Volume III in the series originated by I.T. Harrison and S. Harrison

Compendium of Organic Synthetic Methods

By Louis S. Hegedus and Leroy G. Wade, Jr.

Compendium of Organic Synthetic Methods

Volume 3

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PREFACE

By their compilation of Volumes 1 and 2 of this *Compendium*, Ian and Shuyen Harrison filled one of the greatest needs of the synthetic community: a method for rapidly retrieving needed information from the literature by reaction type rather than by the author's name or publication date. We are honored by the opportunity to bring this useful work up to date.

Compendium of Organic Synthetic Methods, Volume 3, presents the functional group transformations and difunctional compound preparations of 1974, 1975, and 1976. We have attempted to follow as closely as possible the classification schemes of the first two volumes; the experienced user of the *Compendium* will require no additional instructions on the use of this volume.

Perhaps it is fitting here to echo the Harrisons' request stated in Volume 2 of the *Compendium*: The synthetic literature would become more easily accessible and more useful if chemists could write well-organized, concise papers with charts and diagrams that allow the reader to assess quickly and easily the scope of the published research. In addition, the reporting of actual, isolated yields and detailed experimental conditions will save a great deal of wasted effort on the part of other chemists hoping to apply the reported reactions to their own synthetic problems.

Anyone who has ever typed a research paper with structures can understand what a Gargantuan project the preparation of the camera-ready copy for this volume has been. Linda Benedict and Jackie Swinehart completed the entire project almost more quickly than our proofreaders, Gary Allen, Joel Slade and Robert Williams, could make corrections. The authors would like to express their thanks to these people for their dedicated work.

Louis S. Hegedus
Leroy Wade

Fort Collins, Colorado
June, 1977

CONTENTS

ABBREVIATIONS

The authors have attempted to use only abbreviations whose meaning will be readily apparent to the reader. Some of those more commonly used are the following:

Ac	acetyl
Bu	butyl
Bz	benzyl
Cp	cyclopentadienyl
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DIBAL	diisobutylaluminum hydride
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
Et	ethyl
Hex	hexyl
HMPA, HMPT	hexamethylphosphoramide (hexamethylphosphoric triamide)
L	triphenylphosphine ligand (if not specified)
LDA	lithium diisopropylamide
MCPBA	*meta*-chloroperbenzoic acid
Me	methyl
Ms	methanesulfonyl
MVK	methyl vinyl ketone
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
Ni	Raney nickel
Oct	octyl
Ph, ϕ	phenyl
Pr	propyl
Pyr	pyridine

Sia	*secondary*-isoamyl
Tf	trifluoromethane sulfonate
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
THP	tetrahydropyranyl
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl

INDEX, MONOFUNCTIONAL COMPOUNDS

Sections—heavy type
Pages—light type

FROM ↓ / PREPARATION OF →	Acetylenes	Carboxylic acids, acid halides, anhydrides	Alcohols, phenols	Aldehydes	Alkyls, methylenes, aryls	Amides	Amines	Esters	Ethers, epoxides	Halides, sulfonates	Hydrides (RH)	Ketones	Nitriles	Olefins
Acetylenes	**1**	**16**	**31**	**46**	**61**	**76**		**106**		**136**		**166**		**196**
	1	8	24	66	88	134		178		218		248		305
Carboxylic acids, acid halides, anhydrides		**17**	**32**	**47**	**62**	**77**	**92**	**107**		**137**		**167**	**182**	**197**
		8	25	67	89	135	149	178		218		249	296	308
Alcohols, phenols		**18**	**33**	**48**	**63**	**78**	**93**	**108**	**123**	**138**	**153**	**168**	**183**	**198**
		13	26	69	89	138	150	186	204	219	235	254	296	309
Aldehydes		**19**	**34**	**49**	**64**	**79**	**94**	**109**	**124**	**139**		**169**	**184**	**199**
		13	26	74	90	138	150	188	208	222		261	296	312
Alkyls, methylenes, aryls				**50**	**65**									**200**
				76	91									315
Amides		**21**		**51**		**81**	**96**	**111**				**171**	**186**	
		14		76		139	153	189				263	299	
Amines						**82**	**97**			**142**	**157**	**172**	**187**	**202**
						143	154			223	239	264	299	316
Esters	**8**	**23**	**38**	**53**	**68**			**113**			**158**	**173**	**188**	**203**
	4	15	32	77	92			190			240	266	300	316
Ethers, epoxides			**39**	**54**	**69**		**99**	**114**	**129**	**144**		**174**		**204**
			33	78	93		160	194	210	223		267		317
Halides, sulfonates, sulfates	**10**	**25**	**40**	**55**	**70**	**85**	**100**	**115**	**130**	**145**	**160**	**175**	**190**	**205**
	5	17	37	78	94	146	161	195	210	224	242	268	300	319
Hydrides (RH)		**26**	**41**	**56**	**71**	**86**	**101**	**116**		**146**		**176**	**191**	
		19	38	82	105	146	163	197		227		272	301	
Ketones	**12**	**27**	**42**		**72**	**87**	**102**	**117**	**132**	**147**		**177**		**207**
	6	19	40		107	147	163	198	212	231		273		324
Nitriles			**43**	**58**		**88**	**103**	**118**				**178**	**193**	
			51	83		147	165	201				285	301	
Olefins		**29**	**44**	**59**	**74**		**104**	**119**	**134**	**149**		**179**	**194**	**209**
		20	51	83	111		166	201	215	232		286	303	331
Miscellaneous compounds	**15**	**30**	**45**	**60**	**75**		**105**			**150**		**180**	**195**	**210**
	7	20	55	84	133		167			234		289	303	332

PROTECTION

	Sect.	Pg.
Acetylenes		
Carboxylic acids	30A	21
Alcohols, phenols	45A	56
Aldehydes	60A	85
Amides	90A	148
Amines	105A	172
Esters		
Ketones	180A	291
Olefins	210A	333

Blanks in the table correspond to sections for which no additional examples were found in the literature.

INDEX, DIFUNCTIONAL COMPOUNDS

Sections—heavy type

Pages—light type

Blanks in the table correspond to sections for which no examples were found in the literature.

INTRODUCTION

Relationship between Volume 3 and Previous Volumes. *Compendium of Organic Synthetic Methods, Volume 3* presents over 1000 examples of published methods for the preparation of monofunctional compounds, updating the 4000 in Volumes 1 and 2. In addition, Volume 3 contains over 1000 additional examples of preparations of difunctional compounds and various functional groups, updating these sections which were initially introduced in Volume 2. The same systems of section and chapter numbering are used in the two volumes.

Classification and Organization of Reactions Forming Monofunctional Compounds. Examples of published chemical transformations are classified according to the reacting functional group of the starting material and the functional group formed. Those reactions that give products with the same functional group form a chapter. The reactions in each chapter are further classified into sections on the basis of the functional group of the starting material. Within each section reactions are listed in a somewhat arbitrary order, although an effort has been made to put chain-lengthening processes before degradations.

The classification is unaffected by allylic, vinylic, or acetylenic unsaturation, which appears in both starting material and product, or increases or decreases in the length of carbon chains; for example, the reactions *t*-BuOH → *t*-BuCOOH, $PhCH_2OH$ → PhCOOH and PhCH=$CHCH_2OH$ → PhCH=CHCOOH would all be considered as preparations of carboxylic acids from alcohols. Entries in which conjugate reduction or alkylation of an unsaturated ketone, aldehyde, ester, acid, or nitrile occurs have generally been placed in category 74, Alkyls from Olefins.

The terms hydrides, alkyls, and aryls classify compounds containing reacting hydrogens, alkyl groups, and aryl groups, respectively; for example, RCH_2-H → RCH_2COOH (carboxylic acids from hydrides), RMe → RCOOH (carboxylic acids from alkyls), RPh → RCOOH (carboxylic acids from aryls). Note the distinction between R_2CO → R_2CH_2 (methylenes from ketones) and RCOR′ → RH (hydrides from ketones). Alkylations which involve additions across a double bond are found in section 74, Alkyls from Olefins.

The following examples illustrate the application of the classification scheme to some potentially confusing cases:

$RCH{=}CHCOOH \rightarrow RCH{=}CH_2$	(hydrides from carboxylic acids)
$RCH{=}CH_2 \rightarrow RCH{=}CHCOOH$	(carboxylic acids from hydrides)
$ArH \rightarrow ArCOOH$	(carboxylic acids from hydrides)
$ArH \rightarrow ArOAc$	(esters from hydrides)
$RCHO \rightarrow RH$	(hydrides from aldehydes)
$RCH{=}CHCHO \rightarrow RCH{=}CH_2$	(hydrides from aldehydes)
$RCHO \rightarrow RCH_3$	(alkyls from aldehydes)
$R_2CH_2 \rightarrow R_2CO$	(ketones from methylenes)
$RCH_2COR \rightarrow R_2CHCOR$	(ketones from ketones)
$RCH{=}CH_2 \rightarrow RCH_2CH_3$	(alkyls from olefins)
$RBr + RC{\equiv}CH \rightarrow RC{\equiv}CR$	(acetylenes from halides; also acetylenes from acetylenes)
$ROH + RCOOH \rightarrow RCOOR$	(esters from alcohols; also esters from carboxylic acids)
$RCH{=}CHCHO \rightarrow R_2CHCH_2CHO$	(alkyls from olefins)
$RCH{=}CHCN \rightarrow RCH_2CH_2CN$	(alkyls from olefins)

Yields quoted are overall; they are occasionally reduced to allow for incomplete conversion and impurities in the product.

Reactions not described in the given references, but required to complete a sequence, are indicated by a dashed arrow.

Reactions are included even when full experimental details are lacking in the given reference. In some cases the quoted reaction is a minor part of a paper or may have been investigated from a purely mechanistic aspect.

How to Use the Book to Locate Examples of the Preparation or Protection of Monofunctional Compounds. Examples of the preparation of one functional group from another are located via the monofunctional index on p. ix, which lists the corresponding section and page. Thus Section 1 contains examples of the preparation of acetylenes from other acetylenes; Section 2, acetylenes from carboxylic acids; and so forth.

Sections that contain examples of the reactions of a functional group are found in the horizontal rows of the index. Thus Section 1 gives examples of the reactions of acetylenes that form other acetylenes; Section

16, reactions of acetylenes that form carboxylic acids; and Section 31, reactions of acetylenes that form alcohols.

Examples of alkylation, dealkylation, homologation, isomerization, transposition are found in Sections 1, 17, 33, and so on, which lie close to a diagonal of the index. These sections correspond to such topics as the preparation of acetylenes from acetylenes, carboxylic acids from carboxylic acids, and alcohols and phenols from alcohols and phenols. Alkylations which involve conjugate additions across a double bond are found in section 74, Alkyls from Olefins.

Examples of name reactions can be found by first considering the nature of the starting material and product. The Wittig reaction, for instance, is in Section 199 on olefins from aldehydes and Section 207 on olefins from ketones.

Examples of the protection of acetylenes, carboxylic acids, alcohols, phenols, aldehydes, amides, amines, esters, ketones, and olefins are also indexed on p. ix.

The pairs of functional groups alcohol, ester; carboxylic acid, ester; amine, amide; carboxylic acid, amide can be interconverted by quite trivial reactions. When a member of these groups is the desired product or starting material, the other member should, of course, also be consulted in the text.

A few reactions already presented in Volumes 1 and 2 are given again in Volume 3 when significant new publications have appeared. In such cases the starting material and product are shown in a contracted form; for example, ROH instead of $PhCH_2CH_2OH$.

The original literature must be used to determine the generality of reactions. A reaction given in this book for a primary aliphatic substrate may also be applicable to tertiary or aromatic compounds.

The references usually yield a further set of references to previous work. Subsequent publications can be found by consulting the Science Citation Index.

Classification and Organization of Reactions forming Difunctional Compounds. This chapter considers all possible difunctional compounds formed from the groups acetylene, carboxylic acid, alcohol, aldehyde, amide, amine, ester, ether, epoxide, halide, ketone, nitrile, and olefin. Reactions that form difunctional compounds are classified into sections on the basis of the two functional groups of the product. The relative positions of the groups do not affect the classification. Thus preparations of 1,2-aminoalcohols, 1,3-aminoalcohols and 1,4-aminoalcohols are included in a single section. It is recommended that the following illustrative examples of the classification of difunctional compounds be scrutinized closely.

Difunctional Product	*Section Title*
$RC{\equiv}C\text{-}C{\equiv}CR$	Acetylene—Acetylene
$RCH(OH)COOH$	Carboxylic Acid—Alcohol
$RCH(COOH)CH_2COOMe$	Carboxylic Acid—Ester
$RCH(OAc)COOH$	Carboxylic Acid—Ester
$RCH{=}CHOMe$	Ether—Olefin
$RCH(OMe)_2$	Ether—Ether
$RCHF_2$	Halide—Halide
$RCH(Br)CH_2F$	Halide—Halide
$RCH(OAc)CH_2OH$	Alcohol—Ester
$RCH(OH)COOMe$	Alcohol—Ester
$RCOCOOEt$	Ester—Ketone
$RCOCH_2OAc$	Ester—Ketone
$RCH{=}CHCH_2COOMe$	Ester—Olefin
$RCH{=}CHOAc$	Ester—Olefin
$RCH(Br)COOEt$	Ester—Halide
$RCH(Br)CH_2OAc$	Ester—Halide
$RCH{=}CHCH_2CH{=}CH_2$	Olefin—Olefin

How to Use the Book to Locate Examples of the Preparation of Difunctional Compounds. The difunctional index on p. x gives the section and page corresponding to each difunctional product. Thus Section 327 (Alcohol—Ester) contains examples of the preparation of hydroxyesters; Section 323 (Alcohol—Alcohol) contains examples of the preparation of diols.

Some preparations of olefinic and acetylenic compounds from olefinic and acetylenic starting materials can, in principle, be classified in either the monofunctional or difunctional sections; for example, $RCH{=}CHBr \rightarrow RCH{=}CHCOOH$, Carboxylic acids from Halides (monofunctional sections) or Carboxylic acid—Olefin (difunctional sections). In such cases both sections should be consulted.

Reactions applicable to both aldehyde and ketone starting materials are in many cases illustrated by an example that uses only one of them.

Many literature preparations of difunctional compounds are extensions of the methods applicable to monofunctional compounds. Thus the reaction $RCl \rightarrow ROH$ can clearly be extended to the preparation of diols by using the corresponding dichloro compound as a starting material. Such methods are not fully covered in the difunctional sections.

The user should bear in mind that the pairs of functional groups alcohol, ester; carboxylic acid, ester; amine, amide; carboxylic acid, amide can be interconverted by quite trivial reactions. Compounds of the type $RCH(OAc)CH_2OAc$ (Ester—Ester) would thus be of interest to anyone preparing the diol $RCH(OH)CH_2OH$ (Alcohol—Alcohol).

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Chapter 1 PREPARATION OF ACETYLENES

Section 1 Acetylenes from Acetylenes

$$PhC{\equiv}CH \xrightarrow[\substack{2)\ Bu_3B \\ 3)\ MeSOCl}]{1)\ BuLi} PhC{\equiv}CBu \qquad 80\%$$

Tetrahedron (1974) 30 2159

$$HC{\equiv}CCH_2OH \xrightarrow[2)\ \underline{n}\text{-}C_6H_{13}Br]{1)\ LiNH_2,\ NH_3} \underline{n}\text{-}C_6H_{13}\text{-}C{\equiv}CCH_2OH \qquad 60\%$$

JOC USSR (1975) 11 517

$$PhC{\equiv}CH \quad + \quad PhI \xrightarrow[Et_2NH]{(Ph_3P)_2\ PdCl_2/CuI} PhC{\equiv}CPh \qquad 90\%$$

Tetr Lett (1975) 4467

$$PhI \quad + \quad \underline{n}\text{-}PrC{\equiv}CH \xrightarrow[NaOMe,\ DMF]{Pd(PPh_3)_4} PhC{\equiv}C\text{-}\underline{n}\text{-}Pr \qquad 97\%$$

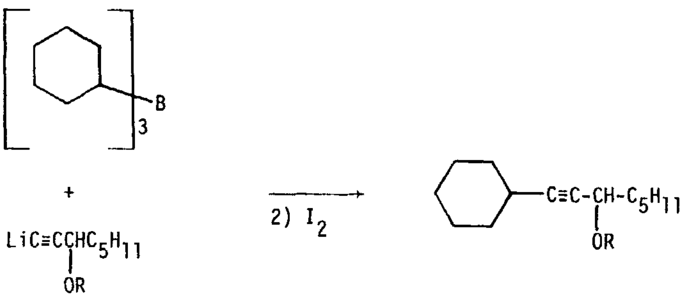
J Organometal Chem (1975) 93 253, 259

$[Bu_3BC\equiv CPh]Li \xrightarrow{I_2} BuC\equiv CPh$ 85%

JOC (1974) 39 731

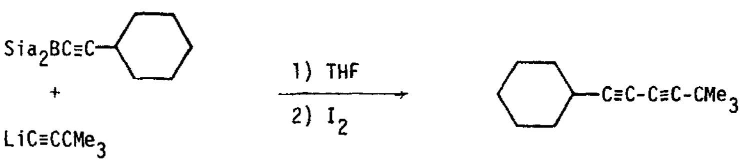
$\underline{i}\text{-}Bu_3B + LiC\equiv CCl \xrightarrow[2)\ NaOH/H_2O_2]{1)\ I_2,\ -78°} \underline{i}\text{-}BuC\equiv C\text{-}Bu\text{-}\underline{i}$ 85%

Tetr Lett (1975) 1961



65%

JOC (1976) 41 3947

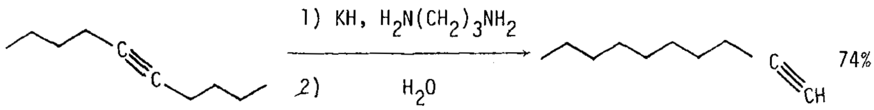


70%

JOC (1976) 41 1078

$\underline{t}\text{-}BuCl + (BuC\equiv C)_3Al \xrightarrow[0°]{CH_2Cl_2} \underline{t}\text{-}BuC\equiv C\text{-}Bu$ 98%

JACS (1975) 97 7385



JACS (1975) 97 891

Section 2 Acetylenes from Carboxylic Acids

No additional examples

Section 3 Acetylenes from Alcohols

No additional examples

Section 4 Acetylenes from Aldehydes

No additional examples

Section 5 Acetylenes from Alkyls, Methylenes and Aryls

No examples

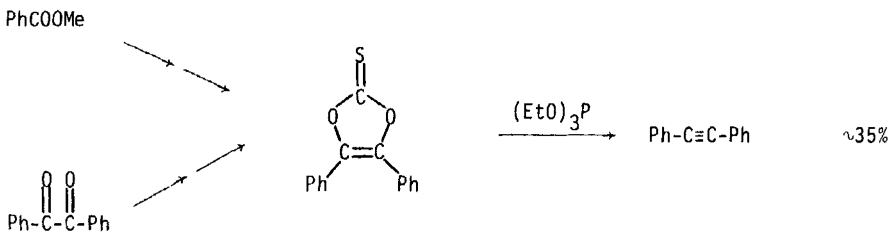
Section 6 Acetylenes from Amides

No additional examples

Section 7 Acetylenes from Amides

No additional examples

Section 8 Acetylenes from Esters



JOC (1976) 41 2640

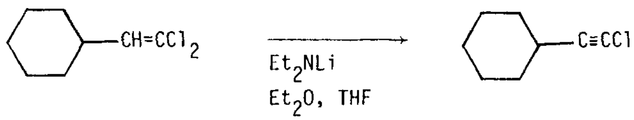
Section 9 Acetylenes from Ethers

No examples

Section 10 Acetylenes from Halides

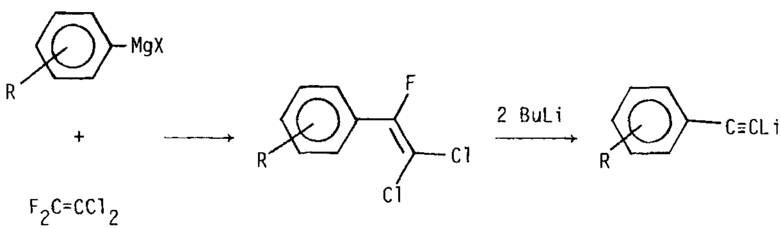
$$HCBr{=}CBrH \xrightarrow[\text{rfx}]{\text{2 eq. } Ph_2PLi\text{, THF}} HC{\equiv}CH \qquad 80\%$$

Tetr Lett (1975) 4709



80%

Synthesis (1975) 458



JOC (1976) 41 1487 ∿60-80%

$$\underset{CH_2Cl}{EtOCH}(CH_2)_{11}Me \xrightarrow[Et_2O\text{/hexane}]{\text{BuLi}} HC{\equiv}C(CH_2)_{11}CH_3 \qquad 81\%$$

Synth Comm (1975) 5 331

Section 11 Acetylenes from Hydrides

No examples

For examples of the reaction $RC{\equiv}CH \rightarrow RC{\equiv}C\text{-}C{\equiv}CR'$ see section 300 (Acetylene - Acetylene)

Section 12 Acetylenes from Ketones

$$\mathrm{Ph{-}\overset{\overset{NNH_2}{\|}}{C}{-}\underset{\underset{NNH_2}{\|}}{C}{-}Ph} \xrightarrow[\mathrm{Cu_2Cl_2}]{\mathrm{O_2,\ pyr}} \mathrm{Ph{-}C{\equiv}C{-}Ph} \qquad 90\%$$

Chem Lett (1976) 147

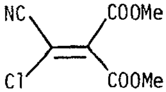
Section 13 Acetylenes from Nitriles

No examples

Section 14 Acetylenes from Olefins

No additional examples

Section 15 Acetylenes from Miscellaneous Compounds



$\xrightarrow[\text{crown ether, 150°}]{\text{KCl, sulfolane}}$ NC-C≡C-COOMe 16%

Tetr Lett (1975) 2429

Section 15A Protection of Acetylenes

No additional examples

Compendium of Organic Synthetic Methods, Volume 3
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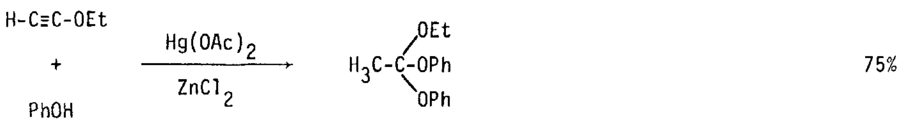
Chapter 2 PREPARATION OF CARBOXYLIC ACIDS ACID HALIDES AND ANHYDRIDES

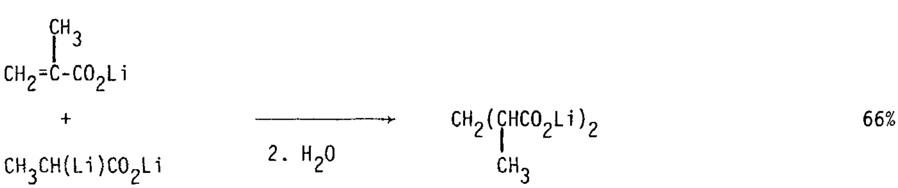
Section 16 Carboxylic Acids from Acetylenes



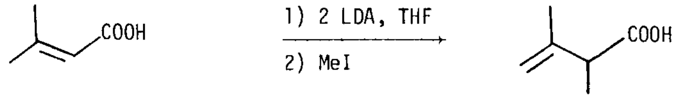
Rec Trav Chim (1975) 94 209

Also via: Esters - Section 106, Amides - Section 76. Also see any relevant Difunctional Compounds.

Section 17 Carboxylic Acids, Acid Halides and Anhydrides from Carboxylic Acids



Gazz Chim Ital (1976) 106 201



99%

Gazz Chim Ital (1974) 104 625

$Me_3SiCH_2COOH \xrightarrow[\text{2) } \underline{n}\text{-BuI}]{\text{1) 2 LDA}} Me_3SiCH(Bu)COOH$ 87%

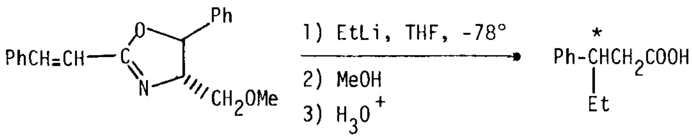
JCS Chem Comm (1975) 537

$PhSCH_2COOH \xrightarrow[\text{2) } \underline{i}\text{-PrI}]{\text{1) 2 LDA}} PhSCH(\underline{i}\text{-Pr})\text{-}COOH$ 99%

JCS Chem Comm (1975) 714

$MeSCH_2COOH \xrightarrow[\text{2) } \underline{i}\text{-BuBr}]{\text{1) LDA}} MeSCH(\underline{i}\text{-Bu})COOH$ 80%

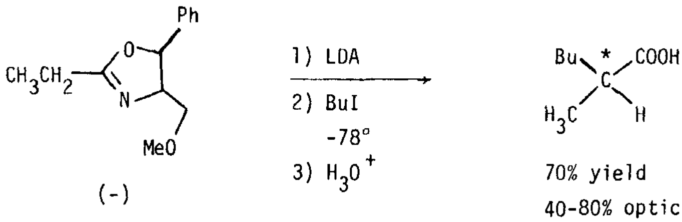
Tetr Lett (1975) 3797



66%

(high optical yield)

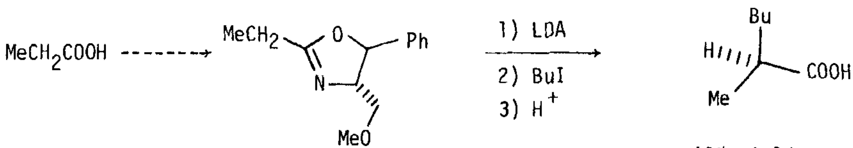
JACS (1975) 97 6266



70% yield

40-80% optical yields

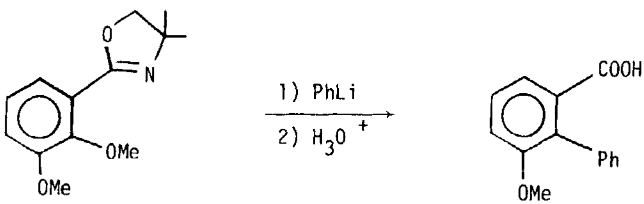
JACS (1974) 96 6508
JOC (1974) 39 2778
Tetr Lett (1974) 3495



42% yield

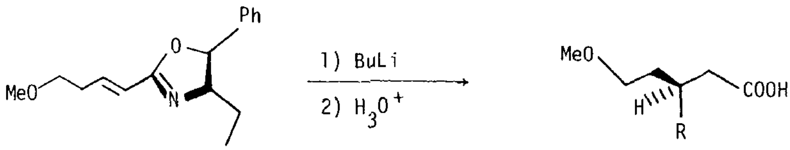
75% optical purity

JACS (1974) 96 268, 6508
JOC (1974) 39 618, 2778



70%

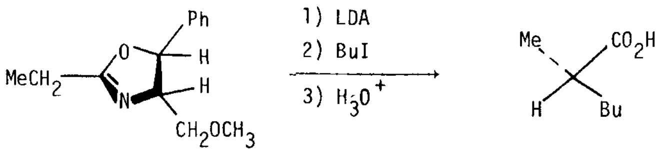
JACS (1975) 97 7383



S 81% ee

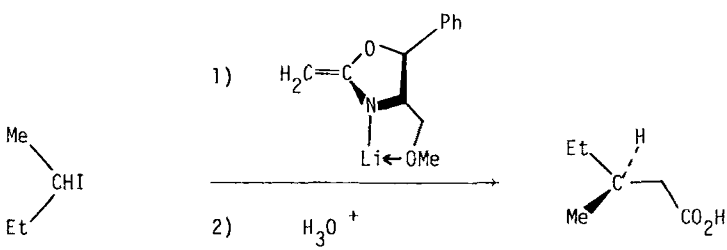
65%

Tetr Lett (1976) 1947



92%
~66% ee

JACS (1976) 98 567

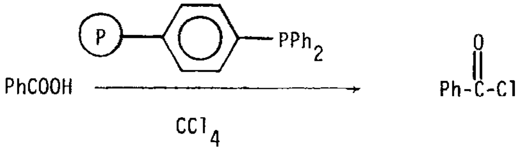


(±)

86%
34% ee

JACS (1976) 98 2290

Carboxylic Acids may be alkylated and homologated via ketoacid, ketoester and olefinic acid intermediates. See section 320 (Carboxylic Acid - Ketone), section 360 (Ester - Ketone) and section 322 (Carboxylic Acid - Olefin). Conjugate reductions of unsaturated acids are listed in Section 74 (Alkyls from Olefins).



90%

JCS Chem Comm (1975) 622

$RCOOH \xrightarrow{\text{Polymer-}PCl_2} RCOCl$

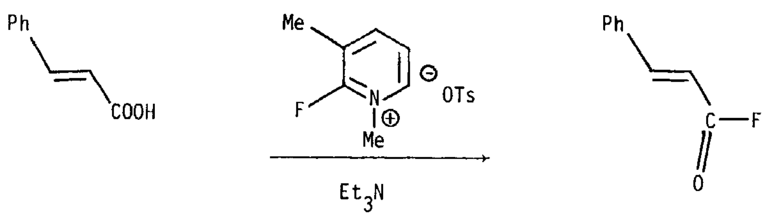
JACS (1974) <u>96</u> 6469

$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \xrightarrow{Cl_2CHOCH_3} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$ 54%

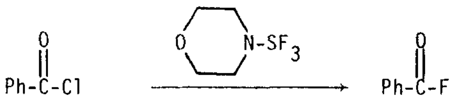
Synthesis (1975) 163

RCOOH or $(RCO)_2O$ + SeF_4 $\longrightarrow$ $R\overset{O}{\overset{\|}{C}}\text{-}F$ 80-95%

JACS (1974) <u>96</u> 925



Chem Lett (1976) 303



70%

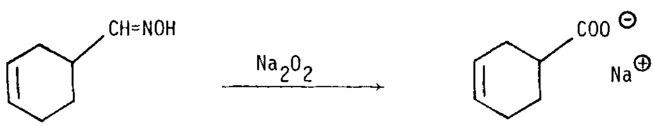
Synthesis (1975) 801

Section 18 Carboxylic Acids from Alcohols

$PhH + aq.\ KMnO_4 + Bu_4\overset{\oplus}{N}\overset{\ominus}{Br} \longrightarrow$ "Purple Benzene" $\xrightarrow{PhCH_2OH} PhCOOH$

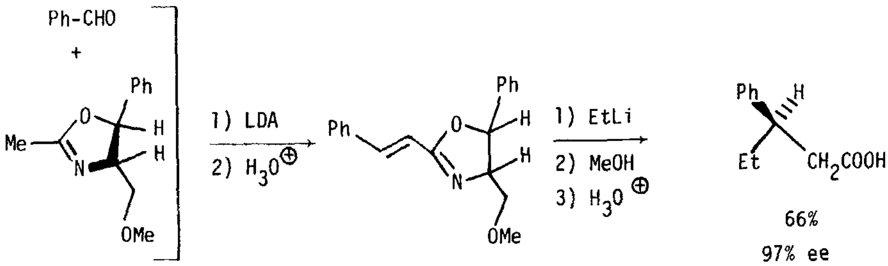
Tetr Lett (1974) 1511

Section 19 Carboxylic Acids and Anhydrides from Aldehydes



74%

Synthesis (1976) 807



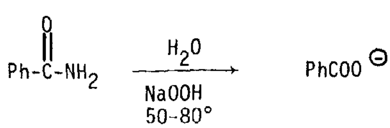
JACS (1975) 97 6266

Related methods: Carboxylic Acids from Ketones (Section 27). Also via: Esters - Section 105, Amides - Section 79. Also see any relevant Difunctional Compounds.

Section 20 Carboxylic Acids from Alkyls

No additional examples

Section 21 Carboxylic Acids from Amides



85%

JOC (1975) 40 1187

$$Ph\text{-}\overset{O}{\overset{\|}{C}}NHNH_2 \xrightarrow[Cu(OAc)_2]{O_2,\ CH_3OH} PhCOOH \qquad 95\%$$

Chem Lett (1975) 437

Section 22 Carboxylic Acids, Acid Halides and Anhydrides from Amines

No additional examples

Section 23 Carboxylic Acids from Esters

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR' \xrightarrow{BBr_3} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

R' = Me, Et, *t*-Bu, $PhCH_2$, *p*-NO_2-$PhCH_2$

JOC (1974) 39 1427

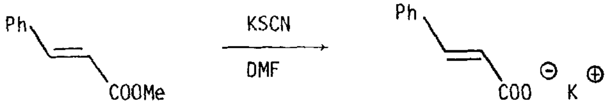
$$C_7H_{15}COO\text{-}\underline{t}\text{-}Bu \xrightarrow[2)\ H_3O^{\oplus}]{1)\ KO_2\text{-crown ether}} C_7H_{15}COOH \qquad 96\%$$

JOC (1976) 41 586

$$R\text{-}COOCH_3 \xrightarrow{KH,\ DMSO} RCOOH \qquad 63\%$$

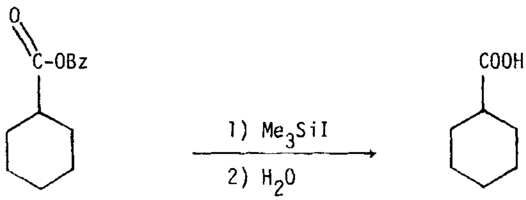
$RCOOCH_3$ = methyl podocarpa-8,11,13-trien-19-oate

Synth Comm (1976) 6 469



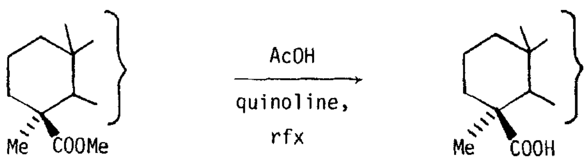
74%

Synth Comm (1975) 5 305



90%

Angew Int Ed (1976) 15 774

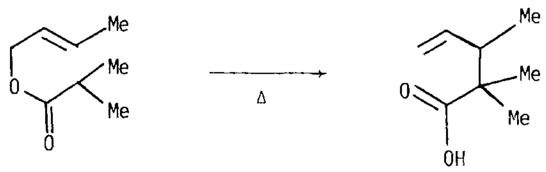


85%

Synthesis (1975) 330

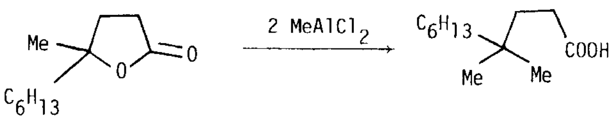
$PhCH_2CO_2Me + LiI \xrightarrow{Pyr} PhCH_2CO_2Li$ 93%

Org React (1976) 24 187



80%

JACS (1976) 98 2868



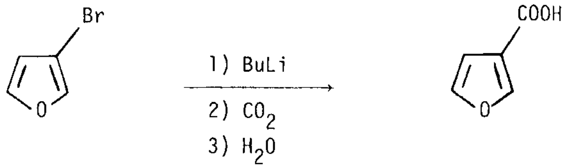
91%

J Prakt Chem (1974) 316 215

Section 24 Carboxylic Acids from Ethers

No additional examples

Section 25 Carboxylic Acids from Halides



97%

Synthesis (1974) 443

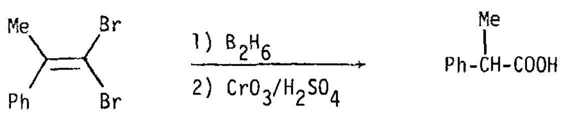
$$PhCuMgX_2 \xrightarrow[\text{2) } CO_2 \text{ 3) } H^{\oplus}]{\text{1) } (EtO)_3P,\ Et_2O/HMPA} PhCOOH \qquad 95\%$$

J Organometal Chem (1975) 94 463

$$RX + CO + 2\ NaOH \xrightarrow[NR_4^{\oplus}X^{\ominus}]{Pd(PPh_3)_4} RCOONa$$

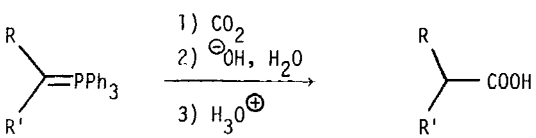
R = Bz, Ar, vinyl, heterocyclic

J Organometal Chem (1976) 121 C55



45%

Synth Comm (1976) 6 349

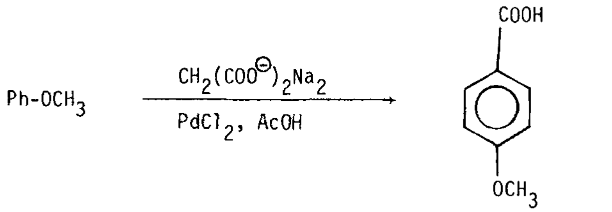


80-90%

Tetr Lett (1974) 1275

Also via: Esters - Section 115, Amides - Section 85. Also see any relevant Difunctional Compounds.

Section 26 Carboxylic Acids from Hydrides



55%

JOC (1976) 41 2049

$(CH_2)_3CHCOOH$ (NHR, NHR) → 1) Cl-COOEt 2) CH_2N_2 3) AgOCOPh 4) $^{\ominus}OH$ → $(CH_2)_3CHCH_2COOH$ (NHR, NHR)

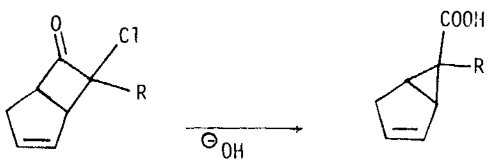
R = $PhCH_2OC(=O)-$

or t-$BuOC(=O)-$

Bull Chem Soc Japan (1975) 48 2401

Also via: Esters (Section 116)

Section 27 Carboxylic Acids from Ketones



97%

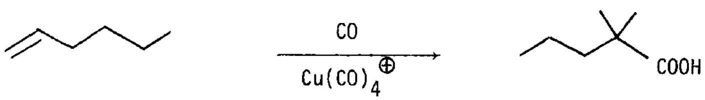
JCS Perkin I (1974)-927

Also via: Esters - Section 117. See also relevant Difunctional Compounds.

Section 28 Carboxylic Acids from Nitriles

No additional examples

Section 29 Carboxylic Acids from Olefins



60%

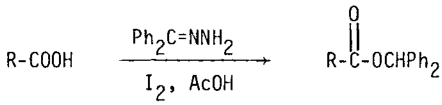
Bull Chem Soc Japan (1976) 49 3296

Section 30 Carboxylic Acids from Miscellaneous Compounds

Review: "Syntheses of Tetracarboxylic Acids"

Russ Chem Rev (1973) 42 939

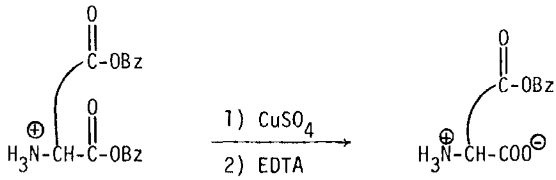
Section 30A Protection of Carboxylic Acids



>90%

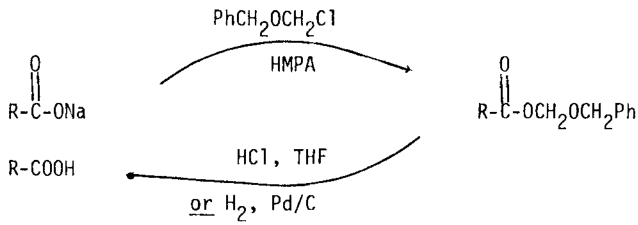
Useful for protecting amino acids.

JCS Perkin I (1975) 2019

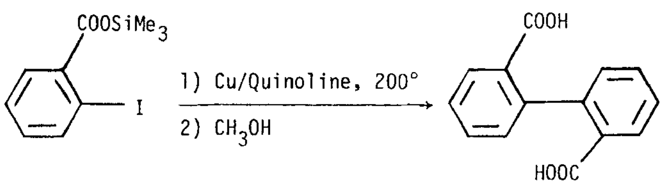


~74%

JOC (1975) 40 3287



JOC (1975) 40 2962



70%

Synthesis (1976) 40

$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}NHCH_2\overset{O}{\overset{\|}{C}}\text{-}OCH_2CCl_3} \xrightarrow[\text{pH 5.5}]{\text{Zn, THF/}H_2O} \mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}NHCH_2COOH} \qquad 83\%$$

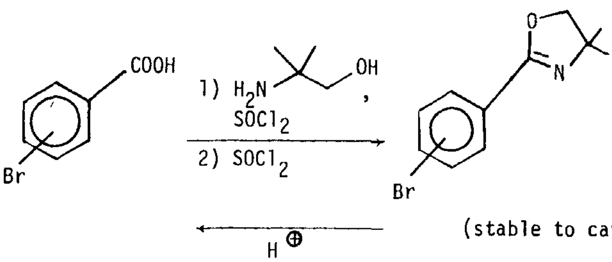
Synthesis (1976) 457

$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2Cl} \xrightarrow{\text{Co(I)phthalocyanine}} \mathrm{PhCOOH} \qquad 66\%$$

Angew Int Ed (1976) 15 681

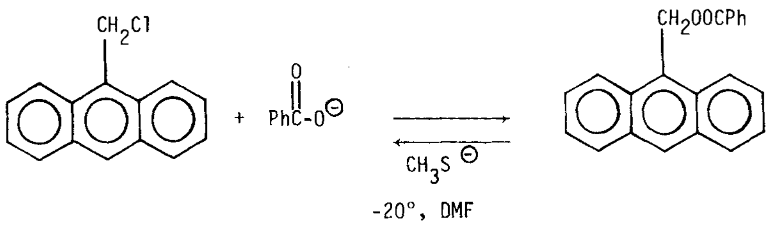
Use of the trimethylsilyl group to protect the carboxyl function of penicillin sulfoxides during their conversion to deacetoxycephalosporins.

JOC (1975) 40 1346



(stable to carbanions)

JOC (1974) 39 2787



JACS (1974) 96 590

Use of TlOR to cleave protected peptides from Merrifield resin.

Can J Chem (1974) 52 2832

Other reactions useful for the protection of carboxylic acids are included in Section 107 (Esters from Carboxylic Acids and Acid Halides) and Section 23 (Carboxylic Acids from Esters).

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 3 PREPARATION OF ALCOHOLS AND PHENOLS

Section 31 Alcohols from Acetylenes

$$Bu_3B \xrightarrow[\substack{2)\ aq.\ HCl,\ \Delta \\ 3)\ NaOH,\ H_2O_2}]{1)\ LiC{\equiv}CH} CH_3C(Bu)_2OH \qquad 82\%$$

JOC (1975) 40 2845

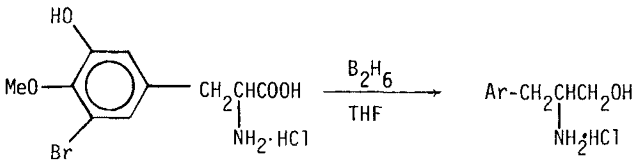
$$MeC{\equiv}CEt \xrightarrow[\substack{3)\ HCl \\ 4)\ NaOH/H_2O_2}]{\substack{1)\ Bu_2BH \\ 2)\ MeLi}} MeCH_2\overset{\substack{Bu \\ |}}{\underset{\substack{| \\ OH}}{C}}\text{-}Et \qquad 70\%$$

Synthesis (1974) 339

Section 32 Alcohols from Carboxylic Acids

$$\mathrm{PhCOCl} \xrightarrow{\overset{\oplus}{\mathrm{Bu_4N}}\ \overset{\ominus}{\mathrm{BH_4}}} \mathrm{PhCH_2OH} \qquad 100\%$$

JOC (1976) 41 690

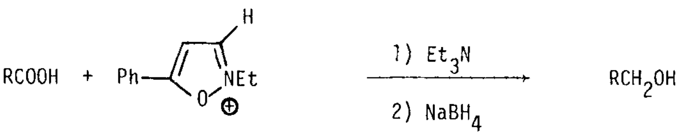


80%

JCS Perkin I (1974) 191

$$\mathrm{PhCOOH} + \mathrm{BH_3{\cdot}MeSH} + \mathrm{B(OMe)_3} \longrightarrow \mathrm{PhCH_2OH}$$

JOC (1974) 39 3052



80-100%

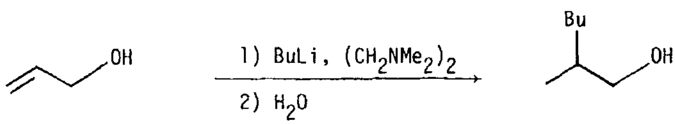
JOC (1974) 39 111

$$CH_2Cl_2 \xrightarrow[\text{2) PhCOCl, -78°} \\ \text{3) MeOH/HOAc}]{\text{1) BuLi, -100°}} PhC(OH)\text{-}(CHCl_2)_2$$

Chem Ber (1975) 108 328

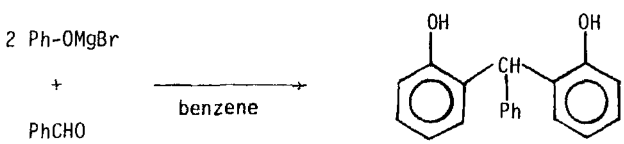
Also via: Esters (Section 38)

Section 33 Alcohols from Alcohols and Phenols



Org Synth (1976) 55 1

Section 34 Alcohols and Phenols from Aldehydes

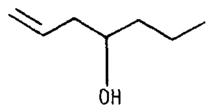


JCS Chem Comm (1976) 309

$$RCHO + Me_2CuLi \xrightarrow[(MeO)_3P]{Et_2O/HMPA} RCHOHMe$$ >90%

Tetr Lett (1975) 2353

$$CH_3(CH_2)_2CHO \xrightarrow[TiCl_4,\ CH_2Cl_2]{Me_3SiCH_2CH{=}CH_2}$$



87%

Tetr Lett (1976) 1295

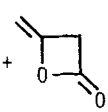
$$PhCH_2SH \xrightarrow[2)\ PhCHO]{1)\ BuLi} PhCHSH\text{—}CH(OH)\text{—}Ph$$ 70%

Angew Int Ed (1974) 13 202

$$Me_2NCH_2CO_2\text{-}\underline{t}\text{-}Bu \xrightarrow[2)\ CH_3CHO]{1)\ LDA,\ -78°} CH_3CH(OH)CH(NMe_2)CO_2\text{-}\underline{t}\text{-}Bu$$ 85%

Tetr Lett (1975) 1477

PhCHO +



$$\xrightarrow[2)\ MeOH]{1)\ TiCl_4,\ CH_2Cl_2} PhCH(OH)CH_2COCH_2COOMe$$ 91%

Chem Lett (1975) 161

$MeCOCCl_3 \xrightarrow[2)\ EtCHO]{1)\ LDA,\ THF,\ -75°} MeCOCCl_2CH(OH)Et$ 73%

Bull Soc Chim France (1975) 1876

$MeN(NO)Me \xrightarrow[2)\ PhCHO]{1)\ LDA,\ THF,\ -80°} MeN(NO)CH_2CH(OH)Ph$ 85%

Chem Ber (1975) 108 1293

$MeCH{=}C(NMePh)CN \xrightarrow[2)\ PhCHO]{1)\ LDA} PhCH(OH)CH_2CH{=}C(NMePh)CN$ 81%

Synthesis (1975) 512

$PhCHO + n\text{-}Bu_3SnCCl_3 \xrightarrow[2)\ H_2O]{1)\ 80°} PhCHOHCCl_3$ 63%

J Organometal Chem (1975) 102 423

$Cl_3CCO_2\text{-}i\text{-}Pr \xrightarrow[2)\ Me_2CHCHO]{1)\ Et_2NLi,\ THF\text{-}ØH\text{-}HMPA} Me_2CHCH(OH)CCl_2CO_2\text{-}i\text{-}Pr$ 71%

Synthesis (1975) 524, 533

$$\mathrm{CH_2Br_2} \xrightarrow[\text{2) PrCHO}]{\text{1) LDA, THF/Et}_2\text{O, -90°}} \underset{\displaystyle \mathrm{OH}}{\mathrm{PhCH}}\mathrm{-CHBr_2} \qquad 63\%$$

Bull Soc Chim France (1975) 1797

$$\mathrm{PhCHO + CHCl_3} \xrightarrow{\underline{\text{t}}\text{-BuOK, NH}_3\text{, -75°}} \underset{\displaystyle \mathrm{OH}}{\mathrm{PhCH}}\mathrm{-CCl_3} \qquad 84\%$$

J Gen Chem USSR (1974) 44 2590

$$\mathrm{PhSCH_2SePh} \xrightarrow[\text{2) PhCHO}]{\text{1) BuLi}} \mathrm{PhSCH_2}\text{-}\underset{\displaystyle \mathrm{OH}}{\mathrm{CHPh}} \qquad 94\%$$

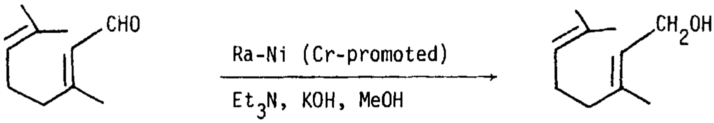
Tetr Lett (1975) 1617
Angew Int Ed (1975) 14 350, 700

$$\mathrm{PhSe(O)}\overset{\displaystyle \mathrm{Li}}{\mathrm{C}}\mathrm{HCH_2CH_2Ph} + \mathrm{EtCHO} \xrightarrow{\mathrm{NaI}} \mathrm{PhSe(O)}\underset{\displaystyle \mathrm{HC(OH)Et}}{\mathrm{C}}\mathrm{HCH_2CH_2Ph} \qquad 87\%$$

JCS Chem Comm (1975) 790

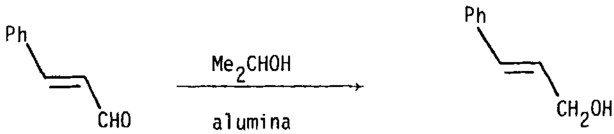
$$(\underline{n}\text{-}\mathrm{C_6H_{13}})_2\mathrm{BCl} + \mathrm{Bu}\underset{\displaystyle \mathrm{Li}}{\mathrm{C}}\mathrm{=N}\text{-}\underline{t}\text{-}\mathrm{Bu} \xrightarrow[\substack{\text{2) HSCH}_2\text{COOH} \\ \text{3) NaOH, diglyme} \\ \text{4) NaOH, H}_2\text{O}_2}]{\text{1) Et}_2\text{O, -78°}} (\underline{n}\text{-}\mathrm{C_6H_{13}})_2\underset{\displaystyle \mathrm{Bu}}{\mathrm{C}}\mathrm{-OH} \qquad 87\%$$

JOC (1975) 40 3644
Tetr Lett (1975) 2689



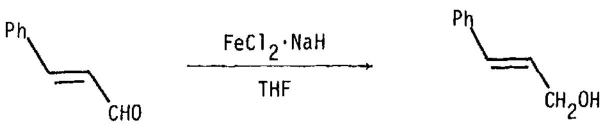
88%

Tetr Lett (1976) 4681



82%

Tetr Lett (1975) 3601



Chem Lett (1976) 581

$$RCHO + Et_3SiH \xrightarrow{H^{\oplus}} RCH_2OH$$

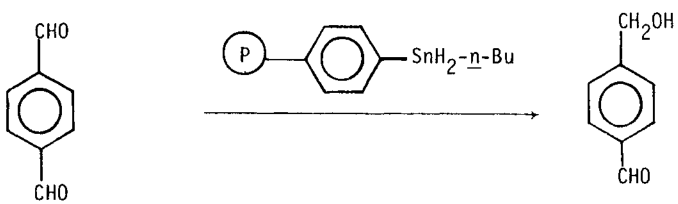
JOC (1974) 39 2740

Benzaldehyde is reduced in preference to acetophenone by $NaBH(OAc)_3$.

