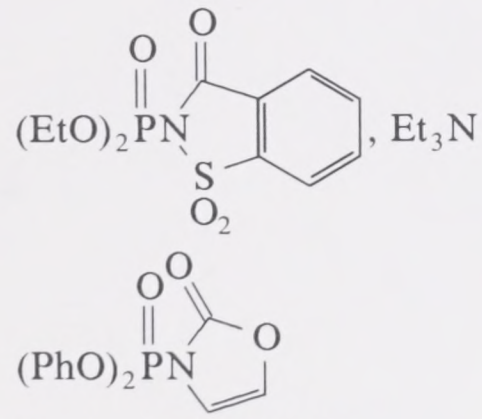
TL *21* 1467 (1980)


, Et_3N

CC 1029 (1980)


, Et_3N

TL *26* 1341 (1985)


, Et_3N

CL 123 (1985)

TL *22* 1257 (1981)

$(PhO)_2PON_3$, Et_3N

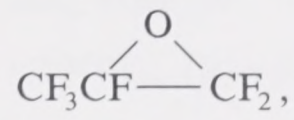
JACS *94* 6203 (1972)

$(EtO)_2POCN$, Et_3N

TL 1595 (1973)

$Me_3SiC{\equiv}COEt$, cat HgO

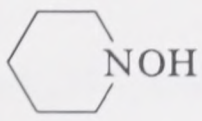
JOC *51* 4150 (1986)



CL 483 (1977)

ROCOCl (R = Me, *i*-Bu)

Syn 385 (1980)
JOC *50* 2323 (1985)
TL *28* 939 (1987)

MeO_2CCl, 

TL 2697 (1971)

EtO_2CCl, Et_3N

Ann *673* 186 (1964)
JCS C 3540 (1971)
JCS Perkin I 2909 (1982)

t-BuCOCl, Et_3N

Tetr *11* 39 (1960)

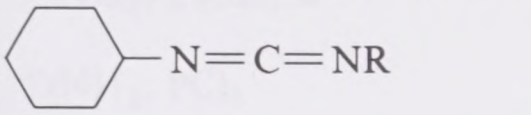
t-BuCOCl, DMAP, py

TL *28* 1131 (1987)

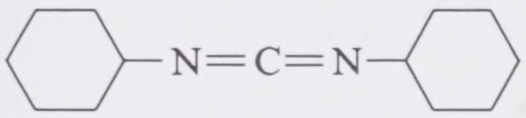


Angew Int *1* 351 (1962)

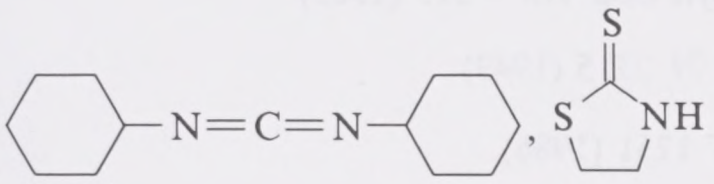
1-cyclohexyl-3-(2-morpholinoethyl)-carbodiimide metho-4-*p*-toluenesulfonate — TL *28* 3163 (1987)



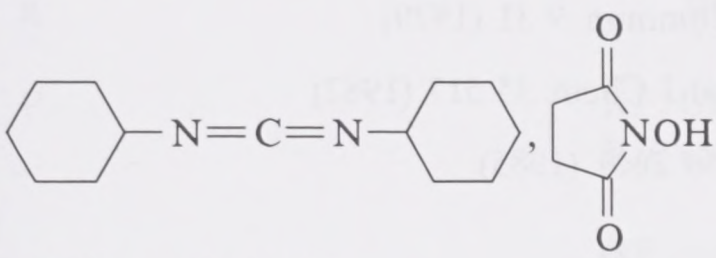
JOC *21* 439 (1956)



Chem Ind 1087 (1955)
JACS *77* 1067 (1955); *78* 1367 (1956)
Ber *92* 2813 (1959)
Tetr *37* 233 (1981) (review)
Chem Rev *81* 589 (1981) (review)
JOC *52* 5717 (1987)



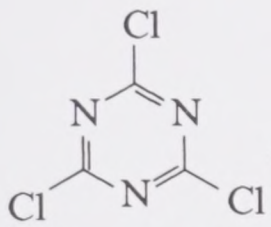
TL *21* 841 (1980)
Pure Appl Chem *53* 1141 (1981)



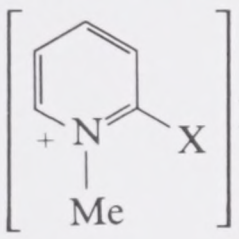
JCS Perkin I 2909 (1982)

PhCCl=NNMePh — JACS *102* 4537 (1980)

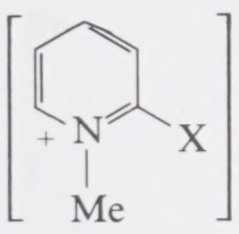
$2,4,6\text{-}(NO_2)_3C_6H_2F$ — CL 647 (1977)
BCSJ *51* 1866 (1978)



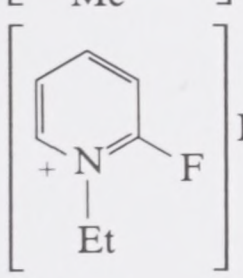
, Et_3N — TL 3037 (1979)



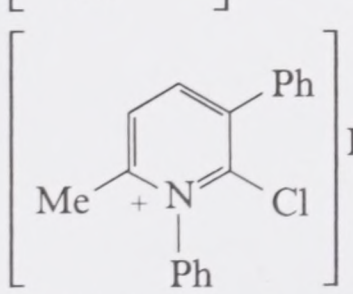
I^- (X = Cl, Br, I), *n*-Bu_3N — JCS 4650 (1964)
CL 1163 (1975)



OTs^- (X = F, Cl), *n*-Bu_3N — CL 57 (1976)

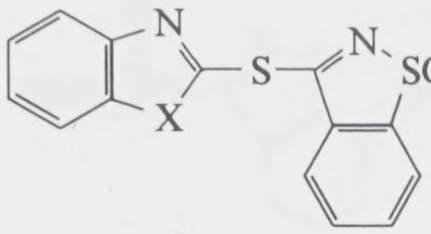


BF_4^-, CsF — CL 391 (1980)



BF_4^-, — CL 1551 (1981)

proton sponge, cat DMAP



SO_2 (X = O, S) — Syn 933 (1982)

$$RCOH \longrightarrow RCNR'R''$$

$HCONH_2$, Δ (R′ = R″ = H)	JACS *71* 2215 (1949)
NH_2CONH_2, Δ (R′ = R″ = H)	JACS *71* 2215 (1949) Org Syn Coll Vol *4* 513 (1963)
$CH_3CONHCONH_2$, Δ (R′ = R″ = H)	JACS *71* 2215 (1949)
R′NCO (R″ = H)	TL *27* 1251 (1986)
$R'R''NPOCl_2$ (R′ = R″ = Me or Et)	Syn Commun *9* 31 (1979)
$(Me_2N)_3P \cdot I_2$, HMPA (R′ = R″ = Me)	Austral J Chem *35* 517 (1982)
$R'N_3$, Ph_2PX (X = Ph, OEt; R″ = H)	JOC *50* 2601 (1985)

$$HCONa \xrightarrow[2.\ RNH_2 \text{ or } (RNH_3)Cl]{1.\ t\text{-BuCOCl, 18-crown-6}} HCNHR$$

Recl J R Neth Chem Soc *101* 460 (1982)