JCS Chem Comm (1975) 535

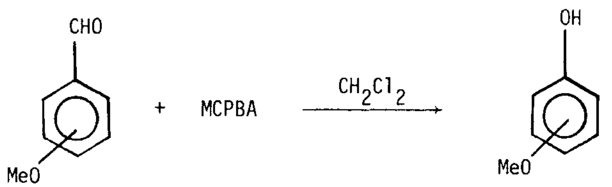
$LiAlH(O\text{-}\underline{t}\text{-}Bu)_3$ reduce benzaldehyde in the presence of acetophenone,
$NaBH_4$ and butanal in the presence of 2-butanone.
$LiBH_4$

Aust J Chem (1975) 28 1383



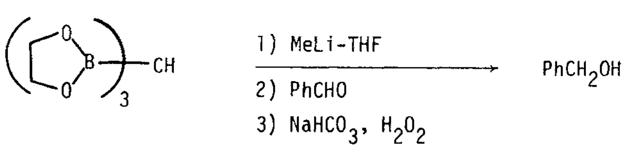
78%

JOC (1975) 40 1966



60-90%

JCS Perkin I (1974) 1353



97%

JACS (1975) 97 5608

Related methods: Alcohols from Ketones (Section 42)

Section 35 Alcohols and Phenols from Alkyls, Methylenes and Aryls

No examples of the reaction RR' → ROH (R'=alkyl, aryl, etc.) occur in the literature. For reactions of the type RH → ROH (R=alkyl or aryl) see Section 41 (Alcohols and Phenols from Hydrides).

Section 36 Alcohols and Phenols from Amides

No additional examples

Section 37 Alcohols and Phenols from Amines

No additional examples

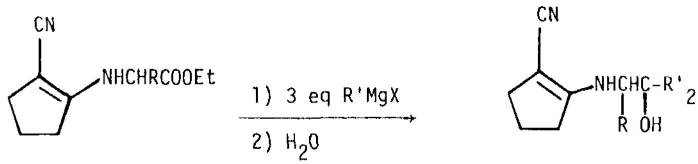
Section 38 Alcohols from Esters

$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OMe} \xrightarrow[\text{THF, rfx 20 hrs.}]{NaBH_4,\ HSCH_2CH_2SH} \mathrm{PhCH_2OH} \qquad 100\%$$

Tetr Lett (1975) 3295

$$PhCH_2CH_2COOEt \xrightarrow[CH_2Cl_2]{Na^{\oplus}[OBH_3C(CH_3)NPh]^{\ominus}} Ph(CH_2)_3OH \qquad 97\%$$

Chem Pharm Bull (1976) 24 1059

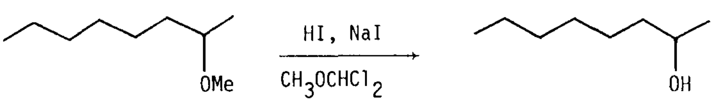


"excellent yield"

Comptes Rendus C (1975) 280 123

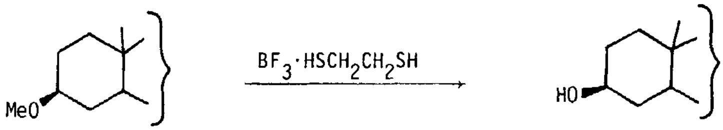
Related methods: Carboxylic Acids from Esters - Section 23,
Protection of Alcohols - Section 45A

Section 39 Alcohols and Phenols from Ethers and Epoxides



84%

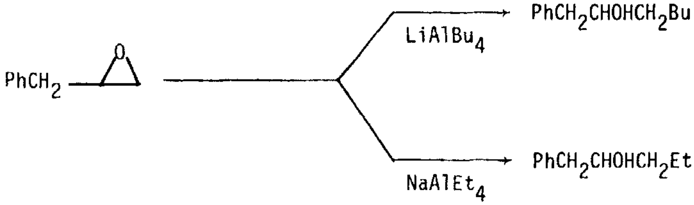
JOC (1976) 41 367



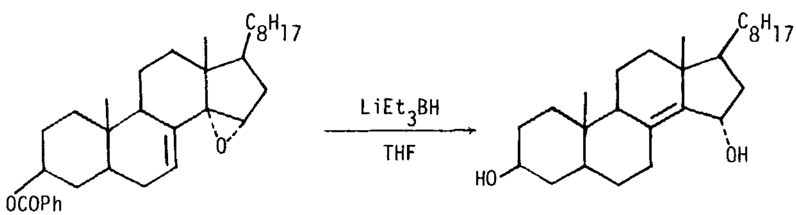
~80%

JCS Perkin I (1976) 2237

Additional examples of ether cleavages may be found in Section 45A (Protection of Alcohols and Phenols).

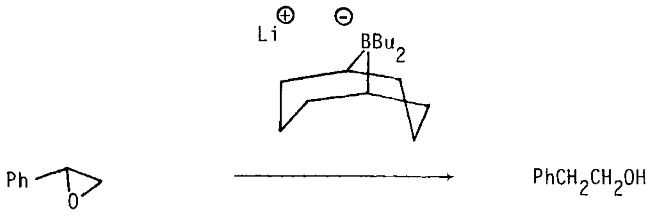


Tetr Lett (1975) 2521



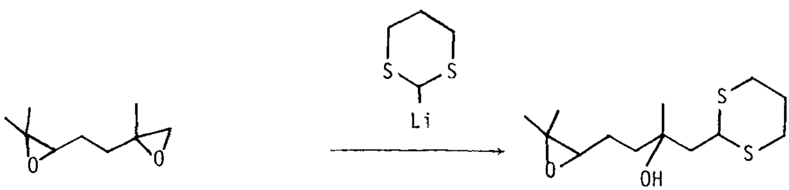
91%

Tetr Lett (1976) 3775



99%

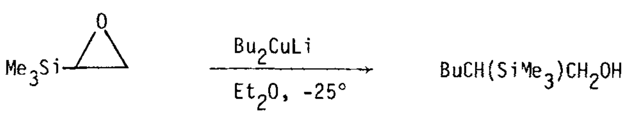
JCS Chem Comm (1976) 672



98%

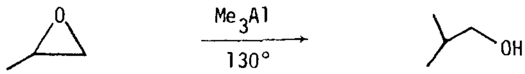
Used in juvenile hormone synthesis.

JOC (1974) 39 3645



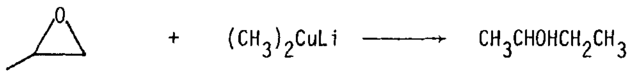
88%

JOC (1975) 40 2263



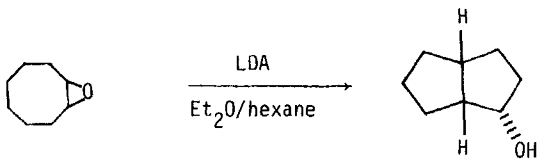
90%

J Organometal Chem (1974) 73 187



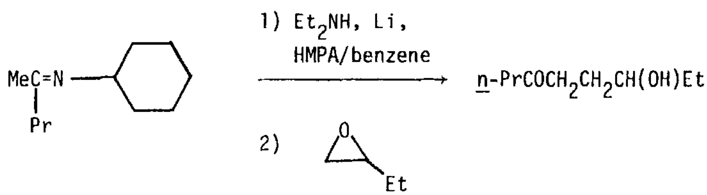
89%

Org React (1975) 22 253



80%

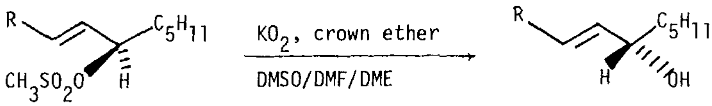
Synthesis (1975) 602



95%

Synthesis (1975) 256

Section 40 Alcohols and Phenols from Halides and Sulfonates



75%

Tetr Lett (1975) 3183

$$\underset{\text{(S)}}{C_6H_{13}\text{-}\overset{*}{C}HCH_3(OTs)} \xrightarrow[\text{2) } H_2O]{\text{1) } KO_2\text{, DMSO, crown ether}} \underset{\text{(R)}}{C_6H_{13}\text{-}\overset{*}{C}HCH_3(OH)}$$

75%

JOC (1975) 40 1678

$$RBr + HgClO_4 + H_2O \longrightarrow ROH$$

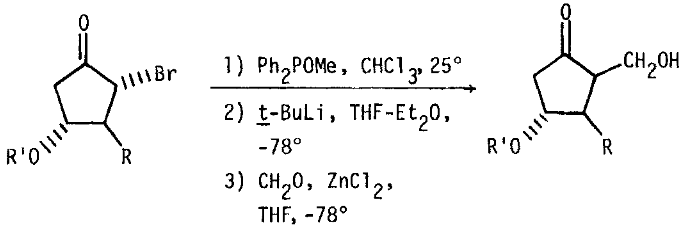
64-98%

21 cases

Tetrahedron (1974) 30 2467

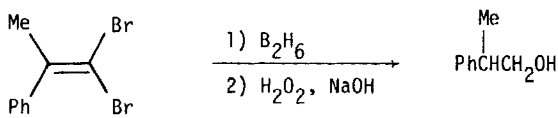
$$\underline{n}\text{-BuSnCH}_2OH \xrightarrow[\text{2) } \underline{n}\text{-Oct Cl}]{\text{1) 2 } \underline{n}\text{-BuLi}} \underline{n}\text{-Oct-CH}_2OH$$

Angew Int Ed (1976) 15 438



80-90%

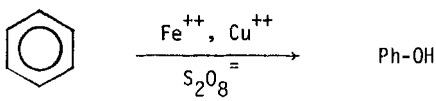
JACS (1975) 97 4745, 6260



97%

Synth Comm (1976) 6 349

Section 41 Alcohols and Phenols from Hydrides

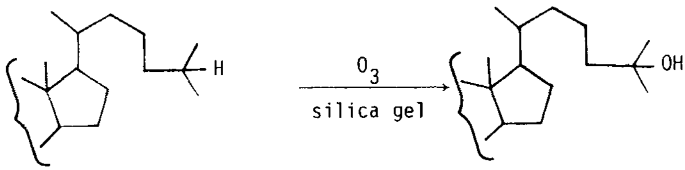


64%

JACS (1975) 97 1603

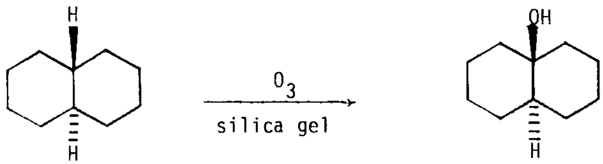
PhH + $Tl(OCOCF_3)_3$ ⟶ $PhTl(OCOCF_3)_2$ $\xrightarrow[\text{2) } H_2O]{\text{1) } B_2H_6}$ PhOH 58%

JCS Chem Comm (1975) 36



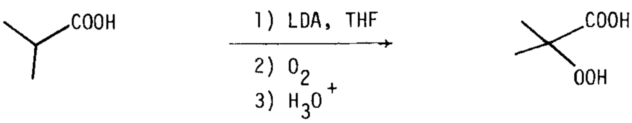
51% yield
11% conversion

JOC (1976) 41 2651



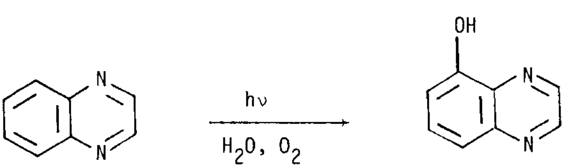
72%

JOC (1975) 40 2141



∿80%

JOC (1976) 41 370



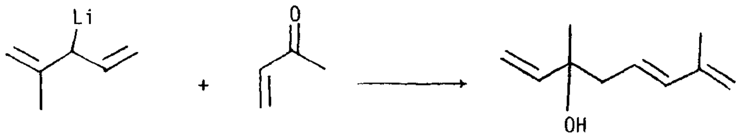
∿80%

Rec Trav Chim (1976) 95 285

Review: Photochemical Hydroxylation of Aromatic Compounds

Synthesis (1974) 173

Section 42 Alcohols from Ketones



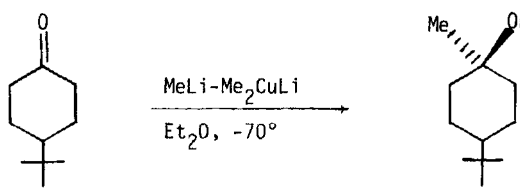
35%

JOC (1976) 41 3209

$$Me_2CO \quad + \quad BrCH_2CMe{=}CHCOOEt \xrightarrow[\text{2) } \Delta \text{ 3) } H^{\oplus}]{\text{1) Zn, HgI}_2} Me_2C(OH)\underset{\displaystyle COOEt}{\underset{|}{C}}HCMe{=}CH_2$$

70%

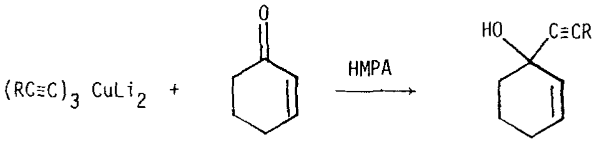
J Organometal Chem (1975) 96 149



91%

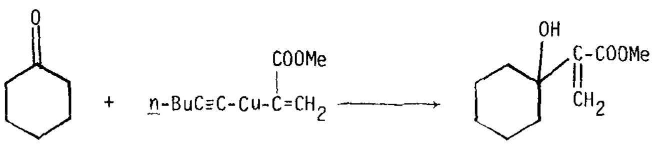
(high yield axial OH)

JACS (1975) 97 5280



~85%

JCS Chem Comm (1975) 892

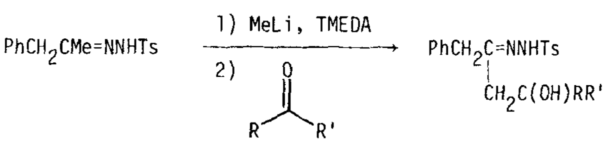


100%

Tetr Lett (1975) 3897

Review: Stereochemistry of Organometallic Compound Addition to Ketones

Chem Rev (1975) 75 521



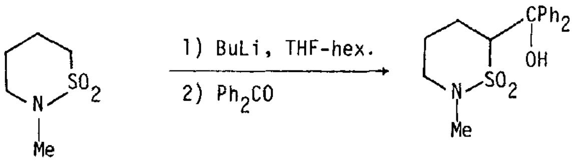
Tetr Lett (1975) 1811

$$PhCOCH_3 \xrightarrow[R\ =\ (-)\text{-N-methylephedrine}]{LiAl(\underline{n}\text{-Bu})_3OR} Ph\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}\underline{n}\text{-Bu}$$

56%

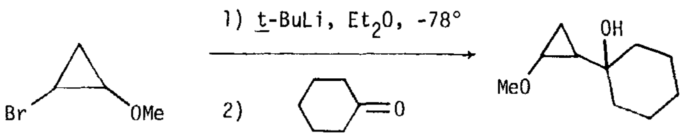
31% ee

Tetr Lett (1976) 4781



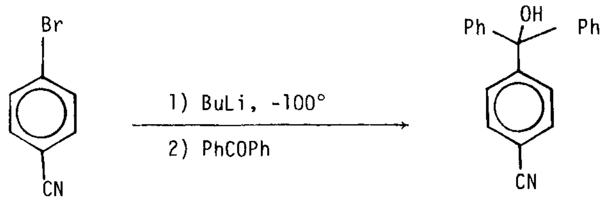
91%

JOC (1975) 40 1342
Synthesis (1975) 333



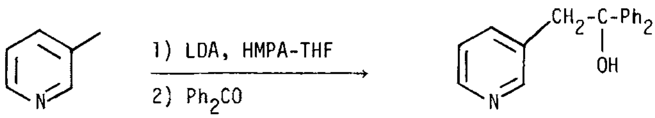
92%

Tetr Lett (1975) 3685



83%

JOC (1976) 41 1187



79%

Synthesis (1975) 705

$$MeCOCH{=}CH_2 \xrightarrow[\text{liq } NH_3/EtO]{NaC{\equiv}CH,\ MgSO_4} Me\text{-}\underset{\underset{\displaystyle CH{=}CH_2}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-}C{\equiv}CH$$

70%

Can J Chem (1975) 53 2157

$$CH_3COS\text{-}\underline{t}\text{-}Bu \xrightarrow[\text{2) } Ph_2CO]{\text{1) LDA, } -78^\circ} Ph_2C(OH)CH_2COS\text{-}\underline{t}\text{-}Bu$$

80%

Tetr Lett (1975) 3255

$$\text{Et-C(Me)(Cl)CO}_2\text{-}\underline{i}\text{-Pr} \xrightarrow[\text{2) (CH}_3)_2\text{CO}]{\text{1) Li, THF}} \text{EtC(Me)(Me}_2\text{COH)-CO}_2\text{-}\underline{i}\text{-Pr}$$

71%

J Organometal Chem (1975) 102 129

$$\text{NCCH}_2\text{CH}_2\text{COOH} \xrightarrow[\text{2) Ph}_2\text{CO}]{\text{1) LiNH}_2\text{, liq NH}_3} \text{Ph}_2\text{C(OH)—CH(CN)CH}_2\text{COOH}$$

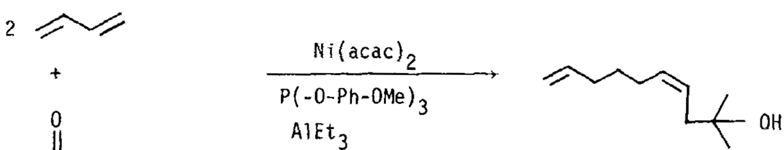
61%

J Organometal Chem (1975) 92 125

$$\text{PhC(=O)CH}_3 \xrightarrow[\text{2) NH}_4\text{Cl}]{\text{1) NaAlEt}_4\text{, NiCl}_2} \text{Ph-C(Et)(OH)-CH}_3$$

84%

Tetr Lett (1976) 993



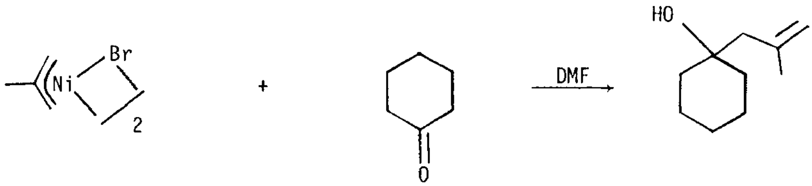
62%

Bull Chem Soc Japan (1976) 49 3646

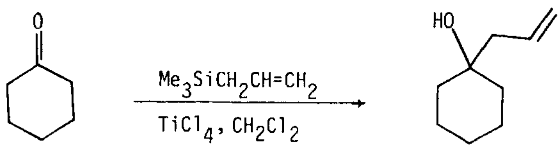
$$\text{Ph}_2\text{CO} \xrightarrow[\text{Ni(acac)}_2]{\text{Me}_3\text{Al}} \text{Ph}_2\text{C(Me)OH}$$

58%

Aust J Chem (1974) 27 2569

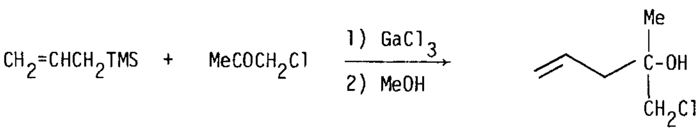


JOC (1975) 40 593



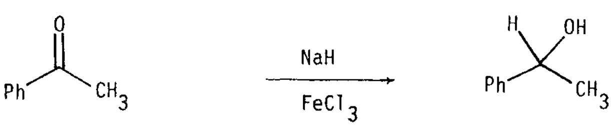
70%

Tetr Lett (1976) 1295



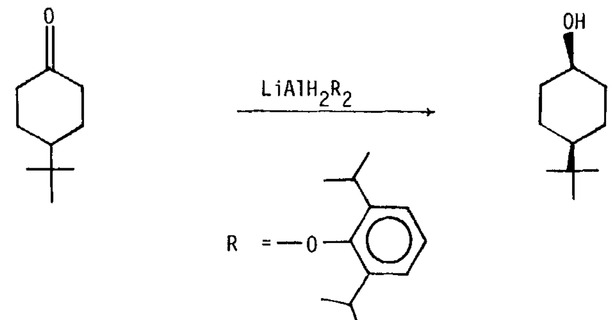
60%

J Organometal Chem (1975) 93 43



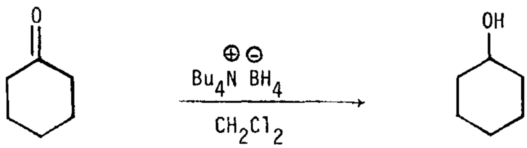
72%

JOC (1976) 41 1667



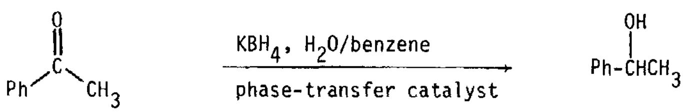
70%

JOC (1975) 40 926



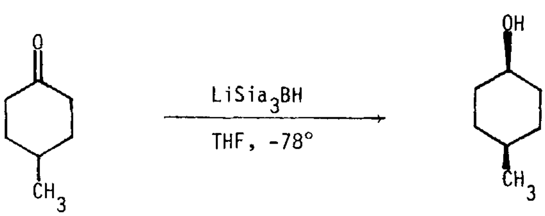
98%

JOC (1976) 41 690



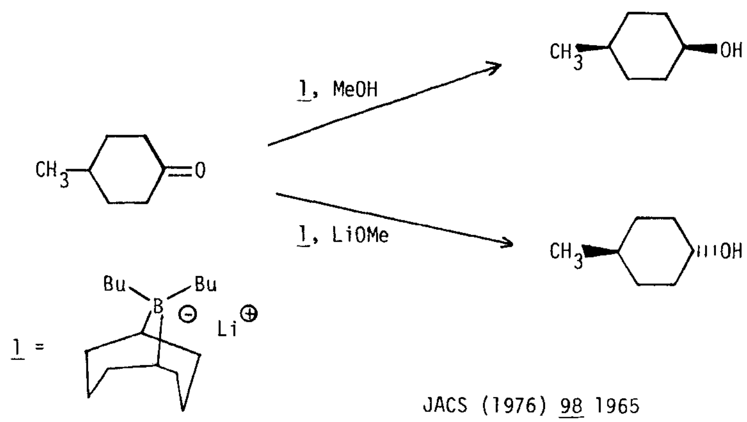
97%

Synthesis (1975) 531



99%

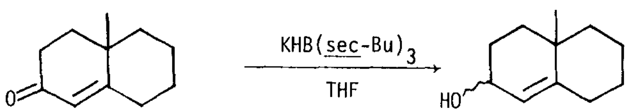
JACS (1976) 98 3383



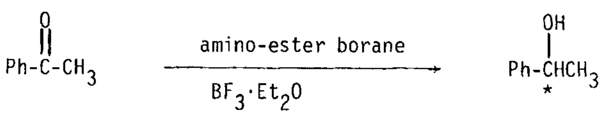
84%

90%

JACS (1976) 98 1965



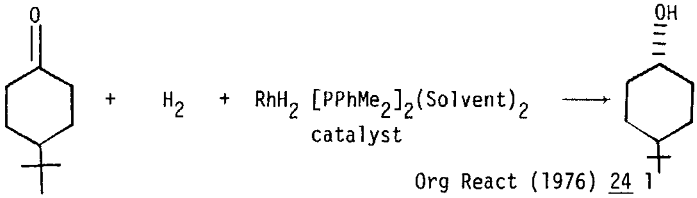
JOC (1975) 40 146



48%

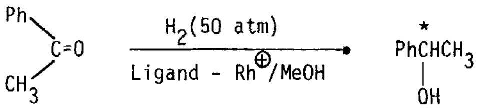
17% ee

Tetr Lett (1976) 295



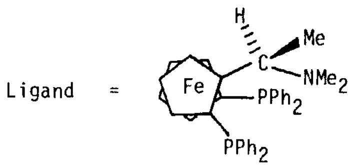
86%

Org React (1976) 24 1

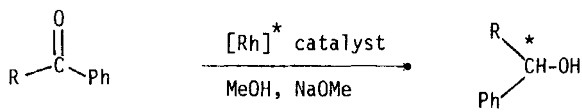


96%

R 43% ee



Tetr Lett (1976) 4351

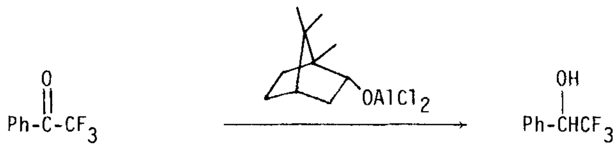


>95%

R = 1°,2°,3° alkyl

up to 58% ee

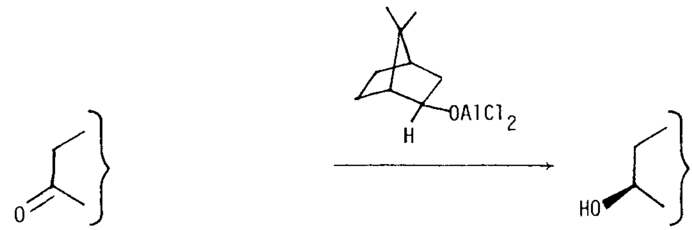
J Organometal Chem (1976) 122 83



88%

(S) 68% ee

Synthesis (1975) 701

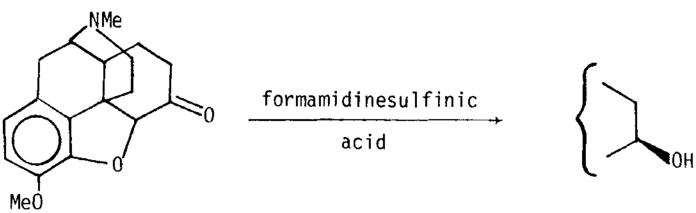


~70%

(various 3-oxo triterpenoids)

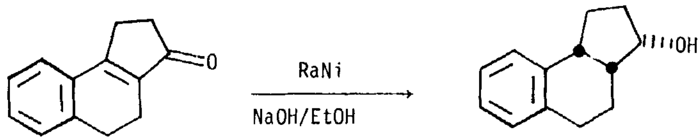
75-100% axial alcohol

JCS Perkin I (1976) 321



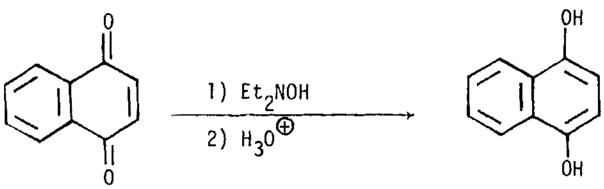
63%

JOC (1976) 41 3624



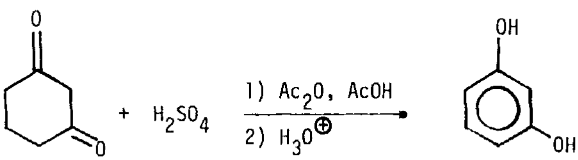
95%

Synthesis (1975) 702

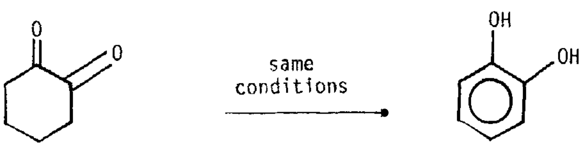


83%

Tetr Lett (1975) 1695



95%

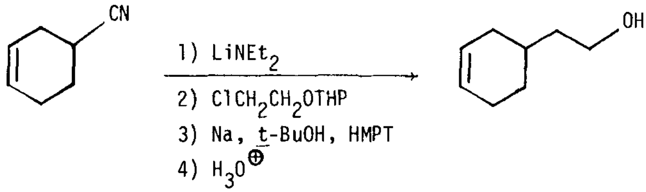


95%

JOC (1974) 39 3697

Related methods: Alcohols from Aldehydes (Section 34)

Section 43 Alcohols and Phenols from Nitriles

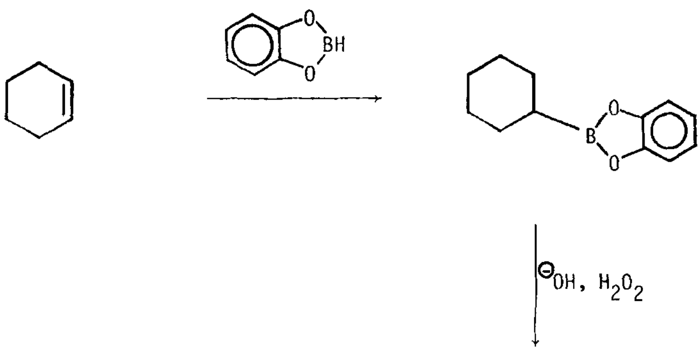


90%

Synthesis (1976) 391

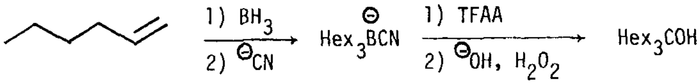
Section 44 Alcohols from Olefins

For the preparation of diols from olefins see Section 323 (Alcohol-Alcohol)



cyclohexanol 90%

JACS (1975) 97 5249



96%

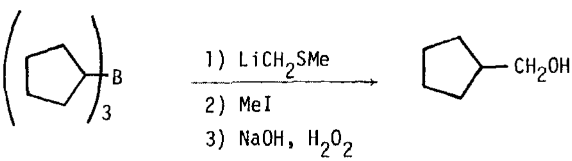
JCS Perkin I (1975) 138

$(\underline{n}\text{-hexyl})_3B + \underset{(-)}{R'C(SR'')_2} \xrightarrow[2)\ H_2O_2,\ ^{\ominus}OH]{1)\ HgCl_2} (\underline{n}\text{-hexyl})_2\underset{\underset{R'}{|}}{C}\text{-}OH$ ~80%

JCS Chem Comm (1974) 863

Use of $BH_3 \cdot Me_2S$ as a hydroboration agent.

JOC (1974) <u>39</u> 1437



97%

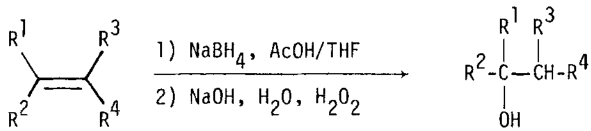
JOC (1975) <u>40</u> 814

$R_3B \xrightarrow[\substack{2)\ HCl,\ -78^\circ \\ 3)\ NaOH,\ H_2O_2}]{1)\ LiCH{=}CH_2} R_2\underset{\underset{OH}{|}}{C}\text{-}Me$ 87-94%

JACS (1975) <u>97</u> 5017

$$(C_6H_{13})_3B \quad + \quad Me_3\overset{\oplus}{N}-\overset{\ominus}{O} \longrightarrow 3\ C_6H_{13}OH \qquad 95\%$$

JOC (1975) 40 1776



Simplified hydroboration procedure

Synthesis (1974) 340

Review: Thexylborane, A Highly Versatile Reagent for Organic Synthesis via Hydroboration

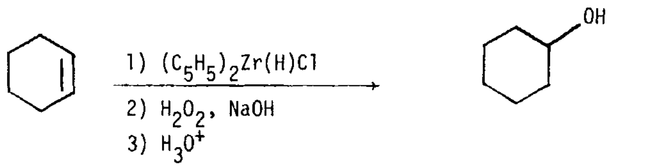
Synthesis (1974) 77

Review: Organoboranes as Reagents for Organic Synthesis

Chem Soc Rev (1974) 3 443

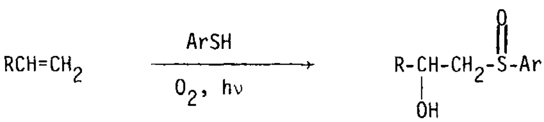
Full experimental details for preparation and use of 9-BBN as a highly selective reagent for hydroboration of olefins.

JACS (1974) 96 7765



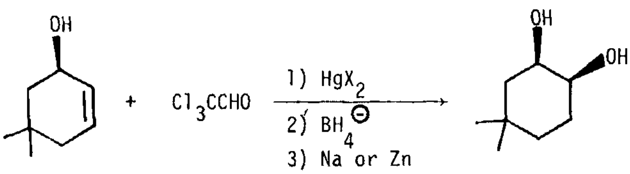
76%

Tetr Lett (1975) 3041



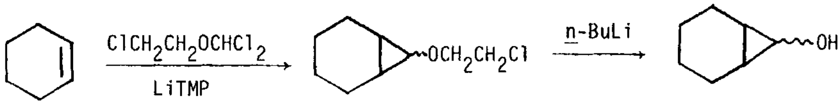
54-92%

JOC (1974) 39 1170



moderate yield

JOC (1974) 39 1474

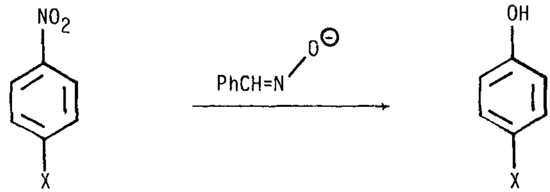


58%

no yield

Tetr Lett (1976) 3783

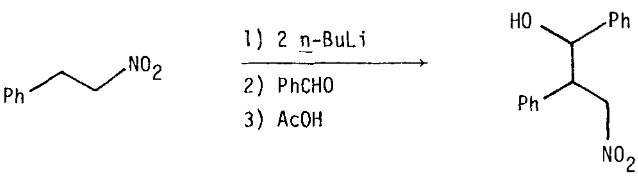
Section 45 Alcohols from Miscellaneous Compounds



20-94%

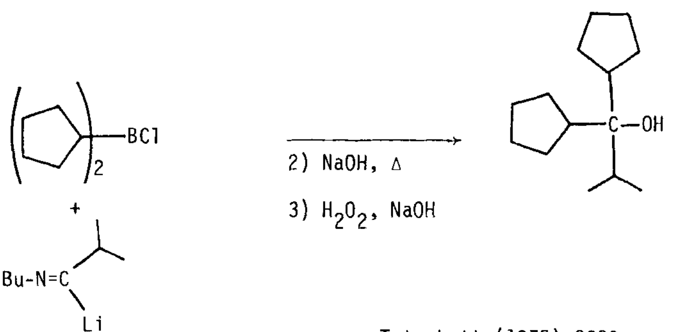
X = COOR, NO_2, CN, $COCH_3$,
CHO, $CONR_2$

JOC (1974) 39 3343



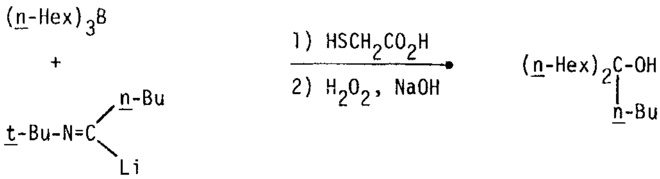
80%

Helv Chim Acta (1976) 59 2213



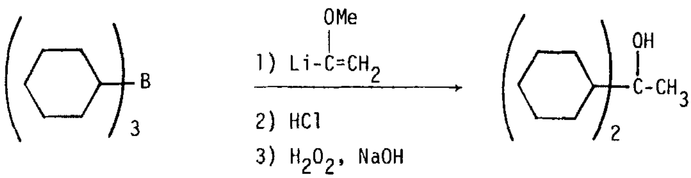
77%

Tetr Lett (1975) 2689



87%

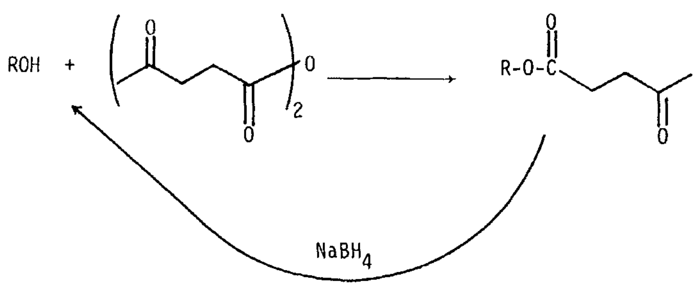
JOC (1975) 40 3644



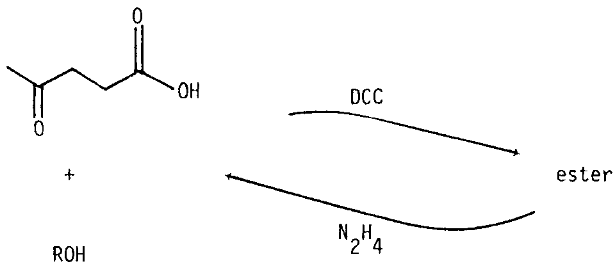
94%

Tetr Lett (1976) 2201

Section 45A Protection of Alcohols and Phenols



JACS (1975) 97 1614



Synth Comm (1975) 5 91

$$Ar\text{-}(CH_2)_4\text{-}\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{C}}}}\text{-}OH \;\underset{HgCl_2,\ CH_3CN/H_2O}{\overset{Ac_2O,\ DMSO}{\rightleftarrows}}\; Ar\text{-}(CH_2)_4\text{-}\underset{Me}{\overset{Me}{\overset{|}{\underset{|}{C}}}}\text{-}OCH_2SCH_3 \qquad 90\%$$

Tetr Lett (1976) 65

$$RO^{\ominus} + ClCH_2SCH_3 \xrightarrow{NaI} ROCH_2SCH_3$$

Stable to base and mild acid.

$$ROCH_2SCH_3 \xrightarrow[\text{or } Ag^+]{Hg^{++}} ROH$$

Tetr Lett (1975) 2643, 3269

$$ROH \xrightarrow{DMSO,\ HOAc,\ Ac_2O} ROCH_2SCH_3$$

$$ROCH_2SCH_3 \xrightarrow{CH_3I,\ NaHCO_3,\ H_2O} ROH$$

R = 1°,2°,3° alkyl

Tetr Lett (1976) 3067

Use of the β-methoxymethyl (MEM) group for the protection of alcohols.

$$ROH + MEM\text{-}Cl + (\underline{i}\text{-}Pr)_2NEt \longrightarrow RO\text{-}MEM$$

$$ROH + MEM\text{-}\overset{\oplus}{N}Et_3\ \overset{\ominus}{Cl} \xrightarrow[rfx]{MeCN} RO\text{-}MEM$$

$$RO^{\ominus} + MEM\text{-}Cl \longrightarrow RO\text{-}MEM$$

$$MEM = -CH_2OCH_2CH_2OCH_3$$

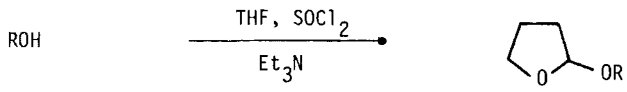
Stable to strong bases, reducing agents, some oxidizing agents, and mild acids. Removed by $ZnBr_2$ or $TiCl_4$ in CH_2Cl_2.

Tetr Lett (1976) 809

$$R\text{-}OH + CH_2(OMe)_2 \xrightarrow{P_2O_5} ROCH_2OCH_3 \qquad 94\text{-}99\%$$

R = 1°,2° alkyl

Synthesis (1975) 276



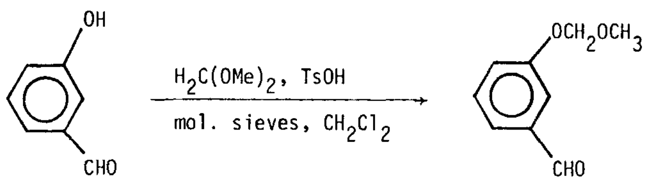
Removed with mild acid.

Tetr Lett (1976) 1725

$$ROH \xrightarrow[AgNO_3,\ MeCN]{PhSeCH_2CH_2Br} ROCH_2CH_2SePh$$

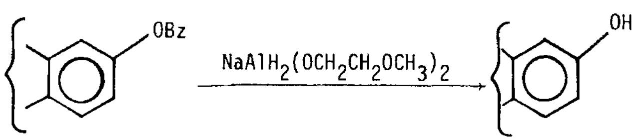
$ROCH_2CH_2SePh \xrightarrow[2)\ HCl]{1)\ H_2O_2} ROH$

Synth Comm (1975) 5 367



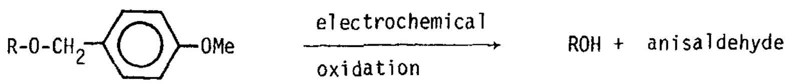
~70%

Synthesis (1976) 244



~50%

JOC (1976) 41 2545



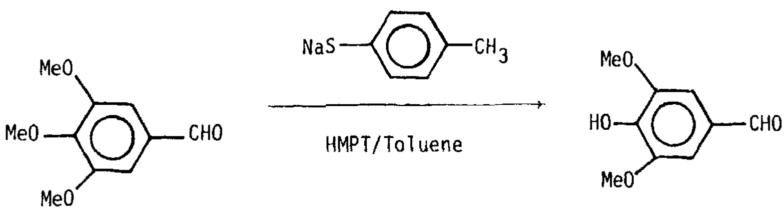
74-98%

R = alkyl, benzyl, propargyl, etc.

JOC (1975) 40 1356

$\underline{n}\text{-}C_8H_{17}OBz \xrightarrow{UF_6} \underline{n}\text{-}C_8H_{17}OH$ 69%

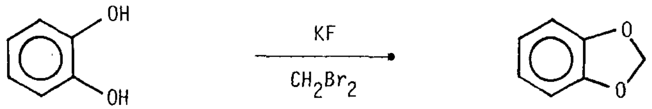
JACS (1976) 98 6717



90%

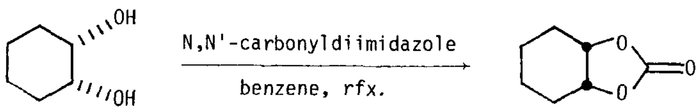
Synthesis (1976) 191

Further examples of ether cleavages are included in Section 39 (Alcohols and Phenols from Ethers and Epoxides)



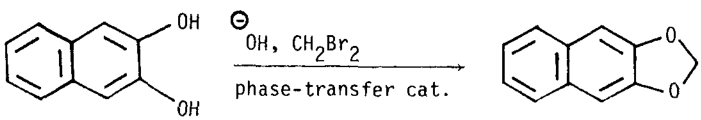
84%

Tetr Lett (1976) 3361



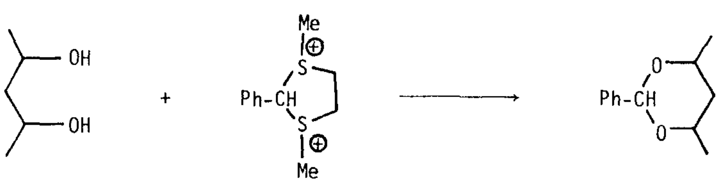
94%

Synth Comm (1975) 5 47



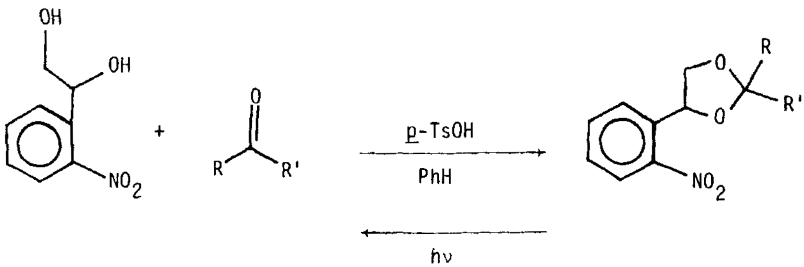
82%

Tetr Lett (1975) 3489

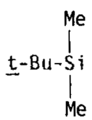


82%

Tetr Lett (1975) 4543



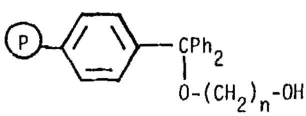
Can J Chem (1974) 52 187



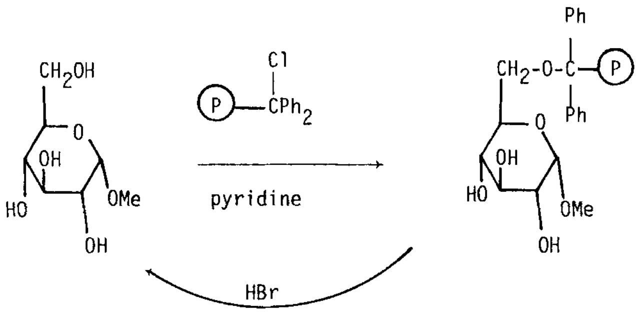
cannot be used for protecting hydroxy groups in molecules where there is an undesired opportunity for acyl migration, e.g. acyl glycerols.

JCS Chem Comm (1975) 249

Use of polymer-bound trityl chloride residues to block selectively one primary OH group of a polyhydroxy alcohol

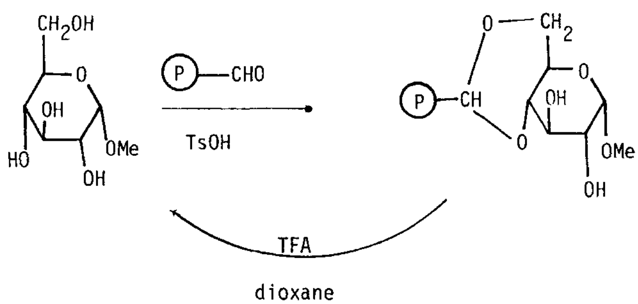


Can J Chem (1976) 54 926, 935

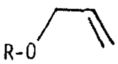


Tetr Lett (1975) 3055

Use of a polymer to protect glucose OH groups:



JCS Chem Comm (1975) 225

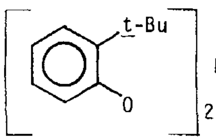

$\xrightarrow[H_2O \text{ or } MeOH]{Pd/C}$ ROH 78-95%

R = alkyl, aryl

Angew Int Ed (1976) 15 558

Allyl ether as a protecting group in carbohydrate chemistry.

JCS Perkin I (1974) 1446

5'-nucleotide + 
POCl $\underset{H_2/Pd}{\rightleftarrows}$ 5'-phosphate

Highly selective for 1° OH over 2° OH

Stable to dil. base, acid

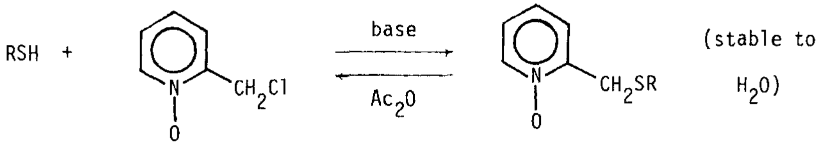
JOC (1974) 39 3767

Use of (t-Bu)$SiMe_2$ and (i-PrO)$_3$Si as protecting groups for 2', and 2',5'-positions of ribonucleosides.

Tetr Lett (1974) 2861, 2865

Use of $HgCl_2/H_2S$ for removal of the S-trityl group from α-SR β lactams.

JCS Chem Comm (1974) 12



RSH = cysteine, glutathione, thiouridine.