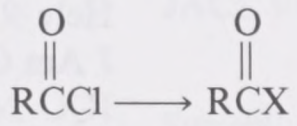
5. Carboxylic Acids to Nitriles

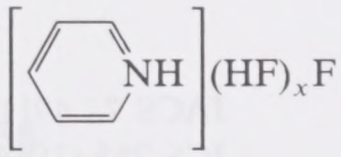
$$RCOH \longrightarrow RCN$$

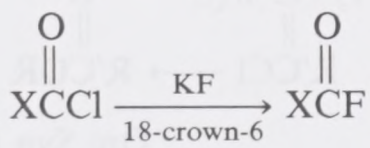
NH_3, silica gel, Δ	Org Syn Coll Vol *4* 62 (1963)
NH_3, ethyl polyphosphate, Δ	Syn 142 (1983)
NH_2CONH_2/Δ	Org Syn Coll Vol *3* 768 (1955)
ArCN, Δ (R = aryl)	JOC *23* 1350 (1958)
$NCCH_2CH_2CHMeCN$, cat H_3PO_4, Δ	JOC *36* 3050 (1971)
CH_3SO_2Cl, $py/NH_3/CH_3SO_2Cl$	Org Prep Proc Int *14* 396 (1982)
$ClSO_2NCO$/DMF	Ber *100* 2719 (1967) Tetr *24* 1063 (1968) Org Syn *50* 18 (1970) Syn Commun *12* 25 (1982)
$ClSO_2NCO/Et_3N$	TL 1631 (1968)

$PhSO_2NH_2$, Δ	JCS 763 (1946)
$TsNH_2$, TsOH, Δ	JCS 763 (1946)
$TsNH_2$, PCl_5	Org Syn Coll Vol *3* 646 (1955)

6. Acid Halides to Other Acid Halides



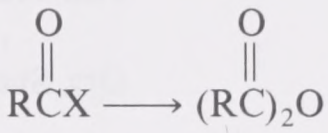
X	Reagent(s)	
F	KF, CH_3CN	CL 761 (1981)
	KF, cat 18-crown-6	JACS *96* 2250 (1974) JOC *44* 1016 (1979)
	KF, cat $(Et_3NCH_2Ph)Cl$	Syn Commun *12* 513 (1982)
	KF, CF_3COCF_3	JOC *31* 2316 (1966)
	KF, CaF_2, sulpholane	CC 791 (1986)
	n-Bu_4NF	JOC *49* 3217 (1984)
	ZnF_2, py	BCSJ *51* 1267 (1978)
	KHF_2	Ber *89* 862 (1956)
		JOC *44* 3872 (1979)
	Na_2SiF_6, Δ	Angew *71* 274 (1959)
	KSO_2F	Ber *91* 2553 (1958)
	R_2NSF_3	Syn 801 (1975)
Br	HBr	Ber *46* 1417 (1913)
	Me_3SiBr	Syn 216 (1981)
I	HI	Ber *46* 1417 (1913) JACS *55* 374 (1933)
	NaI, CH_3CN	Syn 715 (1981); 237 (1982)
	Me_3SiI	Syn 216 (1981)



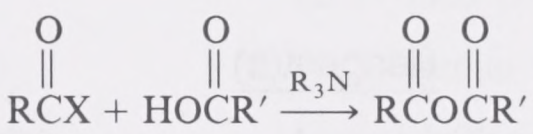
X = OR, NR_2

JOC *44* 1016 (1979)

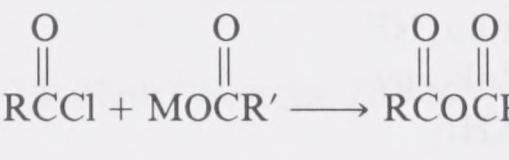
7. Acid Halides to Acid Anhydrides



H_2O, py	JACS *71* 2242 (1949)
H_2O, py, $NaHCO_3$ (R = Ar)	Angew Int *7* 465 (1968)
H_2O, Cl_3CCOCF_3/py	JOC *51* 3390 (1986)
py/H_2O	Org Syn Coll Vol *3* 28 (1955)
Ac_2O	Helv *9* 177 (1926) J Am Oil Chem Soc *31* 151 (1954) JOC *24* 388 (1959)

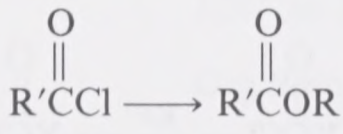


Org Syn *26* 1 (1946)
JCS 2117 (1953)
Org Syn Coll Vol *3* 28 (1955)
CL 145 (1979)
TL *27* 4933 (1986); *28* 4711 (1987)



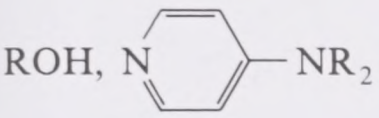
M	
Na	JACS *73* 4911 (1951) JCS 755 (1964) Rec Trav Chim *85* 627 (1966) Org Syn *50* 1 (1970)
K	JACS *61* 684 (1939); *69* 2231 (1947)
Tl	JACS *90* 2422 (1968)
Ag	JACS *75* 232 (1953)

8. Acid Halides to Esters



ROH	Org Syn Coll Vol *5* 1 (1973) JACS *108* 468 (1986)
ROH, Et_3N	Org Syn Coll Vol *5* 258 (1973)
ROH, py	JACS *73* 5487 (1951); *109* 6726, 7838 (1987) JOC *21* 1362 (1956)

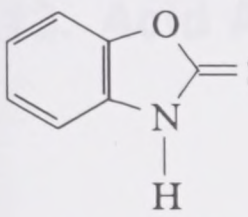
ROH, $PhNMe_2$ — JACS *54* 2088 (1932); *65* 986 (1943)
Org Syn Coll Vol *3* 142 (1955); *5* 171 (1973)

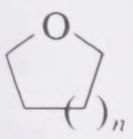
ROH,  — Angew Int *17* 569 (1978)
Tetr *34* 2069 (1978)
JACS *107* 3279 (1985); *109* 6726 (1987)
JOC *50* 2390 (1985)

ROH, Mg — Org Syn Coll Vol *3* 144 (1955)

LiOR — JOC *35* 1198 (1970); *52* 2927 (1987)
Org Syn *51* 96 (1974)

TlS-*t*-Bu/ROH, $Hg(O_2CCF_3)_2$ — JACS *97* 3515 (1975)

 — Syn 991 (1981)

 ($n = 1, 2$), NaI [$R = I(CH_2)_{n+3}$] — TL *23* 681 (1982)

$$RCX \xrightarrow{2\ Me_2\overset{+}{S}O\bar{C}H_2} RCO\bar{C}H\overset{+}{S}OMe_2 \xrightarrow[R'OH]{h\nu} RCH_2COR'$$

X = halogen, OPh

JACS *86* 1640 (1964)

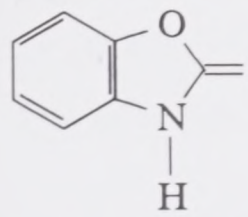
9. Acid Halides to Amides

$$RCCl \longrightarrow RCNR'_2$$

NH_3 ($R' = H$) — JACS *71* 2215 (1949)
Org Syn Coll Vol *3* 490 (1955)

R'_2NH — JACS *71* 2215 (1949); *108* 1039 (1986)
Org Syn Coll Vol *4* 339 (1963); *5* 387 (1973)

R'_2NH, NaOH — Org Syn Coll Vol *1* 99 (1941)

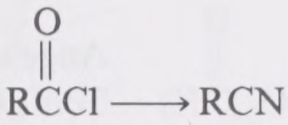
 — Syn 991 (1981)

polymer-ArOH, py/R'_2NH — Syn Commun *12* 709 (1982)

$$RCF + Me_3SiNR_2 \xrightarrow{\text{cat } n\text{-}Bu_4NF} RCNR_2$$

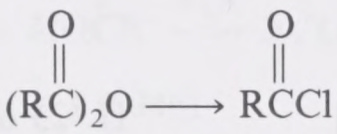
TL *28* 5099 (1987)

10. Acid Halides to Nitriles



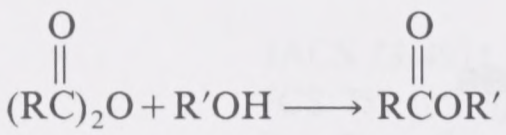
H_2NCONH_2, Δ	Org Syn Coll Vol *3* 768 (1955)
H_2NCONH_2, H_2NSO_3H, Δ	Chimia *25* 94 (1971)
$H_2NSO_2NH_2$, Δ	TL *23* 1505 (1982)
$TsNH_2$, PCl_5, Δ	Org Syn Coll Vol *3* 646 (1955)
$(PNCl_2)_n$ ($n = 3, 4$), Δ	TL 3825 (1973)

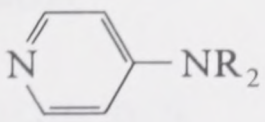
11. Acid Anhydrides to Acid Halides

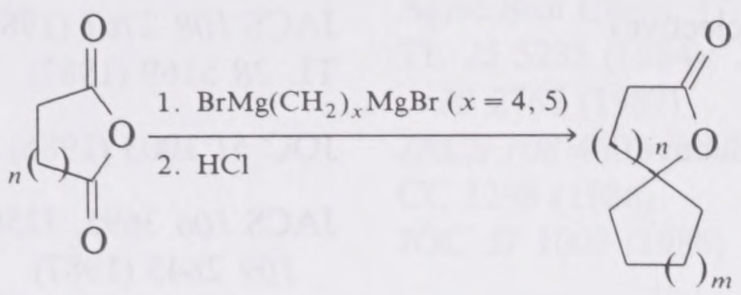


PCl_5	Org Syn Coll Vol *2* 528 (1943)
	Ber *96* 1387 (1963) Z Chem *22* 126 (1982) (review)

12. Acid Anhydrides to Esters



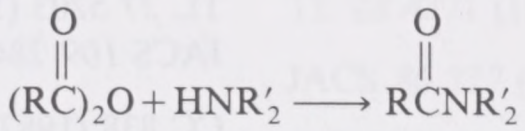
Δ	Org Syn Coll Vol *3* 169 (1955)
TsOH	Org Syn Coll Vol *4* 304 (1963)
TsOH, RCO_2H	JACS *75* 3489 (1953)
Zn, Mg or $ZnCl_2$	JACS *54* 2088 (1932)
$ZnCl_2$	Org Syn Coll Vol *3* 141 (1955)
cat $COCl_2$	CC 114 (1987)
Me_3SiCl	TL *24* 1189 (1983) JOC *52* 5034 (1987)
NaOAc	Org Syn Coll Vol *1* 285 (1941)
py	JACS *109* 7838 (1987)
	Angew Int *8* 981 (1969); *17* 569 (1978) Syn 619 (1972) Tetr *34* 2069 (1978) JACS *108* 4603 (1986) JOC *52* 3784, 4495 (1987)



$n = 1, 2;\ m = 1, 2$

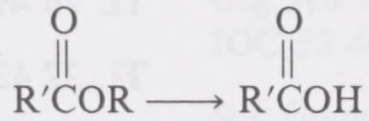
CC 125 (1980)
TL *21* 4167 (1980); *22* 2611 (1981); *28* 4997 (1987)
JOC *46* 309 (1981); *47* 3953 (1982)

13. Acid Anhydrides to Amides



Δ	Org Syn Coll Vol *2* 11 (1943)
py	Org Syn Coll Vol *4* 5 (1963)
RCO_2H, H_2O	Org Syn Coll Vol *3* 661 (1955)
polymer-ArOH, py	Syn Commun *12* 709 (1982)
cat $CoCl_2$	CC 114 (1987)

14. Esters to Carboxylic Acids

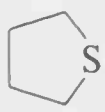


Reviews:

Org Rxs *24* 187 (1976) (S_N2-type)
Tetr *36* 2409 (1980)
Ann Rep Med Chem *19* 263 (1984) (enzymes)
Angew Int *24* 617 (1985) (enzymes)

cholesterol esterase (enantioselective)	JOC *52* 1765, 2608 (1987)
pig liver esterase (enantioselective)	JACS *104* 7294 (1982); *106* 3695 (1984); *108* 4603 (1986) Helv *66* 2501 (1983) Angew Int *23* 64, 66, 67 (1984) CC 236 (1984); 808, 1545 (allenic esters) (1986); 1041 (1987) (diester) TL *26* 2073, 4957, 5831 (1985); *27* 2543, 4639, (1986); *28* 781, 1887, 2767, 3103, 4661 (1987) JOC *51* 1003, 2047 (1986); *52* 4565 (1987) Bioorg Chem *14* 176 (1986) Chimia *40* 314 (1986) Ann 687 (1986)

protease subtilisin (enantioselective)	JACS *108* 2767 (1986) TL *28* 5169 (1987)
various cellulases (enantioselective)	JOC *51* 1003 (1986)
porcine pancreatic lipase (enantioselective)	JACS *106* 3695, 7250 (epoxy esters) (1984); *109* 2845 (1987) CC 1563 (1985); 1298 (1986); 1080 (1987) TL *26* 2073 (1985); *27* 5707 (1986); *28* 531, 1973, 2767, 2989, 3471, 4661, 4669 (1987) JOC *52* 1765 (1987)
Candida cylindracea lipase (enantioselective)	JOC *51* 1003 (1986); *52* 1765 (1987) JACS *108* 6421 (1986); *109* 2845 (1987) TL *27* 2843 (1986); *28* 2767, 2989, 4661 (1987)
Mucor meihei lipase (enantioselective)	CC 1298 (1986) TL *27* 5203 (1986) JACS *109* 2845 (1987)
Pseudomonas fluorescens lipase (enantioselective)	CC 838 (1987)
lipase-MY (enantioselective)	JOC *52* 3211 (1987) (trifluoromethyl carbinol esters)
lipase Amano A or Amano A-6 (enantioselective)	TL *27* 5241 (1986)
lipase Amano P (enantioselective)	JOC *52* 5079 (1987)
α-chymotrypsin (enantioselective)	JACS *83* 4228 (1961); *90* 3495 (1968); *108* 2767 (1986) JOC *49* 3657 (1984); *51* 1003 (1986) TL *26* 4957 (1985); *28* 4661, 4935 (1987)
baker's yeast (enantioselective)	TL *27* 4293 (1986)
pancreatin (enantioselective)	Agric Biol Chem *46* 1593 (1982) JOC *52* 5079 (1987)
steapsin (enantioselective)	Agric Biol Chem *46* 1593 (1982) JOC *52* 5079 (1987)
Trichoderma S (enantioselective)	Agric Biol Chem *37* 1687, 1691, 1695 (1973); *38* 1961, 1965 (1974); *39* 89 (1975)
Saccharomyces sp. (enantioselective)	Biochim Biophys Acta *316* 363 (1973)
Bacillus subtilis var. *Niger* (enantioselective)	Agric Biol Chem *37* 1687, 1691, 1695 (1973); *38* 1961, 1965 (1974); *39* 89 (1975) Tetr *36* 91 (1980) JACS *108* 4603 (1986)
bacterium *Corynebacterium equi* (IFO 3730) (enantioselective)	TL *25* 5235 (1984); *28* 1303 (1987) (α-benzyloxy esters) CL 217 (1986) (arylsulfinyl esters)
mold *Rhizopus nigricans* (enantioselective)	JOC *48* 3017 (1983); *49* 675 (1984); *52* 2400 (1987)