Chem Pharm Bull (1974) 22 2889

Review: "Photosensitive Protecting Groups"

Israel J Chem (1974) 12 103

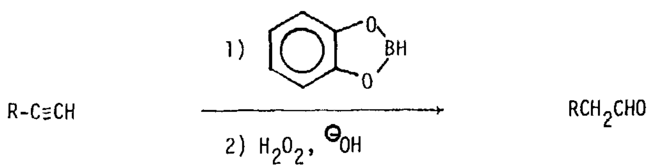
Review: "Electro-Deprotection--Electrochemical Removal of Protecting Groups"

Angew Int Ed (1976) 15 281

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 4 PREPARATION OF ALDEHYDES

Section 46 Aldehydes from Acetylenes

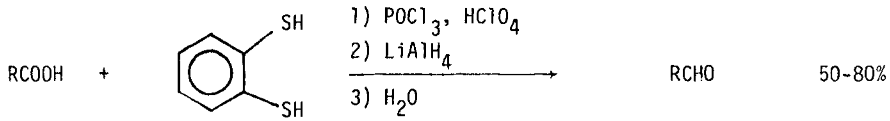


JACS (1975) 97 5249

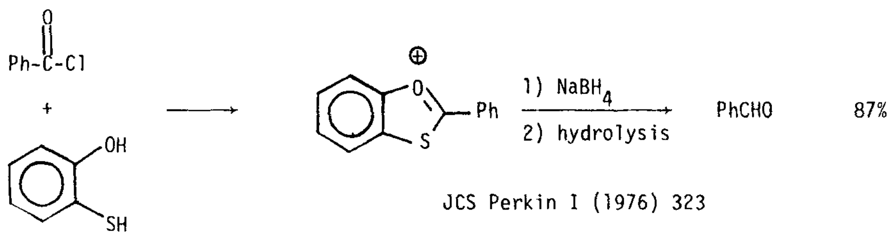
$$H\text{-}C{\equiv}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_3 \xrightarrow[NaCN]{MeOH} (MeO)_2CHCH_2COOCH_3 \qquad 75\%$$

JOC (1976) 41 3765

Section 47 Aldehydes from Carboxylic Acids and Acid Halides



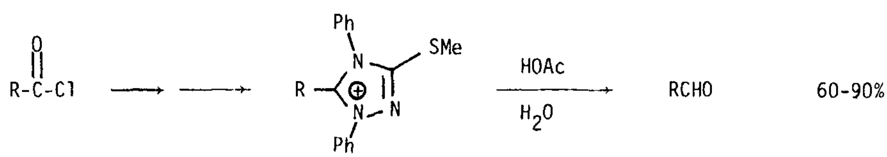
J Het Chem (1974) 11 943



JCS Perkin I (1976) 323

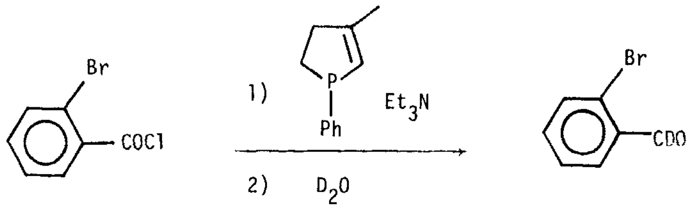
$$PhCH{=}CHCOCl \; + \; PhNHN{=}C(SMe)NHPh \xrightarrow[2)\ H_3O^{\oplus}]{1)\ NaBH_4} PhCH{=}CHCHO \qquad \sim 65\%$$

Tetr Lett (1974) 2649



R = alkyl, aryl, cinnamoyl

Tetrahedron (1976) 32 2549



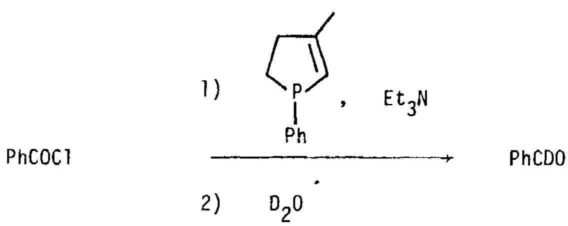
58%

Synth Comm (1976) 6 135

$$\underline{n}\text{-}C_{11}H_{23}\overset{\overset{\large O}{\|}}{C}\text{-}Cl \xrightarrow[\text{2,6-lutidine}]{H_2/\text{Pd-C, THF}} \underline{n}\text{-}C_{11}H_{23}\overset{\overset{\large O}{\|}}{C}\text{-}H$$

95%

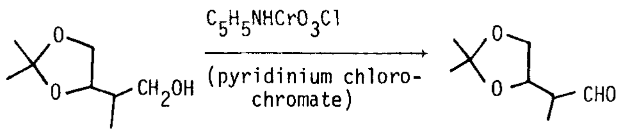
Synthesis (1976) 767



80%

JCS Chem Comm (1975) 459

Section 48 Aldehydes from Alcohols and Phenols



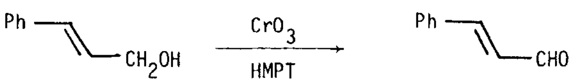
85%

Tetr Lett (1975) 2647

R-CH_2OH $\xrightarrow{CrO_2Cl_2}$ R-CHO ~80%

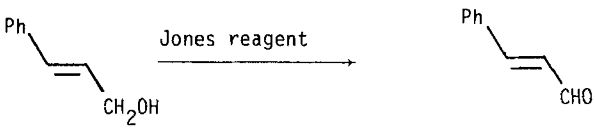
May isomerize double bonds.

JACS (1975) 97 5927



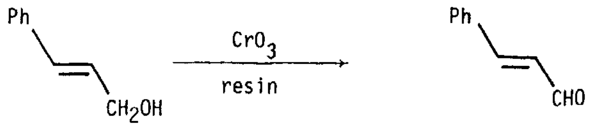
92%

Synthesis (1976) 394



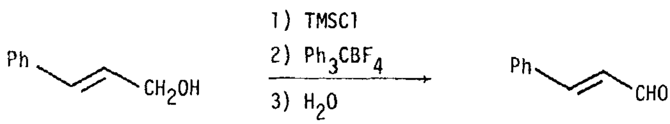
~80%

JOC (1975) 40 1664



96%

JACS (1976) 98 6737



100%

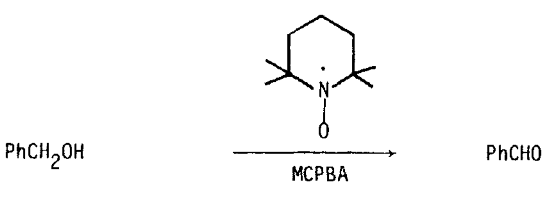
JOC (1976) 41 1479

$$R\text{-}CH_2OH \xrightarrow[\text{celite}]{Ag_2CO_3} R\text{-}CHO$$

50-97%

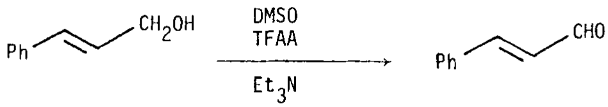
R = pyridine, pyrrole, indole, furyl, etc.

J Het Chem (1976) 13 525



76%

JOC (1975) 40 1860



83%

JOC (1976) 41 957

$Me_3C\text{-}CH_2OH \xrightarrow[\text{TFAA}]{\text{DMSO}} Me_3C\text{-}CHO$ 81%

JOC (1976) 41 3329

$Ph\text{-}CH_2OH \xrightarrow{Br_2/\text{HMPT}} Ph\text{-}CHO$ 86%

Synthesis (1976) 811

$PhCHO \xrightarrow[CH_2Cl_2]{\overset{\oplus}{}\overset{\ominus}{}\ Bu_4N\ BH_4} PhCH_2OH$ 92%

JOC (1976) 41 690

$Ph\text{-}CH_2OH \xrightarrow[CH_2Cl_2]{\overset{\oplus}{NO}\ \overset{\ominus}{BF_4}} PhCHO$ 62%

Synthesis (1976) 609

$PhCH_2OH \xrightarrow[\text{tetrabutylammonium bisulfate}]{\text{NaOCl}} PhCHO$ 76%

Tetr Lett (1976) 1641

$$PhCH_2OSnBu_3 \xrightarrow[CCl_4]{NBS} PhCHO \qquad 86\%$$

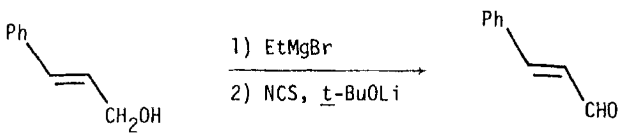
JACS (1976) 98 1629

$$PhCH_2OH \longrightarrow PhCH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow[C_6H_6]{h\nu} PhCHO \qquad 95\%$$

Synth Comm (1976) 6 281

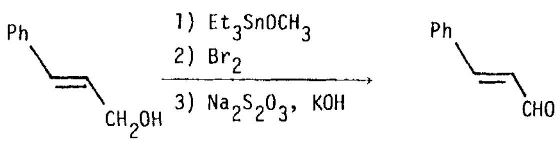
$$CH_3(CH_2)_5CH_2OH \xrightarrow[2)\ h\nu]{1)\ CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl,\ pyridine} CH_3(CH_2)_5CHO \qquad 77\%$$

JOC (1976) 41 3030



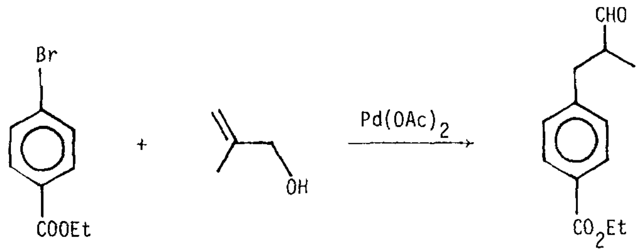
98%

Chem Lett (1975) 691



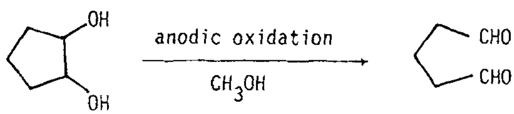
92%

Chem Lett (1975) 145



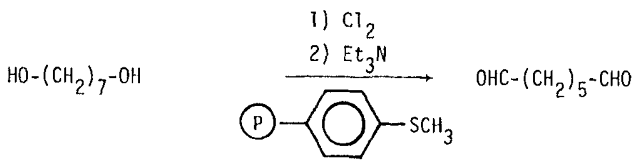
82%

JOC (1976) 41 1206



dialdehyde	56%
acetals	40%

JACS (1975) 97 2546



40%

JACS (1975) 97 2232

Related methods: Ketones from Alcohols and Phenols (Section 168)

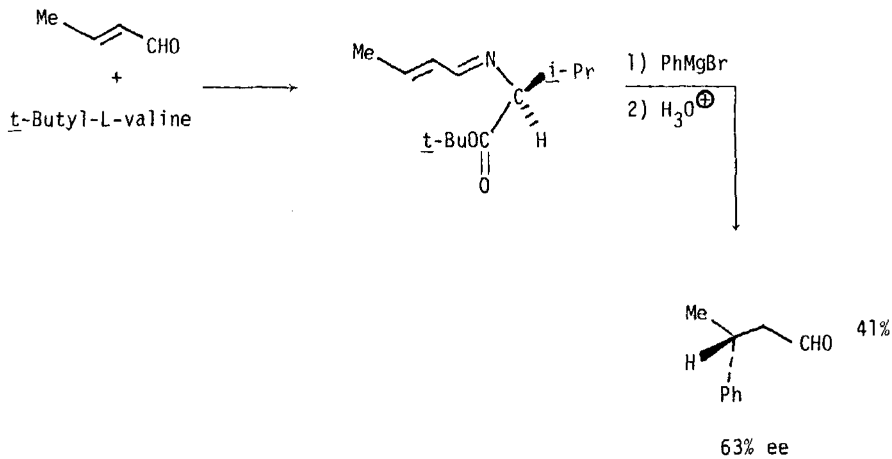
Section 49 Aldehydes from Aldehydes

$Me_2CHCHO \dashrightarrow Me_2CHCH{=}N\text{-}\underline{t}\text{-}Bu \xrightarrow[\text{2) } PhCH_2Br \quad \text{3) } H^{\oplus}]{\text{1) LDA, DME}} PhCH_2C(Me_2)CHO$ 76%

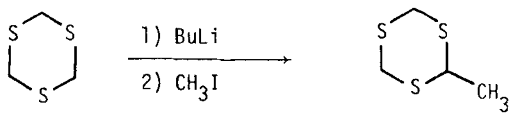
JOC (1974) 39 3102

$Me_2CHCHO \xrightarrow[\text{3) BzCl}]{\text{1) } Me_3CNH_2,\ K_2CO_3 \quad \text{2) EtMgBr}} Bz\text{-}C(Me)(Me)\text{-}CHO$ 30%

Org Synth (1974) 54 46

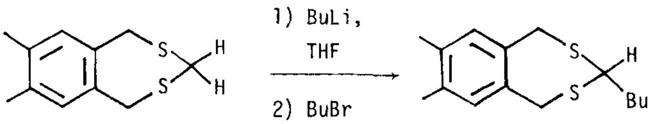


JACS (1976) 98 7450



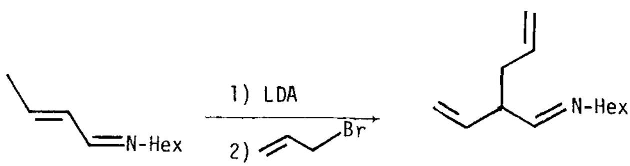
92%

Chem Ber (1974) 107 367



92%

Synthesis (1975) 720

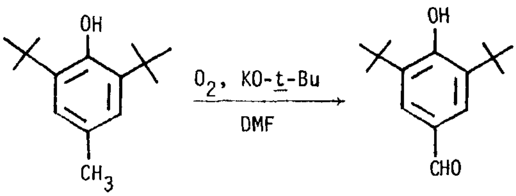


100%

Tetr Lett (1976) 597

Related methods: Aldehydes from Ketones (Section 57), Ketones from Ketones (Section 177). Also via: Olefinic aldehydes (Section 341).

Section 50 Aldehydes from Alkyls



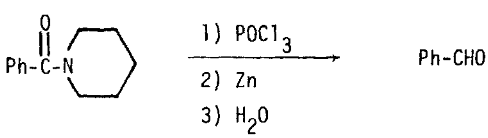
90%

Angew Int Ed (1975) 14 356

Section 51 Aldehydes from Amides

71%

Chem Lett (1975) 875



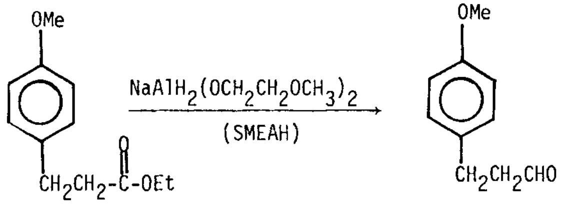
95%

JCS Chem Comm (1976) 594

Section 52 Aldehydes from Amines

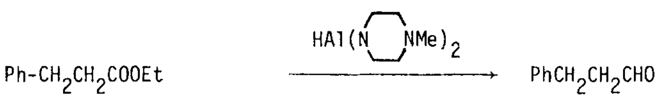
No additional examples

Section 53 Aldehydes from Esters



88%

Synthesis (1976) 526

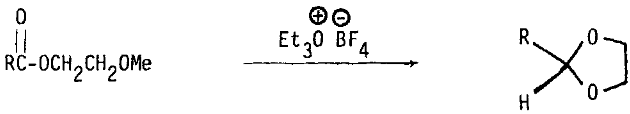


76%

Chem Lett (1975) 215

$$\text{Cbz-NH-}\underset{}{\overset{\text{Bz}}{\overset{|}{\text{CH}}}}\text{-COOMe} \xrightarrow{\text{DIBALH}} \text{Cbz-NH-}\overset{\text{Bz}}{\overset{|}{\text{C}}}\text{HCHO} \qquad 55\%$$

Chem Pharm Bull (1975) <u>23</u> 3081



76-91%

Synthesis (1974) 808

Section 54 Aldehydes from Ethers and Epoxides

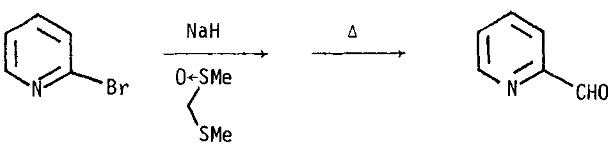
$$PhCH_2OCH_3 \xrightarrow{UF_6} PhCHO \qquad 78\%$$

JACS (1976) 98 6717

Section 55 Aldehydes from Halides

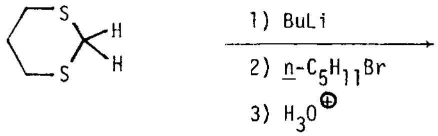
$$Ph(CH_2)_3Br \xrightarrow[2)\ H_2O_2]{1)\ Me_3Si\overset{Li}{\overset{|}{C}}HSePh} Ph(CH_2)_3CHO \qquad 66\%$$

Tetr Lett (1976) 4223



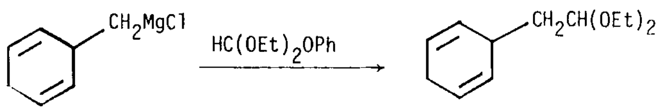
70%

JCS Chem Comm (1974) 410



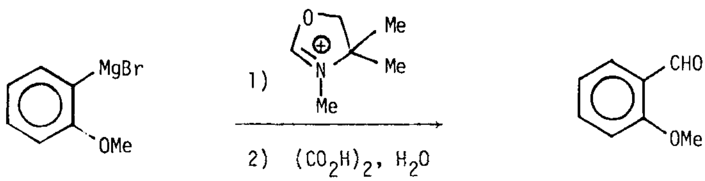
~90%

JOC (1975) 40 231



68%

Chem Ber (1974) 107 2295



Org Synth (1974) 54 42

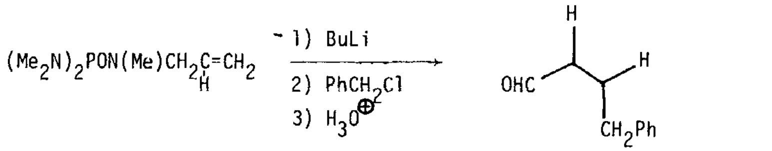
$$RCH_2Br \; + \; AgBF_4 \xrightarrow[2)\ Et_3N]{1)\ DMSO} RCHO$$

60-85%

Tetr Lett (1974) 917

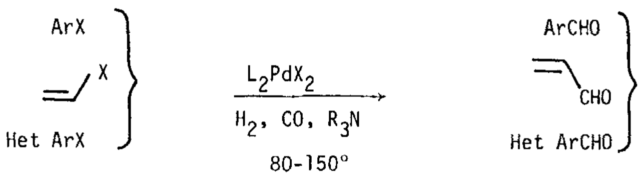
$$\underline{n}\text{-}C_5H_{11}I \; + \; LiCH(SMe)\underset{\Large\|\atop S}{C}NMe_2 \longrightarrow \xrightarrow[\text{MeOH}]{Hg^{++}} \underline{n}\text{-}C_5H_{11}CH(OMe)_2 \qquad 70\%$$

Synthesis (1974) 705



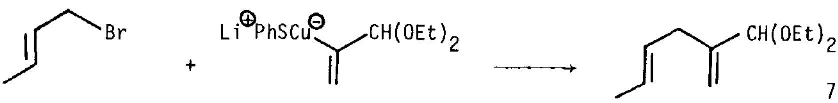
70%

Comptes Rendus (1974) 279 609



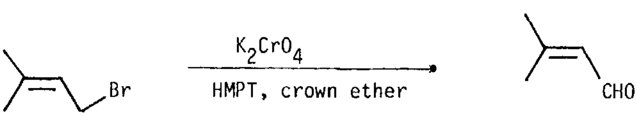
60-90%

JACS (1974) 96 7761



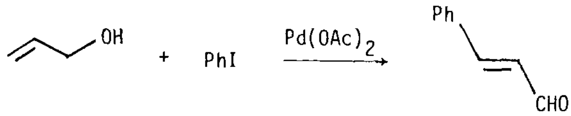
74%

JOC (1976) 41 726



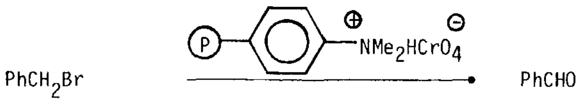
78%

JCS Chem Comm (1976) 190



84%

JOC (1976) __41__ 265
JOC (1976) __41__ 273



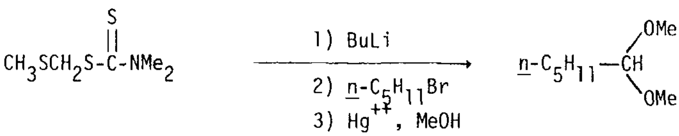
98%

Tetr Lett (1976) 3985

$PhCH_2Br + Hg_2(NO_3)_2 \xrightarrow[\ominus OH]{aq.\ EtOH} PhCHO$ 70-95%

(OMe, NO_2, CN, $COOR$ groups are incompatible)

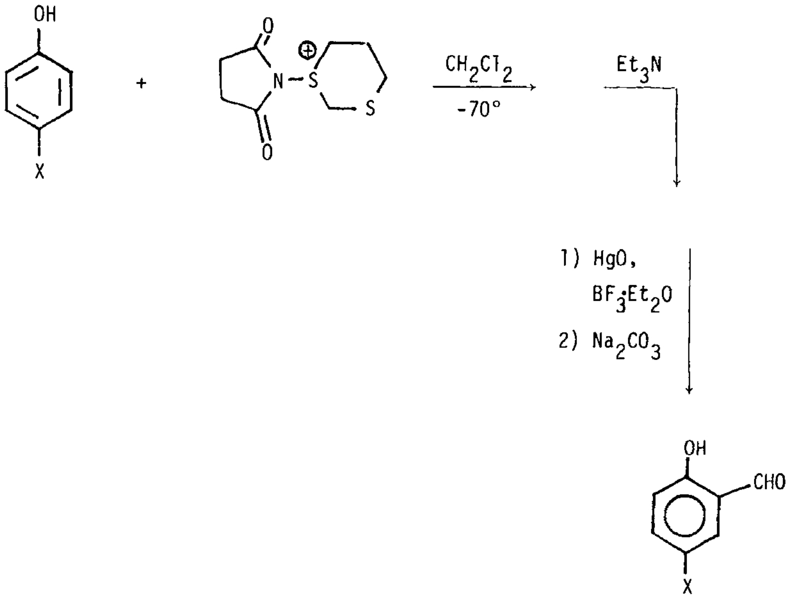
Synth Comm (1974) 45



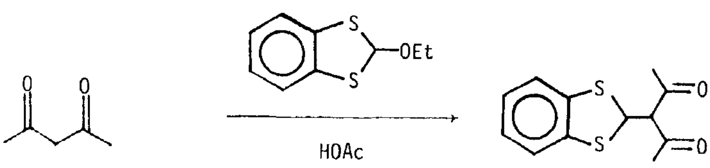
70%

Synthesis (1974) 705

Section 56 Aldehydes from Hydrides

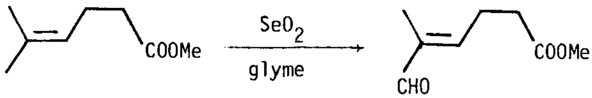


Tetr Lett (1974) 3463 20-40%



90%

JCS Perkin I (1976) 540



41%

Org React (1976) 24 261

Section 57 Aldehydes from Ketones

No additional examples

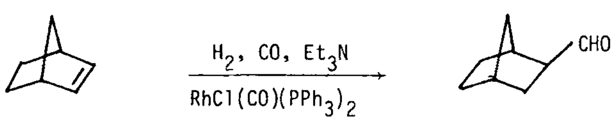
Section 58 Aldehydes from Nitriles

$$n\text{-BuCN} + Et_3\overset{\oplus}{O}\ \overset{\ominus}{BF_4} \xrightarrow[2)\ H_3O^{\oplus}]{1)\ Et_3SiH} n\text{-BuCHO}$$

71%

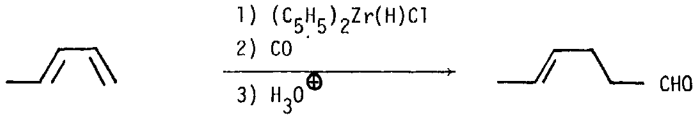
JCS Chem Comm (1974) 45

Section 59 Aldehydes from Olefins



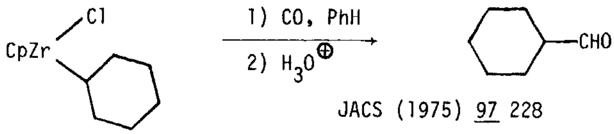
82%

Synth Comm (1976) 6 199



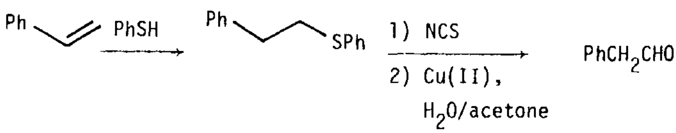
81%

JACS (1976) 98 262



97%

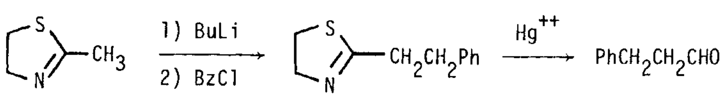
JACS (1975) 97 228



60%

JOC (1976) 41 2769

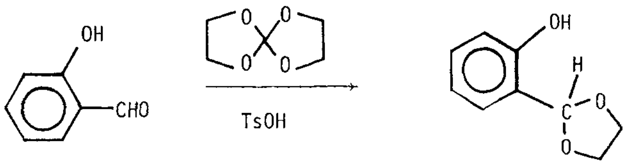
Section 60 Aldehydes from Miscellaneous Compounds



56%

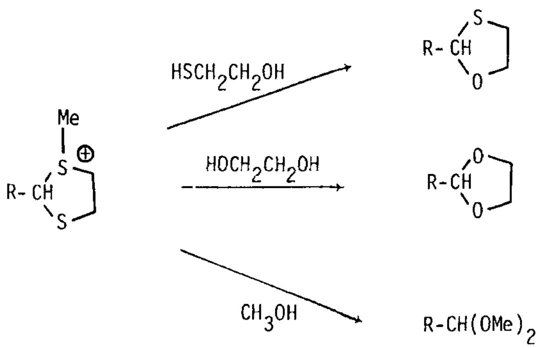
JOC (1975) 40 2021

Section 60A Protection of Aldehydes

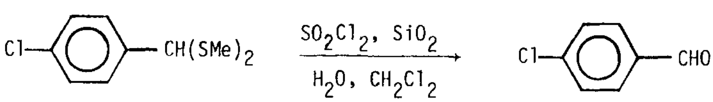


∿80%

JCS Chem Comm (1975) 432

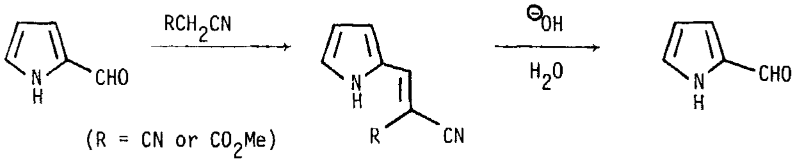


Tetr Lett (1975) 3267



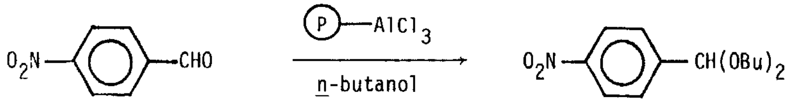
98%

Synthesis (1976) 678



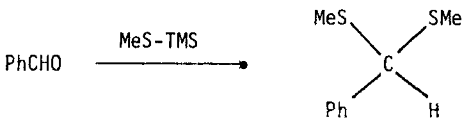
(R = CN or CO_2Me)

JOC (1976) 41 2826



48%

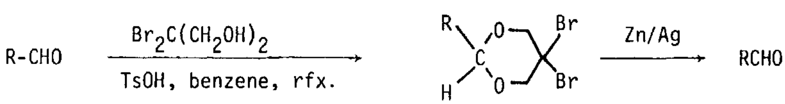
JOC (1975) 40 959



90%

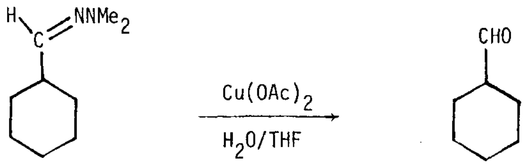
No acid catalyst required.

JACS (1975) 97 3229



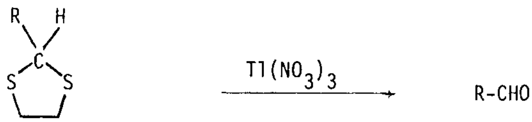
>90%

Tetr Lett (1976) 4577



100%

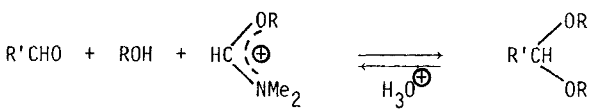
Tetr Lett (1976) 3667



73-99%

R = H, alkyl, aryl

Chem Pharm Bull (1976) 24 1115



60-80%

Liebigs Ann Chem (1974) 690

Related methods: Protection of Ketones - Section 180A, Enol Ethers - Section 367

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 5 PREPARATION OF ALKYLS METHYLENES AND ARYLS

This chapter lists the conversion of functional groups into Me, Et..., CH_2, Ph, etc.

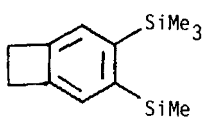
Section 61 Alkyls, Methylenes and Aryls from Acetylenes

$$R\text{-}C{\equiv}CH \xrightarrow{FeCl_2\text{-}NaH} RCH_2CH_3 \qquad 60\text{-}90\%$$

R = alkyl, aryl

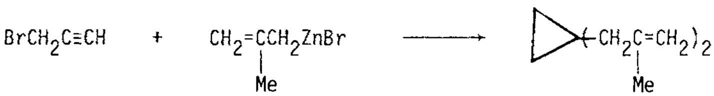
Chem Lett (1976) 581

$$HC{\equiv}CCH_2CH_2C{\equiv}CH \xrightarrow[\substack{CpCo(CO)_2 \\ \text{octane, rfx}}]{Me_3SiC{\equiv}CSiMe_3}$$



60%

JACS (1975) 97 5600
Angew Int Ed (1975) 14 712



68%

Comptes Rendus C (1975) 280 1389, 1473

Section 62 Alkyls and Aryls from Carboxylic Acids

$$CH_3(CH_2)_{14}COOH \xrightarrow[\Delta]{Me_3Al} CH_3(CH_2)_{14}CMe_3 \qquad 91\%$$

Aust J Chem (1974) 27 1665

Section 63 Alkyls from Alcohols

Reactions in which hydroxyl groups are replaced by alkyl, e.g., ROH → RMe, are included in this section. For the conversion ROH → RH see Section 153 (Hydrides from Alcohols and Phenols)

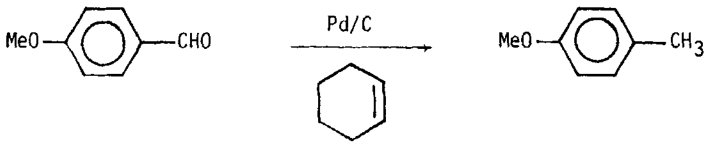
$$R_3COH \xrightarrow[100\text{-}200°]{\text{excess } Me_3Al} R_3CCH_3$$

Aust J Chem (1974) 27 1639

$$PhCH_2OH \xrightarrow[THF]{TiCl_3\text{-}LiAlH_4} PhCH_2CH_2Ph \qquad 78\%$$

JOC (1975) 40 2687

Section 64 Alkyls from Aldehydes

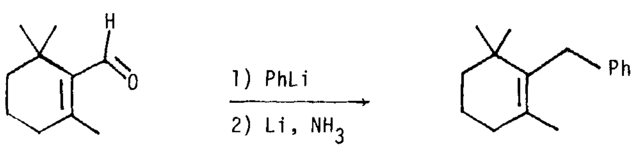


80%

JCS Chem Comm (1976) 757

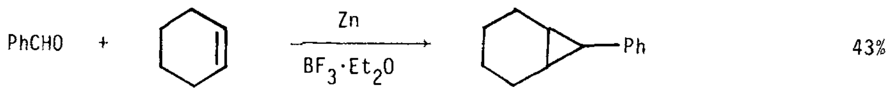
$$Cp_2TiCl_2 \quad + \quad Na \xrightarrow{PhH} [Cp_2Ti]_{1-2} \xrightarrow{RCHO} RCH_3$$

JACS (1974) 96 5290



99%

JOC (1976) 41 3465



Tetrahedron (1975) 31 2785

Review: "New Alkylation Methods Using Cyclopropyl Ylides"

Accts Chem Res (1974) 7 85

Related methods: Alkyls and Methylenes from Ketones (Section 72)

Section 65 Alkyls and Aryls from Alkyls and Aryls

Review: "Photosubstitution Reactions of Aromatic Compounds"

Chem Rev (1975) 75 353

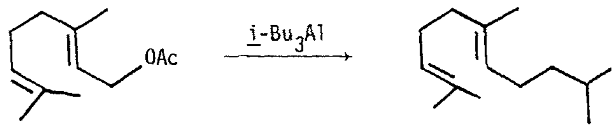
Section 66 Alkyls, Methylenes and Aryls from Amides

No additional examples

Section 67 Alkyls, Methylenes and Aryls from Amines

No additional examples

Section 68 Alkyls, Methylenes and Aryls from Esters

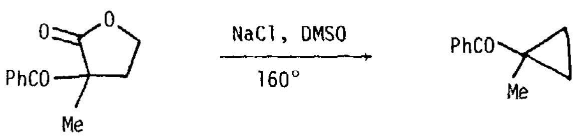


66%

Tetr Lett (1976) 2615

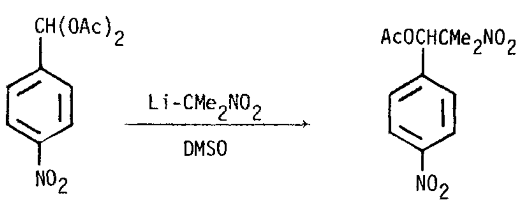
$$Cp_2TiCl_2 + Na \xrightarrow{PhH} [Cp_2Ti]_{1-2} \xrightarrow{RCOOR'} RCH_3$$

JACS (1974) 96 5290



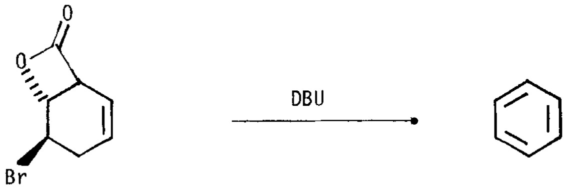
82%

Tetr Lett (1975) 4389
Chem Lett (1975) 1149



80%

Tetr Lett (1975) 431

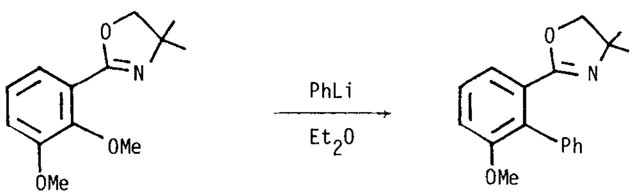


~100%

Tetr Lett (1976) 4435

Section 69 Alkyls and Aryls from Ethers

The conversion ROR → RR' (R'=alkyl, aryl) is included in this section.



100%

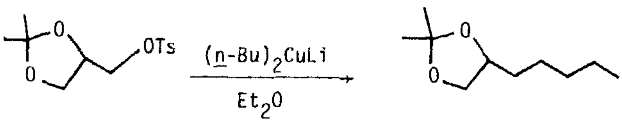
JACS (1975) 97 7383

$Me_2C{=}CHCH_2OEt \xrightarrow[\text{5\% CuBr}]{\underline{n}\text{-}C_7H_{15}MgCl} Me_2C{=}CHCH_2C_7H_{15}$ 80%

Tetr Lett (1975) 3837

Section 70 Alkyls and Aryls from Halides

The replacement of halogen by alkyl or aryl groups is included in this section. For the conversion RX → RH (X=halo) see Section 160 (Hydrides from Halides and Sulfonates)



80%

Tetr Lett (1976) 1161

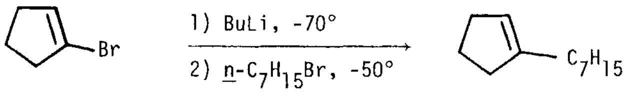
$\underline{n}$-$C_5H_{11}Br$ $\xrightarrow{(\underline{sec}\text{-}Bu)_2CuLi}$ 3-Methyloctane 94%

(alkenyl, alkynyl, aryl, benzyl, allyl, and propargyl halides also work well)

Org React (1975) 22 253

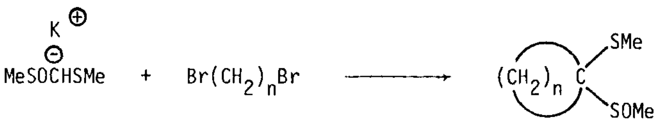
$\underline{n}$-$C_8H_{17}CH{=}C{=}CHBr$ $\xrightarrow[\text{2) MeI}]{\text{1) BuLi}}$ $\underline{n}$-$C_8H_{17}CH{=}C{=}CHCH_3$ 90%

JCS Chem Comm (1975) 561



75%

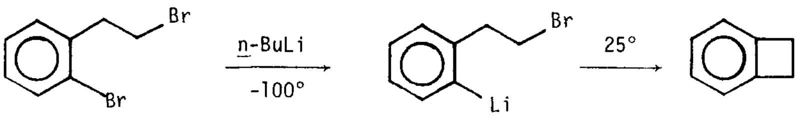
Synthesis (1975) 434



~80%

n = 3-5

Tetr Lett (1975) 2767



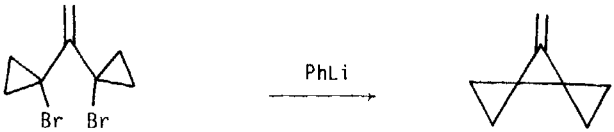
68%

JOC (1976) 41 1184

$$Me_3SiC{\equiv}CCH_2N{=}CHPh \xrightarrow[\text{2) } HC\equiv CCH_2Br]{\text{1) BuLi, THF}} \begin{array}{l} Me_3SiC{\equiv}CCH\text{-}N{=}CHPh \\ \quad\quad\quad\;\; | \\ \quad\quad\quad CH_2C{\equiv}CH \end{array}$$

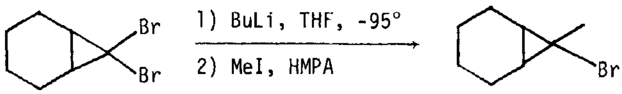
62%

Tetr Lett (1975) 3337



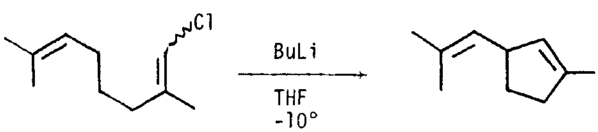
52%

Angew Int Ed (1976) 15 762



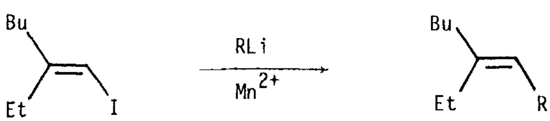
86%

JACS (1975) 97 949



62%

Tetr Lett (1974) 1207

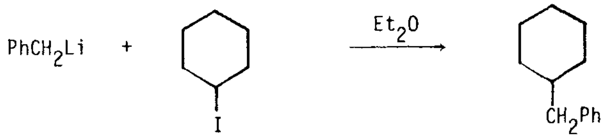


85-90%

J Organometal Chem (1976) 113 99

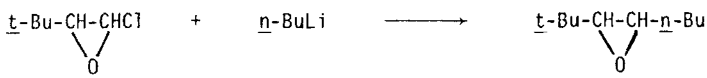
$$\mathrm{EtMgBr} + \mathrm{C_6H_{11}OTs} \xrightarrow[-78^\circ \text{ to } 25^\circ]{\mathrm{Li_2CuCl_4}} \mathrm{Et\text{-}C_6H_{11}} \qquad 98\%$$

Angew Int Ed (1974) 13 82

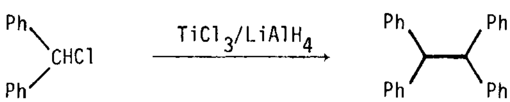


86%

JOC (1974) 39 1168

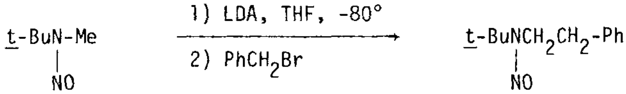


Tetr Lett (1974) 951



85%

Synthesis (1976) 607

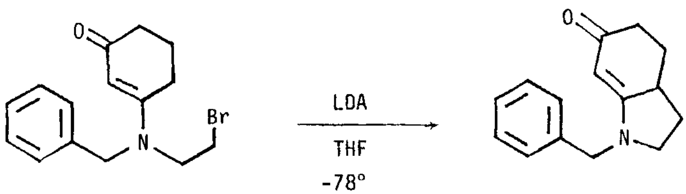


95%

Chem Ber (1975) 108 1293

$$(PhS)_2CH_2 \quad + \quad \underline{n}\text{-}BuBr \xrightarrow[\text{THF, HMPA}]{NaNH_2} (PhS)_2CBu_2 \qquad 84\%$$

Synthesis (1975) 387

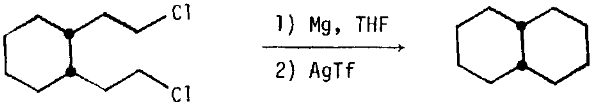


35%

Tetr Lett (1974) 3963

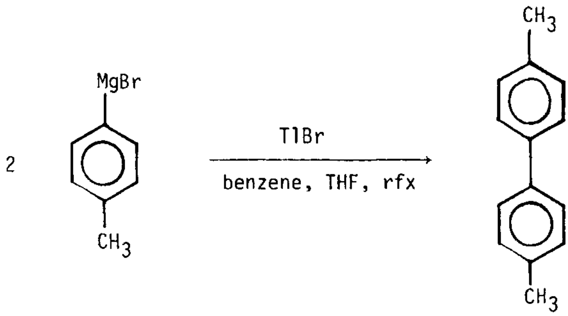
$$\begin{array}{c} Bu_3\overset{\ominus}{B}CH_3\overset{\oplus}{L}i \\ + \\ PhCH_2Br \end{array} \xrightarrow{CuCN} PhCH_2Bu \qquad 68\%$$

Synthesis (1976) 618



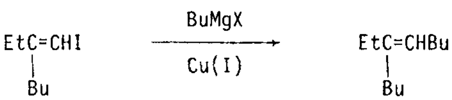
57%

JOC (1976) 41 2882



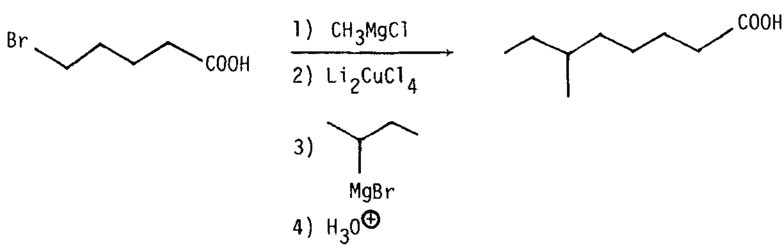
80%

Org Synth (1976) 55 48



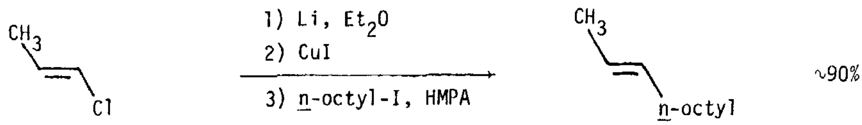
73%

Comptes Rendus (1974) 278 967

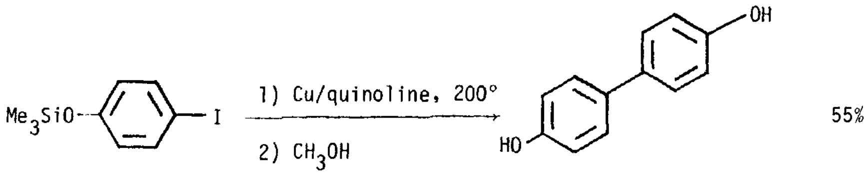


88%

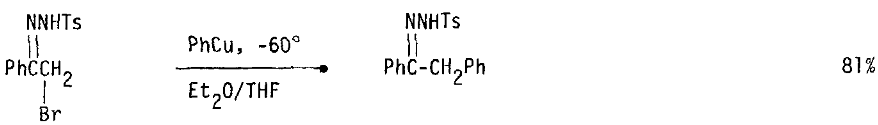
Tetr Lett (1976) 4697



Org Synth (1976) 55 103



Synthesis (1976) 40



JACS (1975) 97 7372

<u>t</u>-BuCO-C(<u>t</u>-Bu)Br_2 + Me_2CuLi ⟶ $\xrightarrow{H_2O}$ <u>t</u>-BuCOCH(Me)(<u>t</u>-Bu) 90%

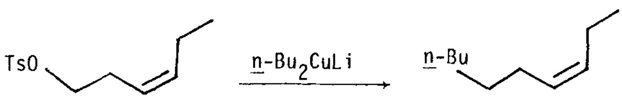
Comptes Rendus (1975) 280 217

t-BuCHBrCOCHBr-t-Bu + Me_2CuLi

$\xrightarrow{H_2O}$ t-Bu(Me)CHCOCH$_2$(t-Bu) 85%

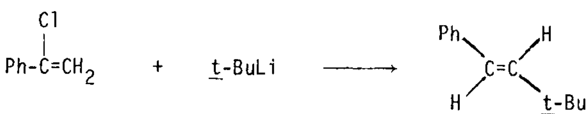
$\xrightarrow{MeI}$ t-Bu(Me)CHCOCH(Me)t-Bu 80%

Tetrahedron (1975) 31 1223, 1227



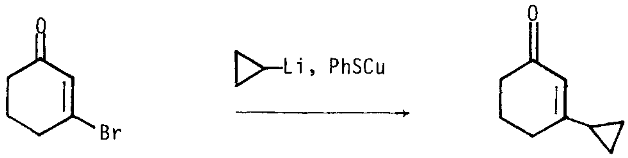
94%

Tetrahedron (1976) 32 2281



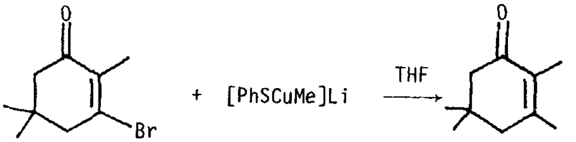
45%

Tetr Lett (1974) 2935



93%

Tetr Lett (1976) 3233, 3241, 3245



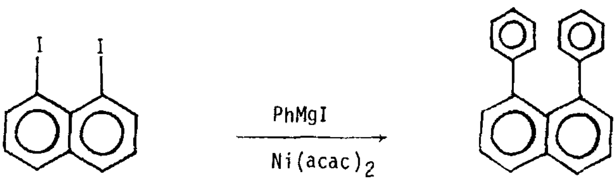
82%

JOC (1975) 40 2694

$$\mathrm{BzBr} \xrightarrow[\text{benzene}]{AgClO_4} \mathrm{Ph{-}CH_2{-}Ph}$$

52%

Coll Czech (1976) 41 1777



70%

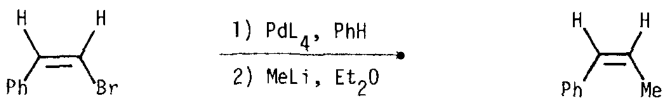
JOC (1976) 41 2252

$$(Ph_3P)_2NiCl_2 \xrightarrow[\text{2) ArX}]{\text{1) } Ph_3P\text{, Zn, DMF}} \text{Ar-Ar} \qquad 50\text{-}80\%$$

Tetr Lett (1975) 3375
JCS Perkin I (1975) 121
[$Pd(OAc)_2$ catalyst]
JACS (1975) <u>97</u> 3873
(intramolecular biaryl formation)

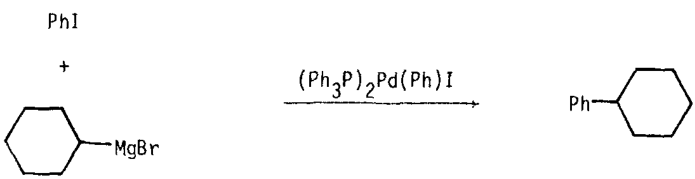
$$\text{PhMgX} + \text{Mesityl Br} \xrightarrow{Ni(dpp)_2Cl_2} \text{Ph-mesityl} \qquad 78\%$$

Chem Lett (1975) 133



88%

J Organometal Chem (1975) <u>91</u> C39

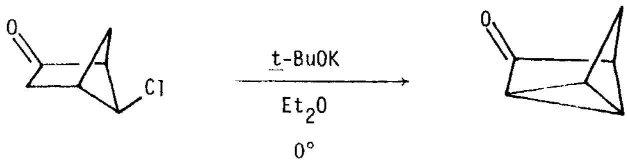


51%

J Organometal Chem (1976) <u>118</u> 349

$PhSO_2CHBr_2 + PhCH_2Cl \xrightarrow[\text{TEBA}]{\text{50\% aq. NaOH}} PhSO_2C(CH_2Ph)Br_2$ 75%

JOC (1975) 40 266



80%

JACS (1974) 96 7355

(allyl-SPh)$^{\ominus}$ + allyl'Cl ⟶ biallyl

Synthesis (1974) 129
Tetrahedron (1974) 30 715

Review: "Oxidative Coupling via Organocopper Compounds"

Angew Int Ed (1974) 13 291

Review: "The Ullmann Synthesis of Biaryls"

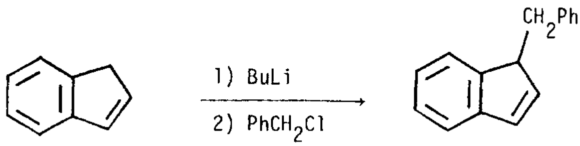
Synthesis (1974) 9

Review: "Activation of Grignard Reagents by Transition Metal Compounds"

Tetrahedron (1975) 31 2735

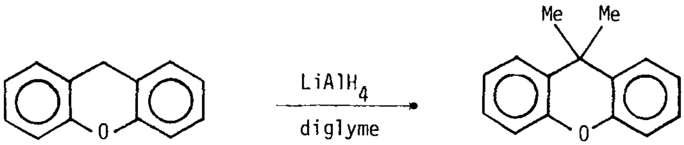
Section 71 Alkyls and Aryls from Hydrides

This section lists examples of the reaction RH → RR' (R,R'=alkyl or aryl). For the reaction C=CH → C=CR (R=alkyl or aryl) see Section 209 (Olefins from Olefins).



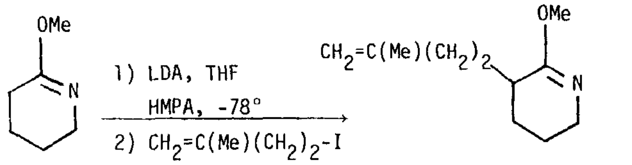
84%

Acta Chem Scand (1974) B28 295



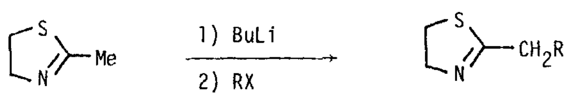
50%

JCS Perkin I (1976) 2380



60%

JACS (1975) <u>97</u> 7152



80-95%

JOC (1975) <u>40</u> 2021

$$Ph_2TlOCOCF_3 \xrightarrow[\text{benzene}]{h\nu} Ph\text{-}Ph$$

95%

JOC (1975) <u>40</u> 2351

$$PhCr(CO)_3 \xrightarrow[2)\ I_2]{1)\ \underline{t}\text{-BuLi}} Ph\text{-}C(CH_3)_3$$

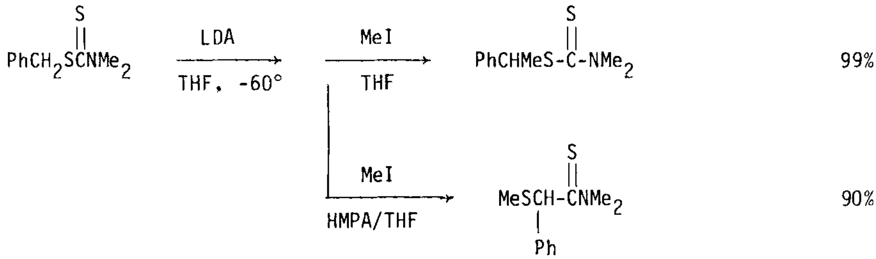
97%

JACS (1975) <u>97</u> 1247

$$2\ PhHgOAc + Cu \xrightarrow[PdCl_2,\ 115°C]{\text{pyridine}} Ph\text{-}Ph$$

86%

JOC (1976) <u>41</u> 2661



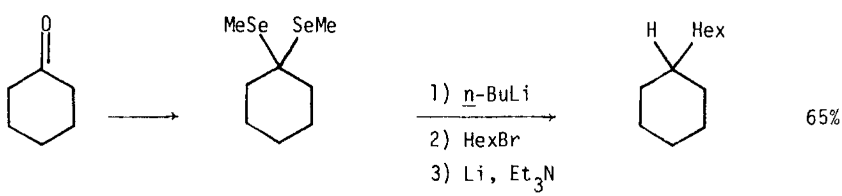
JACS (1975) 97 1608

Review: "Alkylation and Arylation of Unsaturated Compounds with the Aid of Transition Metal Complexes"

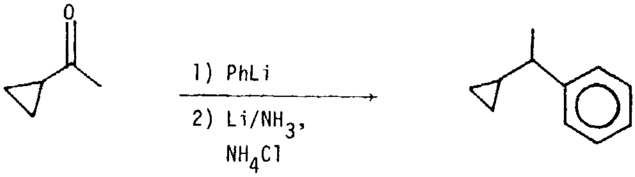
Russ Chem Rev (1975) 44 552

Section 72 Alkyls and Methylenes from Ketones

The conversions $R_2CO \rightarrow RR$, R_2CH_2, R_2CHR', etc. are listed in this section.

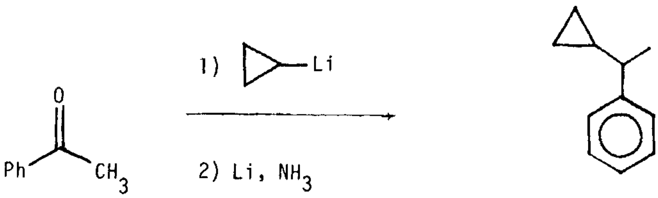


Tetr Lett (1976) 2643



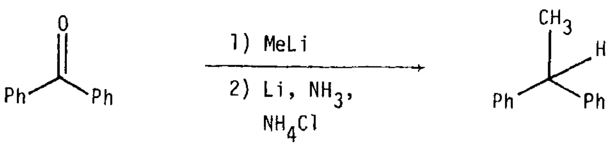
91%

JOC (1975) 40 271



82%

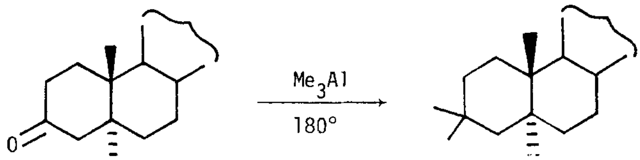
JOC (1976) 41 1494



Org Synth (1976) 55 7

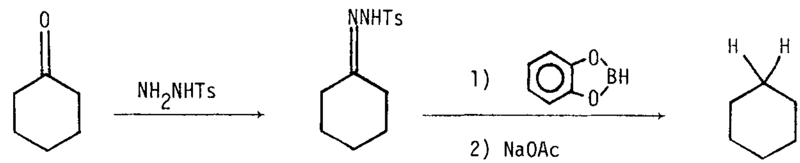
$$RCOR' \xrightarrow[\text{2) Li, liq. } NH_3\text{, } NH_4Cl]{\text{1) PhLi, } Et_2O} RR'CHPh$$ (20 examples)

JOC (1975) 40 271
Synth Comm (1975) 5 441



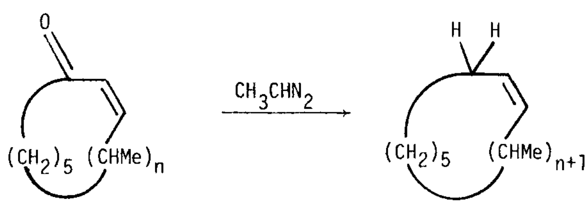
78%

Aust J Chem (1974) 27 1655



92%

JOC (1975) 40 1834

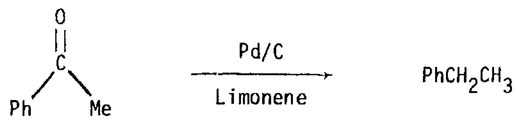


~60%

JCS Chem Comm (1975) 142

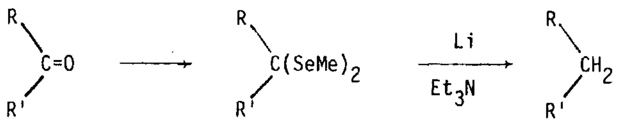
$$\mathrm{Ph\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Et} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Na^{\oplus}[OBH_3C(CH_3)NPh]^{\ominus}}} \mathrm{PhCH_2Et}$$ 78%

Chem Pharm Bull (1976) 24 1059



100%

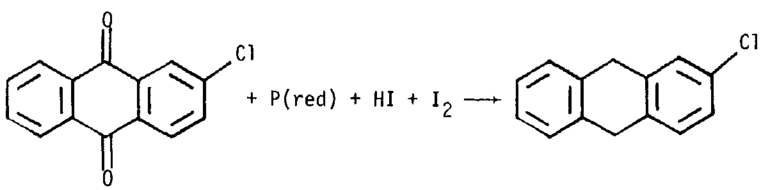
JCS Chem Comm (1976) 757



~65%

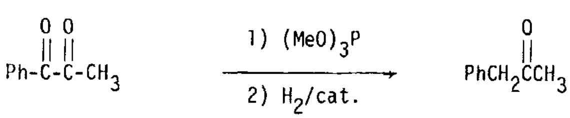
R,R' = n-alkyl

Tetr Lett (1976) 2643



90%

Can J Chem (1974) 52 1229



100%

JOC (1976) 41 2928

Related methods: Alkyls from Aldehydes (Section 64)

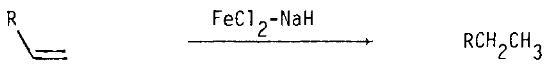
Section 73 Alkyls, Methylenes and Aryls from Nitriles

No additional examples

Section 74 Alkyls, Methylenes and Aryls from Olefins

The following reaction types are included in this section:

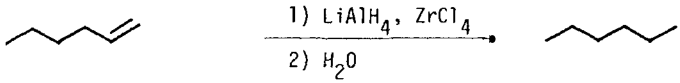
1. Hydrogenation of olefins (and aryls).
2. Dehydrogenations to form aryls.
3. Alkylations and arylations of olefins.
4. Conjugate reductions of conjugated aldehydes, ketones, acids, esters and nitriles.
5. Conjugate alkylations.
6. Cyclopropanations, including halocyclopropanations.



60-90%

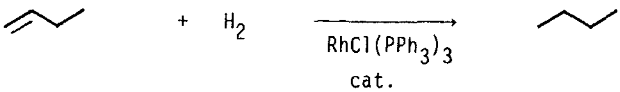
R = alkyl, aryl

Chem Lett (1976) 581



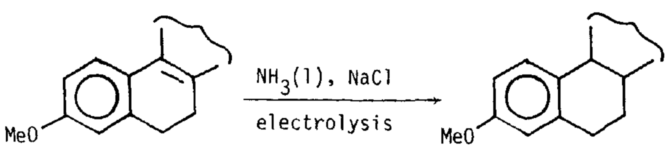
$\sim$90%

J Organometal Chem (1976) 122 C25

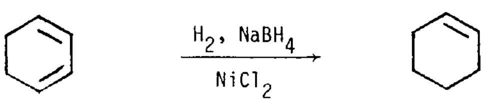


100%

Org React (1976) 24 1

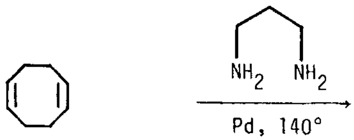


Chem Ber (1976) 109 395



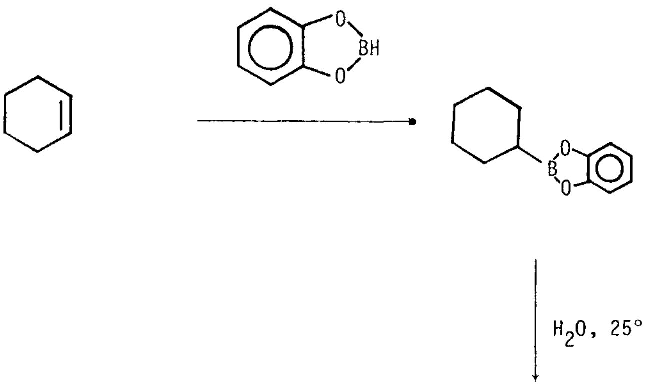
95%

Z Naturforsch B (1975) 30 643



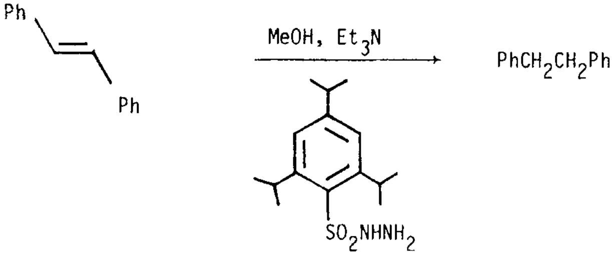
60%

Tetr Lett (1975) 4235



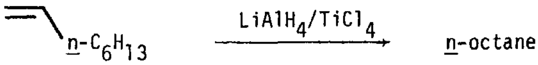
cyclohexane

JACS (1975) 97 5249

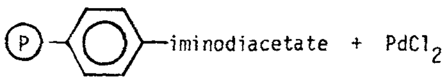


90%

Tetrahedron (1976) 32 2157



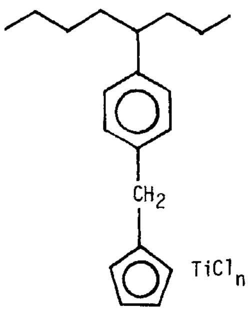
Tetr Lett (1976) 15



Catalyst for reduction of conjugated diolefins to monoolefins at 30° and 1 atm. H_2.

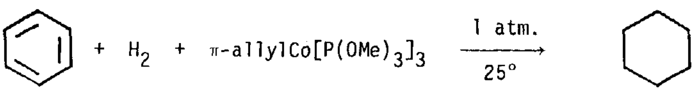
Chem Lett (1976) 165

Use of



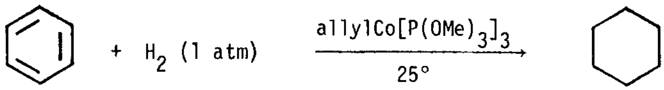
for catalytic hydrogenation of olefins. Rate is 20-30 times greater than that for the free catalyst.

J Organometal Chem (1976) 120 49

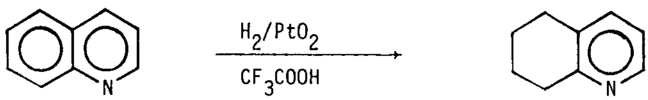


catalyst

Org React (1976) 24 1

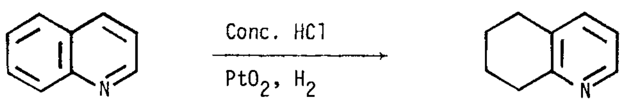


JACS (1974) 96 4063



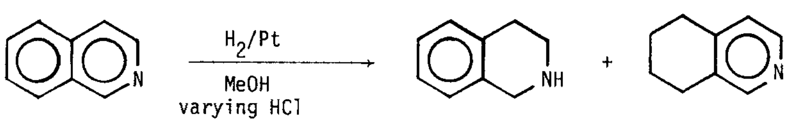
70%

JOC (1975) 40 2729



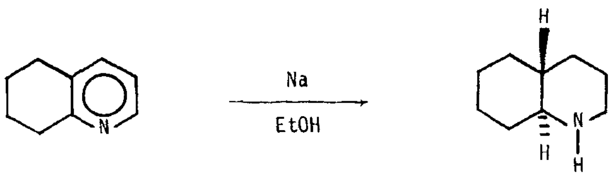
70%

JACS (1974) 96 2256



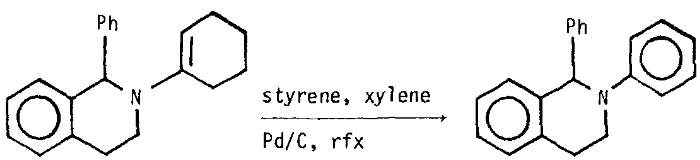
87:13 without HCl
13:87 with 4N HCl

JOC (1975) 40 1191



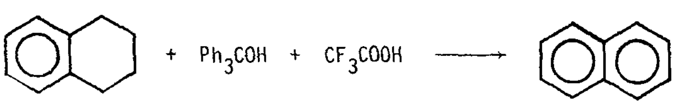
90%

JOC (1975) 40 2734

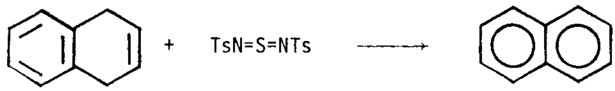


35%

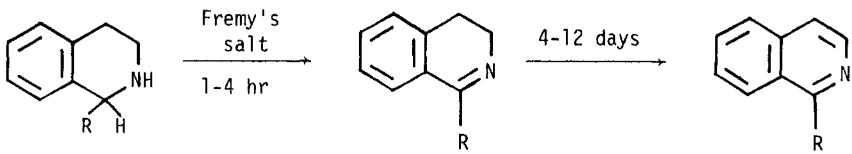
Bull Soc Chim Belges (1976) 85 1



Tetr Lett (1974) 3217

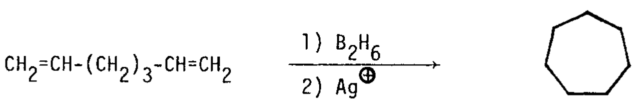


Liebigs Ann Chem (1974) 847



87-94% 30-74%

Synthesis (1974) 288



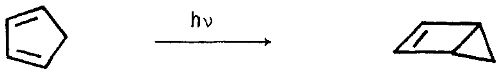
67%

Tetr Lett (1976) 463

$$Ph_2C{=}CH_2 \xrightarrow[\text{2) } PhCH_2Br,\ -78^\circ]{\text{1) Na, THF}} Ph_2C(CH_2Ph)\text{-}CH_2CH_2\text{-}CPh_2(CH_2Ph)$$

95%

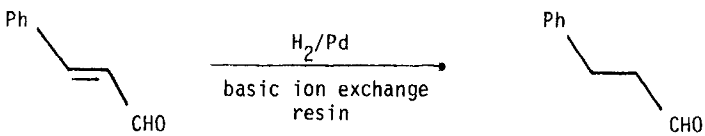
JCS Perkin I (1975) 1474



Org Synth (1976) 55 15

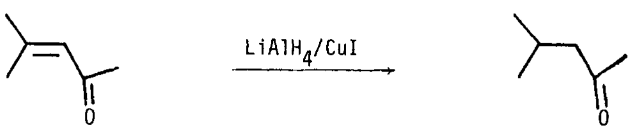
Review: "Cyclobutanes from Dimerization of Olefins"

Synthesis (1974) 539



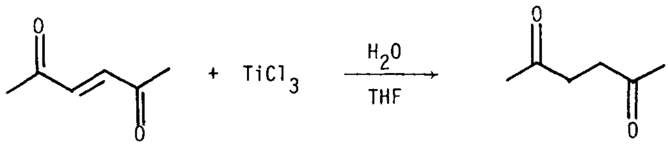
up to 100% selectivity

Bull Soc Chim France (1975) 2133



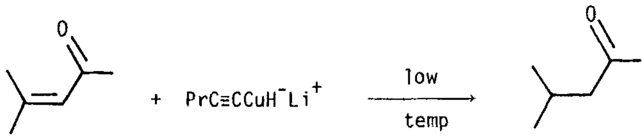
78%

Tetr Lett (1975) 4453



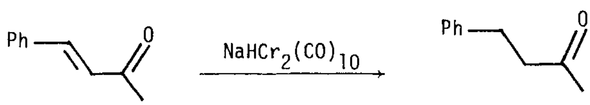
86%

JOC (1974) 39 258



80%

JACS (1974) 96 1625



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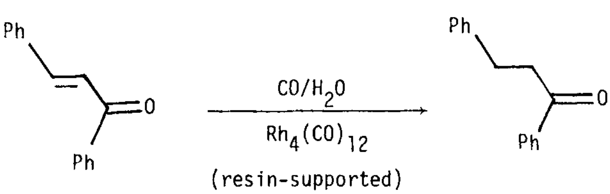
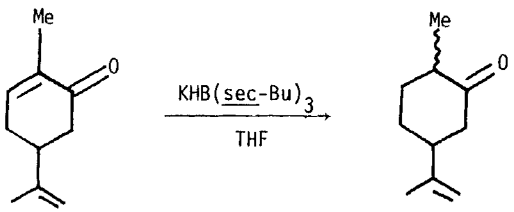
Synthesis (1976) 596



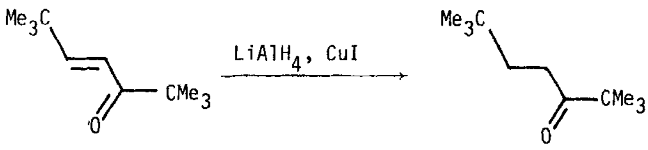
83%

Chem Lett (1975) 203



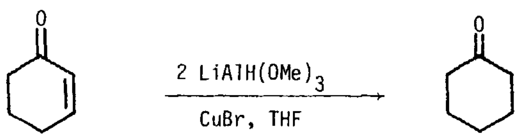
98%

JOC (1975) 40 146



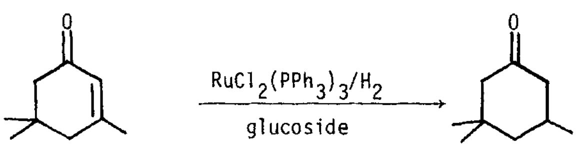
99%

JOC (1976) 41 1939



84%

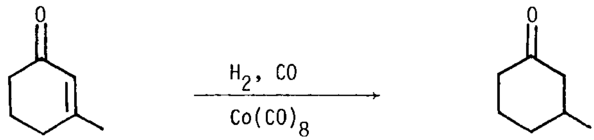
JOC (1975) 40 3619



40%

S 34% ee

Tetr Lett (1976) 4083

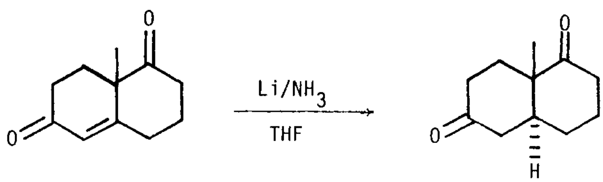


100%

Comptes Rendus C (1975) 281 877

PhCH=CHCOPh $\xrightarrow[Et_2O]{K/NH_3}$ $PhCH_2CH_2COPh$ 98%

Org React (1976) 23 1



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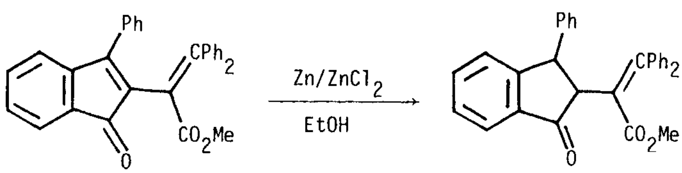
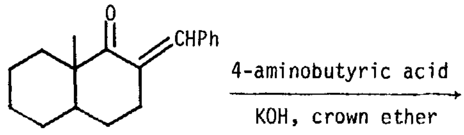
Org React (1976) 23 1



71%

Chem Lett (1976) 695



56%

Synth Comm (1976) 6 113

$\underline{i}$-PrCH=C(NHCOPh)COOH + RhCl (chiral diphos.) cat. $\xrightarrow{H_2}$ $\underline{i}$-PrCH$_2$CH(NHCOPh)CO$_2$H

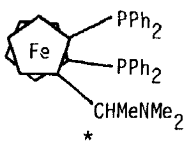
optically active

Org React (1976) 24 1

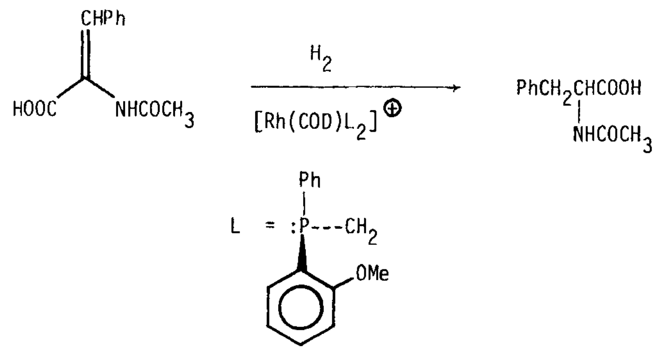
PhCH=C(NHCOMe)-COOH $\xrightarrow{H_2,\ \underline{I}}$ PhCH$_2$-C*H(NHCOMe)COOH ∿90%

(S 93% ee)

I =

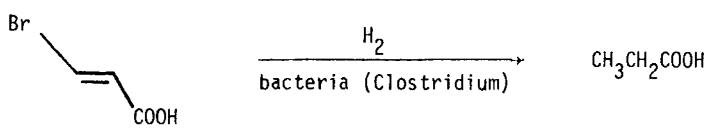


Tetr Lett (1976) 1133



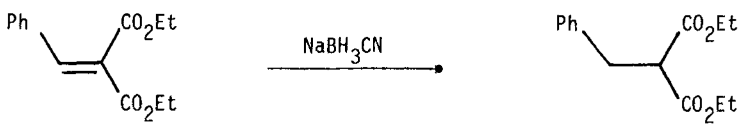
>90% ee

JACS (1975) 97 2567



100%

Angew Int Ed (1975) 14 106



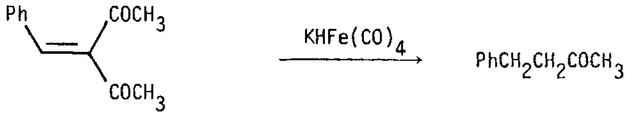
90%

JOC (1976) 41 3279

$$C_6H_{13}CH{=}CHCOOMe \xrightarrow[\text{t-BuOH}]{LiBu_3BH} C_6H_{13}CH_2CH_2COOMe$$

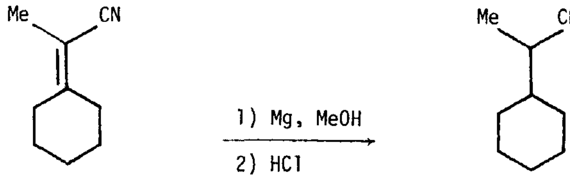
92%

JOC (1975) 40 2846



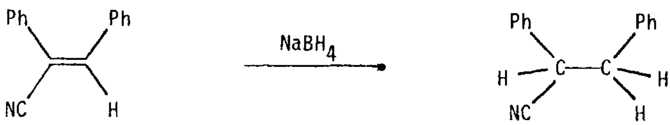
76%

Tetr Lett (1975) 1867



77%

JOC (1975) 40 127



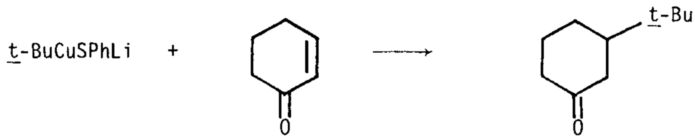
100%

Bull Chem Soc Japan (1976) 49 2643

$$CH_3\text{-}(CH_2)_{10}\text{-}CHO + CH_2{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow[\text{thiazolium salts}]{Et_3N} CH_3\text{-}(CH_2)_{10}\text{-}\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

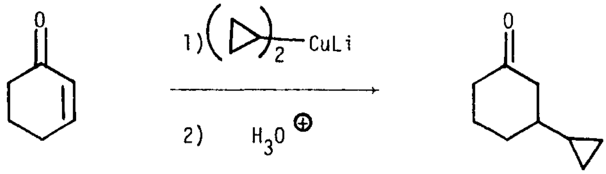
76%

Chem Ber (1976) 109 3426



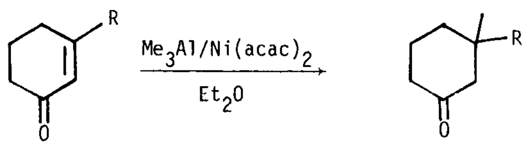
91%

Synthesis (1974) 662



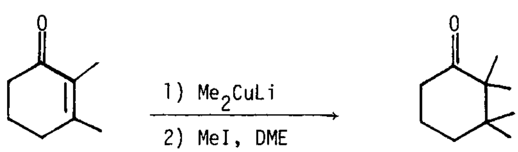
83%

JOC (1976) 41 3629



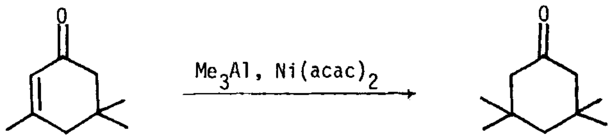
68%

Aust J Chem (1975) 28 801



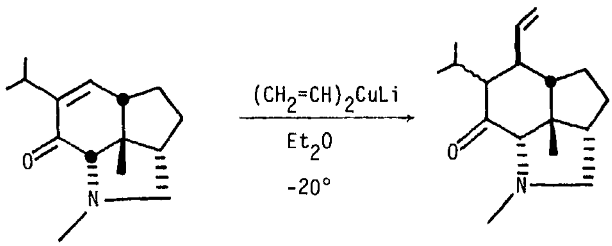
86%

JOC (1974) 39 275



85%

JOC (1974) 39 3297



80%

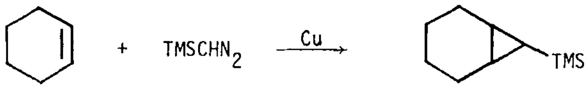
JACS (1974) 96 4334

$PhCH=CHNO_2$ + Me_2CuLi ⟶ $PhCHMeCH_2NO_2$ 54%

Tetr Lett (1975) 3591

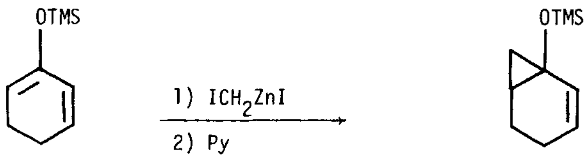
Review: "Catalytic Transfer Hydrogenation"

Chem Rev (1974) 74 567



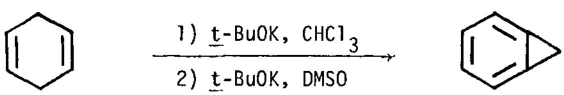
72%

JCS Perkin I (1974) 1440



88%

Tetr Lett (1974) 3329, 3333, 3327



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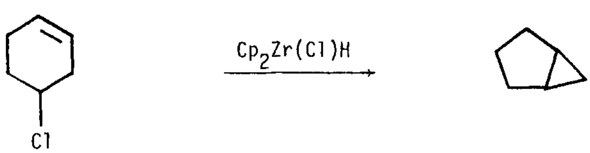
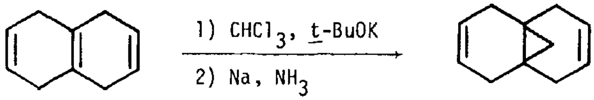
Org Synth (1976) 55 12



45%

J Organometal Chem (1976) 108 C1



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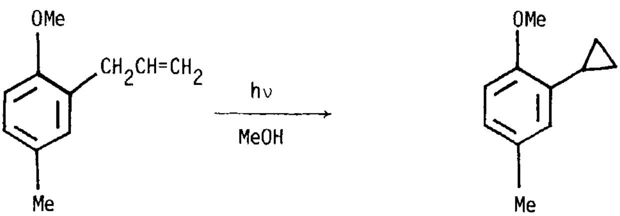
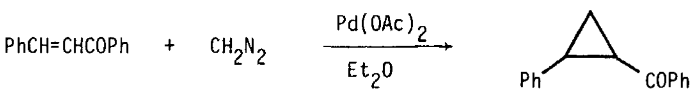
Org Synth (1974) 54 11



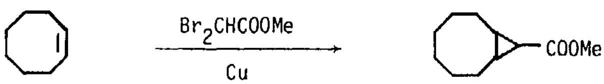
70%

Helv Chim Acta (1975) 58 178



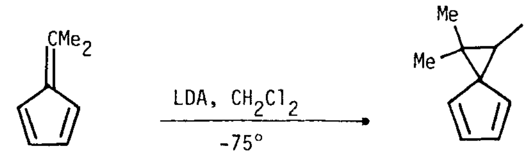
98%

Tetr Lett (1975) 629
Synthesis (1975) 636



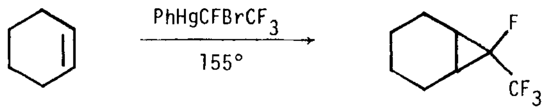
71%

JACS (1976) 98 2676



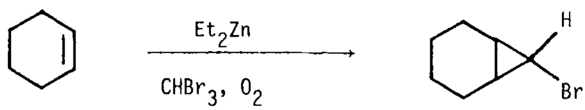
80%

JACS (1975) 97 3830



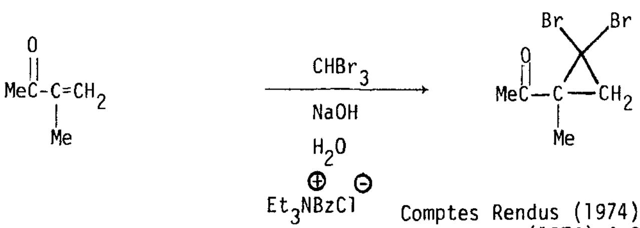
87%

J Organometal Chem (1975) 92 7



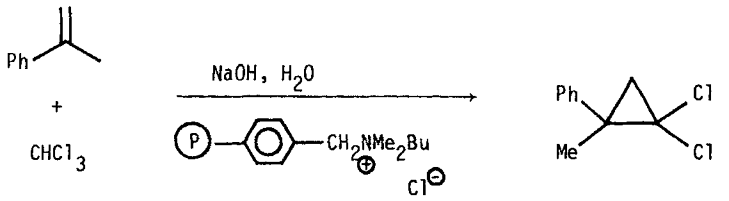
84%

JCS Chem Comm (1975) 364
Bull Chem Soc Japan (1975) 48 3665



85%

Comptes Rendus (1974) 278 621
Synth Comm (1974) 4 341
Synthesis (1974) 736



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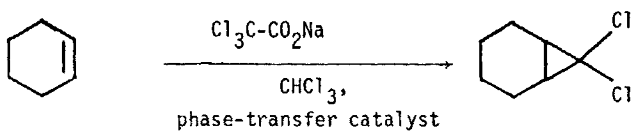
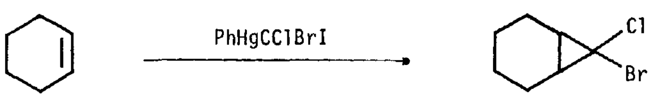
JACS (1975) 97 5956

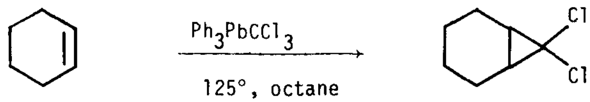


57%

Tetr Lett (1976) 91



JOC (1975) 40 1620



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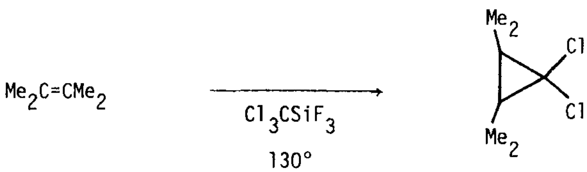
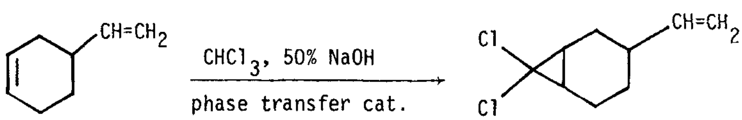
J Organometal Chem (1975) 90 173



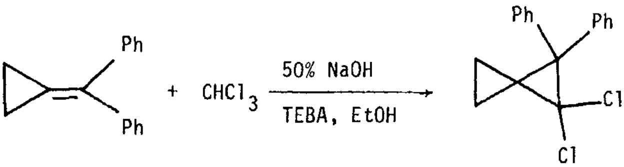
98%

JCS Perkin II (1975) 1051



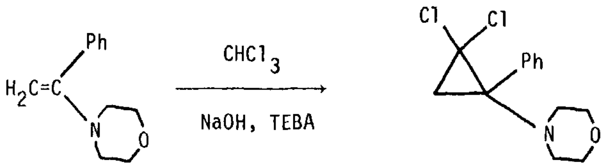
93%

Tetr Lett (1975) 3013



95%

Synthesis (1975) 323



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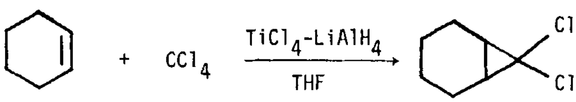
Z Chem (1975) 15 14



79%

Chem Lett (1975) 711

Review: "Cyclopropanation of Silyl Enol Ethers. A Powerful Synthetic Tool"

Pure & Appl Chem (1975) 43 317

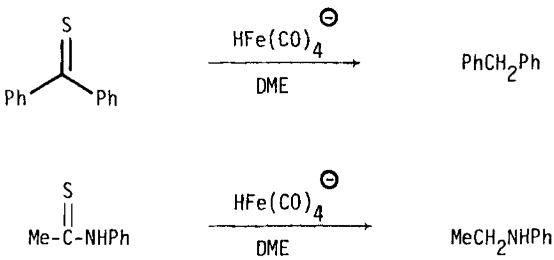
Review: "Chemistry of Phosphorylcarbenes. Cyclopropanation of Various Substrates"

Angew Int Ed (1975) 14 222

Review: "Two-Phase Reactions in the Chemistry of Carbanions and Halocarbenes - A Useful Tool in Organic Synthesis"

Pure & Appl Chem (1975) 43 439

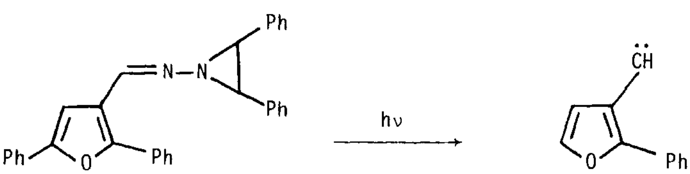
Section 75 Alkyls, Methylenes and Aryls from Miscellaneous Compounds



60%

51%

JOC (1975) 40 2694



JCS Perkin I (1976) 1257

Review: "Novel Approaches to Alkylations"

Pure & Appl Chem (1975) 43 563

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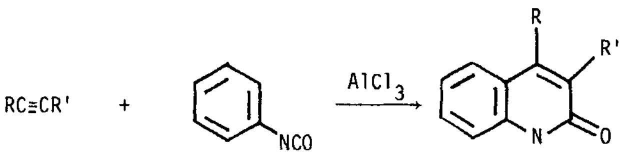
Edited by Louis S. Hegedus, Leroy Wade

Chapter 6 PREPARATION OF AMIDES

Section 76 Amides from Acetylenes



30-40%

Bull Soc Chim France (1974) 1949

$$\text{Ph-C}\equiv\text{C-MgBr} \xrightarrow[\text{2) } H_2O]{\text{1) } Me_3SiNCO} \text{Ph-C}\equiv\text{C-}\overset{O}{\overset{\|}{C}}\text{-}NH_2$$

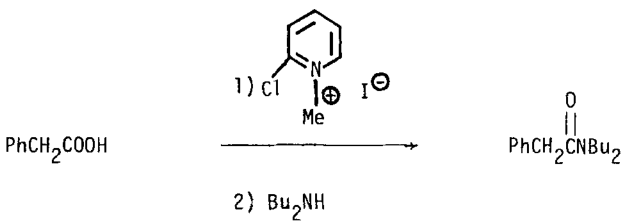
48%

Tetr Lett (1975) 981

Section 77 Amides from Carboxylic Acids and Acid Halides

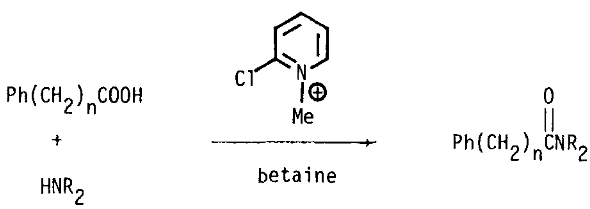
$$CH_3COOH \xrightarrow[2)\ PhNH_2]{1)\ Ph_3P(OTf)_2} CH_3\overset{O}{\overset{\|}{C}}\text{-NHPh} \qquad 80\%$$

Tetr Lett (1975) 277



95%

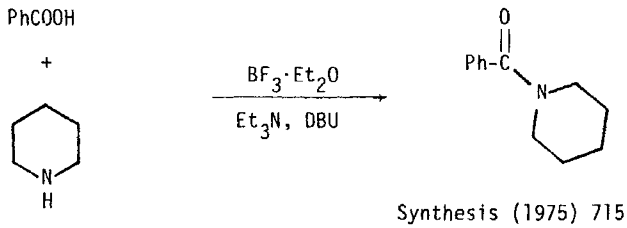
Chem Lett (1975) 1163



n = 0,1,2

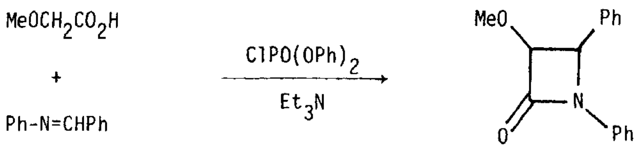
R = Bu, Ph, Bz

Chem Lett (1976) 57



63%

Synthesis (1975) 715



70%

Synth Comm (1976) 6 435

$$RCOOH + N_3PO(OPh)_2 \xrightarrow[R'OH]{Et_3N} RNHCO_2R'$$

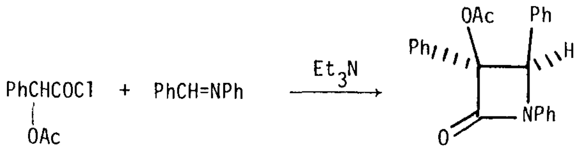
moderate to high yield

Tetrahedron (1974) 30 2151

$$Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + TMS_2NOLi \xrightarrow[2)\ H_3O^{\oplus}]{} ArCONH_2$$

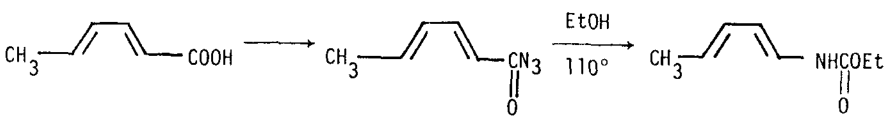
$\sim$50%

Synthesis (1975) 788



90%

Tetr Lett (1974) 2633
Tetr Lett (1974) 3135
JOC (1974) 39 312



80%

Tetr Lett (1976) 3089

Review: "The Azide Method in Peptide Synthesis"

Synthesis (1974) 549

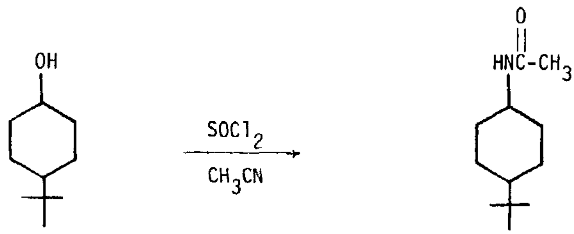
Related methods: Amides from Amines (Section 82)

Section 78 Amides from Alcohols

$$ROH + Ph_2\overset{\oplus}{C}ClSb\overset{\ominus}{C}l_6 \xrightarrow{R'CN} \xrightarrow{H_2O} RNH\text{-}\overset{\overset{O}{\|}}{C}\text{-}R' \qquad 40\text{-}86\%$$

(used with steroidal alcohols)

JCS Perkin I (1974) 2101



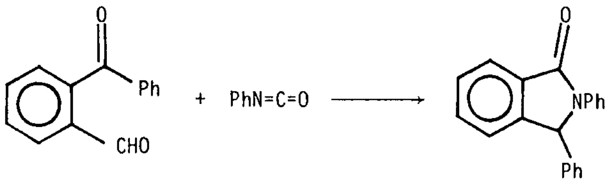
72%

JCS Perkin I (1976) 2205

Section 79 Amides from Aldehydes

$$RCHNOH + \text{silica gel} \xrightarrow{\text{Xylene, rfx}} RCONH_2 \qquad 61\text{-}92\%$$

Tetrahedron (1974) 30 2899



67%

JOC (1974) 39 3924

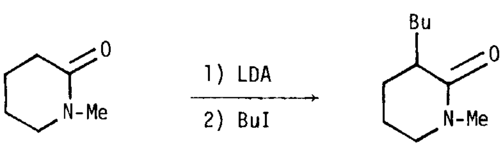
Section 80 Amides from Alkyls, Methylenes and Aryls

No additional examples

Section 81 Amides from Amides

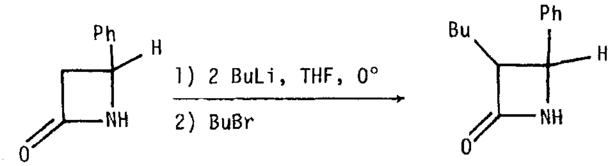
$$Me_2CHCONMe_2 \xrightarrow[\text{2) BuBr}]{\text{1) LDA, HMPA}} Me_2\underset{\displaystyle|\atop\displaystyle Bu}{C}\text{-}CONMe_2 \qquad 86\%$$

Comptes Rendus (1974) 278 1105



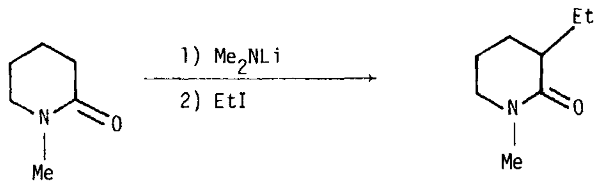
78%

JOC (1974) 39 2475



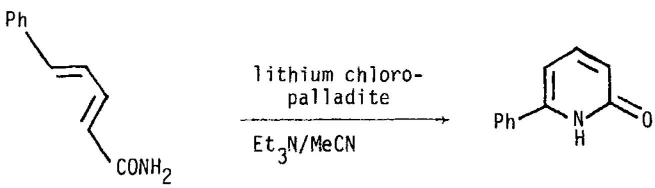
66%

Can J Chem (1974) 52 3206



85%

Can J Chem (1975) 53 1682



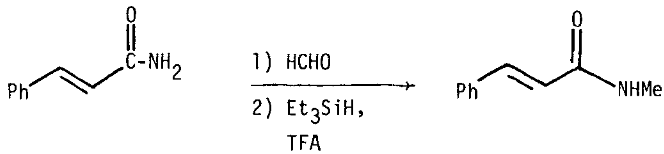
65%

Chem and Ind (1975) 745

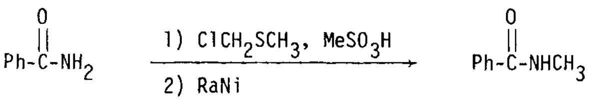
$$RCONH_2 \xrightarrow[-40 \text{ to } -15°]{NaOMe,\ MeOH,\ Br_2} RNHCOCH_3$$ 68-90%

(improved Hoffmann)

Synthesis (1974) 291

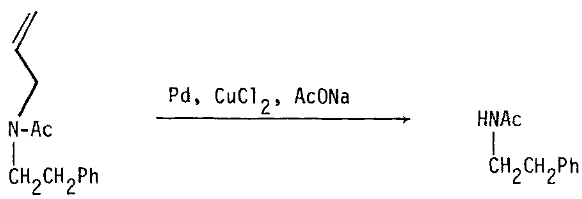


JOC (1976) 41 725

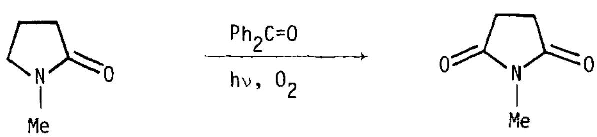


83%

JCS Chem Comm (1975) 320

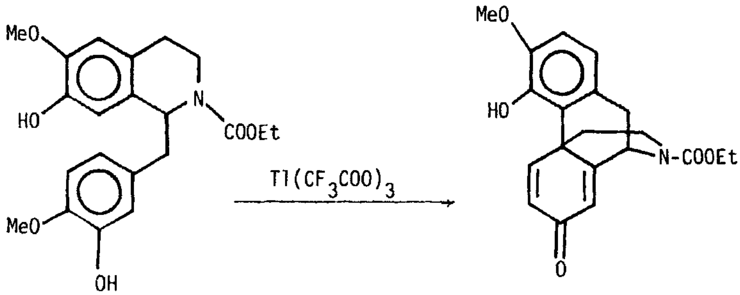


Chem Pharm Bull (1976) 24 1992



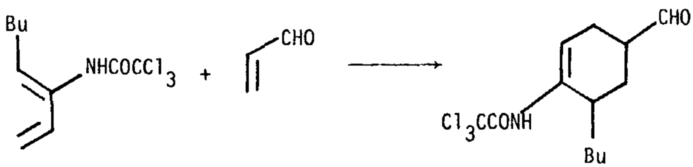
60%

JCS Chem Comm (1976) 194



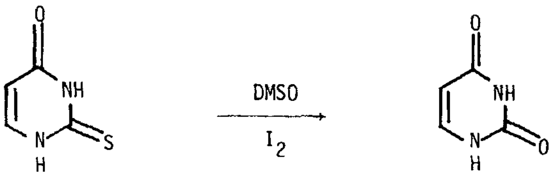
23%

JACS (1975) 97 1239



70%

JACS (1976) 98 2352



80%

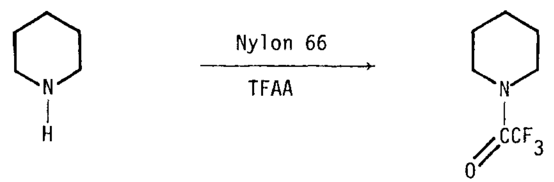
Synthesis (1975) 114

Review: "Alkenylation of Imides and Activated Amides"

Synthesis (1975) 685

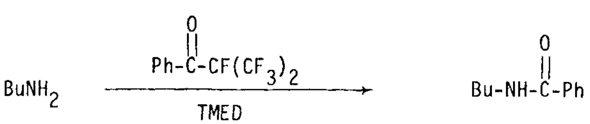
Conjugate reductions of unsaturated amides are listed in Section 74 (Alkyls from Olefins).
Related methods: Amides from Halides (Section 85)

Section 82 Amides from Amines



95%

Angew Int Ed (1976) 15 777



100%

Chem Lett (1976) 673

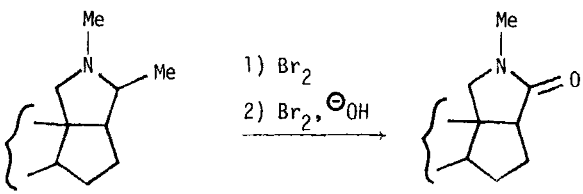
$$Et_2NH \xrightarrow[\text{phase-transfer cat.}]{CHCl_3,\ NaOH} Et_2NCHO \qquad 78\%$$