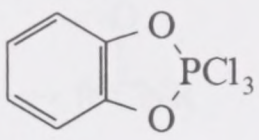
other microbiological reagents (enantioselective)	Agric Biol Chem *37* 1687 (1973) TL *25* 5235 (1984); *27* 5203 (1986); *28* 2767 (1987) JACS *108* 4603 (1986); *109* 2845 (1987) CC 1298 (1986) JOC *51* 1003 (1986)
H_2, cat Pd (R = benzylic)	Org Rxs *7* 263 (1953)
cat Pd-C, 1,4-cyclohexadiene, CH_3OH ($R = CH_2Ph$)	TL *28* 3225 (1987)
$(NH_4)O_2CH$, cat Pd-C ($R = CH_2Ph$)	Syn 929 (1980)
$KO_2CCHEt(CH_2)_3CH_3$, cat $Pd(PPh_3)_4$-PPh_3 (R = allylic)	JOC *47* 587 (1982)
cat $Pd(PPh_3)_4$, R_2NH (R = allylic)	Angew Int *23* 71 (1984) TL *28* 4371 (1987)
Li, NH_3 (R = Me)	JACS *80* 217 (1958)
Zn ($R = CH_2CCl_3$)	Syn 457 (1976) JOC *52* 1790 (1987)
Zn, H_2O, HOAc ($R = CH_2CCl_3$)	JACS *88* 852 (1966)
Zn, MeOH (R = aryl)	TL *22* 335 (1981)
$LiOH/H_3O^+$	JACS *108* 4603 (1986)
$NaOH/H_3O^+$	JACS *58* 1014 (1936); *109* 6726 (1987) Org Syn Coll Vol *1* 379, 391 (1941); *3* 526, 531, 652 (1955); *4* 582, 616, 628 (1963) JOC *50* 2128 (1985)
KOH/H_3O^+	Org Syn Coll Vol *3* 267 (1955); *4* 608, 633 (1963) JOC *52* 4647 (1987)
KOH, Al_2O_3/H_3O^+	Syn Commun *11* 413 (1981)
$Ba(OH)_2/H_3O^+$	Org Syn Coll Vol *4* 635 (1963)
NaO_2, DMSO (R = Me)	JOC *44* 4727 (1979)
KO-*t*-Bu, DMSO (R = Me)	TL 2969 (1964)
2 KO-*t*-Bu, 1 H_2O (R = 1°, 3° alkyl)	JOC *42* 918 (1977) TL *28* 1131 (1987)
Na_2S, H_2O ($R = p\text{-}NO_2C_6H_4CH_2$)	JOC *43* 1243 (1982)
Na_2S, CH_3CN [$R = (CH_2)_nCl$; $n = 4, 5$]	Syn Commun *4* 307 (1974)
KSCN, DMF (R = Me, $PhCH_2$)	JOC *37* 744 (1972) Syn Commun *5* 305 (1975)
EtSH, AlX_3 (X = Cl, Br) (R = Me, $PhCH_2$)	TL 5211 (1978) JOC *46* 1991 (1981)
Me_2S or  , AlX_3 (X = Cl, Br) (R = Me, Et, *n*-Pr, *i*-Pr)	JOC *46* 1991 (1981); *50* 3957 (1985)

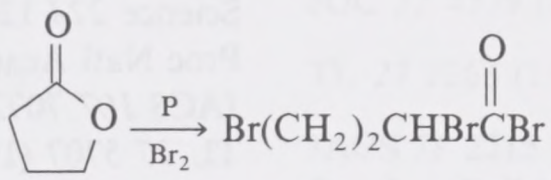
LiSMe (R = Me or lactone)	TL 3859 (1977) JACS *102* 3904 (1980)
NaSMe (R = 9-anthrylmethyl, lactone)	Ber *83* 265 (1950) JACS *96* 590 (1974)
NaSEt, DMF (R = Me)	Austral J Chem *25* 1731 (1972)
LiS-*n*-Pr, HMPA (R = Me)	TL 4459 (1970) JACS *106* 5304 (1984) JOC *52* 4634 (1987)
NaS-*n*-Pr, DMF (R = Me, Et, $PhCH_2$)	JOC *27* 739 (1962)
NaSPh, DMF (R = Me, benzylic, phenacyl)	JOC *29* 2006 (1964)
$(NaSCH_2)_2$, CH_3CN [R = $CH_2CH_2Cl(Br)$]	Syn 510 (1975)
Na_2CS_3, CH_3CN [R = $CH_2CH_2Cl(Br)$]	Syn 715 (1974)
$KSeO_3K$ (lactone)	JOC *31* 1202 (1966)
$LiSeCH_3$, DMF	Syn Commun *13* 617 (1983)
$NaSeCH_3$, DMF	TL *28* 4225 (1987)
$NaSeCH_2Ph$ (lactones)	Arkiv Kemi *24* 415, 573 (1965)
NaSePh (R = 1°, 2° alkyl; benzylic; lactone)	Coll Czech Chem Commun *34* 3801 (1969) TL 4365, 4369 (1977) JACS *102* 3904 (1980) JOC *46* 2605 (1981)
$Me_3SiSePh$, KF, 18-crown-6 (R = Et, lactone)	TL 5087 (1978)
NaCN, HMPA (R = Me)	TL 3565 (1973)
LiI, DMF, (NaOAc or NaCN) (R = Me)	JCS 6655 (1965) Syn Commun *2* 389 (1972)
LiI, various pyridines (R = Me, Et)	Rocz *30* 323 (1956) Helv *43* 113 (1960) Org Syn *45* 7 (1965)
BCl_3, CH_2Cl_2 (R = Me)	CC 667 (1971)
$MeSiCl_3$, NaI (R = Me, *t*-Bu, $PhCH_2$)	JOC *48* 3667 (1983)
Me_3SiOTf, Et_3N/H_2O (R = *t*-Bu)	Syn 545 (1980); 1 (1982) (review)
Me_3SiI (R = 1° alkyl, *t*-Bu, benzylic)/ H_2O	Angew Int *15* 774 (1976) JACS *99* 968 (1977); *106* 5335 (1984) CC 495 (1979)
Me_3SiCl, NaI/H_2O (R = 1°, 2°, 3° alkyl; benzylic)	CC 874 (1978) JOC *44* 1247 (1979)
$Me_3SiSiMe_3$, I_2/H_2O (R = Me, Et, $PhCH_2$)	Angew Int *18* 612 (1979)
$PhSiMe_3$, I_2/H_2O (R = 1°, 2° alkyl; benzylic)	Syn 417 (1977)

$ZnCl_2$ (R = Et)	Helv *36* 1203 (1953)
CF_3CO_2H (R = Me)	Syn Commun *12* 855 (1982)
HCl (R = *t*-Bu)	JACS *73* 4752 (1951); *81* 3089 (1959)
HCl, HBr or H_2SO_4 (phase transfer) (R = 1° alkyl, *t*-Bu)	JOC *47* 154 (1982)
$Na_2S_2O_4$, H_2O, Na_2CO_3 ($R = p\text{-}NO_2C_6H_4CH_2$)	Syn Commun *12* 219 (1982)
$Ar_3N^+_{\cdot}$ (R = benzylic)	Angew Int *21* 780 (1982)
$NOPF_6/H_2O$ (R = benzylic)	Syn 418 (1977)
Me_2CuLi (R = allyl)	Syn Commun *8* 15 (1978) TL *28* 5921 (1987)
$Hg(OAc)_2$, CH_3OH/KSCN (R = cinnamyl)	TL 2081 (1977)

15. Esters to Acid Halides

$$RCOR' \longrightarrow RCX$$

X	R′	Reagent	
F, Cl	$C(CH_3)=CH_2$	HX (X = F, Cl)	JOC *34* 2486 (1969)
Cl	$SiMe_2$(*t*-Bu)	ClCOCOCl	JOC *43* 3972 (1978)
	1° alkyl		Ber *96* 1387 (1963)
Br	$SiMe_3$	Ph_3PBr_2	Syn 684 (1982)
	$SiMe_2$(*t*-Bu)	Ph_3PBr_2	JOC *51* 4941 (1986)

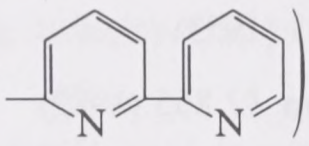


Angew Int *75* 1205 (1963)
JOC *52* 5745 (1987)