Z Chem (1974) 14 434

$$Ac_2O + RCN \xrightarrow[PhH]{\Delta} AcO\text{-}C(CN)_2\text{-}H + RNH_2 \longrightarrow RNH\text{-}C(=O)\text{-}CH_3 \qquad 85\text{-}90\%$$

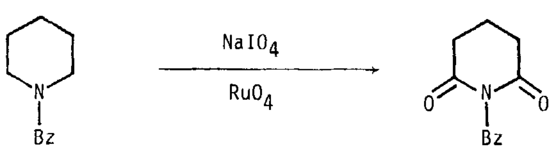
specific for R=alkyl: $ArNH_2$, ArOH unreactive

Synth Comm (1974) 4 351



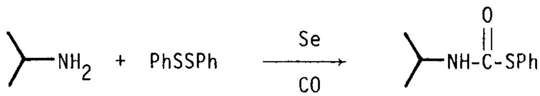
80%

Synthesis (1975) 109



41%

JOC (1976) 41 2780



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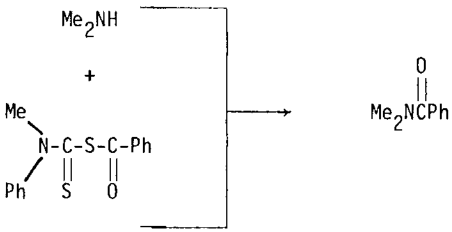
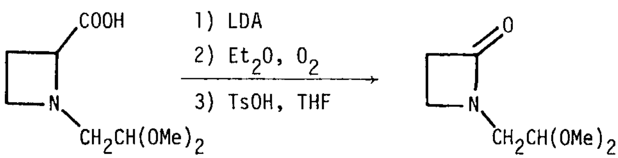
Tetr Lett (1975) 2087



∿60%

Indian J Chem (1975) 13 35



∿50%

Tetr Lett (1976) 4613

Related methods: Amides from Carboxylic Acids and Acid Halides (Section 77)
Protection of Amines (Section 105A)

Section 83 Amides from Esters

No additional examples

Section 84 Amides from Ethers and Epoxides

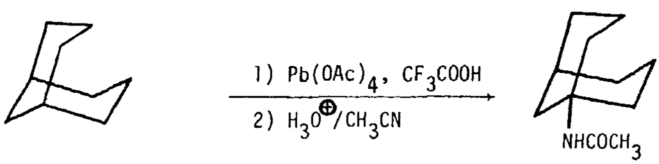
No additional examples

Section 85 Amides from Halides

$$\mathrm{PhMgBr} \xrightarrow[\text{2) } NH_4Cl,\ H_2O]{\text{1) TMSNCO}} \mathrm{PhCONH_2} \qquad 49\%$$

Tetr Lett (1975) 981

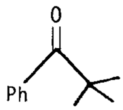
Section 86 Amides from Hydrides



78%

Synthesis (1976) 32

Section 87 Amides from Ketones

 $\xrightarrow[\text{t-BuNH}_2]{h\nu}$ Ph-C(=O)-NH*t*-Bu 95%

JCS Perkin I (1976) 1511

Review: "The Willgerodt Reaction"

$\text{Ar-C(=O)-(CH}_2)_n\text{H} \xrightarrow{\text{S, NH}_4\text{OH}} \text{Ar(CH}_2)_n\text{CONH}_2$

Synthesis (1975) 358

Section 88 Amides from Nitriles

$\text{RCN} + \text{PdCl}_2 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{RCONH}_2$ 60-80%

Synthesis (1974) 574

$\text{Ph-C}\equiv\text{N} \xrightarrow[\text{t-BuOH}]{\text{KOH}} \text{Ph-C(=O)-NH}_2$ 90%

JOC (1976) <u>41</u> 3769

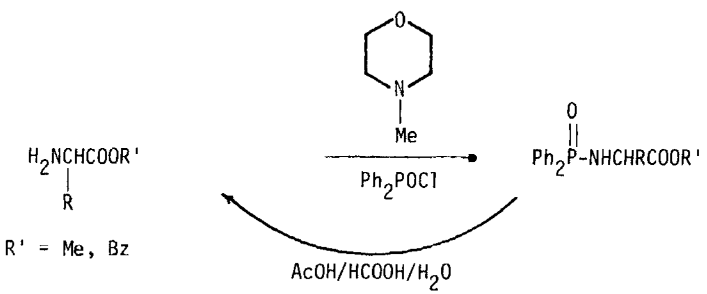
Section 89 Amides from Olefins

No additional examples

Section 90 Amides from Miscellaneous Compounds

No additional examples

Section 90A Protection of Amides



Tetr Lett (1976) 3623

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 7 PREPARATION OF AMINES

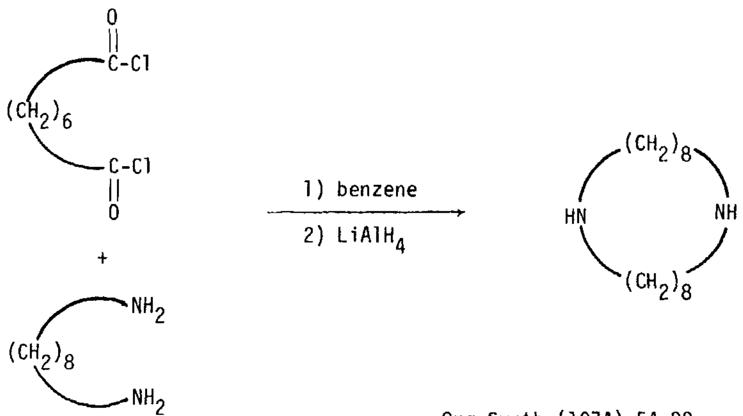
Section 91 Amines from Acetylenes

No additional examples

Section 92 Amines from Carboxylic Acids and Acid Halides

$$ArNH_2 + RCOOH + NaBH_4 \longrightarrow ArNHCH_2R \qquad 60\text{-}90\%$$

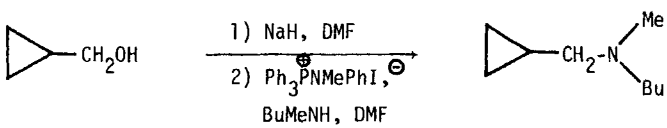
JACS (1974) 96 7814



~40%

Org Synth (1974) 54 88

Section 93 Amines from Alcohols and Phenols



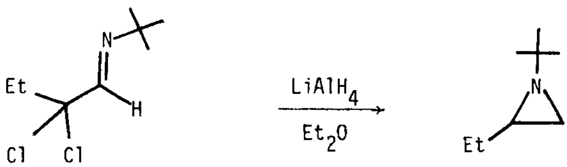
92%

Tetr Lett (1975) 471

Section 94 Amines from Aldehydes

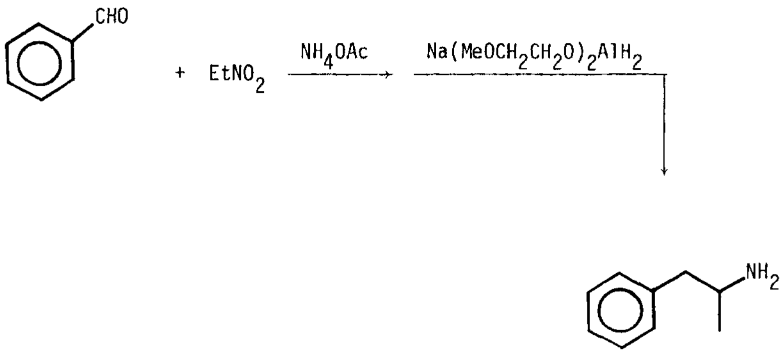
R_2NH + R'CHO + $NaHFe(CO)_4$ $\longrightarrow$ R_2NCH_2R' 60-80%

Synthesis (1974) 733

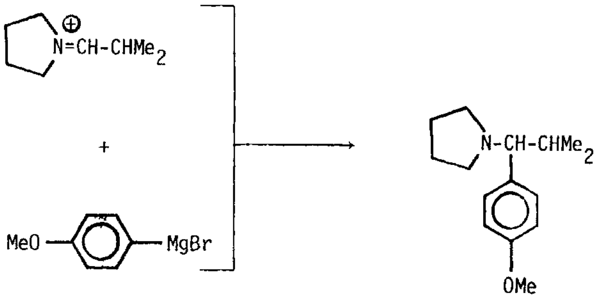


92%

Synth Comm (1975) 5 269

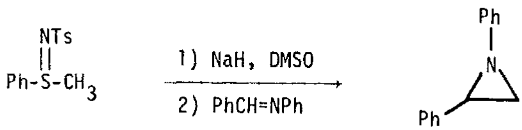


JCS Chem Comm (1974) 307



59%

Chem Ber (1975) 108 2827



47%

Synthesis (1976) 35

Related methods: Amines from Ketones (Section 102)

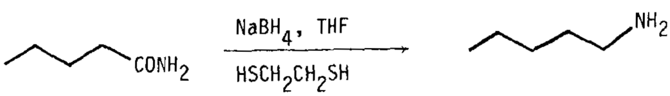
Section 95 Amines from Alkyls, Methylenes and Aryls

No examples

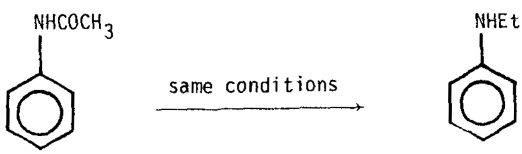
Section 96 Amines from Amides

$$PhC(=O)NHCH_3 \xrightarrow[AcOH]{NaBH_4} PhCH_2NHCH_3 \qquad 82\%$$

Tetr Lett (1976) 763



∿100%



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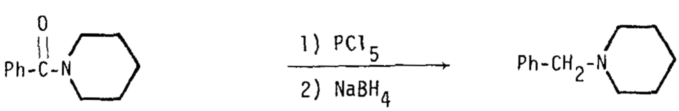
Chem and Ind (1976) 322

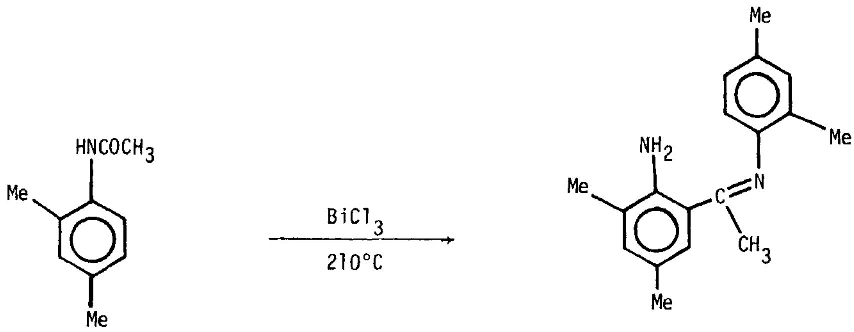


90%

Tetr Lett (1976) 219

$$TsNHCH_2CH_2\text{-}N(COCH_3)\text{-}CH_2CO_2C_6Cl_5 \xrightarrow[2)\ H_3O^{\oplus}]{1)\ BH_3\cdot THF} TsNHCH_2CH_2\text{-}N(CH_2CH_3)\text{-}CH_2COOH$$

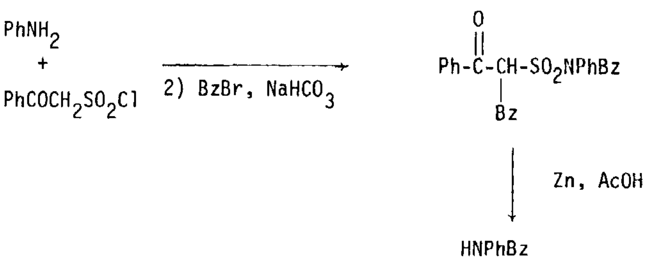
JOC (1976) 41 149



40%

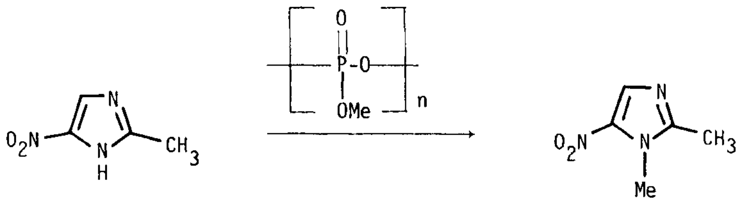
Tetr Lett (1976) 3217

Section 97 Amines from Amines



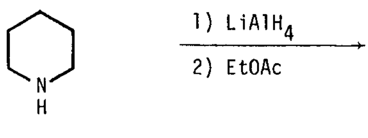
~60%

Tetrahedron (1975) 31 2517



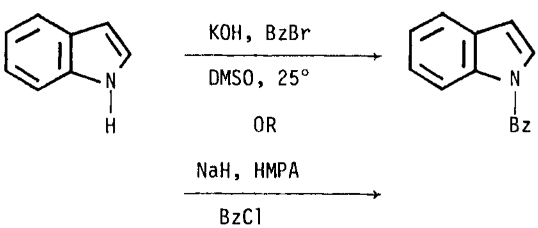
63%

Synthesis (1975) 596



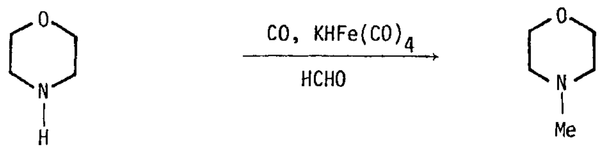
88%

Synthesis (1975) 607



85%

Org Synth (1974) 54 58, 60



~100%

Bull Chem Soc Japan (1976) <u>49</u> 1378

$BzNH_2 \xrightarrow[Et_3N]{Ph_2POCl} Ph_2PONHBz \xrightarrow[\text{2) MeI; 3) MeOH, TsOH}]{\text{1) NaH}} BzNH_2Me^{\oplus}\ OTs^{\ominus}$ 56%

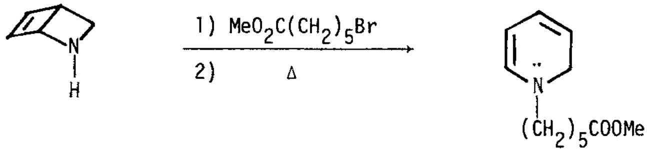
Tetr Lett (1976) 4005

$R\text{-}NH_2 \xrightarrow[MeOH]{NaHCO_3,\ MeI} RNMe_3^{\oplus} I^{\ominus}$ 75-96%

R = amino acid

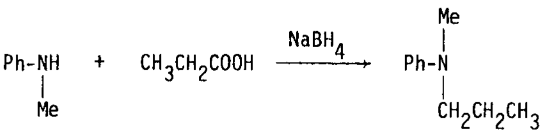
Also works with secondary amines.

Can J Chem (1976) <u>54</u> 3310



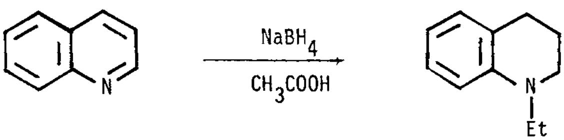
90%

JACS (1976) 98 2344



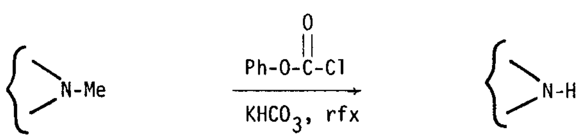
65%

JOC (1975) 40 3453



68%

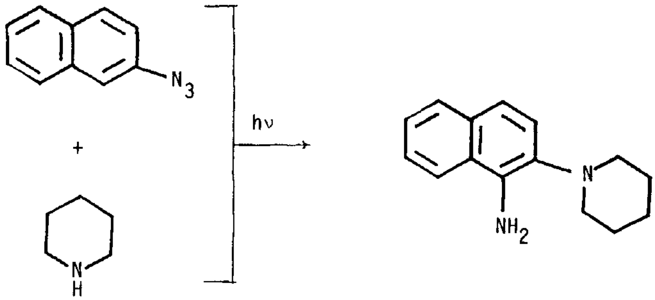
Synthesis (1975) 650



84-89%

morphine, codeine

JOC (1975) 40 1850



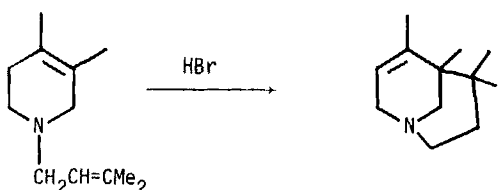
75%

Synthesis (1975) 710

$$CH_3NR_2 \xrightarrow[\text{2) Zn/HOAc}]{\text{1) }Cl_3CCH_2OCOCl} R_2NH \qquad >70\%$$

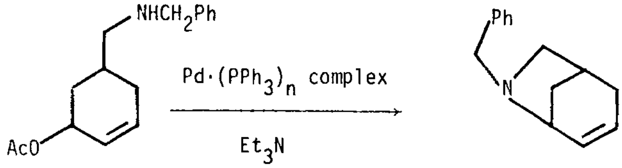
(proceeds in 75% with morphine)

Tetr Lett (1974) 1325



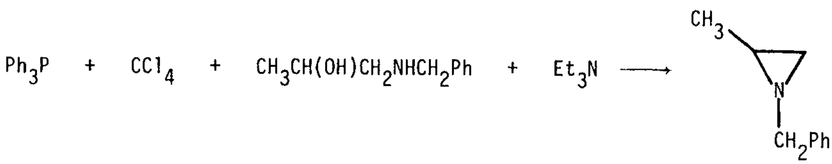
83%

Synthesis (1975) 440



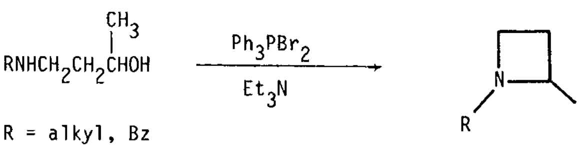
67%

JACS (1976) 98 8516



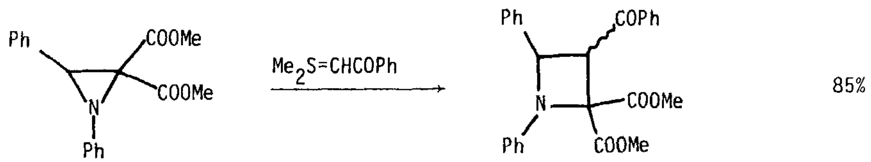
80%

Chem Ber (1974) 107 5



44-65%

Synthesis (1974) 894



JOC (1975) 40 2990

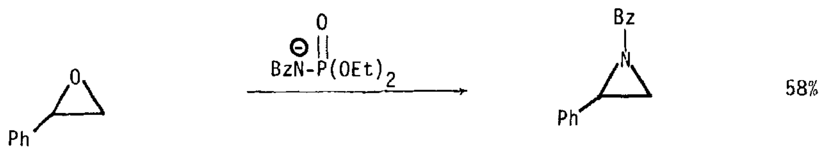
Review: "Umpolung of Amine Reactivity"

Angew Int Ed (1975) 14 15

Section 98 Amines from Esters

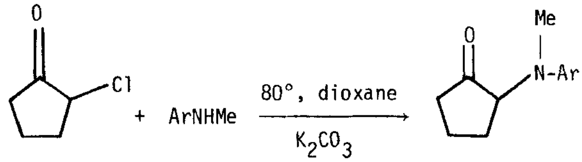
No additional examples

Section 99 Amines from Epoxides



Tetr Lett (1976) 4003

Section 100 Amines from Halides



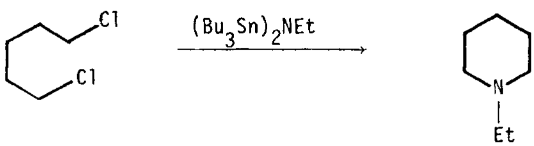
~50%

Monatshefte (1976) 107 401

$$ArI + (Me_3Si)_2NCu \longrightarrow \xrightarrow{MeOH} ArNH_2$$

30-60%

JCS Chem Comm (1974) 256



60%

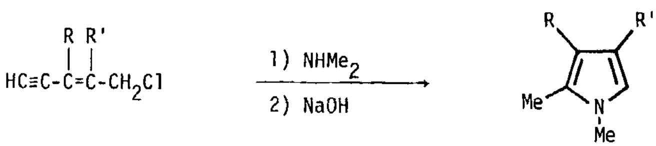
Comptes Rendus C (1975) 281 47

$$PhLi \quad + \quad HMPA \xrightarrow[-30^\circ]{THF} [complex] \xrightarrow{PhLi} PhCH_2NHMe \qquad 75\%$$

JOC (1974) 39 3042

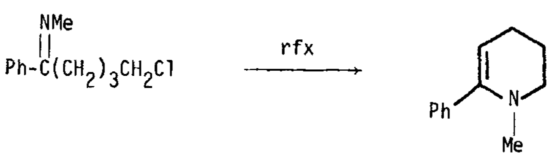
$$NH_2NH_2 \quad + \quad CHCl_3 \quad + \quad KOH \xrightarrow[18\text{-crown-}6]{ether} CH_2N_2 \qquad 40\%$$

Tetr Lett (1974) 2983



55-60%

Comptes Rendus (1974) 278 801

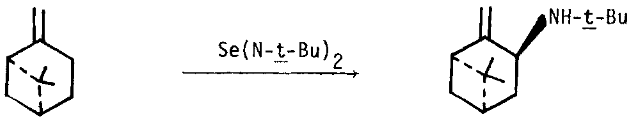


Org Synth (1974) 54 93

$Me_2NNHC(=O)CH_3 \xrightarrow[\text{3) } ^{\ominus}OH,\ H_2O]{\text{1) MeI, 2) EtI}} H_2N\text{-}NMeEt$ ~80%

JOC USSR (1975) 11 56

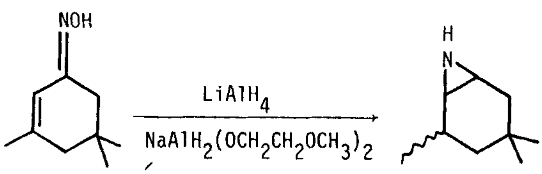
Section 101 Amines from Hydrides



62%

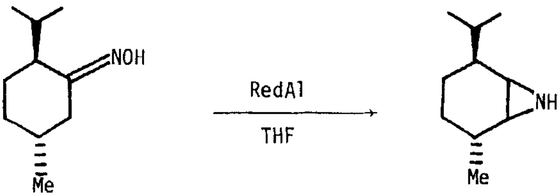
JACS (1976) 98 269

Section 102 Amines from Ketones



54%

Can J Chem (1975) 53 3227

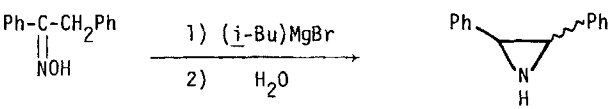


55%

Tetr Lett (1976) 1175

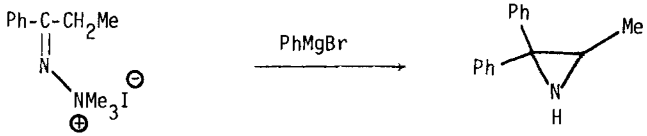
~80%

Tetr Lett (1975) 3263



49%

Chem Pharm Bull (1976) 24 1083



80%

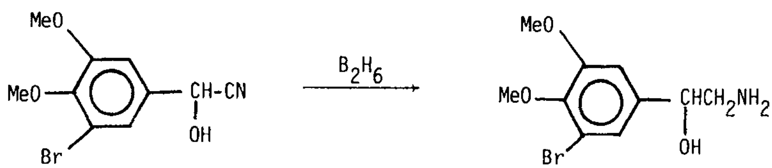
Tetr Lett (1975) 355

Related methods: Amines from Aldehydes (Section 94)

Section 103 Amines from Nitriles

$$PhCH_2CN \xrightarrow[THF]{NaBH_3(OCOCF_3)} PhCH_2CH_2NH_2 \qquad 70\%$$

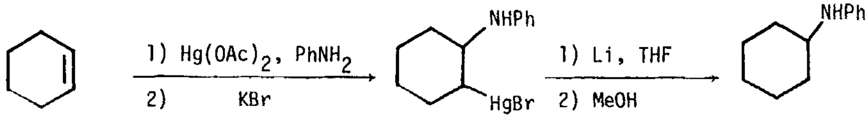
Tetr Lett (1976) 2875



Does not hydrogenolyze halides.

JCS Perkin I (1974) 1015

Section 104 Amines from Olefins

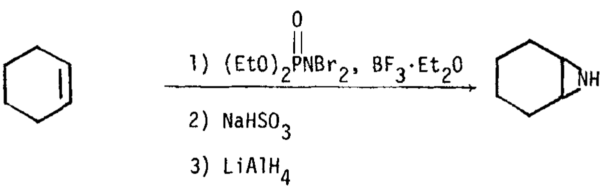


87%

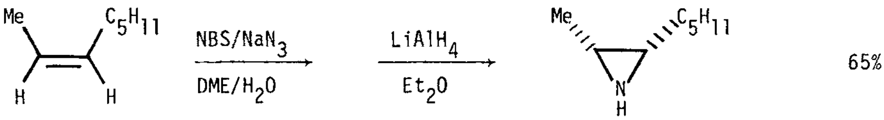
Synthesis (1975) 116

R_3B or R_2BH + $MesSO_3NH_2$ $\longrightarrow$ RNH_2 24-50%

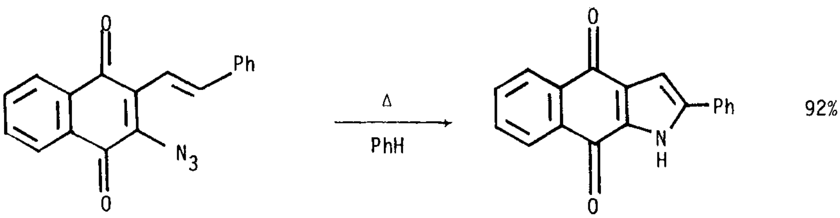
Synthesis (1974) 196



Angew Int Ed (1976) 15 302

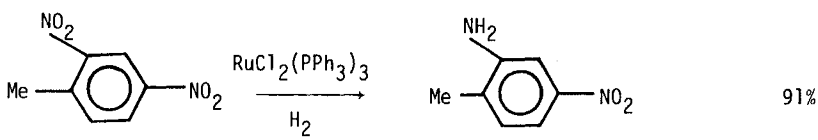


Angew Int Ed (1974) 13 279

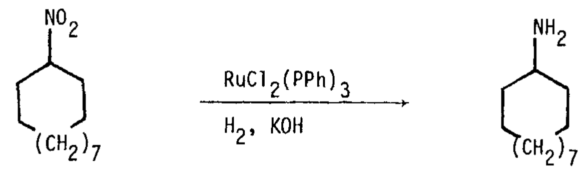


JOC (1974) 39, 775

Section 105 Amines from Miscellaneous Compounds

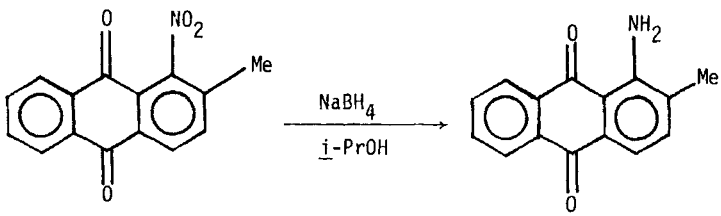


Tetr Lett (1975) 2163



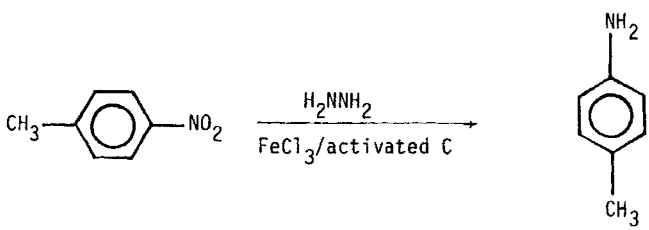
~80%

JOC (1975) 40 519



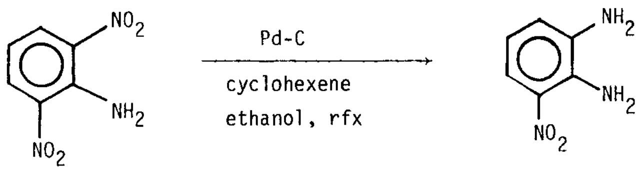
97%

Synthesis (1976) 528



99%

Chem Lett (1975) 259



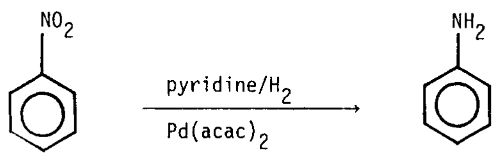
95%

JCS Perkin I (1975) 1300

$$PhNO_2 \xrightarrow[2)\ HF]{1)\ (NH_4)_2S} \underline{p}\text{-F-}PhNH_2$$

30%

JOC (1974) <u>39</u> 1758



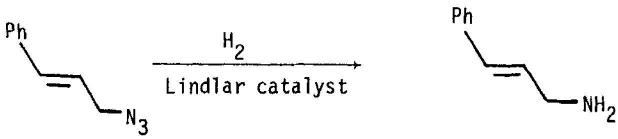
90%

Chem and Ind (1975) 1057

$$Ph\text{-}N_3 \xrightarrow[H_2O/THF]{VCl_2} PhNH_2$$

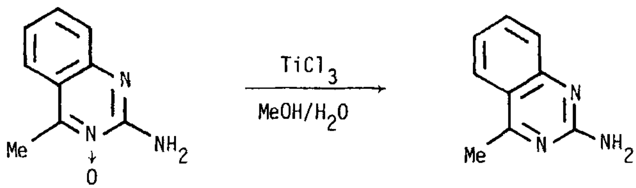
70%

Synthesis (1976) 815



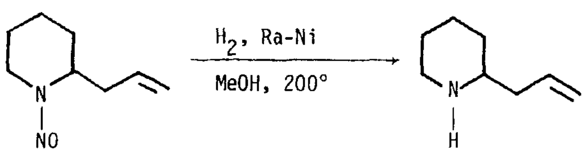
93%

Synthesis (1975) 590



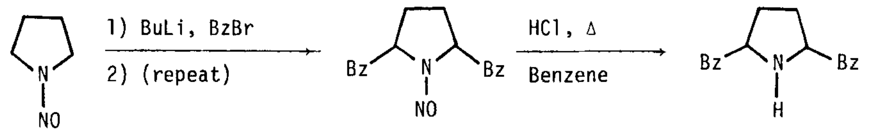
83%

Synthesis (1975) 335



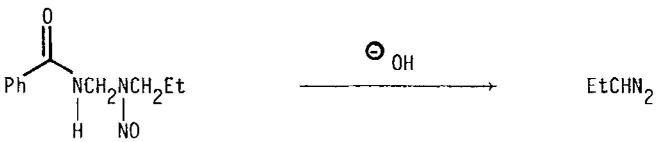
95%

Synthesis (1976) 548



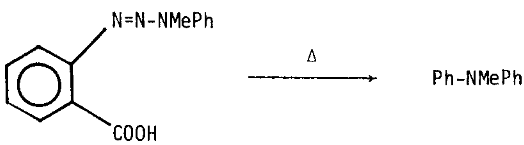
76%

Synthesis (1976) 540



65%

Chem Pharm Bull (1976) 24 369



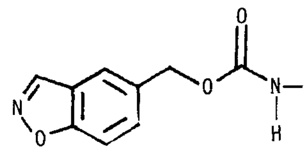
72%

Bull Chem Soc Japan (1975) 48 2397

Section 105A Protection of Amines

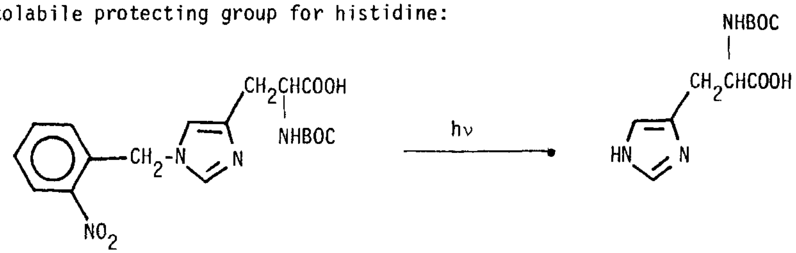
"Bic" protecting group for amine functions in peptide synthesis. Removed by Et_3N/DMF followed by hydrolysis or by hydrogenolysis.

"Bic" =



Tetr Lett (1975) 4625

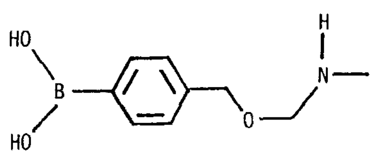
A photolabile protecting group for histidine:



JACS (1975) 97 440

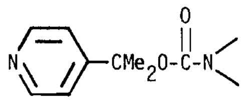
Use of the "Dobz" amine-protecting group to vary solubility properties of reactants and products in peptide synthesis.

"Dobz" =

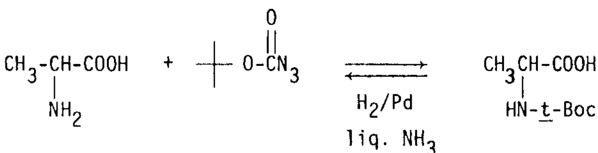


Tetr Lett (1975) 4629

The introduction of tertiary amino substituents into urethane-type amino protecting groups increases their acid-stability and provides a functional group which can be used to alter solubility characteristics.

example: 

JCS Chem Comm (1975) 939



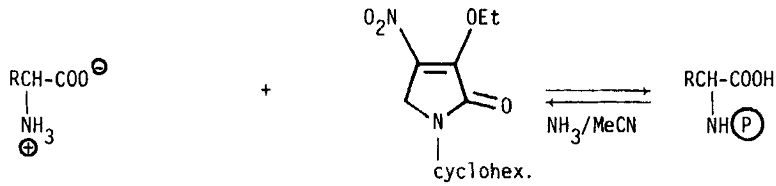
JACS (1974) 96 4978

Cleavage of t-Boc, Z(OMe), and NPS protecting groups by CF_3SO_3H in polypeptide synthesis.

JCS Chem Comm (1974) 107

Use of the 2-(triphenylphosphonio)ethoxycarbonyl group as an amino protective function in peptide chemistry. Stable to acids, removed with base.

Chem Ber (1976) 109 2670



Stable to DCC

JOC (1974) 39 3351

Cleavage of N$^{\alpha}$-benzaloxycarbonyl from methionine via H_2/Pd in liquid NH_3.

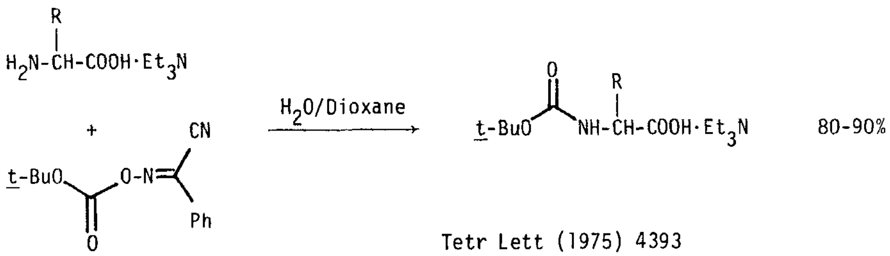
O
||
PhCH$_2$O-C-R, PhCH$_2$OR, PhCH$_2$OC(O)-R are cleaved.

O
||
t-BuO-C-R, *t*-BuO-R, etc. are not cleaved.

Tetr Lett (1974) 3259

Me_3SiClO_4 cleaves the *t*-Butoxycarbonyl (BOC) group selectively in the presence of benzyloxycarbonyl (Z) groups and *t*-butyl esters.

Angew Int Ed (1975) 14 818



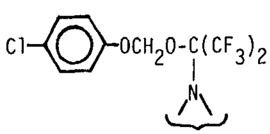
Tetr Lett (1975) 4393

$$H_2N\text{-}\overset{\text{Bz}}{\overset{|}{C}}H\text{-}COOH \xrightarrow[\text{Ni, THF}]{Me_2PhSiH} Me_2PhSi\text{-}NH\text{-}\overset{\text{Bz}}{\overset{|}{C}}H\text{-}COOSiMe_2Ph \qquad 75\%$$

Tetr Lett (1975) 3207

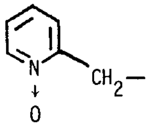
$$Ph\text{-}NH\overset{O}{\overset{||}{C}}\text{-}OCH_2CH_2Cl \xrightarrow{\text{Co(I)phthalocyanine}} PhNH_2 \qquad 83\%$$

Angew Int Ed (1976) 15 681

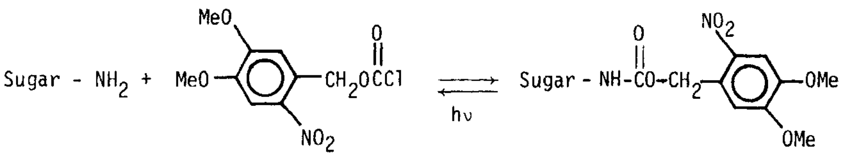
Use of  to block imidazole in histidine

1) stable to saponification and H_2
2) removed by mild H^+
3) derivatives soluble in organic solvents

Tetr Lett (1974) 2637

Use of  as NH_2 or OH protecting group in nucleotides and nucleosides. Removed by Ac_2O followed by NH_3/MeOH.

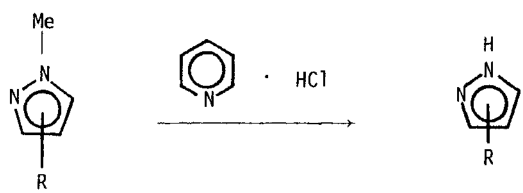
JOC (1974) 39 1250



JOC (1974) 39 192

Use of $PhCH_2$- to protect basic N in alkaloids. Removed by n-PrSLi/HMPA at 0°.

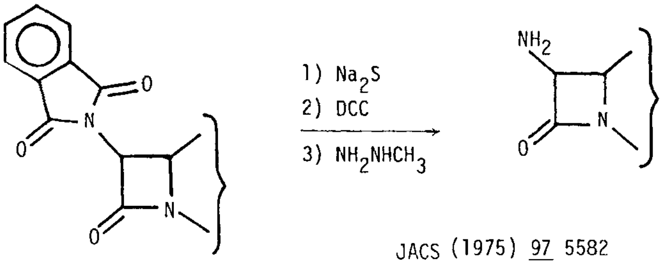
Synth Comm (1974) 4 183



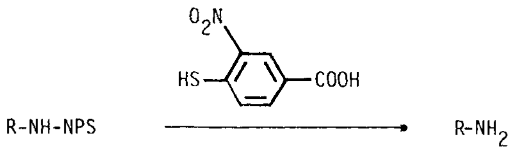
50-70%

R = alkyl

JOC (1975) 40 1353



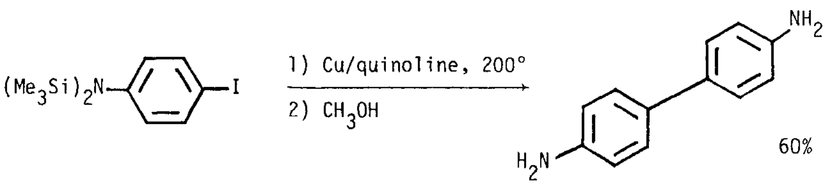
JACS (1975) 97 5582



~100%

NPS = o-nitrophenylsulfenyl

Helv Chim Acta (1976) 59 855



60%

Synthesis (1976) 40

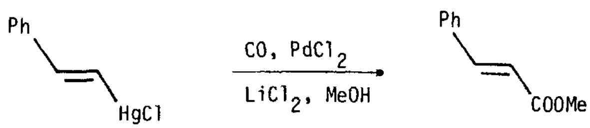
Review: "Stability of Side Chain Protecting Groups in Solid-Phase Peptide Synthesis"

Israel J Chem (1974) 12 79

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 8 PREPARATION OF ESTERS

Section 106 Esters from Acetylenes



100%

JOC (1975) 40 3237

Section 107 Esters from Carboxylic Acids and Acid Halides

The following types of reactions are found in this section:

1. Esters from carboxylic acids (and acid halides) and alcohols.
2. Lactones from hydroxy acids.
3. Esters from carboxlic acids and halides, sulfates, and miscellaneous compounds.

Use of "graphite bisulfate" to catalyze esterification

$$\mathrm{RCOOH} + \mathrm{R'OH} \longrightarrow \mathrm{RCOOR'}$$

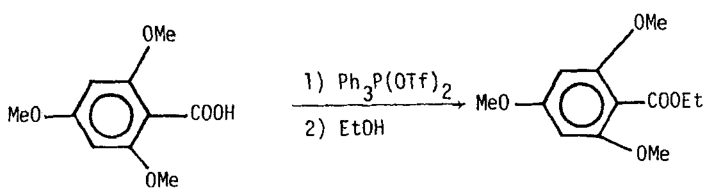
Fast, high yield; excess R'OH is not required.

3° alcohols undergo elimination.

JACS (1974) <u>96</u> 8113

Use of $BF_3 \cdot Et_2O \cdot ROH$ to effect esterification of carboxylic acids.

Synth Comm (1974) <u>4</u> 167



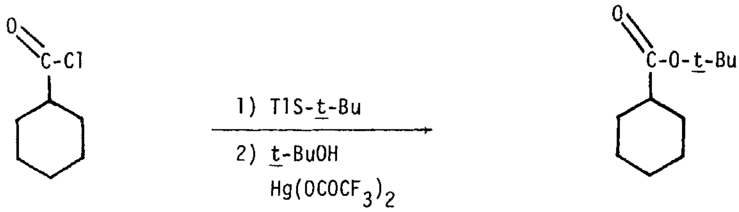
78%

Tetr Lett (1975) 277

$$\mathrm{R{-}COOH} \xrightarrow[\text{BuOH, pyridine}]{\text{BzOH, DCC}} \mathrm{R{-}COOBz} \qquad \sim 85\%$$

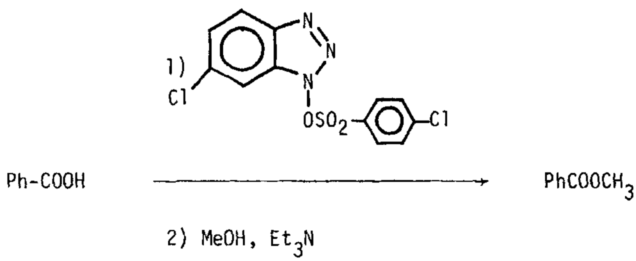
R = N-protected amino acid

Z Naturforsch <u>B</u> (1976) <u>31</u> 1157



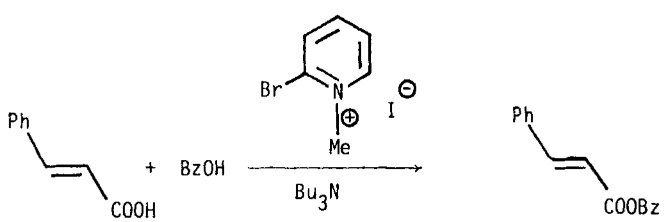
100%

JACS (1975) 97 3515



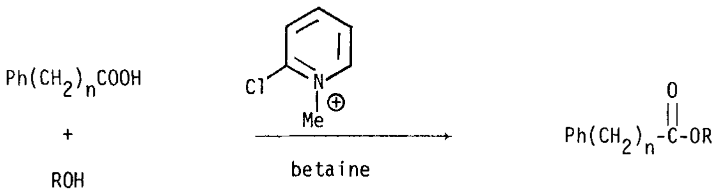
93%

Synthesis (1975) 456



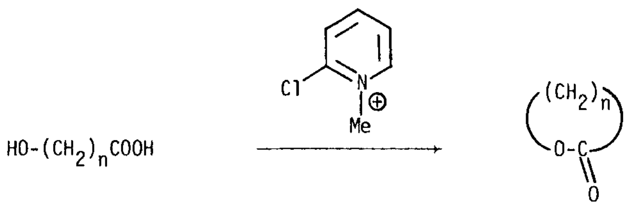
62%

Chem Lett (1975) 1045



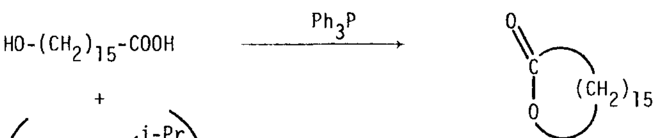
n = 1, 2

R = Ph, alkyl, cinnamyl, etc. Chem Lett (1976) 13

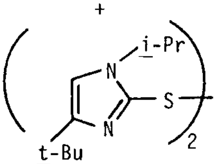


n = 5,7,10,11,14

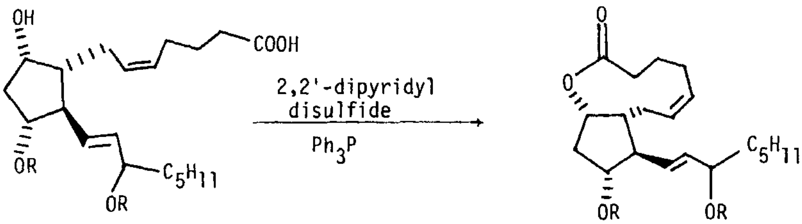
Chem Lett (1976) 49



83%

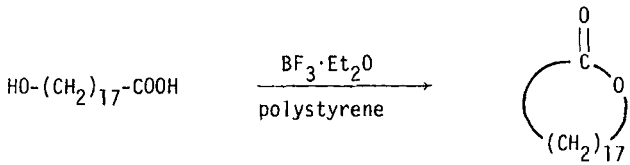


Tetr Lett (1976) 3409



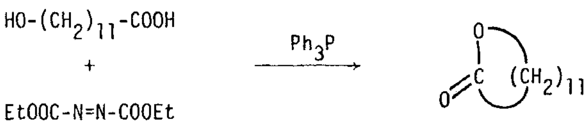
92%

JACS (1975) 97 653, 654



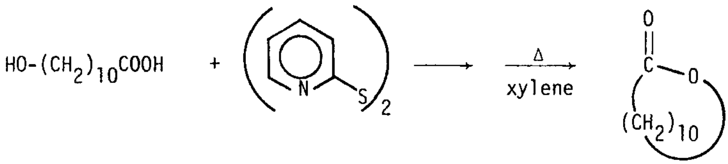
78%

Synthesis (1976) 738



63%

Tetr Lett (1976) 2455



~70%

JACS (1974) 96 5614

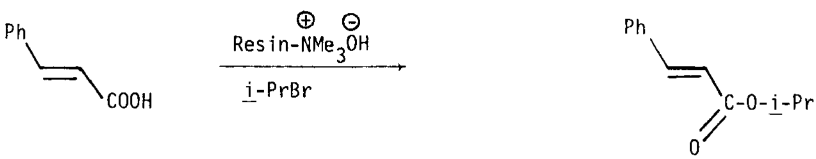
Further examples of the reaction RCOOH + ROH → RCOOR are included in Section 108 (Esters from Alcohols and Phenols) and Section 10A (Protection of Carboxylic Acids).

$$\text{R-COOK} + \text{BzCl} \xrightarrow[\text{TMEDA}]{\text{MeCN}} \text{RCOOBz}$$

~80%

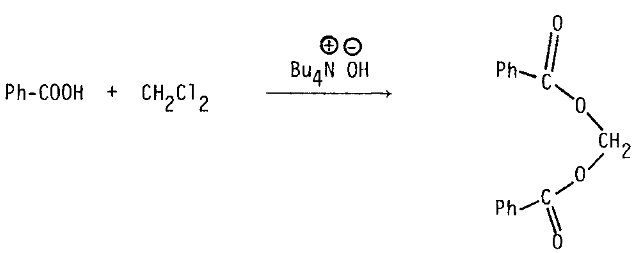
R = hindered alkyl

Comptes Rend C (1976) 283 483



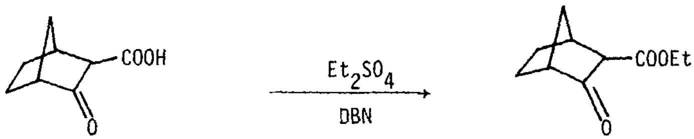
59%

Synthesis (1975) 723



88%

Tetr Lett (1975) 2303

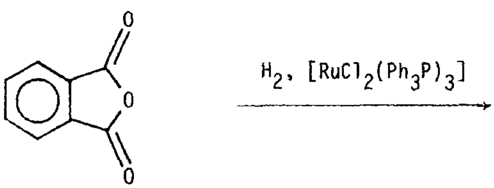


76%

Synth Comm (1976) 6 89

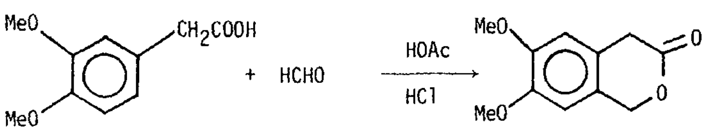
$RCO_2^{\ominus}$ + $PhCH_2\overset{\oplus}{N}(Me)_2Ph$ $\xrightarrow{\Delta}$ RCO_2CH_2Ph 65-80%

Synthesis (1974) 727



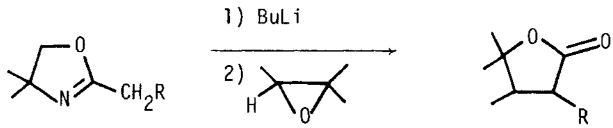
100%

JCS Chem Comm (1975) 412



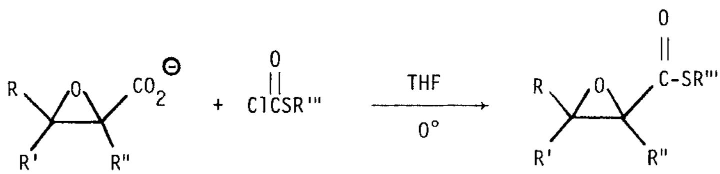
56%

Org Synth (1976) 55 45



high yield

JOC (1974) 39 2783



40-80%

Synthesis (1974) 811

$$\mathrm{RCOOH} + \mathrm{R'SH} \xrightarrow[\mathrm{Et_3N\ in\ DMF}]{\mathrm{NCPO(OEt)_2}} \mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}\text{-}SR'} \qquad 70\text{-}95\%$$

JOC (1974) 39 3302

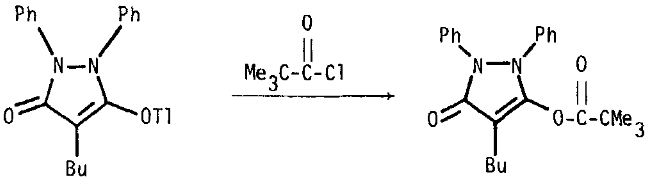
Section 108 Esters from Alcohols and Phenols

$$\underline{n}\text{-}C_{16}H_{33}OTHP \xrightarrow[CH_2Cl_2]{TFAA} \underline{n}\text{-}C_{16}H_{33}OCOCF_3 \qquad 89\%$$

Synth Comm (1976) 6 21

$$MeOH \xrightarrow[TMED]{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF(CF_3)_2} Me\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph \qquad 89\%$$

Chem Lett (1976) 673



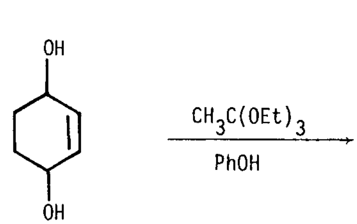
75%

JOC (1976) 41 165

Further examples of the reaction ROH → R'COOR are included in Section 107 (Esters from Carboxylic Acids and Acid Halides) and Section 45A (Protection of Alcohols and Phenols).