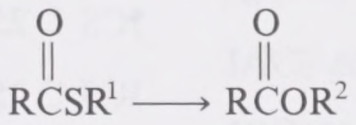
16. Esters to Other Esters

$$R^1COR^2 \longrightarrow R^1COR$$

BBr_3/ROH	TL 3995 (1974)
Me_3SiI, I_2/ROH	Syn 142 (1981)

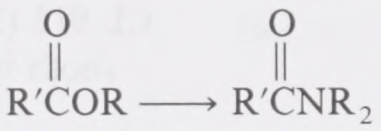
ROH, CsF (R^2 = )	CL 563 (1980)
ROH, TsOH	Org Syn Coll Vol *3* 146 (1955)
ROH, cat KCN	JCS Perkin I 1186 (1972) Syn 790 (1973)
ROH, Al_2O_3 (R^1 = Me, R^2 = Et; R = 1° > 2° alkyl)	Syn 789 (1981) TL *22* 5003, 5007 (1981)
ROH (R = 1°, 2° alkyl), cat $XSn(n\text{-}Bu)_2OSn(n\text{-}Bu)_2OH$ (X = Cl, NCS)	TL *27* 2383 (1986)
ROH, $Ti(OR')_4$ (R′ = Et, *i*-Pr)	Syn 138, 826 (1982) Org Syn *65* 230 (1987)
CH_3OH, cat $(EtO)_3TiOCH_2CH_2OTi(OEt)_3$ (R = Me)	Helv *65* 1197 (1982)
$CH_3CH_2CO_2CH_3$, cat $Ti(OEt)_4$ (R = Me)	Helv *65* 1197 (1982)
MeOH, MeO_2CEt, cat $Ti(OEt)_4$, ($HOCH_2CH_2OH$) (R = Me)	Helv *65* 1197 (1982)
ROH, cat DMAP	JOC *50* 3618 (1985) (β-keto esters) TL *28* 2713, 2717 (1987) JACS *109* 7488 (1987)
ROH, *n*-BuLi (R^1 = aryl, vinylic)	CC 695 (1986)
t-BuOH, KO-*t*-Bu, molecular sieves	Syn 49 (1972)
KOR, NH_3	JOC *39* 855 (1974)
BrMgOR ($R^2 = CH_2SOCH_3$)	JACS *106* 2954 (1984)
ROH, electrolysis ($R^2 = p\text{-}C_6H_4OH$)	TL *22* 3715 (1981)
ROH, porcine pancreatic lipase (enantioselective)	Science *224* 1249 (1984) Proc Natl Acad Sci USA *82* 3192 (1985) JACS *107* 7072 (1985); *109* 3977 (1987) TL *27* 5707 (1986); *28* 1607, 2091, 3471 (1987)
ROH, porcine pancreatic lipase, py (enantioselective)	JACS *108* 5638 (1986)
ROH, porcine pancreatic lipase, molecular sieves ($R^2 = CH{=}CH_2$, enantioselective)	TL *28* 953 (1987)
ROH, porcine pancreatic lipase, solid support (enantioselective)	TL *28* 3563 (1987)
ROH, pig liver esterase, solid support (enantioselective)	JACS *106* 2687 (1984)
ROH, horse liver esterase, solid support (enantioselective)	TL *28* 3563 (1987)

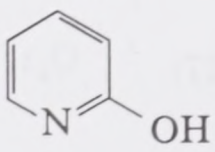
ROH, α-chymotrypsin (enantioselective)	JACS *108* 2767 (1986)
ROH, α-chymotrypsin, solid support (enantioselective)	TL *28* 3563 (1987)
ROH, subtilisin (enantioselective)	JACS *108* 2767 (1986)
ROH, *Candida cylindracea* lipase (enantioselective)	JACS *107* 7072 (1985); *109* 3977 (1987) TL *27* 29 (1986)
ROH, *Candida cylindracea* lipase, solid support (enantioselective)	JACS *106* 2687 (1984) TL *28* 3563 (1987)
ROH, other lipases (enantioselective)	TL *28* 1607 (1987) JOC *52* 5079 (1987) JACS *109* 3977 (1987)



R^2OH, AgO_2CCF_3 (R^1 = *t*-Bu)	TL *24* 5143 (1983) JCS Perkin I 121, 131 (1987)
R^2OH; $Hg(O_2CCF_3)_2$, $HgCl_2(CdCO_3)$ or $Tl(O_2CCF_3)_3$	JACS *97* 3515 (1975)
R^2_2CuLi, O_2 (R^1 = 2-pyridyl)	CC 1231 (1981)

17. Esters to Amides



NH_3	Org Syn Coll Vol *1* 153, 179 (1941); *3* 516, 536 (1955) JOC *52* 4379 (1987)
n-$BuNH_2$, C_6H_6 (R′ = aryl > alkyl)	TL *27* 2263 (1986)
HNR_2, Δ	JACS *71* 2215 (1949) Org Syn Coll Vol *3* 108, 765 (1955); *4* 80 (1963)
HNR_2, cat NaCN	JOC *52* 2033 (1987)
HNR_2, electrolysis	TL *28* 441 (1987)
HNR_2, porcine pancreatic lipase	Proc Natl Acad Sci USA *82* 3192 (1985)
HNR_2, enzymes	TL *28* 1629 (1987)
NH_3, NH_4X	JACS *60* 579 (1938)
NH_4OH, NH_4Cl	Org Syn Coll Vol *4* 486 (1963)
HNR_2, 	JCS C 89 (1969)

HNR_2, $NaOCH_3$	JOC *28* 2915 (1963)
$LiNR_2$	TL 1791 (1970) JOC *52* 5745 (1987)
$NaNR_2$	JACS *77* 469 (1955) TL 321 (1971) Chem Ind 277 (1956)
$XMgNR_2$	JCS 1188 (1954)
R_2AlNR_2	TL 4171 (1977) Org Syn *59* 49 (1980) JACS *107* 1695, 5732 (1985) JOC *52* 4665 (1987)
R_3SnNR_2	JCS A 992 (1969) JCS C 2565 (1969)
$Ti(NR_2)_4$	JCS C 2565 (1969)
BBr_3/R_2NH	TL 3995 (1974)
KOH, *n*-Bu_4NBr/R_2NH, (*o*-$NO_2C_6H_4O)_2POPh$, molecular sieves	CL 285 (1981)

$$RC(=O)SR^1 + H_2NR^2 \longrightarrow RC(=O)NHR^2$$

CuI	JOC *52* 4531 (1987)
AgO_2CCF_3	TL *28* 3019 (1987)
$Hg(O_2CCF_3)_2$	CL 915 (1986); 293 (1987) (both intramolecular)

18. Esters to Nitriles

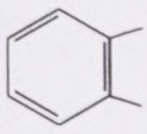
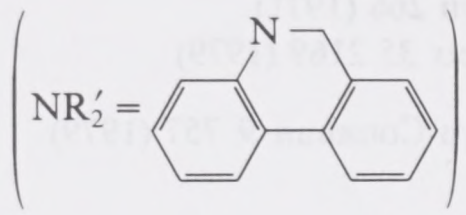
$$RC(=O)OR' \xrightarrow{Me_2AlNH_2} RCN$$

TL 4907 (1979)
JOC *52* 1309 (1987)

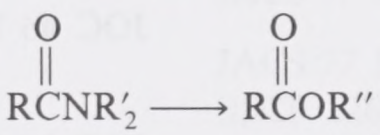
19. Amides to Carboxylic Acids

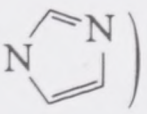
$$RC(=O)NR'_2 \longrightarrow RC(=O)OH$$

H_2SO_4, H_2O	JACS *70* 3091 (1948)
H_3PO_4, H_2O	Rec Trav Chim *46* 600 (1927)