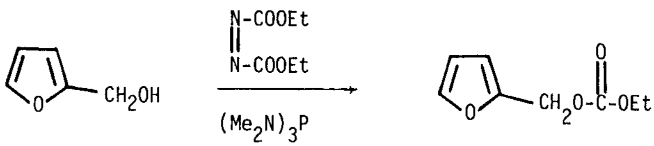
$$BuONa + CO \xrightarrow[BuOH,\ THF]{Se} (BuO)_2CO \qquad 80\%$$

Bull Chem Soc Japan (1975) 48 108



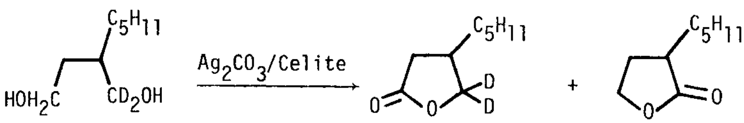
85%

Angew Int Ed (1975) 14 103



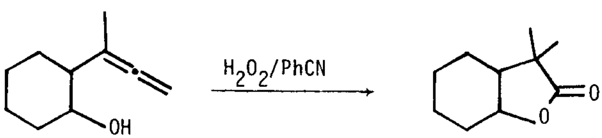
71%

Tetrahedron (1975) 31 1411



90% 10%

Tetrahedron (1975) 31 171



~80%

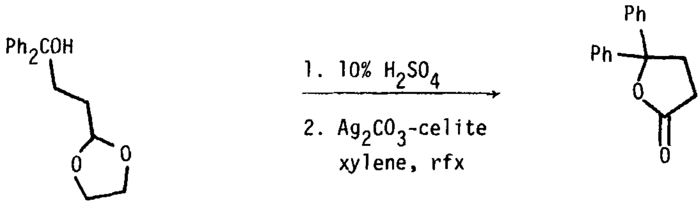
Tetr Lett (1976) 3305

Section 109 Esters from Aldehydes

$$\begin{matrix} ROSnBu_3 \\ + \\ R'CHO \end{matrix} \xrightarrow[CCl_4]{NBS} R'\text{-}\overset{\overset{\displaystyle O}{||}}{C}\text{-}OR \qquad \sim 90\%$$

R = alkyl
R'= alkyl, Ph

JACS (1976) 98 1629



71%

JOC (1975) 40 892

$$PhCH(OCH_2CH{=}CH_2)_2 \xrightarrow{\Delta} Ph\text{-}\overset{\overset{\displaystyle O}{||}}{C}\text{-}OCH_2CH{=}CH_2 \qquad 72\%$$

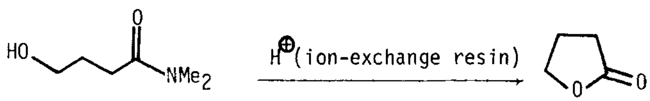
Synth Comm (1975) 5 213

Related methods: Esters from Ketones (Section 117)

Section 110 Esters from Alkyls, Methylenes and Aryls

No examples of the reaction RR → RCOOR' or R'COOR (R,R'=alkyl, aryl, etc.) occur in the literature. For the reaction RH → RCOOR' or R'COOR see Section 116 (Esters from Hyrides).

Section 111 Esters from Amides



86%

Chem Ber (1975) 108 48

$$RCONHR' \xrightarrow{PhS(OR_f)_2} RCO_2R_f + R'N{=}SPh_2$$

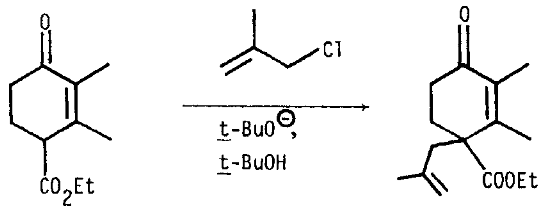
$R_f = PhC(CF_3)_2$

JACS (1975) 97 6137

Section 112 Esters from Amines

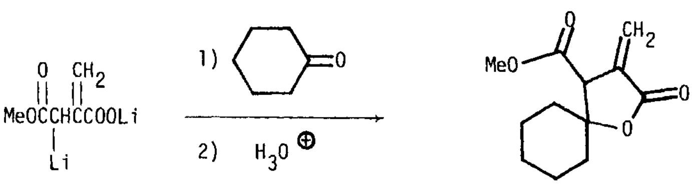
No additional information

Section 113 Esters from Esters



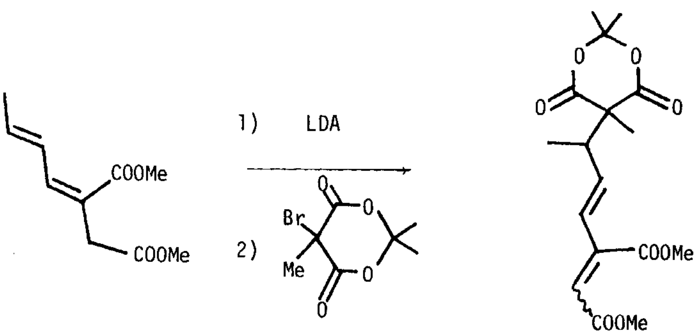
100%

JOC (1974) 39 2323



71%

JOC (1976) 41 4065



66%

JACS (1976) 98 1204

$C_6H_{13}CH{=}CHCOOMe \xrightarrow[\text{2) } PhCH_2Br]{\text{1) L-Selectride}} C_7H_{15}CH(CH_2Ph)CO_2Me$ 50%

JOC (1975) 40 2846

$Et_3SiCH_2COOMe \xrightarrow[\text{2) } MeI]{\text{1) } (Me_3Si)_2NNa} Et_3SiCHMeCO_2Me$ 86%

J Gen Chem USSR (1975) 45 78

$EtCCl_2COO\text{-}\underline{i}\text{-}Pr \xrightarrow[\text{2) } MeI]{\text{1) Li, THF}} EtCCl(Me)CO_2\text{-}\underline{i}\text{-}Pr$ 85%

J Organometal Chem (1975) 102 129

$MeSCH_2CH{=}CHCOOMe \xrightarrow[\text{2) MeI, HMPA}]{\text{1) LDA, THF}} MeSCH{=}CHCHMeCOOMe$ 92%

Tetr Lett (1975) 405

$EtOOCCH_2N{=}C(SMe)_2 + \underline{t}\text{-}BuOK + MeI \longrightarrow EtOOC\text{-}\underset{\displaystyle Me}{\underset{|}{C}H}\text{-}N{=}C(SMe)_2$ 70%

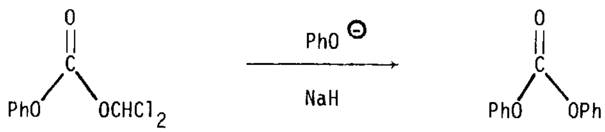
Angew Chem Int Ed (1975) 14 424

$MeC{\equiv}CCOOH \xrightarrow[\text{THF, HMPA}]{\text{1) Li, TMP}} Me_2C{=}CH(CH_2)_2C{\equiv}CCOOMe$ 50%

2) $Me_2C{=}CHCH_2Br$

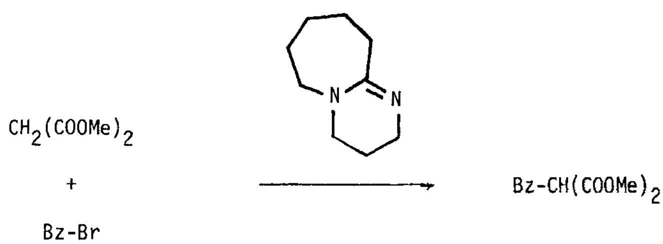
3) MeI

JOC (1975) 40 269



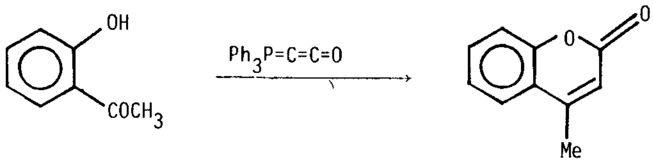
70%

JOC (1976) 41 2039



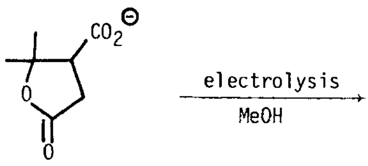
84%

Liebigs Ann Chem (1976) 348



78%

Angew Int Ed (1976) 15 115

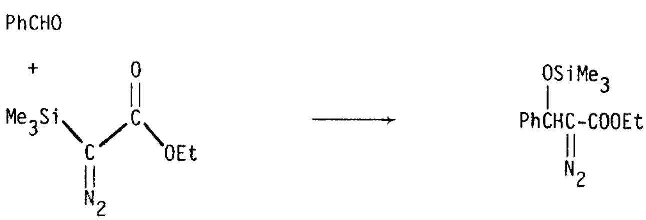


92%

JOC (1974) 39 2486

$$\mathrm{EtO\text{-}\overset{\overset{O}{\|}}{C}\text{-}H} \quad + \quad \mathrm{NaOMe} \quad + \quad \mathrm{O_2} \quad \xrightarrow[\text{cat.}]{\text{Se}} \quad \mathrm{EtO\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMe}$$

Tetr Lett (1974) 804

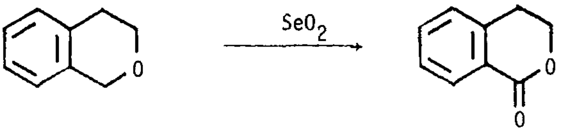


86%

JOC (1976) 41 3335

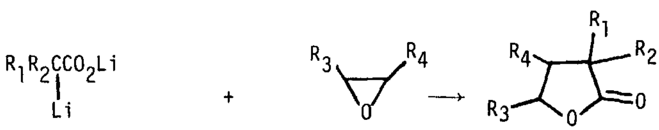
Conjugate reductions of unsaturated esters are listed in Section 74
(Alkyls from Olefins)

Section 114 Esters from Ethers



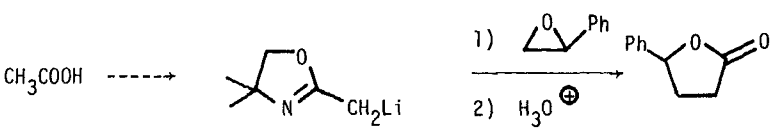
85%

Org React (1976) 24, 261



~80%

Aust J Chem (1974) 27 2205



89%

JOC (1974) 39 2783

$$\text{R-OR'} \xrightarrow{\text{FeCl}_3\text{-Ac}_2\text{O}} \text{ROAc} + \text{R'OAc}$$

(allyl ethers not rearranged or isomerized)

JOC (1974) 39 3728

Section 115 Esters from Halides

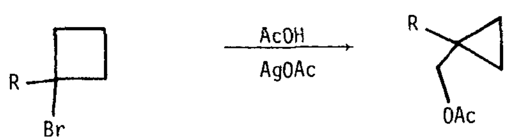
$$\text{ArX} \xrightarrow[\text{MeOH, Et}_2\text{NH}]{\text{Pd}^{++}\text{, CO}} \text{ArCOOMe}$$

Bull Chem Soc Japan (1975) 48 2075
JOC (1975) 40 532

$$\text{PhI} + \text{CO} + \text{EtOH} + \text{Et}_3\text{N} + \text{Pd(0) cat} \longrightarrow \text{PhCOOEt} \qquad 90\%$$

$$\text{MeNH}_2 \longrightarrow \text{PhCONHMe}$$

JOC (1974) 39 3318
JOC (1974) 39 3327



40-60%

JOC (1974) 39 1761

$$RBr + Hg(NO_3)_2 \longrightarrow RONO_2 \qquad 60\text{-}100\%$$

28 cases

Tetrahedron (1974) <u>30</u> 2467

$$RBr + Hg(OAc)_2 + AcOH \longrightarrow ROAc \qquad 88\text{-}98\%$$

15 cases

Tetrahedron (1974) <u>30</u> 2467

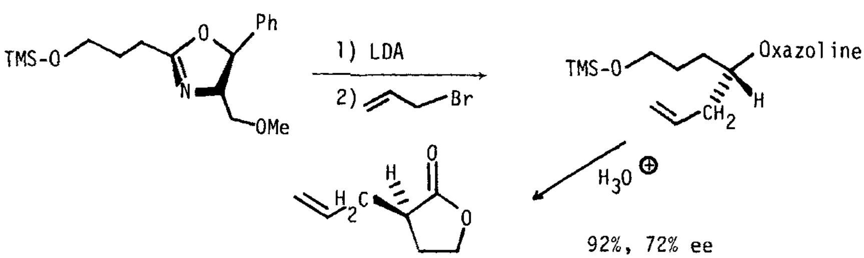
$$RX + Hg(O_2CR')_2 \xrightarrow{B(O_2CR')_3} RO_2CR'$$

$$RX + NaO_2CR' \xrightarrow{HMPA} RO_2CR'$$

$$RX + AgO_2CR' \xrightarrow{THF} RO_2CR'$$

Comparison of these methods.

JOC (1974) <u>39</u> 3721



92%, 72% ee

JOC (1975) <u>40</u> 1186

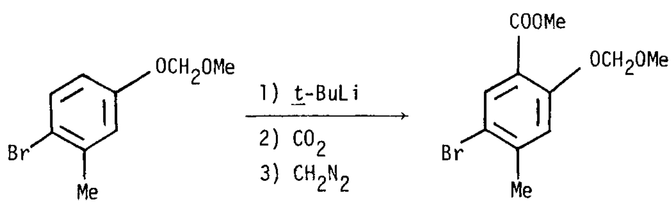
$$HO_2CCH_2COOEt \xrightarrow[\text{2) } PhCH_2Cl]{\text{1) LiICA, THF}} PhCH_2CH_2COOEt \qquad 75\%$$

JOC (1975) 40 2556

Related methods: Carboxylic Acids from Halides (Section 25)

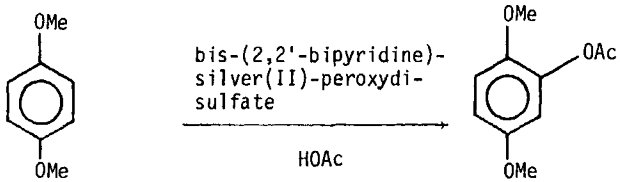
Section 116 Esters from Hydrides

This section contains examples of the reaction RH → RCOOR' or R'COOR (R=alkyl, allyl, aryl, etc.) and ArH → Ar-X-COOR (X=alkyl chain)



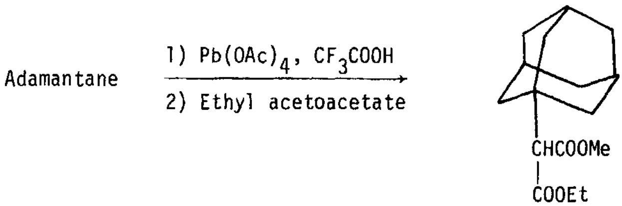
~90%

Tetr Lett (1975) 3973



183% (based on Ag)

Acta Chem Scand B (1975) 29 629

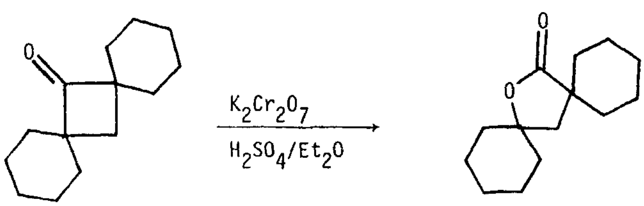


87%

Synthesis (1976) 32

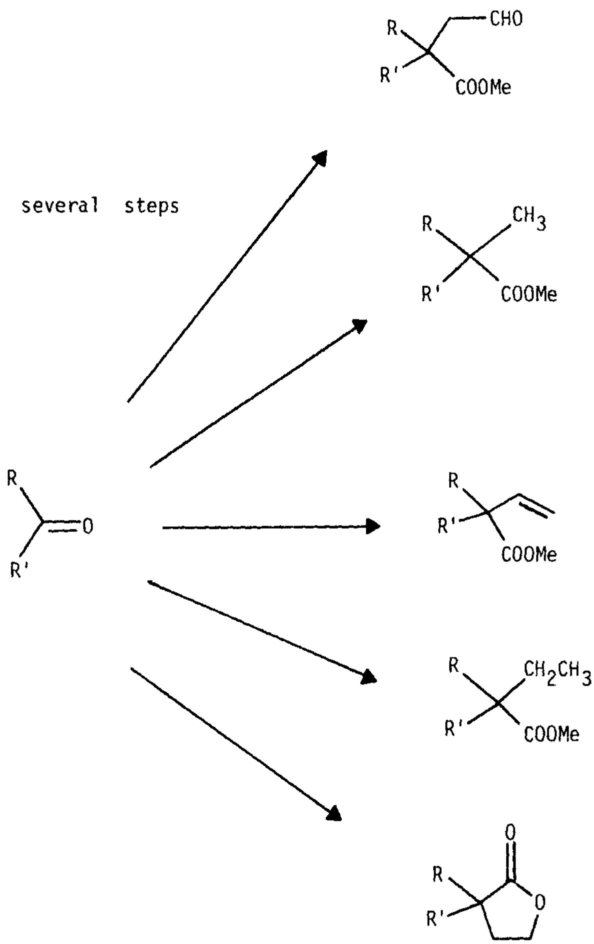
Also via: Carboxylic acids, Section 26; Alcohols, Section 41

Section 117 Esters from Ketones

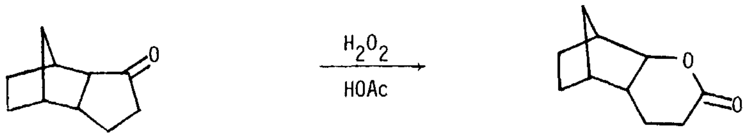


80%

Tetr Lett (1975) 1841

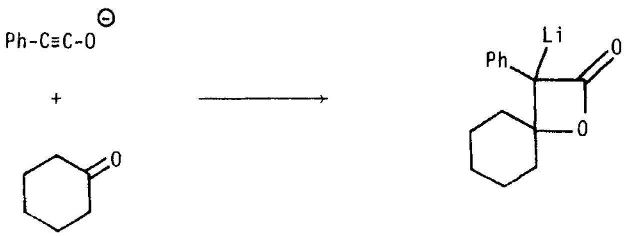


JACS (1975) 97 2218, 2224



85%

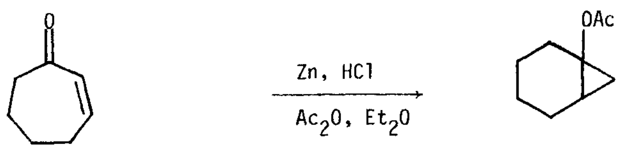
Synthesis (1975) 404



51%

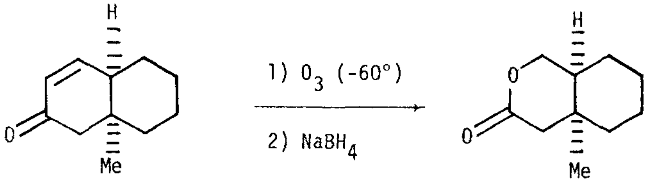
May be protonated, decarboxylated, or further alkylated.

Angew Int Ed (1975) 14 765



40%

Helv Chim Acta (1976) 59 962

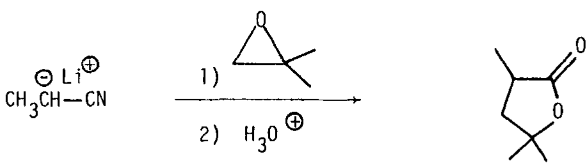


45%

JOC (1975) 40 2970

Also via Carboxylic acids, Section 27

Section 118 Esters from Nitriles



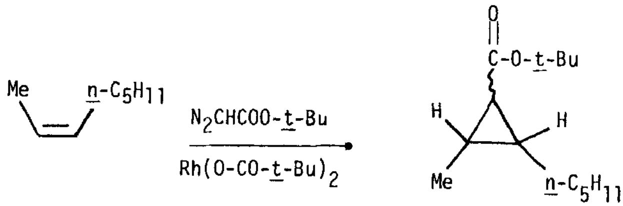
72%

Synthesis (1976) 238

Section 119 Esters from Olefins

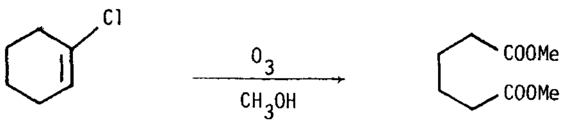
$$BuCH{=}CH_2 \xrightarrow[\text{3) } I_2]{\text{1) 1/3 } BH_3 \quad \text{2) } Hg(OAc)_2} BuCH_2CH_2OAc \qquad 86\%$$

JOC (1974) 39 834



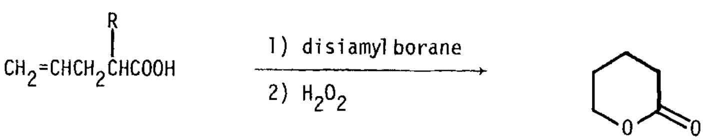
89%

Synthesis (1976) 600



83%

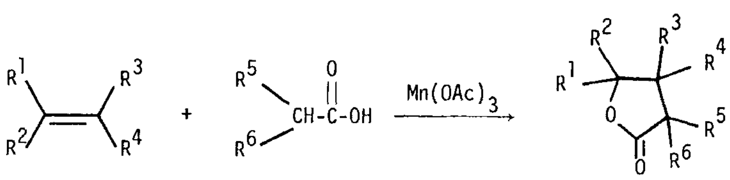
Angew Int Ed (1975) 14 716



54-84%

R = H, 1°, 2°, 3° alkyl

Chem Pharm Bull (1976) 24 538



30-60%

JACS (1974) 96 7977
JOC (1974) 39 3456

Also via Alcohols, Section 44

Section 120 Esters from Miscellaneous Compounds

No additional examples

Section 120A Protection of Esters

No additional examples

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 9 PREPARATION OF ETHERS AND EPOXIDES

Section 121 Ethers and Epoxides from Acetylenes

No examples

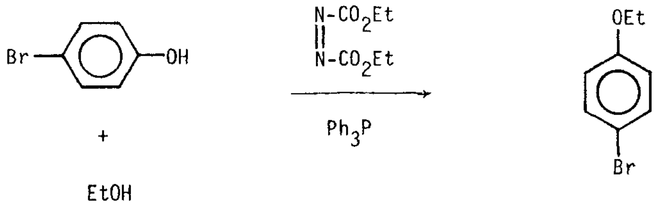
Section 122 Ethers and Epoxides from Carboxylic Acids

No additional examples

Section 123 Ethers and Epoxides from Alcohols and Phenols

$$ROH + CH_3I + NaH \longrightarrow ROCH_3$$ high yields

Synthesis (1974) 434



90%

JCS Perkin I (1975) 461

$RBr + HgClO_4 + R'OH \longrightarrow ROR'$ 74-98%

23 cases

Tetrahedron (1974) 30 2467

$ArOH + RX \xrightarrow[\text{cat.}]{\text{phase transfer}} ArOR$

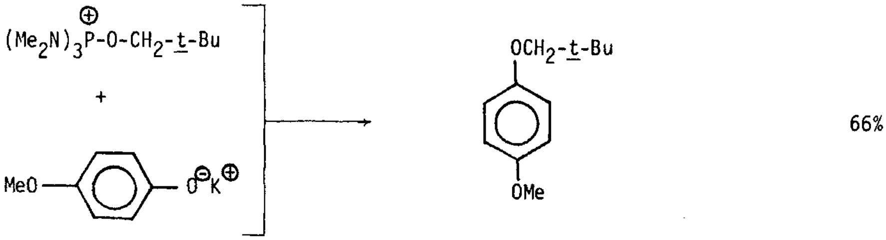
Tetrahedron (1974) 30 1379

$\text{Polyphenol} + Me_2SO_4 + NaOAc \xrightarrow[\text{dioxane}]{\text{acetone-}}$ methylation of most acidic OH group

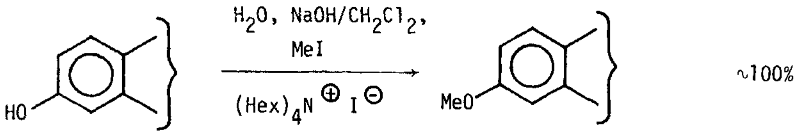
Indian J Chem (1974) 12 893

$PhOH \xrightarrow[\text{N-COOEt} \,||\, \text{N-COOEt}]{CH_3OH,\ Ph_3P} PhOCH_3$ 98%

Chem and Ind (1975) 281

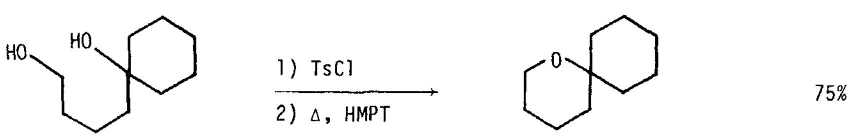


Angew Int Ed (1975) 14 370

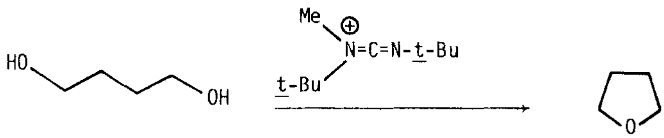


Steroids (1976) 28 481

Related methods: Protection of Alcohols and Phenols (Section 45A)

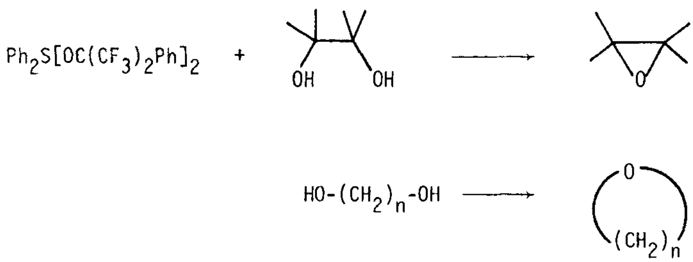


Tetr Lett (1975) 2731



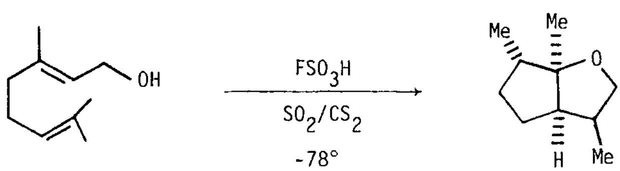
64%

JACS (1975) 97 465



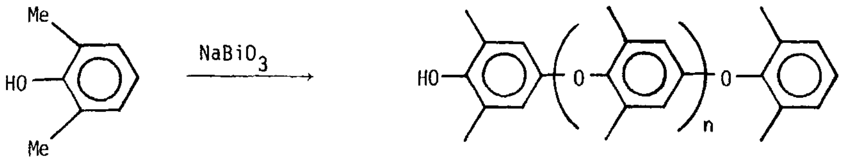
moderate to high yields

JACS (1974) 96 4604



78%

JCS Perkin I (1974) 1637



molecular weight ~10^4

JOC (1975) 40 1515

Section 124 Ethers and Epoxides from Aldehydes

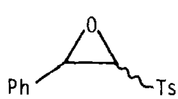
$$RCHO + R'OH \longrightarrow R\text{-}\underset{H}{\overset{OR'}{C}}\text{-}OR' \xrightarrow[THF]{B_2H_6} RCH_2OR' \qquad 60\text{-}90\%$$

Can J Chem (1974) 52 888

$$RCHO + Et_3SiH \xrightarrow[CHCl_3]{AcOH} (RCH_2)_2O$$

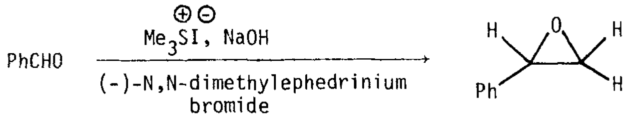
JOC (1974) 39 2740

PhCHO + $TsCH_2Cl$ $\xrightarrow[\text{TEBA}]{\text{50\% aq. NaOH}}$



60%

JOC (1975) 40 266



77%

(R)-67% ee

JACS (1975) 97 1626

Section 125 Ethers and Epoxides from Alkyls, Methylenes and Aryls

No examples of the preparation of ethers and epoxides by replacement of alkyl, methylene and aryl groups occur in the literature. For the conversion of RH → ROR' (R,R'=alkyl) see Section 131 (Ethers from Hydrides)

Section 126 Ethers and Epoxides from Amides

No additional examples

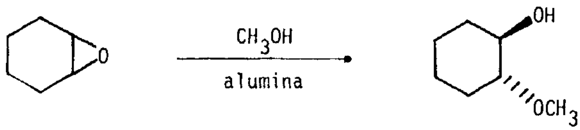
Section 127 Ethers and Epoxides from Amines

No additional examples

Section 128 Ethers and Epoxides from Esters

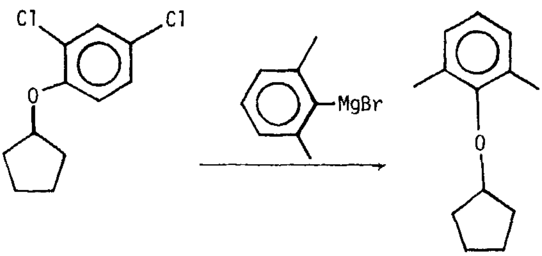
No additional examples

Section 129 Ethers and Epoxides from Ethers and Epoxides



66%

Tetr Lett (1975) 3597



79%

Chem Lett (1975) 1051

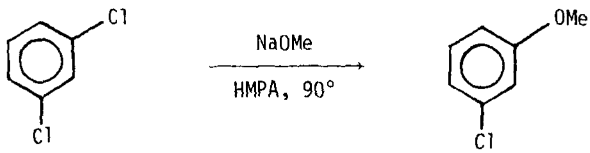
Section 130 Ethers from Halides

$$\text{BzCl} + \text{Bu-OH} \xrightarrow[\text{Bu}_4\text{N}^{\oplus}\,\text{HSO}_4^{\ominus}]{\text{50\% NaOH}} \text{Bu-O-Bz} \qquad 92\%$$

Tetr Lett (1975) 3251

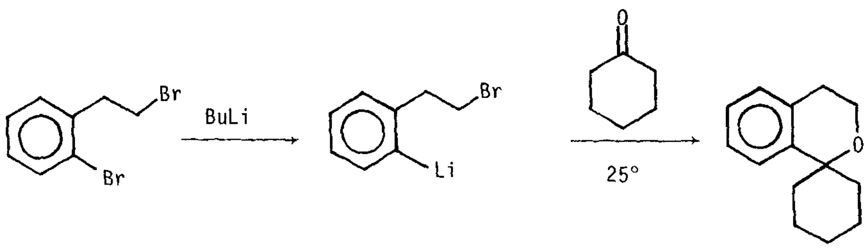
$$MeOCH_2CH_2OH \xrightarrow[\text{2) BzBr, MeCN}]{\text{1) TlOEt}} MeOCH_2CH_2OBz \qquad 81\%$$

Angew Int Ed (1975) 14 762



87%

JOC (1976) 41 732



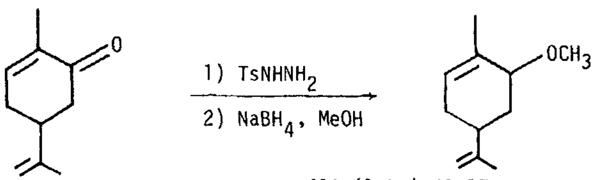
75%

JOC (1976) 41 1184

Section 131 Ethers from Hydrides

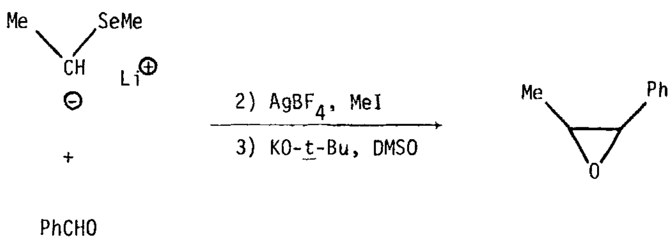
No additional examples

Section 132 Ethers and Epoxides from Ketones



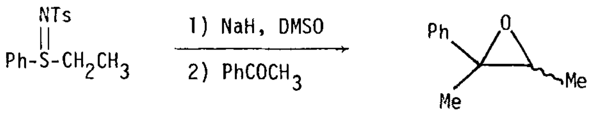
77%

JOC (1976) 41 1755



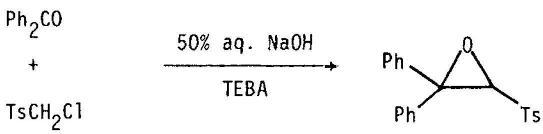
78%

Angew Int Ed (1975) 14 350, 700



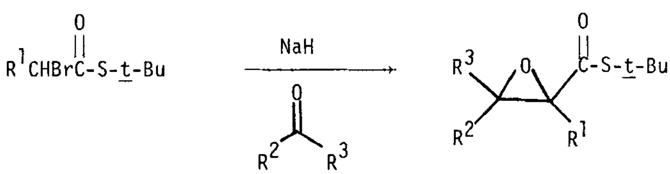
54%

Synthesis (1976) 35

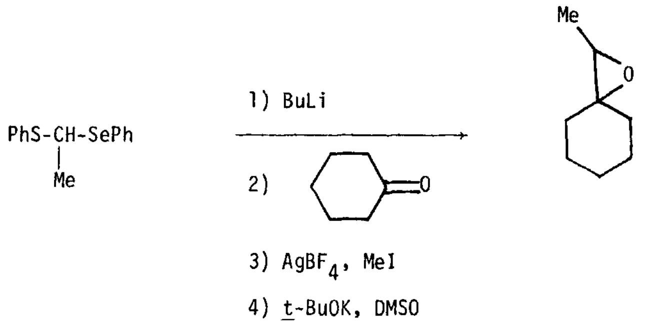


90%

JOC (1975) 40 266

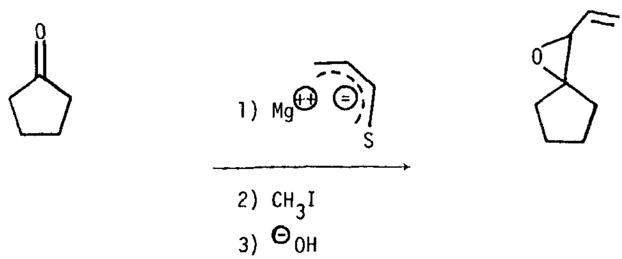


JOC (1975) 40 3173



∿35%

Tetr Lett (1975) 1617



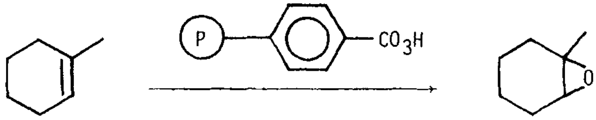
78%

Angew Int Ed (1976) 15 437

Section 133 Ethers and Epoxides from Nitriles

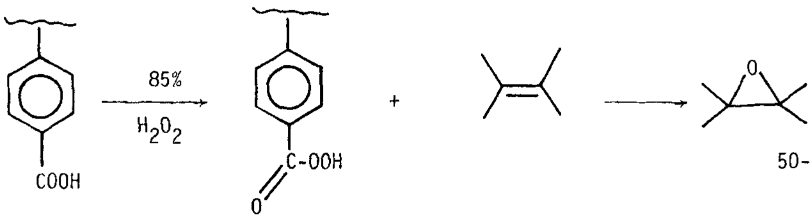
No additional examples

Section 134 Ethers and Epoxides from Olefins



65%

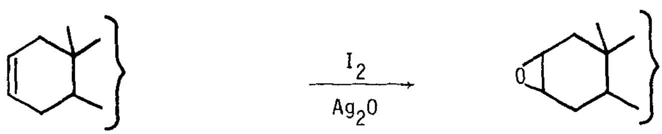
JCS Perkin I (1976) 605



50-90%

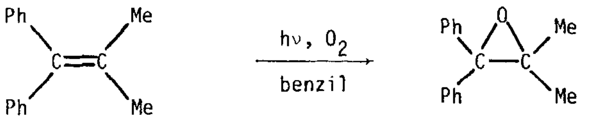
Use of polymer supported peracids to epoxidize olefins.

JCS Chem Comm (1974) 1009



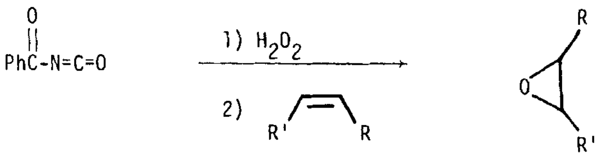
~80%

Tetr Lett (1976) 207

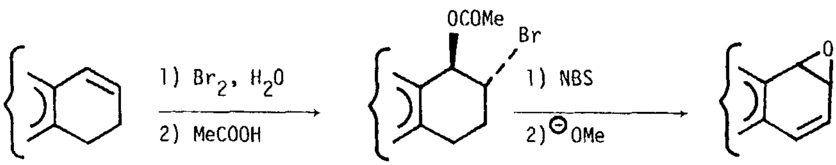


80%

JACS (1976) 98 4193

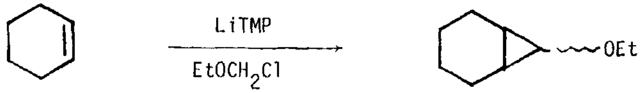


JCS Chem Comm (1974) 711



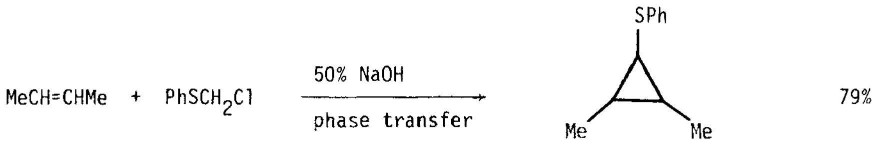
~70%

JACS (1975) 97 3185



55%

Tetr Lett (1976) 3779



Tetr Lett (1975) 4247

Review: "Metal Ketenides in the Catalytic Epoxidation of Olefins"

Chem and Ind (1975) 154

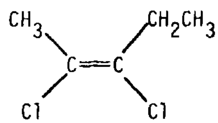
Section 135 Epoxides from Miscellaneous Compounds

No additional examples

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 10 PREPARATION OF HALIDES AND SULFONATES

Section 136 Halides and Sulfonates from Acetylenes

$CH_3\text{-}C{\equiv}C\text{-}CH_2CH_3 \xrightarrow{MoCl_5}$  38%

JACS (1975) 97 1599

Section 137 Halides from Acid Halides

$PhCOCl + SF_4 \xrightarrow{95°} PhCF_3$ 95%

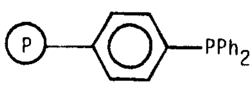
Org React (1974) 21 1

Section 138 Halides and Sulfonates from Alcohols

$$\text{geranyl-OH} \xrightarrow[CCl_4]{Ph_3P} \text{geranyl-Cl} \qquad \sim 80\%$$

or $\xrightarrow[\text{LiCl, HMPA}/Et_2O]{\text{MeLi, TsCl}}$

Org Synth (1974) 54 63, 68

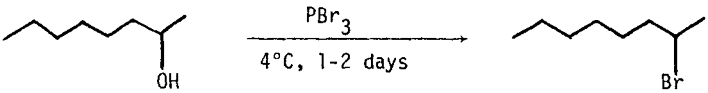


$$PhCH_2OH \xrightarrow[CCl_4]{} PhCH_2Cl \qquad 88\%$$

JCS Chem Comm (1975) 622

$$\textit{n}\text{-BuOH} \xrightarrow[ZnCl_2]{PCl_3,\text{DMF}} \textit{n}\text{-BuCl} \qquad 87\%$$

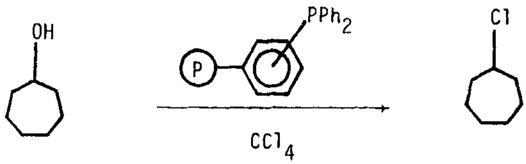
Synthesis (1976) 398



67%

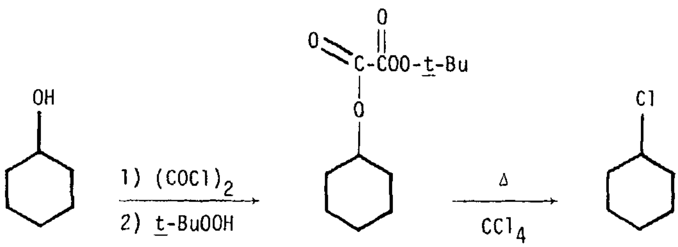
97% retention of configuration

JOC (1976) 41 1071



92%

JOC (1975) 40 1669



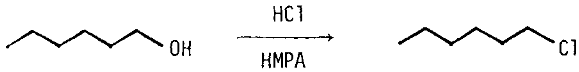
48%

JACS (1975) 97 2281

$$\text{R-OH} + \text{PCl}_5 \xrightarrow[\text{CaCO}_3]{\text{CHCl}_3} \text{R-Cl}$$

R = 3° alkyl — retention of configuration

Aust J Chem (1976) 29 133

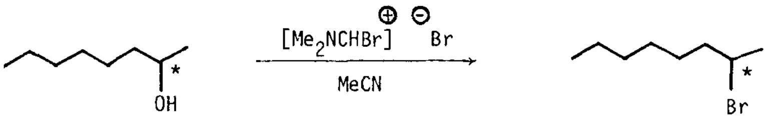


76%

Can J Chem (1975) 53 3620

n-Hexyl-OH + aq. HCl $\xrightarrow[\text{cat.}]{\text{phase transfer}}$ n-Hexyl Cl >90%

Synthesis (1974) 37

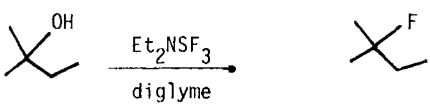


~80% yield

~75% ee (retention)

JCS Perkin I (1976) 754

BzOH $\xrightarrow[CH_2Cl_2]{Et_2NSF_3}$ BzF 100%



88%

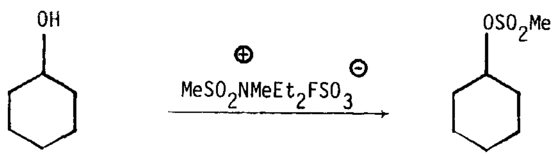
JOC (1975) 40 574

$C_6F_5CH_2OH + SF_4 \xrightarrow{85°} C_6F_5CH_2F$ 80%

Org React (1974) <u>21</u> 1

$ROH + SeF_4 \longrightarrow RF$ 40-90%

JACS (1974) <u>96</u> 925



98%

JACS (1975) <u>97</u> 2566

Section 139 <u>Halides and Sulfonates from Aldehydes</u>

$PhCHO + SF_4 \xrightarrow{160°} PhCHF_2$ 81%

Org React (1974) <u>21</u> 1

Section 140 <u>Halides and Sulfonates from Alkyls</u>

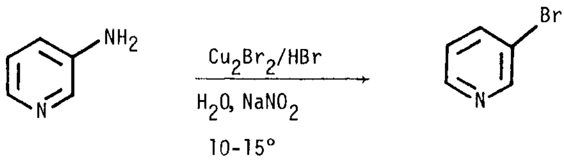
No additional examples

For the conversion RH→RHal see Section 146 (Halides from Hydrides)

Section 141 Halides and Sulfonates from Amides

No additional examples

Section 142 Halides from Amines



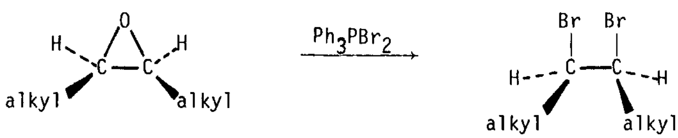
70-90%

Synthesis (1974) 292

Section 143 Halides and Sulfonates from Esters

No additional examples

Section 144 Halides from Ethers



85%

JOC (1976) 41 3279

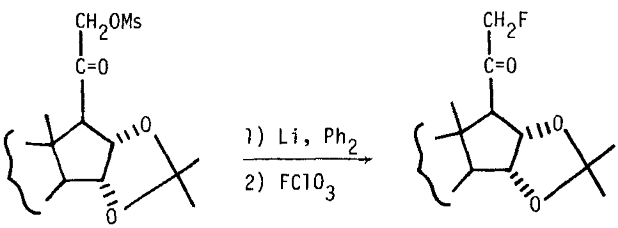
Section 145 Halides from Halides and Sulfonates

$$\mathrm{RX} + \mathrm{KF} \xrightarrow[120\text{-}160^\circ]{\text{phase-transfer catalyst}} \mathrm{RF} \qquad \text{good yield}$$

Synthesis (1974) 428

$$\underline{n}\text{-}C_{16}H_{33}Br \xrightarrow{\text{resin-}\overset{\oplus}{N}Me_3\ F^{\ominus}} \underline{n}\text{-}C_{16}H_{33}F \qquad 77\%$$

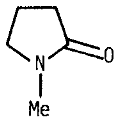
Synthesis (1976) 472



Helv Chim Acta (1976) 59 1027

$$\underset{(R)}{\text{Hex-}\overset{\displaystyle CH_3}{\overset{|}{C}}HOMs} \xrightarrow[\text{phase-transfer catalyst}]{KCl} \underset{\substack{(S) \\ 89\%\ ee}}{\text{Hex-}\overset{\displaystyle CH_3}{\overset{|}{C}}HCl} \qquad 74\%$$

Synthesis (1975) 430



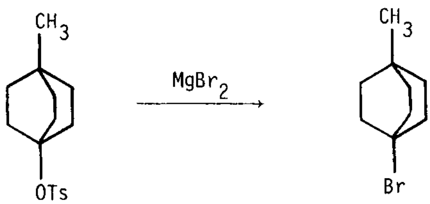
$$R\text{-}Cl \xrightarrow[\text{NaBr, EtBr}]{} R\text{-}Br \qquad \sim 80\%$$

R = 1° alkyl

Bull Chem Soc Japan (1976) 49 1989

$$\underline{n}\text{-}C_{16}H_{33}OTHP \xrightarrow{PPh_3Br_2} \underline{n}\text{-}C_{16}H_{33}Br \qquad 87\%$$

Synth Comm (1976) 6 21

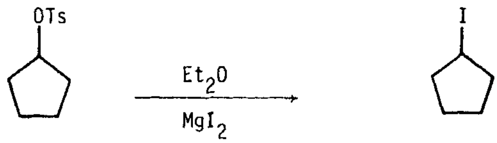


83%

Angew Int Ed (1975) 14 824

$$\underline{t}\text{-}BuCl + FeCl_3 + I^{\ominus} \longrightarrow \underline{t}\text{-}BuI \qquad 95\%$$

Tetr Lett (1974) 2691

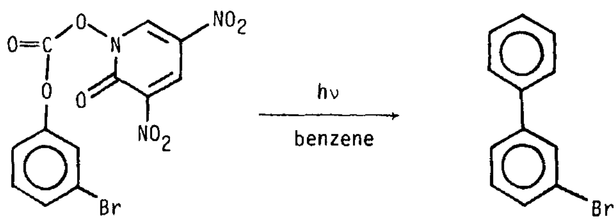


80%

Bull Soc Chim France (1976) 169

$Me_2C(Cl)Et \xrightarrow[ZnCl_2]{NaI,\ CS_2} Me_2C(I)Et$ 96%

JCS Perkin I (1976) 416

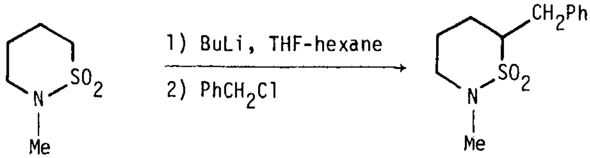


56%

JOC (1976) <u>41</u> 24

$PhSO_2CH_2CH_2OH \xrightarrow[\text{2) Hexyl Br}]{\text{1) BuLi}} PhSO_2CH(Hex)CH_2OH$ ∿100%