HCl, H_2O	Org Syn Coll Vol *3* 66, 88 (1955); *4* 39, 496 (1963)
HCl, HOAc, H_2O	JACS *63* 2494 (1941)
acidic resin, H_2O	Chem Ind 736 (1957) JOC *46* 5351 (1981)
KOH	JOC *52* 4689 (1987)
NaOH, ethylene glycol	JACS *78* 450 (1956); *79* 2530 (1957)
KOH, ethylene glycol	TL *27* 4941 (1986)
KOH, diethylene glycol	JOC *15* 617 (1950)
NaOH/HCl	Org Syn Coll Vol *4* 58 (1963)
Na_2O_2, H_2O/H^+	JOC *40* 1187 (1975)
N_2O_4, HOAc (RCONHR′)	JACS *60* 235 (1938)
$(NO)BF_4$, CH_3CN (RCONHR′)	JOC *30* 2386 (1965) TL *27* 4941 (1986)
n-BuONO, HCl, HOAc (RCONHR′)	JACS *70* 3091 (1948) J Med Chem *9* 603 (1966)
NOCl, Ac_2O, HOAc, py/KOH (RCONHR′)	JACS *83* 1492 (1961)
$NaNO_2$, H_2SO_4	JACS *78* 5416 (1956); *79* 2530 (1957); *107* 2111 (1985)
$HOSO_2ONO$, H_2O ($RCONH_2$)	Org Prep Proc Int *14* 357 (1982)
 ($RCONR'_2$)	Ber *96* 1387 (1963)
$Ce(NH_4)_2(NO_3)_6$ 	CL 1551 (1981)

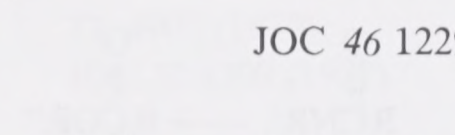
20. Amides to Esters



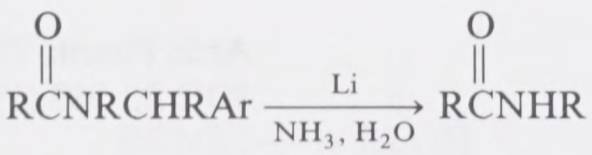
MeOH, $BF_3 \cdot OEt_2$	CC 414 (1969)
MeOH, acidic resin	JOC *46* 5351 (1981)
EtOH, HCl (R″ = Et)	Arch Pharm *290* 218 (1957) JOC *25* 560 (1960); *35* 125 (1970)
R″OH, DBU 	JOC *50* 3224 (1985)
R″Br, H_2O	JOC *34* 3204 (1969)

N_2O_4 or $NaNO_2$-Ac_2O, Δ (on RCONHR′)	JACS *76* 4497 (1954); *77* 6008, 6011 (1955) TL 2627 (1965) JOC *34* 3834 (1969)

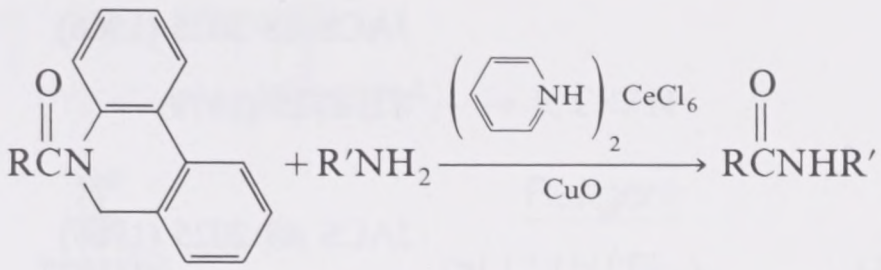
21. Amides to Other Amides



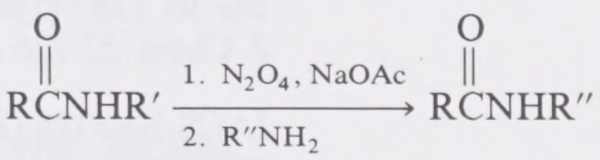
Na, Me_2SO_4 (R = Me)	Ber *68* 751 (1935)
Na, RX (R = 1° alkyl, $PhCH_2$; X = Cl, Br, I)	Ber *10* 327 (1877) JACS *74* 1010 (1952)
NaH, RX (R = 1°, 2° alkyl; allylic; X = Br, I)	JOC *14* 1099 (1949) JACS *74* 1010 (1952)
NaOH, K_2CO_3, C_6H_6, cat (n-Bu_4N)HSO_4, RX (R = 1° alkyl, benzyl; X = Cl, Br)	Syn 527, 549 (1979); 1005 (1981)
NaOH, (Et_3NCH_2Ph)Cl, aq C_6H_6, RX [RX = Me_2SO_4, Et_2SO_4; 1° alkyl and benzylic Cl, Br, I; R^2 = aryl]	Syn 113 (1976)
KOH, acetone, MeI (R^2 = Ar; R = Me)	JACS *74* 1321 (1952)
KOH, EtI (R = Et)	Ber *20* 3422 (1887)
KOH, EtOH, RBr (R = 1° alkyl)	JACS *74* 1010 (1952)
KOH, DMSO, RX (R = 1°, 2° alkyl, $PhCH_2$; X = Cl, Br, I)	Syn 266 (1971) Tetr *35* 2169 (1979)
KO-t-Bu, crown ether/RX (RX = MeI, allyl bromide; R^2 = aryl)	Syn Commun *9* 757 (1979)
n-BuLi/Me_2SO_4 (R = Me)	JOC *38* 1677 (1973)
KF, alumina, RX (RX = MeI, $PhCH_2Cl$)	CL 1143 (1981)
ROH, $EtO_2CN{=}NCO_2Et$, PPh_3 (intramolecular, β-lactam)	JOC *46* 1229 (1981)
$R'_2C(OR'')_2$ (R″ = Me, Et), H_2, cat Pd-C, HOAc, H_2SO_4 (R^2 = H, R = CHR'_2)	JOC *27* 2205 (1962)



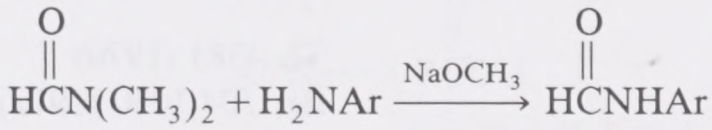
TL *27* 4941 (1986)
JOC *51* 5226 (1986)



CL 991 (1982)

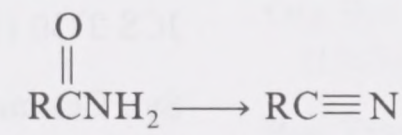


TL *23* 1127 (1982)

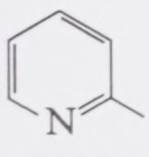


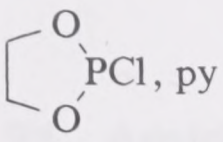
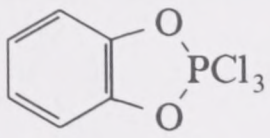
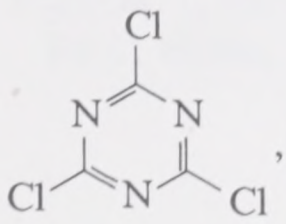
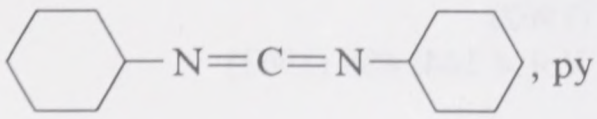
JOC *26* 2563 (1961)

22. Amides to Nitriles



Review: Chem Rev *42* 189 (1948)

$SOCl_2$	JACS *69* 2663 (1947); *82* 2498 (1960); *83* 2354, 2363 (1961) JOC *27* 4608 (1962) Org Syn Coll Vol *4* 436 (1963)
$SOCl_2$, DMF	JOC *24* 26 (1959); *36* 3960 (1971); *50* 2323 (1985) Tetr *21* 2239 (1965) JACS *88* 2025 (1966)
$ClSO_2NCO$, Et_3N	CC 227 (1979)
$PhSO_2Cl$	JCS 763 (1946)
$PhSO_2Cl$, py	JACS *77* 1701 (1955)
TsCl, py	JACS *77* 1701 (1955) BSCF 2262 (1965)
 (R = aryl)	TL *27* 1925 (1986)
$(CF_3CO)_2O$, py	TL 1813 (1977)
P_2O_5	JOC *27* 4608 (1962) Org Syn Coll Vol *4* 144, 486 (1963)
P_2O_5, $Me_3SiOSiMe_3$	Syn 591 (1982)
$(Ph_3PO_3SCF_3)O_3SCF_3$	TL 277 (1975)

$(EtO)_2POP(OEt)_2$	JACS *88* 2025 (1966)
$(EtO)_3PI_2$	TL 1725 (1979)
	JACS *88* 2025 (1966)
	Ber *96* 1387 (1963) Z Chem *22* 126 (1982) (review)
$POCl_3$	JACS *70* 3315 (1948) JOC *27* 4608 (1962); *50* 5451 (1985)
$POCl_3$, DMF/py	Syn Commun *10* 479 (1980)
CCl_4, PPh_3	TL 4383 (1970) Ber *104* 1030 (1971)
CCl_4, Ph_2P-polymer	Syn 41 (1977)
$(PNCl_2)_3$	Can J Chem *50* 3857 (1972)
$P(NEt_2)_3$	CL 577 (1973)
$COCl_2$, py	JCS 3730 (1954)
$COCl_2$, DMF/py	Syn Commun *10* 479 (1980)
ClCOCOCl, DMF/py	Syn Commun *10* 479 (1980)
$ClCO_2Me$	Bull Acad Polon Sci, Ser Sci Chem *10* 227 (1962) [CA *59* 4031g (1963)]
Cl_3CCOCl, Et_3N	Syn 184 (1985)
$Cl_3COCOCl$, $OP(OMe)_3$	TL *27* 2203 (1986)
$Cl_3CN{=}CCl_2$	Syn 599 (1972)
$NaCl \cdot AlCl_3$, Δ	JACS *62* 1432 (1940)
cat $ClRh(PPh_3)_3$ (R = aryl)	TL 1963 (1970)
$TiCl_4/R_3N$	TL 1501 (1971)
$HCCl_3$, NaOH, $(PhCH_2NEt_3)Cl$	TL 2121 (1973)
$HN(SiMe_2)_n$ ($n = 3, 4$)	JOC *35* 3253 (1970)
 , DMF	Syn 657 (1980)
 , py	JOC *26* 3356 (1961); *36* 3960 (1971) JACS *88* 2025 (1966)
$LiAlH_4$	Can J Chem *44* 2113 (1966)

$$R^1\overset{\overset{O}{\|}}{C}NHR^2 \longrightarrow R^1C{\equiv}N$$

R^1	R^2	Reagent	
aryl	benzylic	cat $ClRh(PPh_3)_3$	TL 1963 (1970)
alkyl, aryl, vinylic	*t*-Bu	$POCl_3$	Org Prep Proc Int *15* 297 (1983)

23. Nitriles to Carboxylic Acids

$$RCN \longrightarrow R\overset{\overset{O}{\|}}{C}OH$$

HBr, H_2O	Org Syn Coll Vol *1* 131 (1941)
HCl, H_2O	Org Syn Coll Vol *1* 21, 289, 336, 451 (1941); *3* 84, 114, 591, 851 (1955); *4* 496, 804 (1963)
HCl, H_2O, HOAc	Org Syn Coll Vol *4* 790 (1963)
H_2SO_4, H_2O	Org Syn Coll Vol *1* 406, 436 (1941); *2* 25, 588 (1943); *3* 557 (1955)
H_3PO_4	Rec Trav Chim *46* 600 (1927)
NaOH, H_2O/H^+	Org Syn Coll Vol *1* 321 (1941); *2* 376 (1943)
$Ba(OH)_2$, H_2O/H^+	Org Syn Coll Vol *1* 298 (1941); *3* 34 (1955)
NaOH, H_2O, $MeOH/H^+$	JACS *107* 7967 (1985)
KOH, H_2O, $EtOH/H^+$	Org Syn Coll Vol *2* 292 (1943)
NaOH, ethylene glycol/H^+	JACS *78* 450 (1956) JOC *51* 4169 (1986)
NaOH, diethylene glycol/H^+	JOC *50* 2128 (1985)
KOH, ethylene glycol/H^+	JACS *78* 5413 (1956) Org Syn Coll Vol *4* 93 (1963)
enzyme	TL *28* 4057 (1987) (α-amino acids)

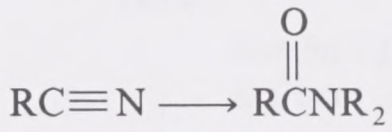
24. Nitriles to Esters

$$RCN \longrightarrow RCO_2R'$$

R′OH, H_2SO_4	JOC *50* 2128 (1985)
R′OH, H_2SO_4, H_2O	Org Syn Coll Vol *1* 270 (1941)
R′OH, HCl	Ber *105* 1778 (1972) JOC *50* 2128 (1985) TL *27* 2103 (1986) JOC *51* 5463 (1986)

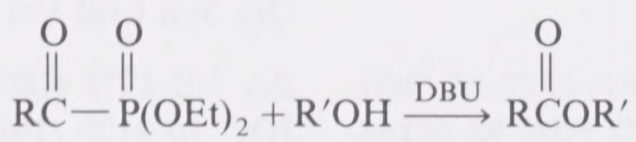
R′OH, TsOH	JOC *23* 1225 (1958)
NaOH/MeI (R′ = Me)	JACS *108* 1039 (1986)

25. Nitriles to Amides

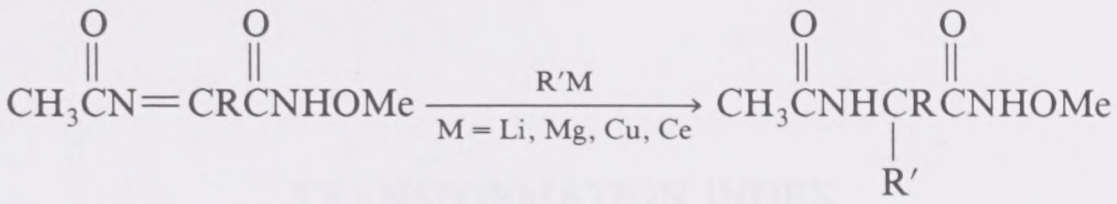


KF, Al_2O_3 ($RCONH_2$)	Syn Commun *12* 177 (1982)
H_2O, cat Cu ($RCONH_2$)	JOC *47* 4812 (1982)
H_2SO_4 ($RCONH_2$)	JACS *78* 5416 (1956); *79* 2530 (1957)
H_2SO_4, R′OH (RCONHR′)	Org Syn Coll Vol *5* 73 (1973)
PPA ($RCONH_2$)	JACS *76* 3039 (1954); *79* 725 (1957)
H_2O, HCl ($RCONH_2$)	Org Syn Coll Vol *3* 66, 88 (1955); *4* 58, 496, 760 (1963)
BF_3, HOAc ($RCONH_2$)	JOC *20* 1448 (1955) JACS *79* 725 (1957)
BF_3, HOAc, H_2O ($RCONH_2$)	JOC *20* 1448 (1955)
NaO_2, DMSO ($RCONH_2$)	JOC *44* 4727 (1979)
H_2O_2, base ($RCONH_2$)	Ber *18* 355 (1885) Org Syn Coll Vol *2* 44, 586 (1943) JACS *75* 3961 (1953), *77* 2519 (1955) JOC *36* 3048 (1971)
H_2O_2, NH_4OH ($RCONH_2$)	JOC *51* 1065 (1986)
H_2O_2, NaOH, (n-Bu_4N)HSO_4 (phase transfer) ($RCONH_2$)	Syn 243 (1980)
KOH, diethylene glycol ($RCONH_2$)	JOC *15* 617 (1950)
KOH, t-BuOH ($RCONH_2$)	JOC *41* 3769 (1976)
KOH, t-BuOH/1° R′X (RCONHR′)	Syn 303 (1978)
$NOPF_6$, R′X (R′ = 1°, 2°, 3° alkyl; benzylic) (RCONHR′)	Syn 274 (1979)
R_2NH, H_2O, cat $H_2Ru(PPh_3)_4$	JACS *108* 7846 (1986)