Bull Soc Chim France (1976) 519



65%

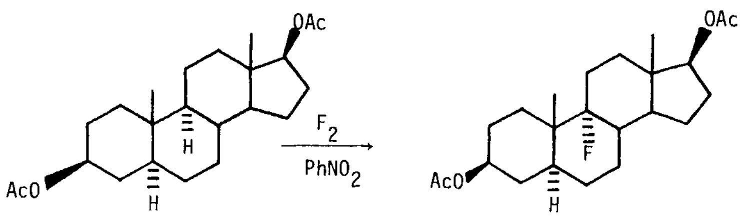
JOC (1975) 40 1342

$$HCBr_3 \xrightarrow[\text{2) BuI}]{\text{1) LDA, THF-}Et_2O\text{-110°}} BuCBr_3$$

90%

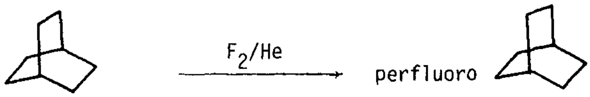
Bull Soc Chim France (1975) 1797

Section 146 Halides from Hydrides



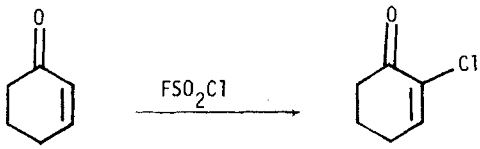
50%

JACS (1976) 98 3036



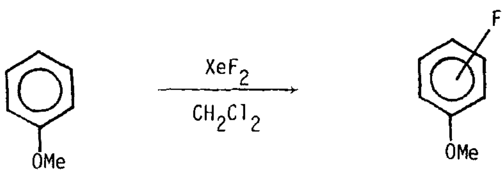
3.5%

JACS (1975) 97 513



70%

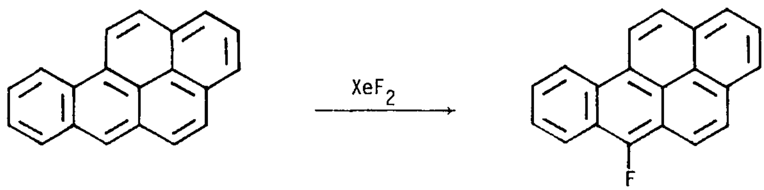
Synthesis (1976) 33



71%

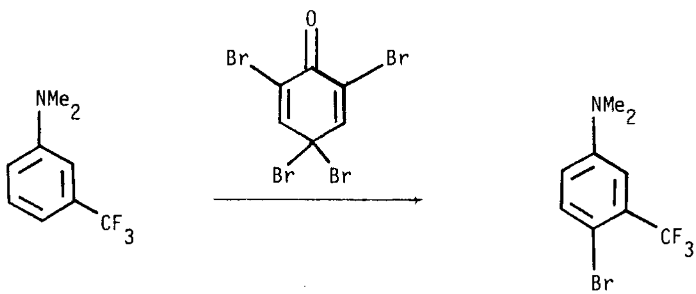
10:1:8
o:m:p

JOC (1975) 40 807



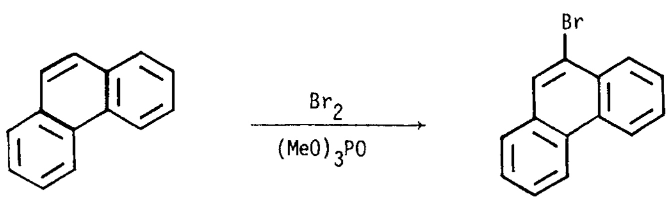
26%

Experientia (1976) 15 417



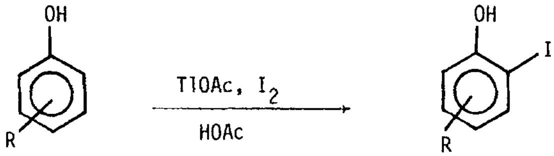
~85%

Org Synth (1976) 55 20



70%

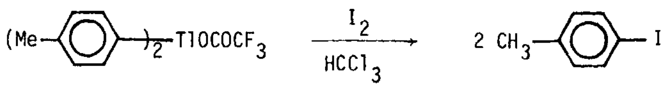
Synthesis (1976) 621



~50%

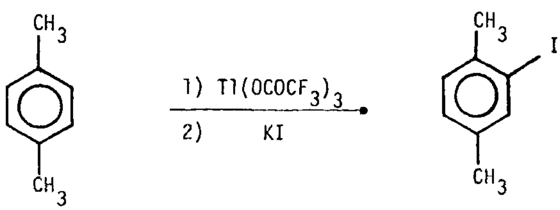
R = H, alkyl, aryl

JCS Perkin I (1976) 1161



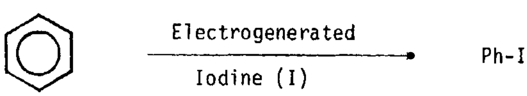
86%

JOC (1975) 2351



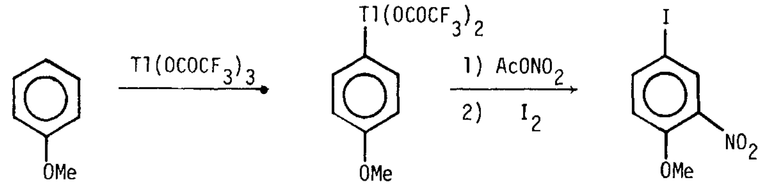
80%

Org Synth (1976) 55 70



91%

JACS (1976) 98 1515



98%

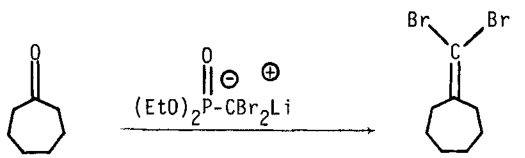
JOC (1975) 40 3441

Section 147 Halides from Ketones

$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R' \quad + \quad SeF_4 \longrightarrow RCF_2R'$$

60-90%

JACS (1974) 96 925



67%

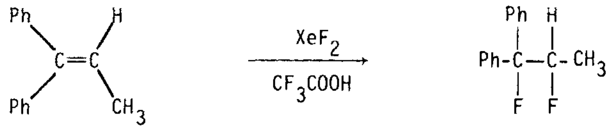
Synthesis (1976) 197

Section 148 Halides and Sulfonates from Nitriles

No examples

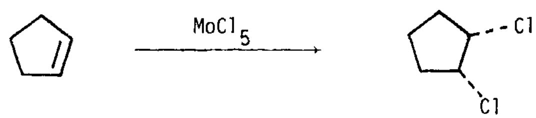
Section 149 Halides from Olefins

For allylic halogenation see Section 146 (Halides from Hydrides)
For halocyclopropanations see Section 74 (Alkyls from Olefins)



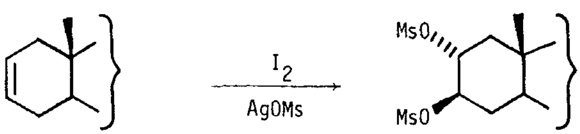
95%

JOC (1976) 41 4002



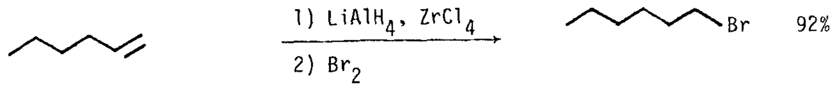
66%

JACS (1975) 97 1599

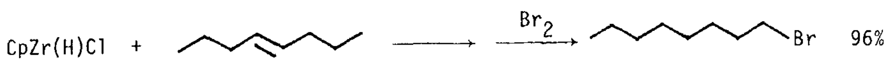


58%

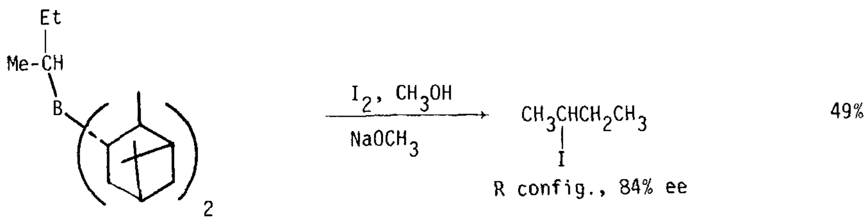
Steroids (1975) 25 619



J Organometal Chem (1976) 122 C25



JACS (1974) 96 8115

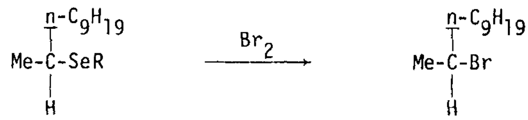


JACS (1976) 98 1290

$$H_2C{=}CH(CH_2)_8COOMe \xrightarrow[\text{2) } I_2,\ NaOCH_3]{\text{1) } B_2H_6,\ THF} I\text{-}CH_2(CH_2)_9COOMe \qquad 68\%$$

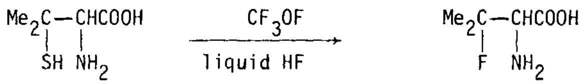
Synthesis (1976) 114

Section 150 Halides from Miscellaneous Compounds



84%

Tetr Lett (1976) 2647



94%

JOC (1976) 41 3107

Review: "Advances in the Synthesis and Investigation of Organo-fluorine Compounds"

Russ Chem Rev (1975) 44 339

Review: "Some Recent Developments in Organic Chlorine Chemistry"

Chem and Ind (1975) 249

Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 11 PREPARATION OF HYDRIDES

This chapter lists hydrogenolysis and related reactions by which functional groups are replaced by hydrogen, e.g. $RCH_2X \rightarrow RCH_2\text{-}H$ or R-H

Section 151 Hydrides from Acetylenes

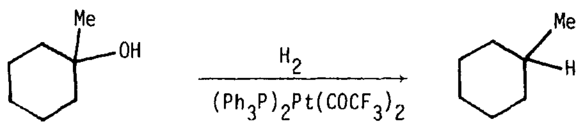
No examples of the reaction $RC{\equiv}CR \rightarrow RH$ occur in the literature

Section 152 Hydrides from Carboxylic Acids

No additional examples

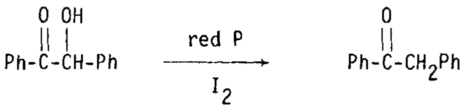
Section 153 Hydrides from Alcohols and Phenols

This section lists examples of the hydrogenolysis of alcohols and phenols, $ROH \rightarrow RH$



83%

Doklady Chem (1974) 219 888



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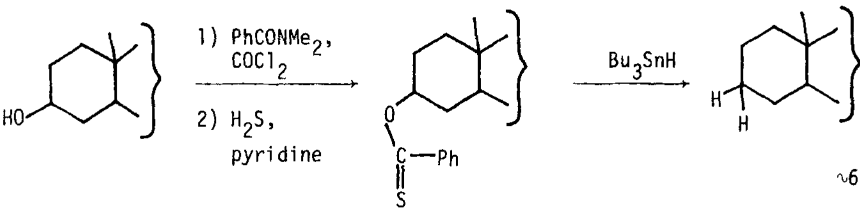
Synthesis (1975) 161



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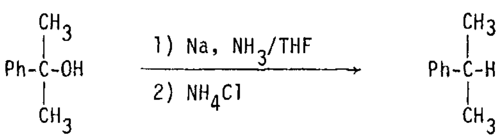
JCS Perkin I (1975) 1574



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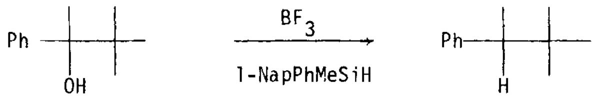
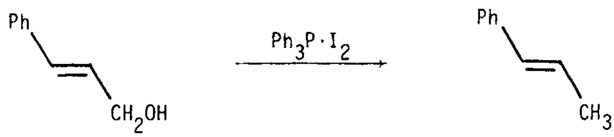
JOC (1975) 40 3151



86%

Tetr Lett (1976) 2955



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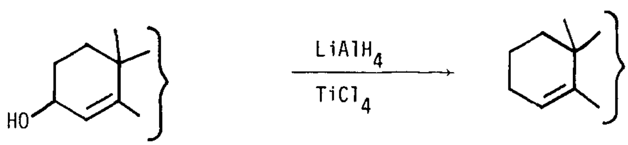
Chem Ber (1976) 109 1586



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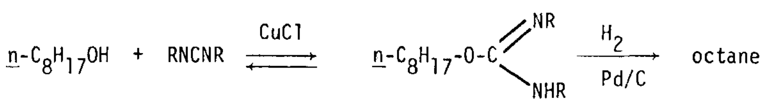
Chem Pharm Bull (1976) 24 825

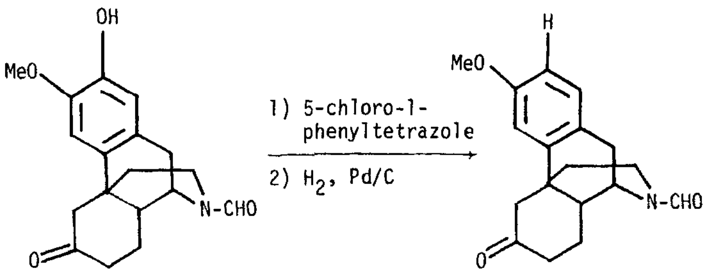


90%

Chem Ber (1974) 107 1353
Chem Ber (1974) 107 907

$$PhOH \longrightarrow PhOSO_3^{\ominus}\ \ NHR_2Ph^{\oplus} \xrightarrow[2)\ RaNi]{1)\ KOH} PhH \qquad 94\%$$

JCS Perkin I (1975) 169



~50%

Rec Trav Chim (1976) 95 43

Also via Halides and Sulfonates, Section 160

Section 154 Hydrides from Aldehydes

No additional examples

For the conversion RCHO → RMe etc. see Section 64 (Alkyls from Aldehydes)

Section 155 Hydrides from Alkyls, Methylenes and Aryls

No additional examples

Section 156 Hydrides from Amides

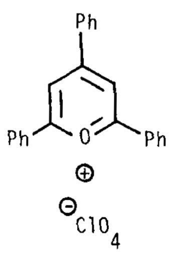
No additional examples

Section 157 Hydrides from Amines

This section lists examples of the conversion $RNH_2 \rightarrow RH$

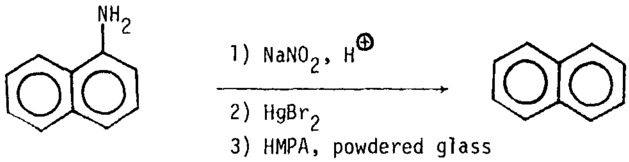
$ArCH_2NH_2$

+



$$\xrightarrow[\text{3) }200^\circ]{\text{2) }NaBH_4} ArCH_3 \qquad 50\%$$

Tetr Lett (1976) 2689



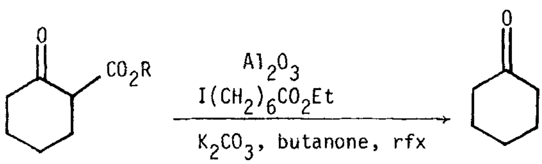
JOC (1974) 39 1317

$C_{10}H_{21}NH_2 \longrightarrow C_{10}H_{21}NTs_2 \xrightarrow[\text{HMPA}]{\text{NaBH}_4} C_{10}H_{22}$ 91%

JOC (1975) 40 2018

Section 158 Hydrides from Esters

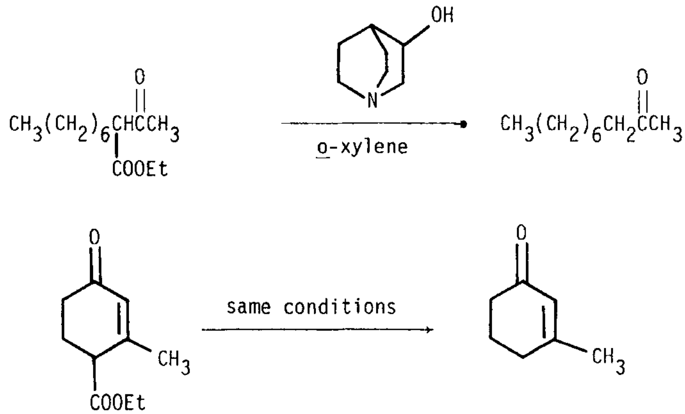
This section lists examples of the reactions RCOOR'→RH and RCOOR'→R'H.



80-90%

R = H, Me, Et

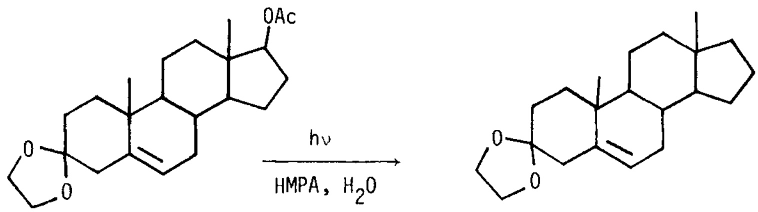
Tetr Lett (1976) 2707



97%

98%

Synth Comm (1975) 5 341



>60%

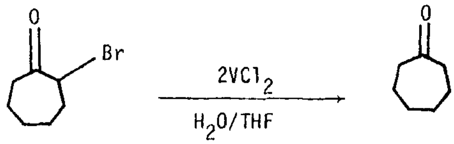
JCS Chem Comm (1975) 439

Section 159 Hydrides from Ethers

No additional examples

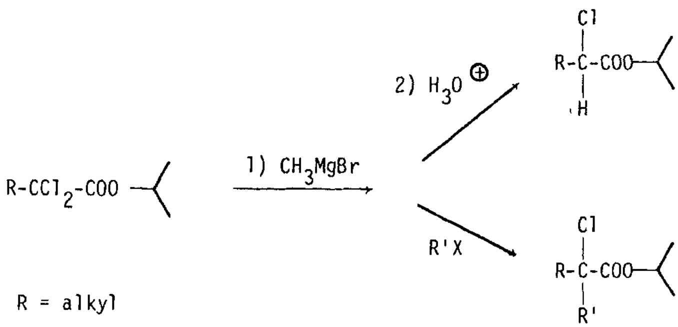
Section 160 Hydrides from Halides and Sulfonates

This section lists the reduction of halides and sulfonates RX → RH



96%

Synthesis (1976) 807



~80%

~80%

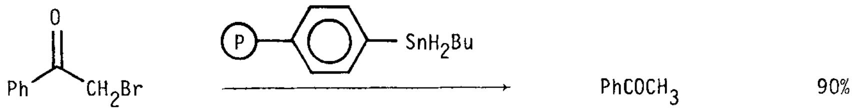
R = alkyl

R' = alkyl, acyl

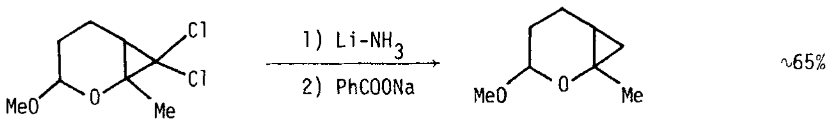
Synthesis (1975) 533

$$Ph(CH_2)_3Br \xrightarrow[NaBH_4,\ h\nu]{Bu_3SnCl\ (0.1\ equiv)} PhCH_2CH_2CH_3 \qquad 88\%$$

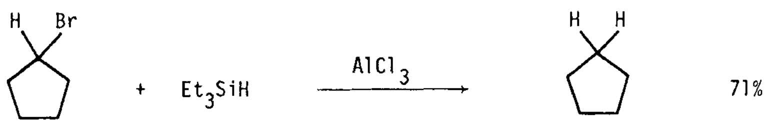
JOC (1975) 40 2554



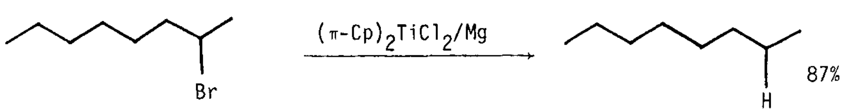
JOC (1975) 40 1966



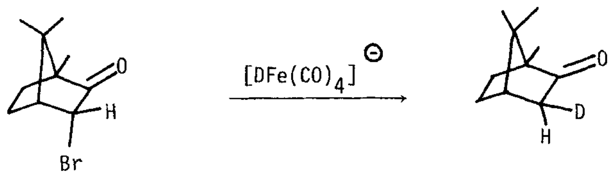
JOC (1975) 40 2238



JOC (1976) 41 1393



JOC (1975) 40 3159

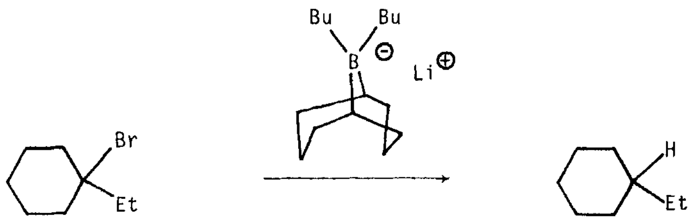


60%

Tetr Lett (1975) 2257

$PhCH_2Br$ + K ($\underline{s}$-Bu)$_3$BH + CuI ⟶ $PhCH_3$ <90%

JCS Chem Comm (1974) 762



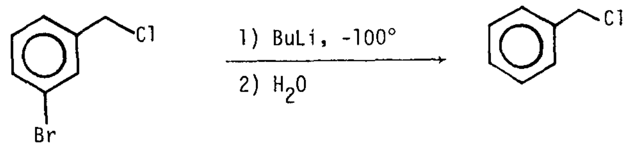
81%

JACS (1975) __97__ 2558

$$RC(Br)_2R' + Zn(Cu) \xrightarrow[D_2O]{THF} R\text{-}C(D)(Br)\text{-}R' + R\text{-}C(D)(D)\text{-}R'$$

60% 20%

JOC (1974) __39__ 2300

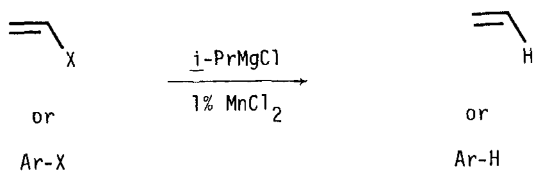


88%

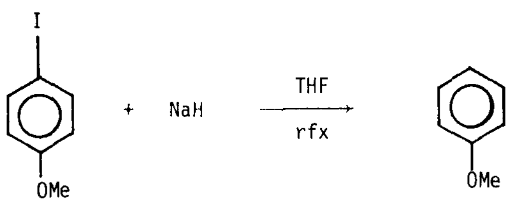
JOC (1976) 41 1184, 1187

$PhCCl{=}CH_2 \xrightarrow[Et_2O]{\underline{t}\text{-BuLi}} PhCH{=}CH\text{-}\underline{t}\text{-}Bu$ 71%

Tetr Lett (1975) 2935

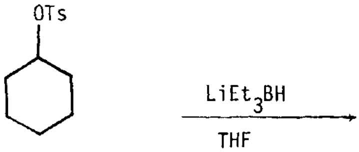


J Organometal Chem (1976) 113 107



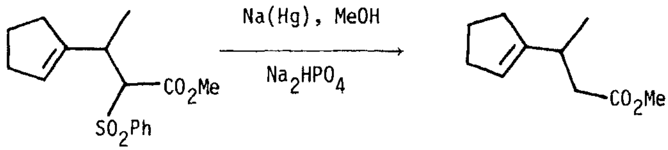
87%

JOC (1974) 39 1425



80%

JOC (1976) 41 3064



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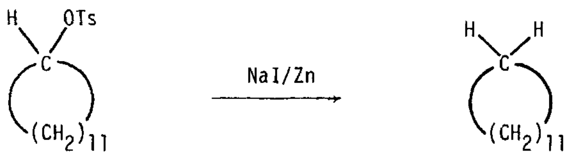
Tetr Lett (1976) 3477



95%

Tetr Lett (1976) 3325

Section 161 Hydrides from Hydrides

No additional examples

Section 162 Hydrides from Ketones

No additional examples

For the conversion $R_2CO \rightarrow R_2CH_2$ or R_2CHR' see Section 72 (Alkyls and Methylenes from Ketones)

Section 163 Hydrides from Nitriles

No additional examples

Section 164 Hydrides from Olefins

No additional examples

Section 165 Hydrides from Miscellaneous Compounds

No additional examples

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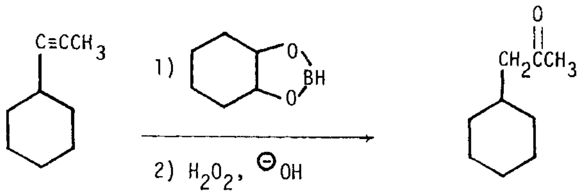
Chapter 12 PREPARATION OF KETONES

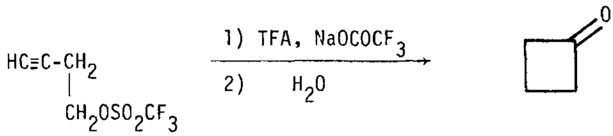
Section 166 Ketones from Acetylenes



JACS (1975) 97 5249

$$R_3B \xrightarrow[\begin{array}{l}2)\ HCl\\ 3)\ NaOH,\ H_2O_2\end{array}]{1)\ LiC\equiv CH} RCOMe \qquad 70\text{-}90\%$$

JACS (1975) 97 5017
Tetr Lett (1975) 3327 (more functionalized alkynes)



~35%

Org Synth (1974) 54 84

75%

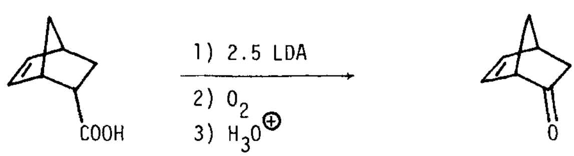
Tetr Lett (1975) 3275

$$\mathrm{Ph{-}C{\equiv}C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3} \xrightarrow[\mathrm{NaCN}]{\mathrm{CH_3OH}} \mathrm{Ph{-}\underset{\displaystyle OMe}{\underset{|}{\overset{\displaystyle OMe}{\overset{|}{C}}}}{-}CH_2COCH_3}$$

86%

JOC (1976) 41 3765

Section 167 Ketones from Carboxylic Acids and Acid Halides



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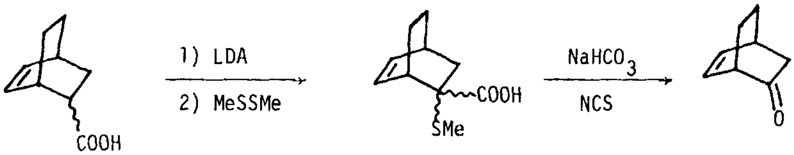
Tetr Lett (1975) 4611



44%

JACS (1975) 97 3528

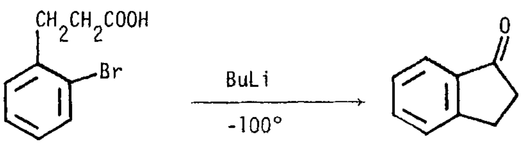
$CH_2{=}CHCMe_2COOH \xrightarrow[Et_2O]{MeLi} H_2C{=}CHCMe_2COMe$ 55%

$CH_2{=}CHCMe_2COOH \xrightarrow[80\%\ THF/20\%\ Et_2O]{MeLi} Me_2C{=}CHCH_2COMe$ 50%

Tetr Lett (1975) 3179

$EtCO_2Li + PhLi \xrightarrow[\text{rfx 24 hrs.}]{Et_2O} EtCOPh$ 82%

JOC (1975) 40 1770

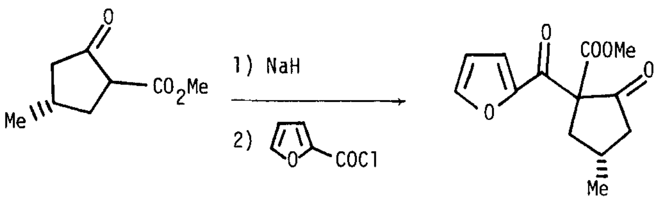


76%

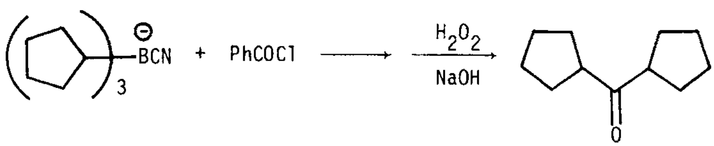
JOC (1975) 40 2394

$$\underline{n}\text{-}C_4H_9CO(CH_2)_4COCl \xrightarrow{(\underline{t}\text{-BuOCuBu-}\underline{t})Li} \underline{n}\text{-}C_4H_9CO(CH_2)_4CO\text{-}\underline{t}\text{-Bu} \qquad 73\%$$

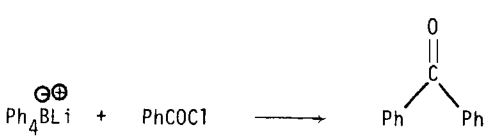
Org React (1975) 22 253



JOC (1974) 39 3241

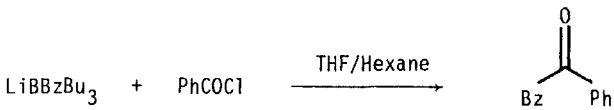


JCS Perkin I (1975) 129, 142



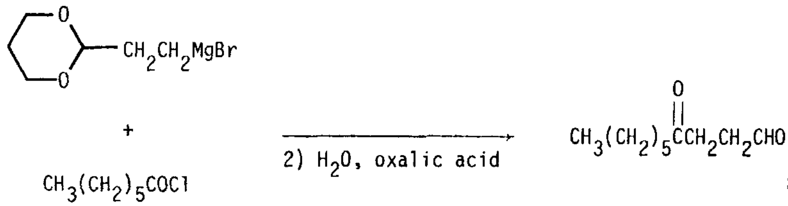
80%

JCS Chem Comm (1975) 138



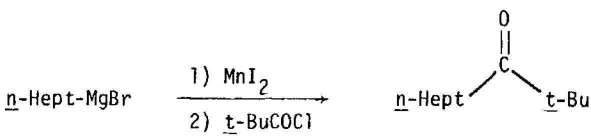
88%

JOC (1975) 40 1676



82%

JOC (1976) 41 560



80%

Tetr Lett (1976) 3155

$\mathrm{Ph\text{-}C(=O)\text{-}Cl} \xrightarrow[\mathrm{THF}]{\mathrm{PhS[Me_3C]CuLi}} \mathrm{Me_3C\text{-}C(=O)\text{-}Ph}$ 85%

Org Synth (1976) 55 122

$\mathrm{CH_2{=}CH_2} + \mathrm{PhCOCl} \xrightarrow{\mathrm{L_3RhH(CO)}} \mathrm{PhCOEt}$ 50-80%

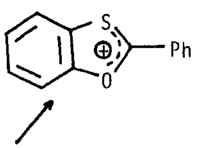
JACS (1974) 96 4721

$$\mathrm{BuLi} + \mathrm{RhCl(CO)(PPh_3)_2} + \mathrm{PhCOCl} \longrightarrow \mathrm{PhCOBu} \qquad 90\%$$

JACS (1975) 97 5448

$$\mathrm{(MeCO)_2C{=}SMe_2} \xrightarrow[\text{2) PhCOCl}]{\text{1) BuLi, THF}} \mathrm{PhCOCH_2CO\overset{\overset{\displaystyle SMe_2}{||}}{C}COMe} \qquad 55\%$$

JCS Chem Comm (1975) 289



PhCOOH

$$\xrightarrow[\text{2) hydrolysis}]{\text{1) } \underline{i}\text{-PrMgX}} \underline{i}\text{-PrCOPh}$$

quant.

Gazz Chim Ital (1975) 105 907

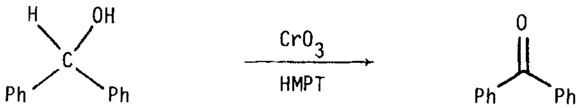
$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{||}}{C}{-}Br} + \mathrm{Et_2Hg} \xrightarrow[\text{HMPA}]{\mathrm{Pd(PPh_3)_4}} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{||}}{C}{-}Et} \qquad 86\%$$

Chem Lett (1975) 951

$$\mathrm{PhCOCl} + \mathrm{PhH} \xrightarrow{\mathrm{CrCl_3 \cdot 5\ DMSO}} \mathrm{PhCOPh} \qquad 80\%$$

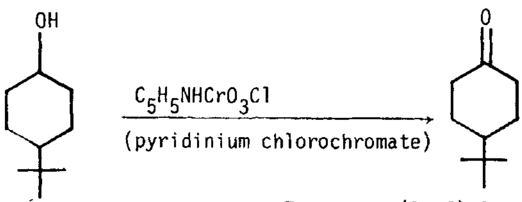
J Gen Chem USSR (1974) 44 2316

Section 168 Ketones from Alcohols and Phenols



100%

Synthesis (1976) 394



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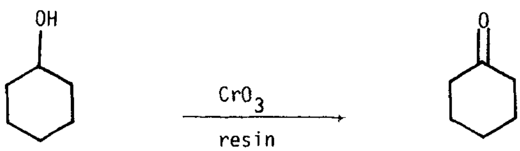
Tetr Lett (1975) 2647



77%

JACS (1976) 98 6737

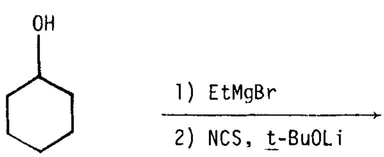
$$\underset{\displaystyle OH}{\underset{|}{RCHR'}} + Na_2Cr_2O_7 \xrightarrow[\text{conc. } H_2SO_4]{\text{DMSO}} \overset{\displaystyle O}{\overset{||}{RCR'}}$$

80-90%

JOC (1974) 39 3304

$$\underset{\text{OH}}{\text{Ph-CHCH}_3} \xrightarrow[\text{3) } Na_2S_2O_3\text{, KOH}]{\text{1) } Et_3SnOCH_3 \quad \text{2) } Br_2} \text{PhCOCH}_3 \qquad 78\%$$

Chem Lett (1975) 145



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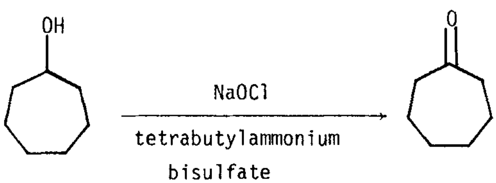
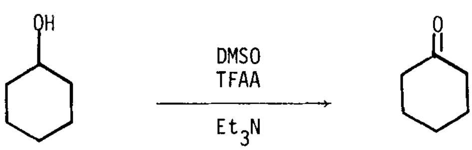
Chem Lett (1975) 691



89%

Tetr Lett (1976) 1641



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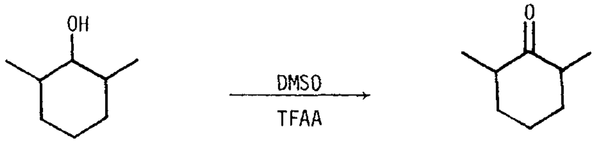
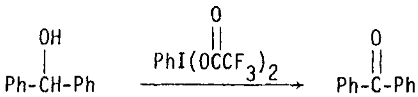
JOC (1976) 41 957



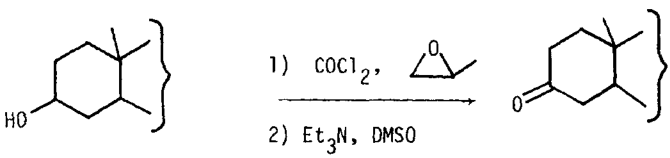
89%

JOC (1976) 41 3329



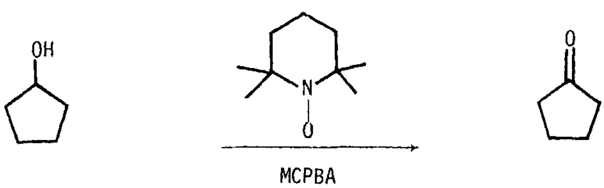
65%

Synthesis (1975) 445



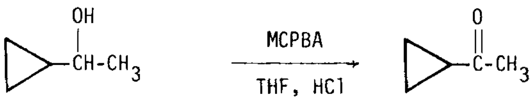
~70%

JCS Perkin I (1975) 1614



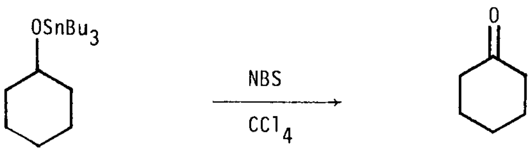
77%

JOC (1975) 40 1860



98%

Tetr Lett (1975) 4115



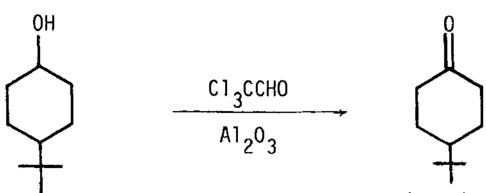
85%

JACS (1976) <u>98</u> 1629

$$\underset{\displaystyle \text{OH}}{\text{RCH-R'}} \xrightarrow[\text{pyridine}]{Cl_2} \overset{\displaystyle \text{O}}{\overset{||}{\text{RCR'}}}$$

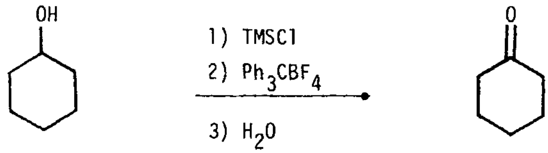
2°>1°

Tetr Lett (1974) 3059



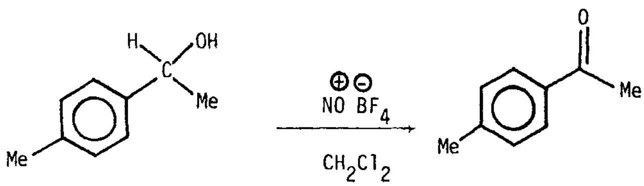
71%

Tetr Lett (1976) 3499



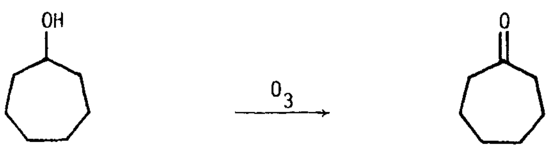
92%

JOC (1976) 41 1479



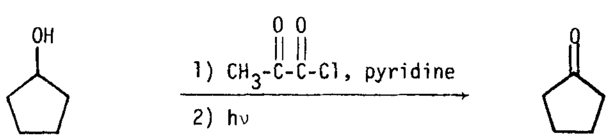
78%

Synthesis (1976) 609



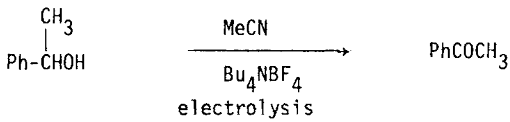
74%

JOC (1976) 41 889



84%

JOC (1976) 41 3030



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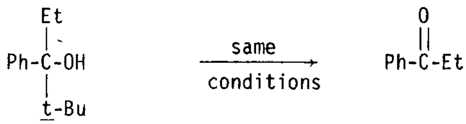
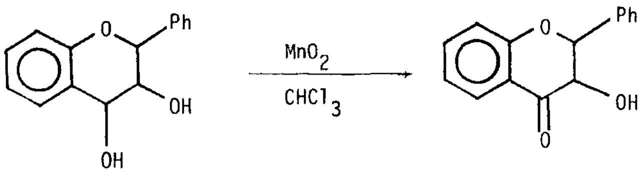
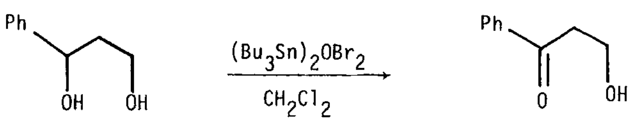


82%

JACS (1975) 97 4012

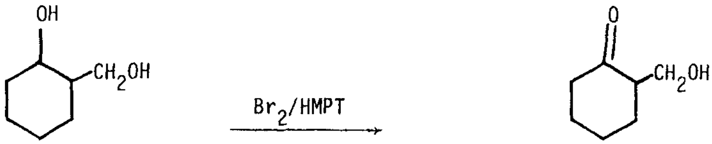


Indian J Chem (1976) 146 143



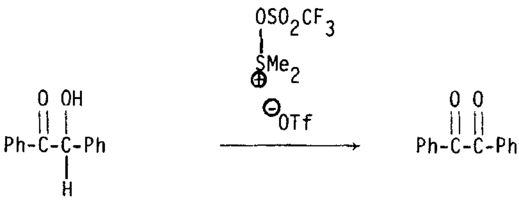
86%

Tetr Lett (1976) 4597



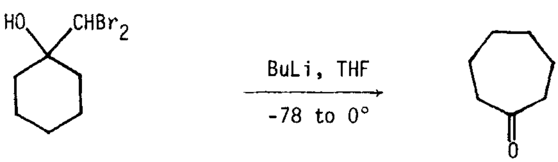
93%

Synthesis (1976) 811



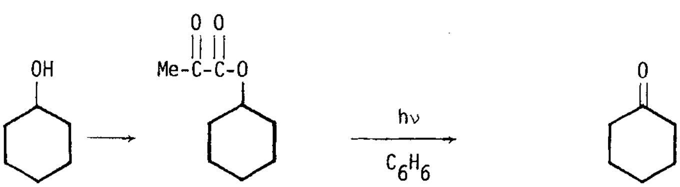
97%

Tetr Lett (1975) 273



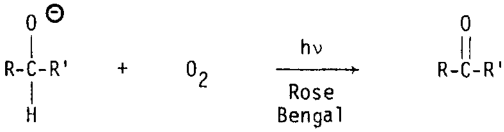
70-90%

JACS (1974) 96 6510



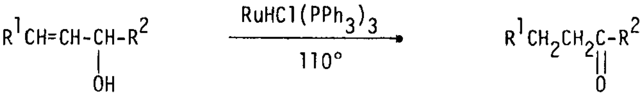
100%

Synth Comm (1976) 6 281



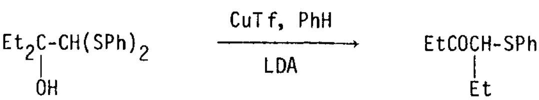
high yield

JACS (1974) 96 585



80-90%

Tetr Lett (1974) 4133

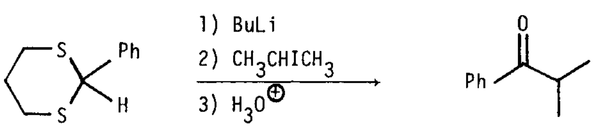


88%

JACS (1975) 97 4749

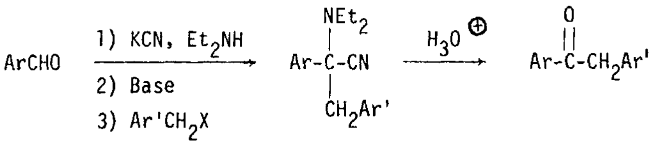
Related methods: Aldehydes from Alcohols and Phenols (Section 48)

Section 169 Ketones from Aldehydes



∿95%

JOC (1975) 40 231



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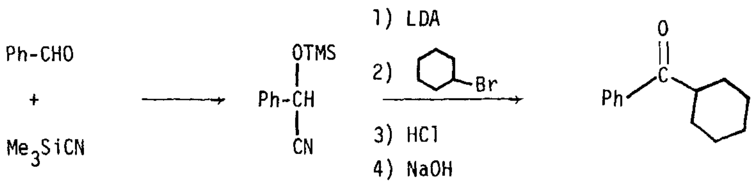
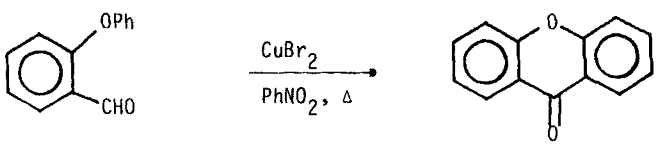
Tetrahedron (1975) 31 1219



48%

Synthesis (1975) 180



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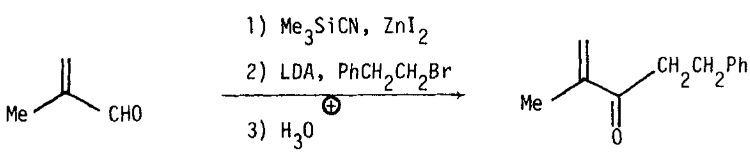
JCS Perkin I (1976) 2241



54%

Synthesis (1976) 416

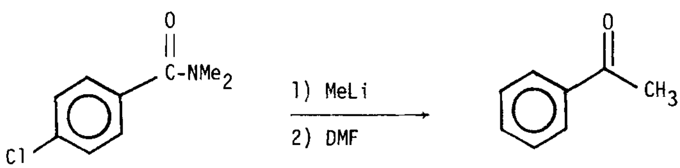
$$Me_2CO + PhCHO \xrightarrow{KHFe(CO)_4} MeCOCH_2CH_2Ph \qquad 70\%$$

JCS Perkin I (1975) 1273

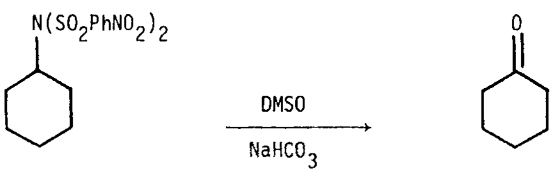
Section 170 Ketones from Alkyls and Methylenes

No additional examples

Section 171 Ketones from Amides

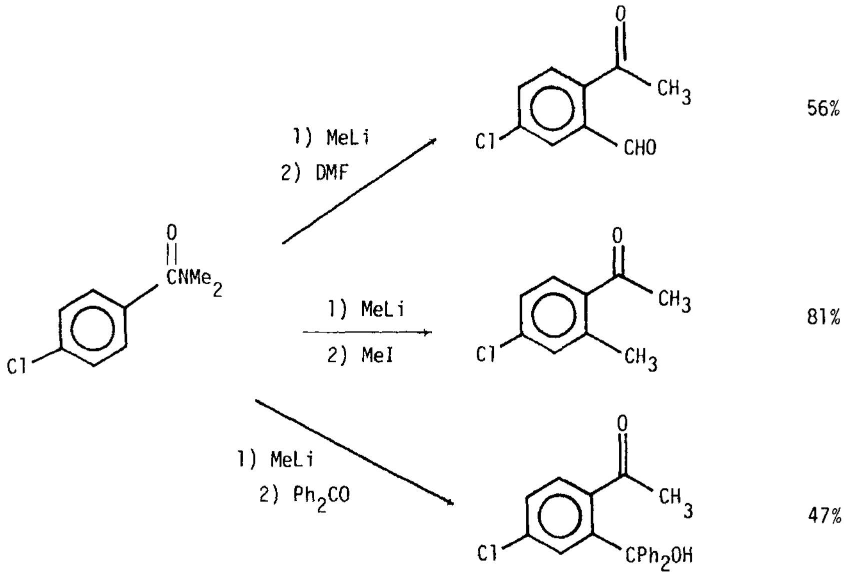


JOC (1976) 41 3651



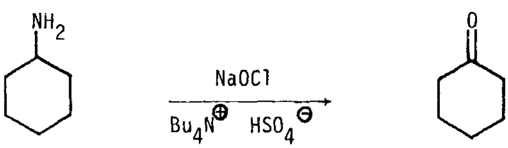
67%

Tetr Lett (1975) 3107

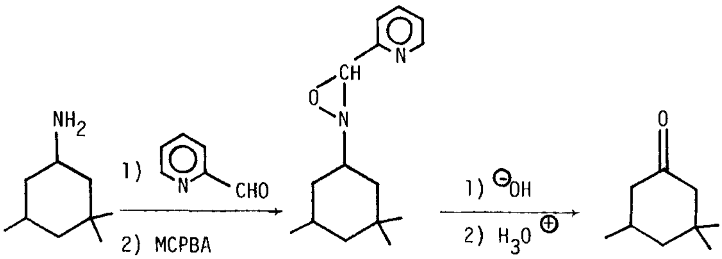


JOC (1976) 41 3651

Section 172 Ketones from Amines

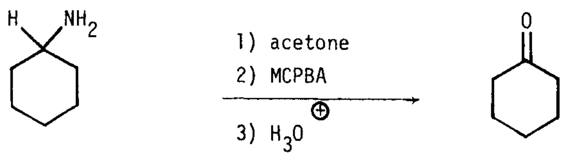


Tetr Lett (1976) 1641



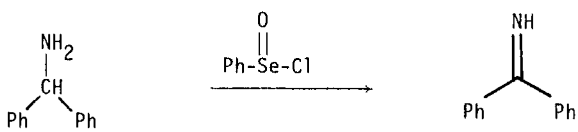
~40%

JACS (1975) 97 6900



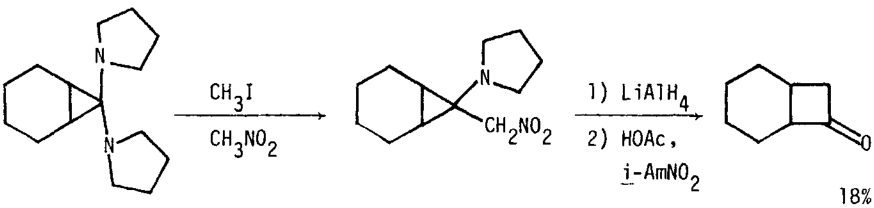
~30%

Aust J Chem (1975) 28 2547

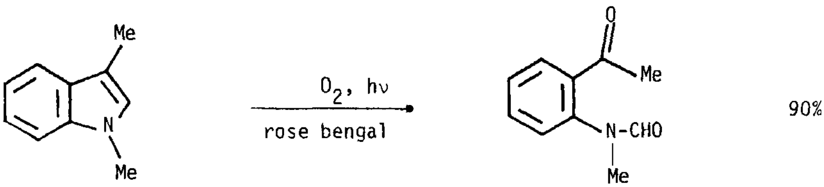


97%

Synth Comm (1976) 6 285



JOC (1976) 41 153



Synthesis (1976) 255

Section 173 Ketones from Esters

$$RC(=O)CH_2C(=O)\text{-}OR \quad + \quad \text{DABCO} \xrightarrow[\text{rfx}]{\text{xylene}} RCOCH_3 \qquad \sim 80\%$$