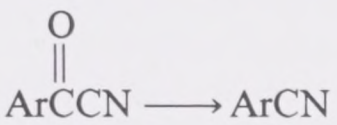
26. Other Interconversions



TL *22* 3617 (1981)



TL *27* 4241 (1986)



cat $ClRh(PPh_3)_3$ JACS *89* 2338 (1967)

cat $Pd(PPh_3)_4$ JOC *51* 898 (1986)

TRANSFORMATION INDEX

The following index tabulates all organic transformations covered in this book. It describes in the first column the organic product of the transformation, in the second column the organic starting material, and in the last column the page on which that transformation occurs. Inorganic reagents have been ignored. Transformations of the type A → B → C have been indexed as follows: to C from B, to C from A, and to B from A. In equations with many variables, such as various electrophiles, nucleophiles and substituents, only those transformations actually reported in the literature have been indexed.

Each transformation has been indexed in its most general form. The reader is cautioned that for reactions whose scope is ill-defined, the author has often had to make assumptions as to a reaction's generality in order to index it. Not only the presence of key functional groups, but also the presence of carbon-carbon double or triple bonds and aryl groups have been considered carefully in the indexing of all transformations. The reader should keep in mind that not all reactions general for both aldehydes and ketones have been illustrated as such in the text. It is, therefore, advisable for the reader to look under both alkanal (aldehyde) and alkanone (ketone) for a given reaction and to check the original literature.

To shorten an already lengthy index and to increase its utility, the names of key functional groups have often been simplified. For example, trimethylsilyl has been shortened to silyl, methylthio or arylthio to thio, etc. The halogens have not been differentiated from one another. Alkyl or aryl groups that are not central to the transformation in question have been ignored.

Current IUPAC and Chemical Abstracts nomenclature has been employed in this index, with the former given preference. Substitutive nomenclature has been given preference over radicofunctional, additive, subtractive, conjunctive or replacement nomenclature except where this becomes unwieldy.

Prefixes for all names are listed in alphabetical order, not in order of complexity. The following less obvious prefixes have been employed for the group or metal indicated; lithio (Li), boryl (B), sodio (Na), magnesio (Mg), aluminio (Al), silyl (Si), thio (SR), mercapto (SH), halo (F, Cl, Br, I), potassio (K), calcio (Ca), titanio (Ti), vanadio (V), chromio (Cr), manganio (Mn), ferrio (Fe), nickelio (Ni), cuprio (Cu), zincio (Zn), germyl (Ge), seleno (Se), zirconio (Zr), niobio (Nb), rhodio (Rh), palladio (Pd), argentio (Ag), cadmio (Cd), stannyl (Sn), telluro (Te), hafnio (Hf), tantalio (Ta), mercurio (Hg), thallio (Tl), plumbyl (Pb), bismuthio (Bi), lanthanio (La), cerio (Ce), ytterbio (Yb).

The suffix is assigned according to the principal functional group, keeping in mind the following priorities: cation > alkanoic acid > alkanoate ester > acyl halide > alkanamide > alkanenitrile > alkanal > alkanone > alkanol.

The principle chain in acyclic compounds has been assigned according to the following criteria applied successively: (1) maximum number of principal groups, (2) maximum number of carbon-carbon double or triple bonds considered together, (3) maximum number of double bonds, (4) highest locant for multiple bonds, (5) lowest locant for all substituents cited as prefixes and (7) lowest locant for substituents cited first as prefix in alphabetical order. Note that this does not follow IUPAC or Chemical Abstracts rules exactly since chain length has been ignored.

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acenaphthalene	acenaphthene	97
acetal	*see* alkanal acetal *or* alkanone acetal	
acetal, bicyclic	halo acetal	86, 91, 126
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acid anhydride	acyl halide	978
acid anhydride	alkanoic acid	965, 966
acid anhydride	maleic anhydride (conjugate addition)	67, 919
acid anhydride	mercurioalkane	67, 919
acid anhydride, aryl	alkanoate sodium salt	858
acid anhydride, aryl	arene	858
acid anhydride, aryl	arenediazonium salt	858
acid anhydride, mixed	acyl halide	966, 978
acid anhydride, mixed	alkanoate 1-alkenyl ester	966
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acid anhydride, mixed	alkanoic acid	552, 694, 966, 978
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acyl	*see* alkanoyl *only when the acyl group is substituted*	
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N-acylalkanamide	*N*-acylalkanamide (*N*-alkylation)	420, 909
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N-acylalkanamide	alkanamide	846
N-acylalkanamide	alkanol	420, 909
N-acylalkanamide	1,ω-bis(tosyloxy)alkane	909
N-acylalkanamide	cuprioalkane	918
N-acylalkanamide	1,ω-dihaloalkane	909
N-acylalkanamide	haloalkane	909
N-acyl-4-alkanelactam	alkanamide	846
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3-acyl-4-alkanolide	2-alken-4-olide	709
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N-acyl-4-alkenamide	1-cuprio-1-alkene	918
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2-acyl-2-alkenoate ester	alkanone	171
2-acyl-2-alkenoate ester	2-alkynoate ester	238
2-acyl-2-alkenoate ester	3-oxoalkanoate ester	171
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2-acyl-4-alkenoate ester	1-boryl-1-alkyne	221
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ω-acyl-ω-alken-ω-olide	2-alken-1-one	957
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2-acyl-3-alkoxy-2-alkenoate ester	acyl halide	187
2-acyl-3-alkoxy-2-alkenoate ester	alkanoate ester	187
2-acyl-3-alkoxy-2-alkenoate ester	3-alkoxy-2-alkenoate ester	187
2-acyl-4-alkynoate ester	2-alkyn-1-ol	301
2-acyl-4-alkynoate ester	2-alkynyl cation cobalt compound	301
2-acyl-4-alkynoate ester	3-oxoalkanoate ester	301

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2-(acylamino)alkanamide	haloalkane	902
2-(acylamino)alkanoate 2-alkenyl ester	2-alken-1-ol	936
2-(acylamino)alkanoate ester	2-(acylamino)alkanoate ester (alkylation)	879
2-(acylamino)alkanoate ester	2-acylamino-2-alkenoate ester	7
2-(acylamino)alkanoate ester	*N*-alkoxyalkanamide	420
2-(acylamino)alkanoate ester	haloalkane	879
2-(acylamino)alkanoate ester	2-hydroxyalkanoate ester	420
3-(acylamino)alkanoate ester	3-(acylamino)alkanoate ester (alkylation)	881
3-(acylamino)alkanoate ester	haloalkane	881
5-(acylamino)alkanoate ester	2-alkenoate ester	919
5-(acylamino)alkanoate ester	*N*-(2-mercurioalkyl)alkanamide	919
2-(acylamino)alkanoic acid	2-(acylamino)alkanoic acid (alkylation)	869
2-(acylamino)alkanoic acid	2-acylamino-2-alkenoic acid	7
2-(acylamino)alkanoic acid	alkanamide	850
2-(acylamino)alkanoic acid	2-alken-1-ol	850
2-(acylamino)alkanoic acid	haloalkane	869
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3-acylamino-2-alkenoate ester	3-acylamino-2-alkenoate ester (substitution)	187
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