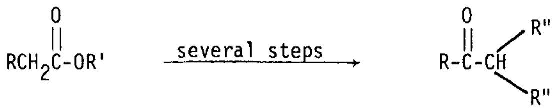
JOC (1974) 39 2647

$$MeCH_2COOEt \xrightarrow[\text{THF}]{\text{KH}} MeCH_2COCH(Me)COOEt \qquad 95\%$$

Synthesis (1975) 326

$BuCO_2Et \xrightarrow[300^\circ]{ThO_2} BuCOBu$ 80%

Bull Soc Chim France (1974) 1455

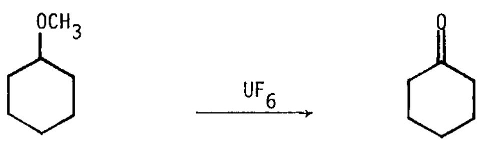


JACS (1975) 97 439

Review: "Reaction of Organomagnesium Compounds with Thiocarbonyl Compounds"

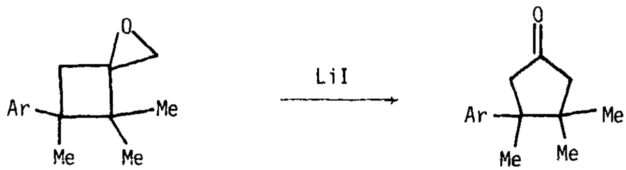
Bull Soc Chim France (1975) 1439

Section 174 Ketones from Ethers and Epoxides



86%

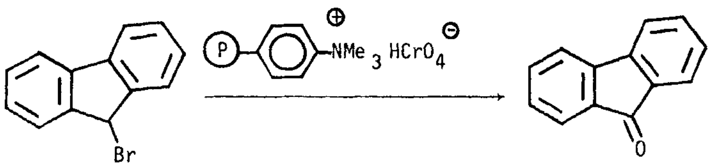
JACS (1976) 98 6717



78%

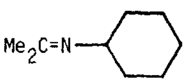
Comptes Rendus C (1975) 280 791

Section 175 Ketones from Halides



97%

Tetr Lett (1976) 3985

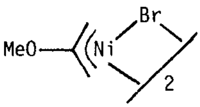


$\xrightarrow[\text{2) } n\text{-}C_8H_{17}Cl \quad \text{3) } H_3O^{\oplus}]{\text{1) LDA, THF}}$ n-$C_8H_{17}CH_2COCH_3$ 80%

Liebigs Ann Chem (1975) 719

$PhCH(Br)COOH$ + Zn + MeCN $\longrightarrow$ $MeCOCH_2Ph$ <80%

J Organometal Chem (1974) 81 139

 + PhI $\xrightarrow[\text{2) } H^{\oplus}]{\text{1) DMF}}$ $PhCH_2COCH_3$ 91%

JACS (1974) 96 3250

RMgX + 1 eq. HMPA $\xrightarrow[\text{30 atm}]{\text{CO}}$

- R = 3° → RCH(OH)-C(=O)-R
- R = 1° → R_2CHCOR 30-50%
- R = 2° → Mixtures

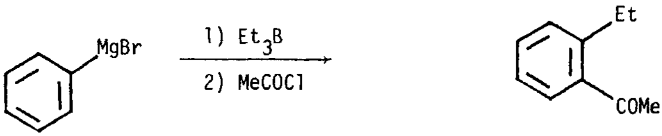
Tetr Lett (1974) 3377

$\underline{n}$-$C_5H_{11}Br$ + $Na_2Fe(CO)_4$ + CH_2CH_2 $\xrightarrow[\text{2) HOAc}]{\text{1) THF}}$ $\underline{n}$-$C_5H_{11}COEt$ 95%

JACS (1975) 97 6863

ArX + KCH_2COMe $\xrightarrow[NH_3(l)]{h\nu}$ $ArCH_2COMe$ ($S_{RN}1$ mechanism)

Chem Pharm Bull (1975) 23 2621



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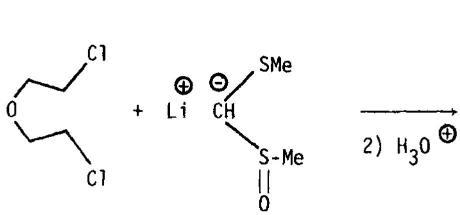
Tetr Lett (1975) 4239

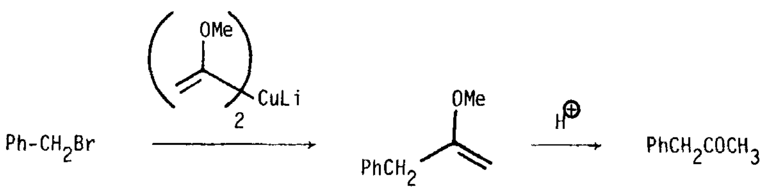
Review: "Disodium Tetracarbonylferrate - A Transition Metal Analog of a Grignard Reagent"

Accts Chem Res (1975) 8 342



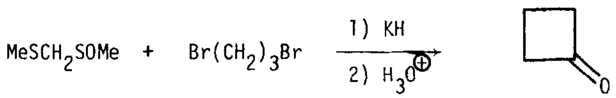
66%

Tetr Lett (1975) 2767



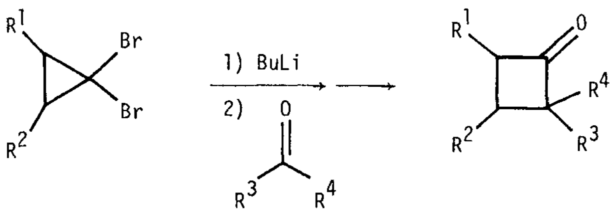
72%

JACS (1975) 97 3822



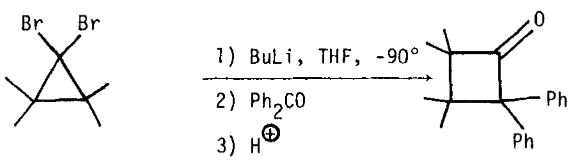
76%

Tetr Lett (1974) 3653



30-40%

Tetr Lett (1974) 3295
Angew Int Ed (1974) 13 277

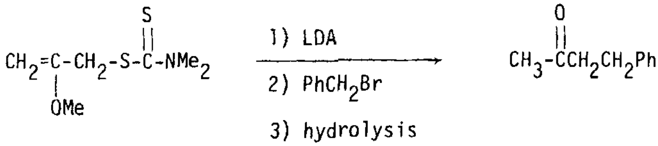


90%

Chem Ber (1975) 108 2368

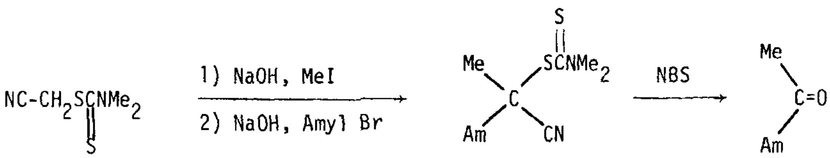
$n\text{-}C_6H_{13}I$ + $\overset{O}{\overset{\|}{\text{MeS}}}\overset{(-)}{\text{CH}}\text{SMe}$ $\longrightarrow$ $\xrightarrow{HCl}$ $C_6H_{13}COC_6H_{13}$ 62%

Synthesis (1974) 117



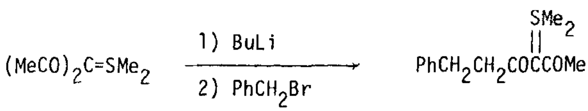
98%

Tetr Lett (1975) 4027



68%

Tetr Lett (1976) 2967



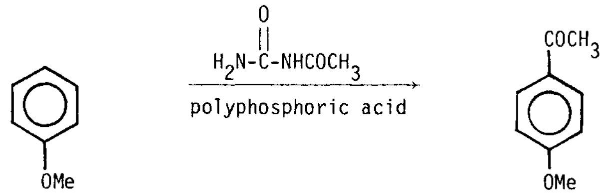
73%

JCS Chem Comm (1975) 289

Related methods: Ketones from Ketones (Section 177), Aldehydes from Halides (Section 55)

Section 176 Ketones from Hydrides

This section lists examples of the replacement of hydrogen by ketonic groups, RH → RCOR'. For the oxidation of methylenes $R_2CH_2 \rightarrow R_2CO$ see Section 170 (Ketones from Alkyls and Methylenes)



51%

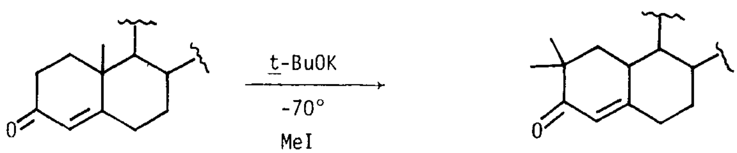
Chem and Ind (1976) 1069

Review: "Friedel Crafts Acylation"

Chem and Ind (1974) 727

Section 177 Ketones from Ketones

This section contains alkylations of ketones and protected ketones, ketone transpositions and annelations, ring expansions and ring openings, and dimerizations. Conjugate reductions and reductive alkylations of enones are listed in Section 74 (Alkyls from Olefins).

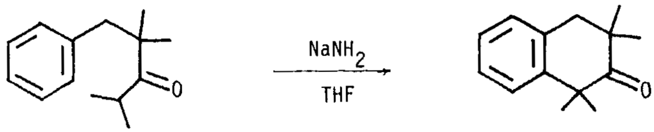


88%

Tetrahedron (1974) 30 3263

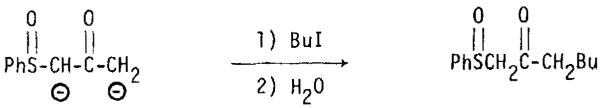
$PhCH_2COMe \xrightarrow[\text{phase transfer catalyst}]{\text{RX, NaOH}} PhCHRCOMe$ high yields

Tetr Lett (1975) 3757
JCS Chem Comm (1975) 393



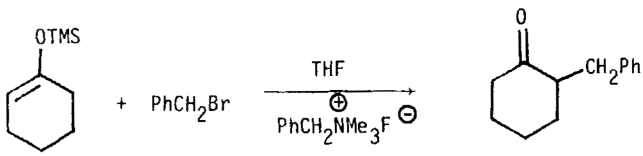
90%

Synthesis (1974) 201



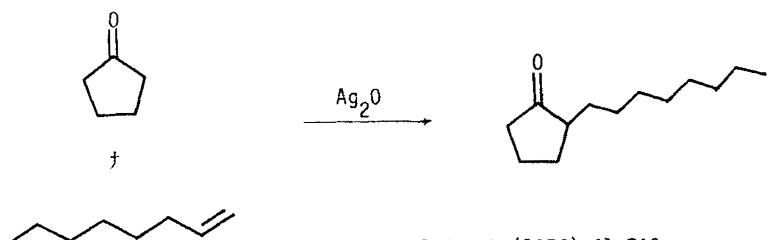
78%

JOC (1974) 39 732



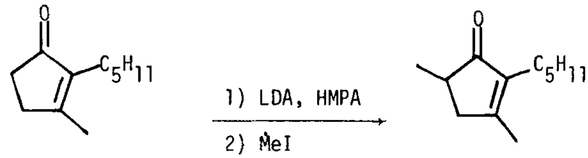
63%

JACS (1975) 97 3257



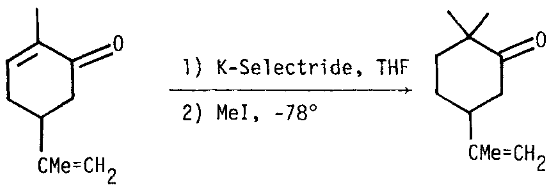
~69%

Coll Czech (1976) 41 746



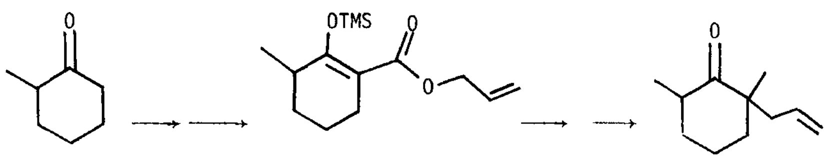
74%

Synth Comm (1975) 5 435

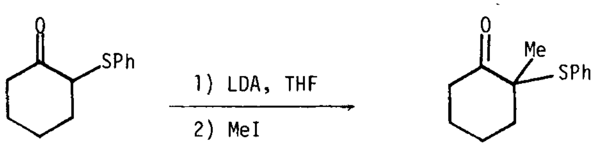


98%

JOC (1975) 40 146

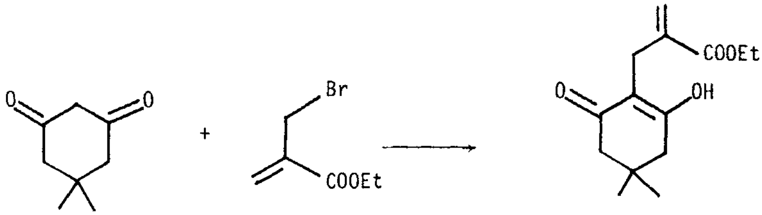


JACS (1975) 97 1619



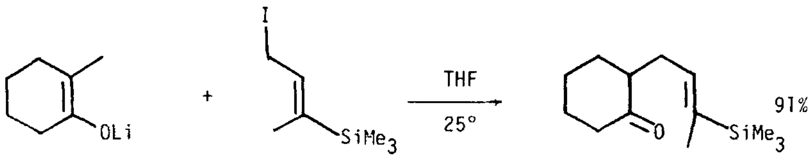
93%

Tetr Lett (1974) 3955



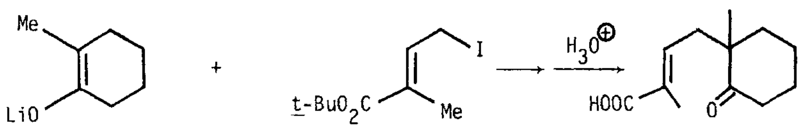
82%

Rec Trav Chim (1974) 93 153



91%

JACS (1974) 96 3684



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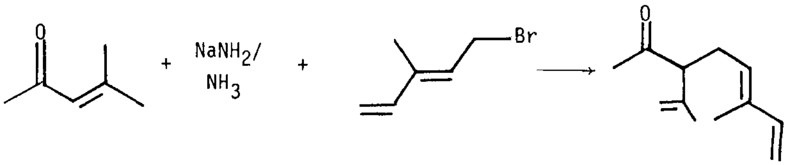
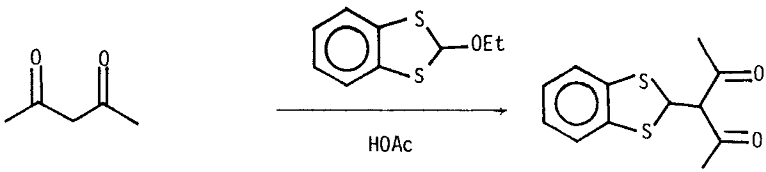
JACS (1974) 96 6524



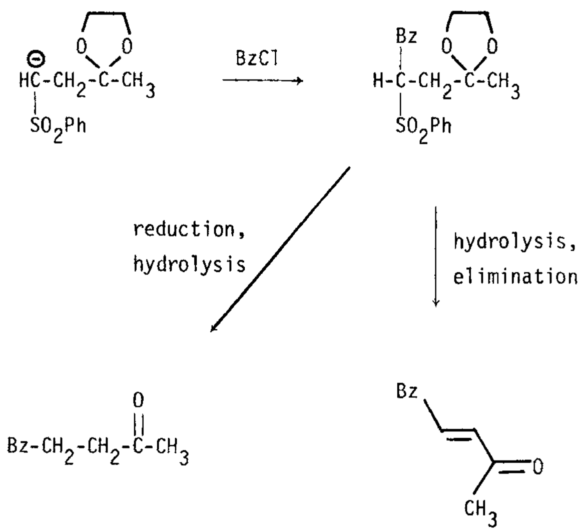
88%

JACS (1974) 96 7573

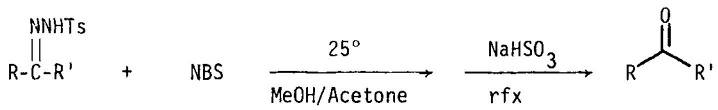


90%

JCS Perkin I (1976) 540

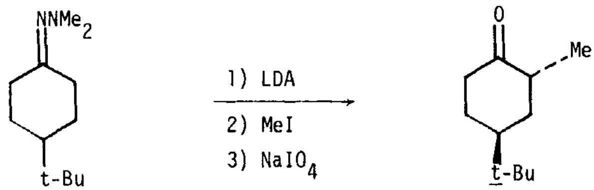


Bull Soc Chim France (1975) 1363



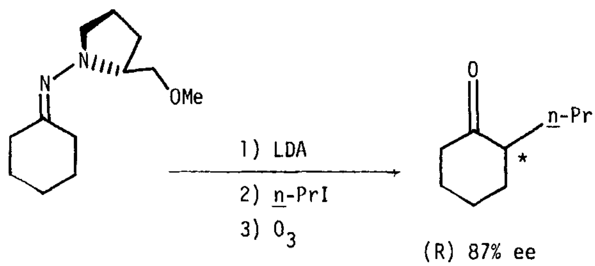
75-91%

JOC (1974) 39 3504



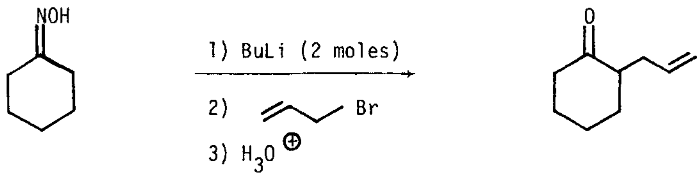
95%

Tetr Lett (1976) 3



73%

Angew Int Ed (1976) 15 549



65%

JOC (1976) <u>41</u> 439

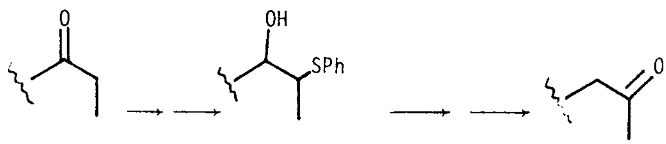
$$R\text{-}\overset{\overset{\displaystyle NOH}{\|}}{C}\text{-}R' \quad + \quad (Ph_3P)_2\,PdO_2 \quad \xrightarrow[\text{benzene}]{} \quad R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R'$$

74-98%

Tetr Lett (1974) 797

For the preparation of enamines from ketones see Section 356 (Amine - Olefin)

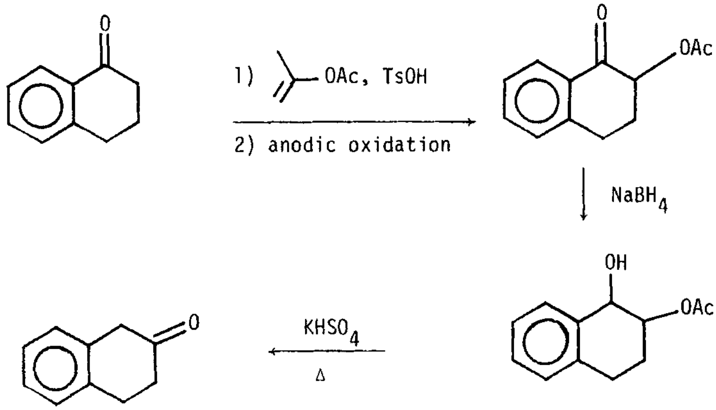
A 1,2-alkylative carbonyl transposition:



60-75%

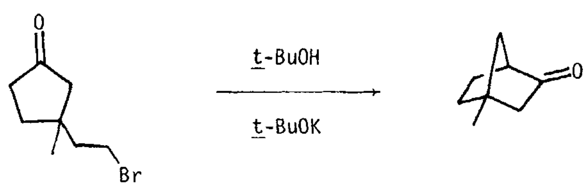
also: $$RCH_2\overset{\overset{\displaystyle O}{\|}}{C}R' \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH(R'')(R')$$

JACS (1975) <u>97</u> 439



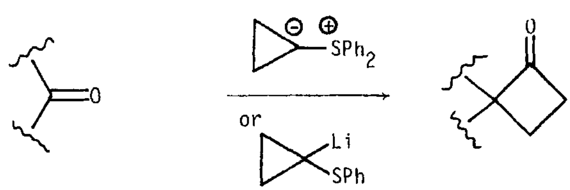
~30% overall

Chem Lett (1976) 1319



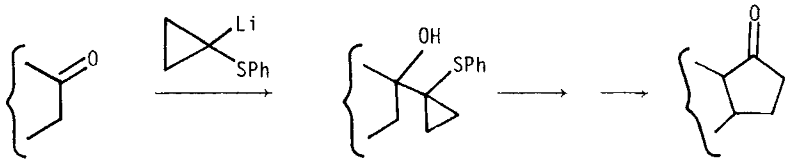
65%

JOC (1974) 39 573



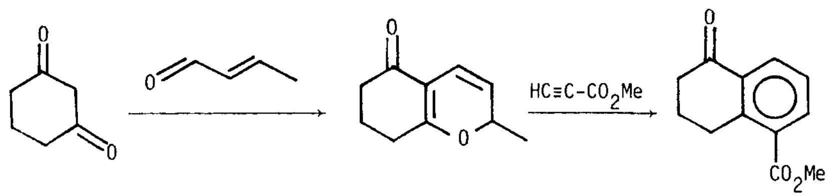
2) Acid

JACS (1975) 97 2218, 2224



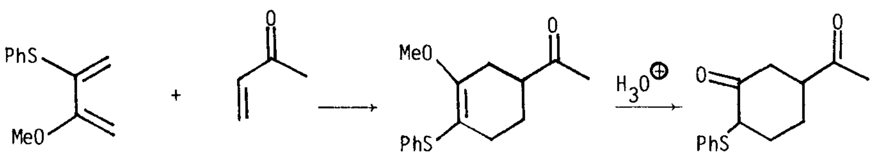
~60%

JACS (1976) 98 248



70% (second step)

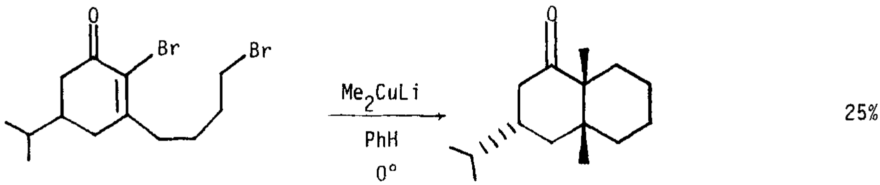
JOC (1976) 41 2918



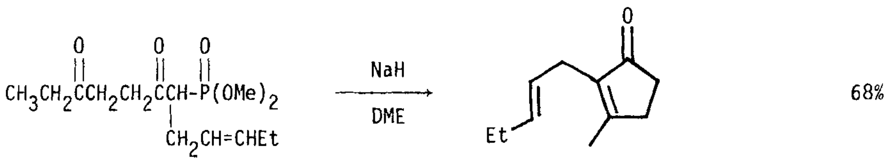
75%

Can be alkylated further, dehydrosulfenylated.

JACS (1976) 98 5017



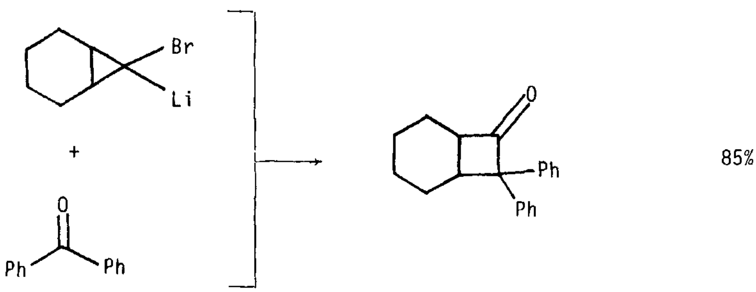
Tetr Lett (1974) 2591



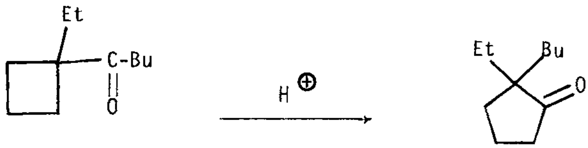
Synth Comm (1975) 5 1

Review: "The Thermal Cyclization of Unsaturated Carbonyl Compounds"

Synthesis (1975) 1

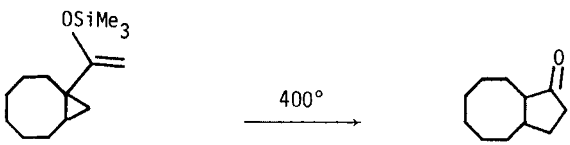


Chem Ber (1975) 108 2368



91%

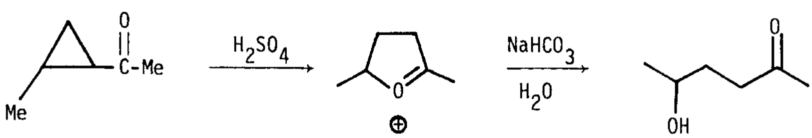
Comptes Rendus C (1975) 280 309



99%

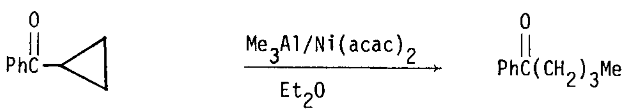
Widely varying yields with other ring sizes.

JOC (1975) 40 858



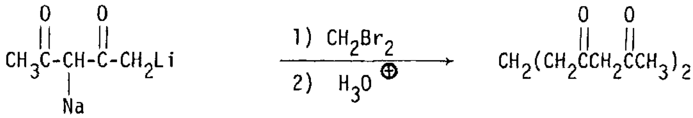
45%

Tetr Lett (1975) 1531



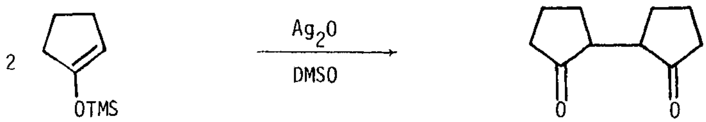
55%

Aust J Chem (1975) 28 821



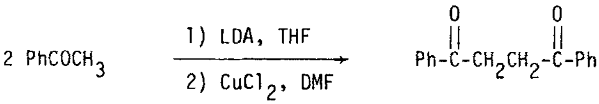
~9%

JOC (1976) 41 2772



61%

JACS (1975) 97 649



83%

JACS (1975) 97 2912

Review: "Inversion of Carbonyl Reactivity"

Chem and Ind (1974) 687

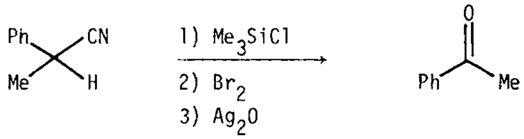
Review: "The Use of Kinetically Generated Unstable Enolate Ions in the Regiospecific Formation of Carbon-Carbon Bonds"

Pure and Appl Chem (1975) 43 553

Ketones may also be alkylated and homologated via olefinic ketones (Section 374)

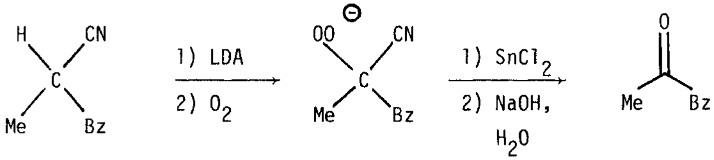
Related methods: Aldehydes from Aldehydes (Section 49)

Section 178 Ketones from Nitriles



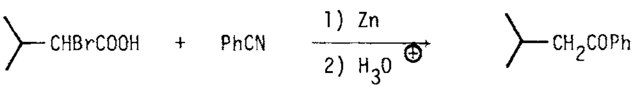
~70%

JOC (1974) 39 2799
Tetr Lett (1974) 3029



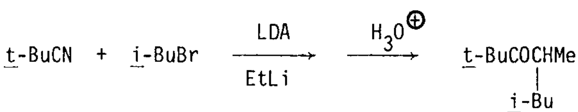
82%

JOC (1975) 40 267



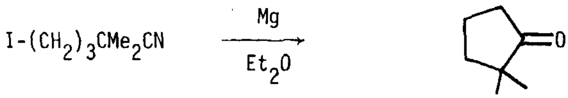
74%

J Organometal Chem (1974) 81 139



73%

Comptes Rendus (1975) 280 889



79%

J Organometal Chem (1975) 87 25

$$PhCN \xrightarrow[Ni(acac)_2]{Me_3Al} PhCOMe$$

80%

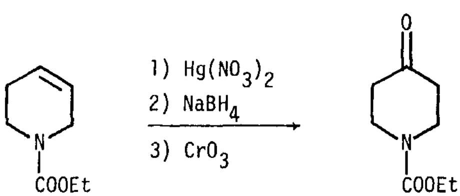
Aust J Chem (1974) 27 2577

Section 179 Ketones from Olefins

$$RCH{=}CHR \xrightarrow[2)\ ^{\ominus}OH]{1)\ HgSO_4,\ H_2O} RCCH_2R \text{ (with C=O)}$$

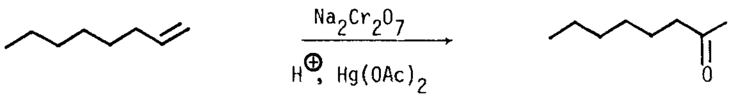
30-70%

JOC (1974) 39 3445



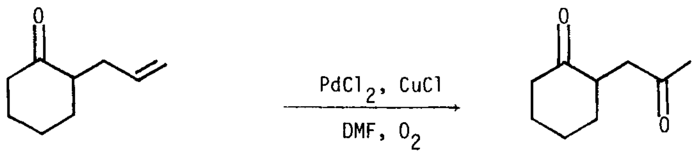
80%

JOC (1974) 39 2674



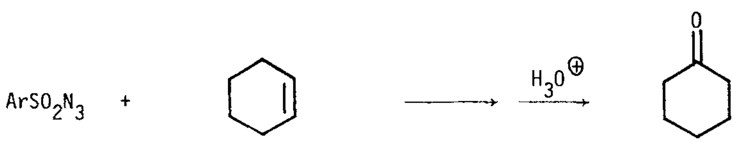
82%

JOC (1975) 40 3577



68%

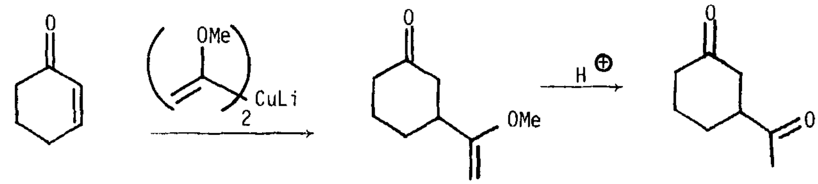
Tetr Lett (1976) 2975



JCS Perkin I (1974) 2169

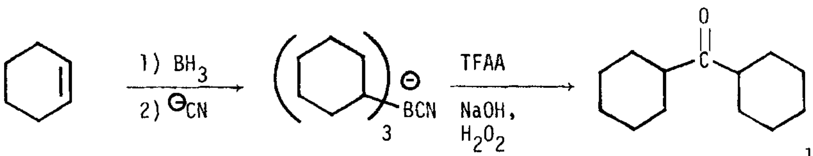
80%

JACS (1974) 96 8115



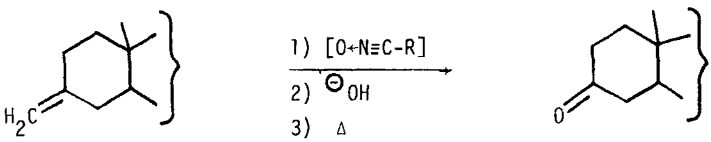
66%

JACS (1975) 97 3822



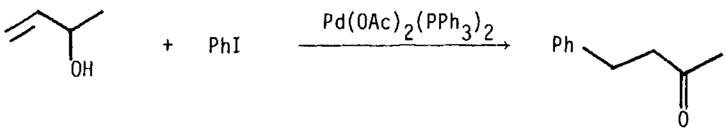
100%

JCS Perkin I (1975) 129



~50%

JCS Chem Comm (1976) 209, 210



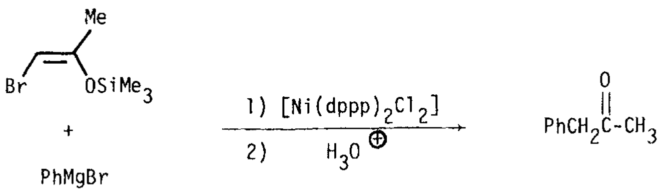
76%

JOC (1976) 41 265
JOC (1976) 41 273

See also section 134 (Ethers and Epoxides from Olefins) and Section 174 (Ketones from Ethers and Epoxides)

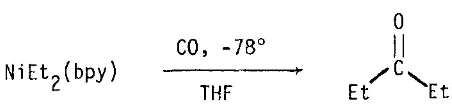
Section 180 Ketones from Miscellaneous Compounds

Conjugate reductions and reductive alkylations of enones are listed in Section 74 (Alkyls from Olefins).



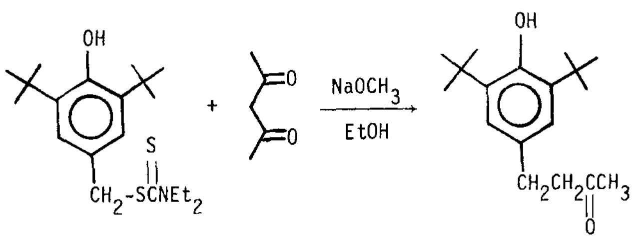
75%

Chem Lett (1976) 1239



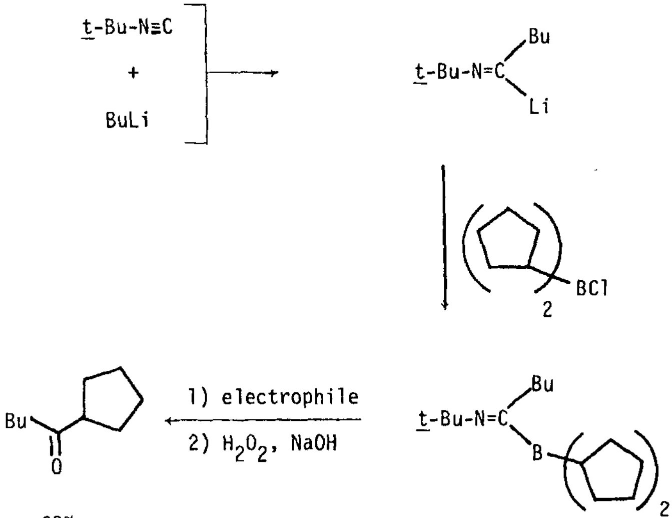
100%

Chem Lett (1976) 1217



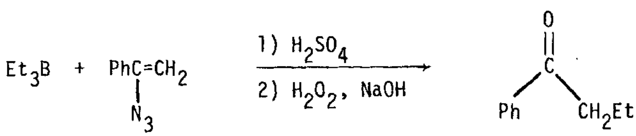
52%

Helv Chim Acta (1976) 59 522



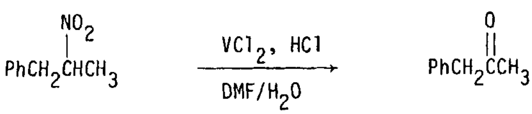
63%

Bull Chem Soc Japan (1975) 48 3682



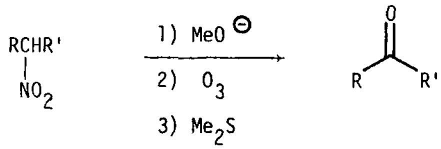
95%

Tetr Lett (1975) 2195



65%

Tetr Lett (1976) 2533

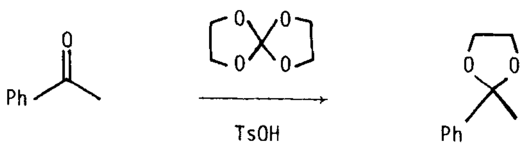


65-88%

JOC (1974) 39 259

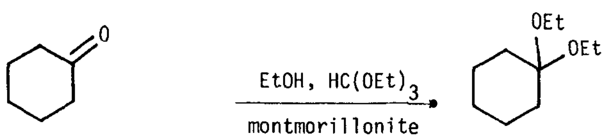
Section 180A <u>Protection of Ketones</u>

This section covers ketals, thioketals, and hydrazones. See also Section 363 (Ether-Ether) for ketals and Section 367 (Ether-Olefin) for enol ethers. Some of the methods in Section 60A (Protection of Aldehydes) are also applicable to ketones.



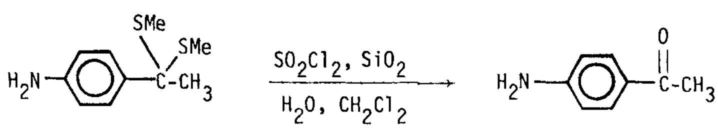
74%

JCS Chem Comm (1975) 432



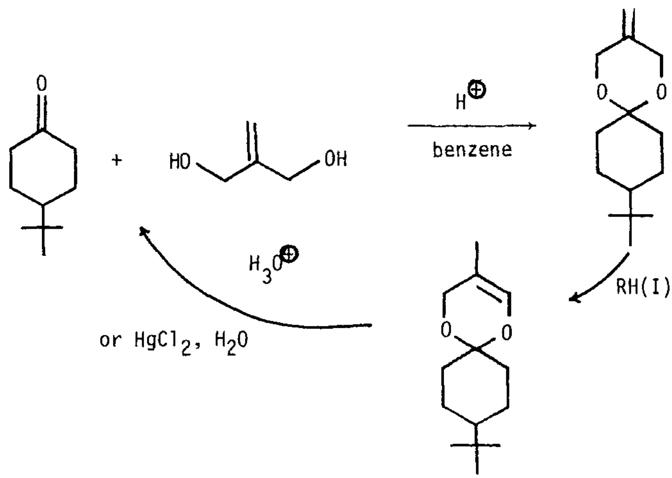
78%

Bull Soc Chim France (1975) 2558

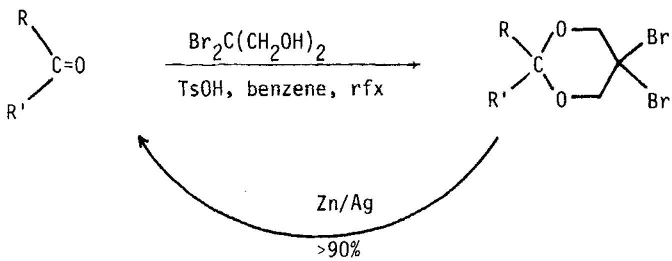


100%

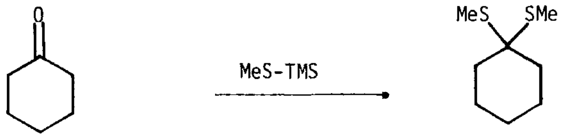
Synthesis (1976) 678



Tetr Lett (1975) 3775



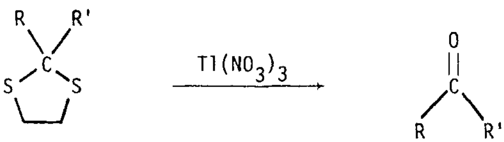
Tetr Lett (1976) 4577



90%

No acid catalyst required.

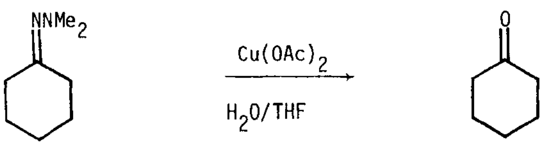
JACS (1975) 97 3229



73-99%

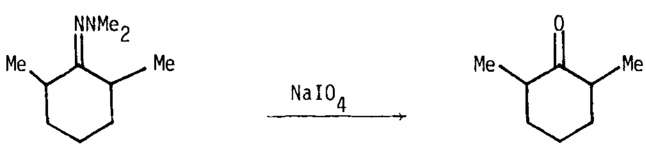
R,R' = H, alkyl, aryl, cyclic

Chem Pharm Bull (1976) 24 1115



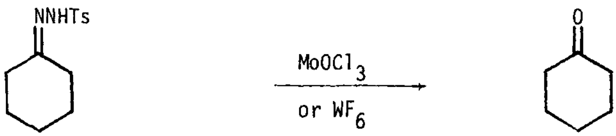
96%

Tetr Lett (1976) 3667



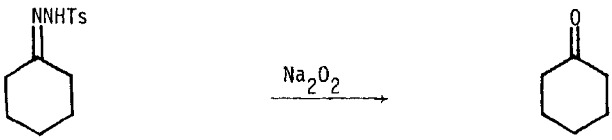
100%

Tetr Lett (1976) 3



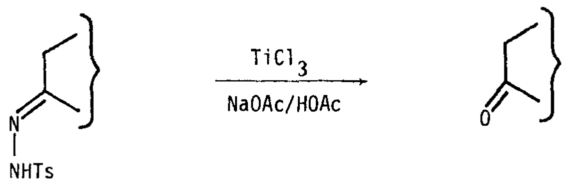
74%

Synthesis (1976) 808, 809



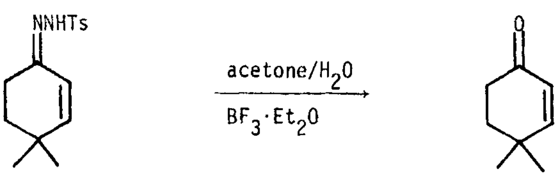
72%

Synthesis (1976) 611



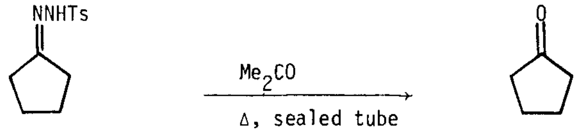
~90%

Chem and Ind (1975) 87



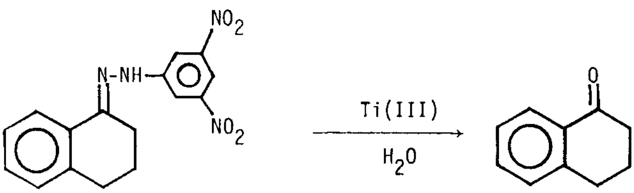
83%

Synthesis (1976) 456



75%

JOC (1975) 40 3302



98%

JOC (1975) 40 1502

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Edited by Louis S. Hegedus, Leroy Wade

Chapter 13 PREPARATION OF NITRILES

Section 181 Nitriles from Acetylenes

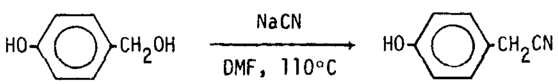
No additional examples

Section 182 Nitriles from Carboxylic Acids and Acid Halides

$$BuCH_2COOH \xrightarrow[NaNO_2]{(CF_3CO)_2O} BuC{\equiv}N \qquad 60\%$$

JOC USSR (1975) 11 653

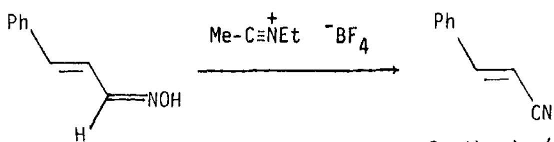
Section 183 Nitriles from Alcohols



67%

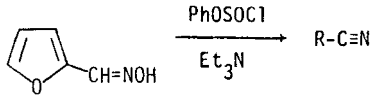
JOC (1976) 41 2502

Section 184 Nitriles from Aldehydes



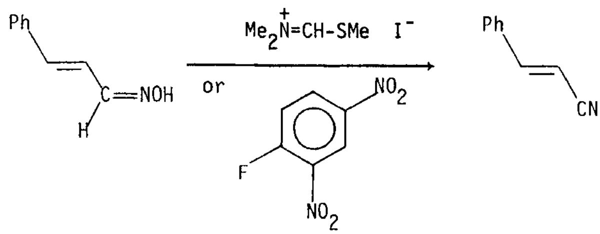
56%

Synthesis (1975) 401



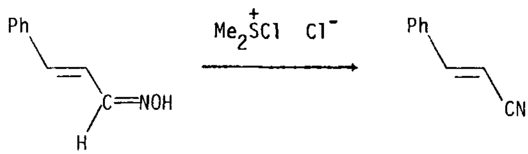
92%

Synthesis (1975) 502



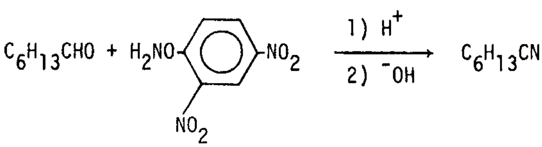
71%

Synth Comm (1975) 5 299



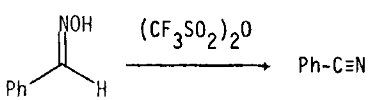
89%

Synth Comm (1975) 5 423



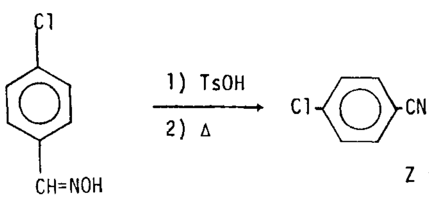
91%

JOC (1975) 40 126



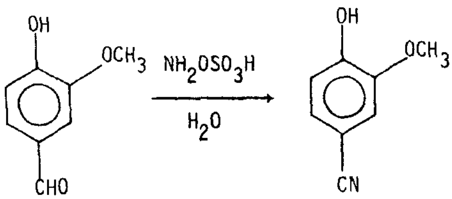
90%

Tetr Lett (1976) 603



81%

Z Chem (1976) 16 17



89%

Helv Chim Acta (1976) 59 2786

$RCHO + NH_2OSO_3H \xrightarrow[65°]{H_2O} RCN$ 60-90%

Tetr Lett (1974) 3187

$MeCH{=}NOH + Me_2N{=}CCl_2^{+}\ Cl^{-} \xrightarrow[\substack{CHCl_3 \\ 2\text{-}4\ hr}]{rfx} RC{\equiv}N$ 82-97%

Synthesis (1974) 563

$Ph\text{-}CHO \longrightarrow PhCH{=}NTs \xrightarrow[HMPA]{NaCN} PhC{\equiv}N$ 77%

Tetr Lett (1976) 1781

$RCHO \longrightarrow RCH{=}NOH \xrightarrow[\substack{CuCl_2 \\ Et_3N}]{DCC} RCN$ 55-92% (44 cases)

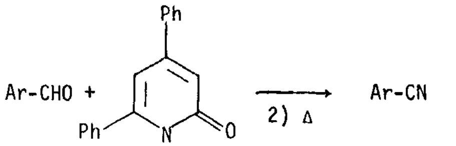
Chem Ber (1974) 107 1221

$RCH{=}NOH + R'C(OEt)_3 \xrightarrow{H^+} RCN$ >90%

JOC (1974) 39 3424

$$Et_2CH\text{-}CH{=}NNMe_2 \xrightarrow[\text{2) } H_2O]{\text{1) Li, } Et_2NH\text{, HMPT}} Et_2CH\text{-}CN \qquad 71\%$$

Synthesis (1976) 237 and 238



~80-90%

Tetr Lett (1976) 2691

Section 185 Nitriles from Alkyls, Methylenes and Aryls

No additional examples

Section 186 Nitriles from Amides

$$\text{Polymer-}PCl_2 \xrightarrow{RCONH_2} RCN$$

JACS (1974) 96 6469

$$PhCONH_2 \xrightarrow{Ph_3P(OTf)_2} PhCN \qquad 70\%$$

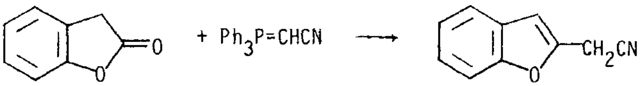
Tetr Lett (1975) 277

Section 187 Nitriles from Amines

$$PhCH_2NH_2 \xrightarrow{PhSeOCl} PhCN \qquad 85\%$$

Synth Comm (1976) 6 285

Section 188 Nitriles from Esters



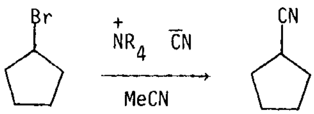
89%

Aust J Chem (1975) 28 1097; 2499

Section 189 Nitriles from Ethers and Epoxides

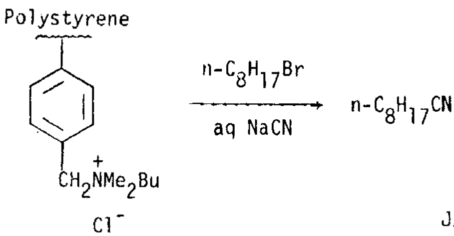
No additional examples

Section 190 Nitriles from Halides



68%

Synthesis (1975) 605



92%

JACS (1975) 97 5956

$$Br(CH_2)_4Br + Et_4N^+CN \xrightarrow{CH_2Cl_2} NC\text{-}(CH_2)_4CN$$ 90%

Synthesis (1975) 605

$$CH_3(CH_2)_5Br \xrightarrow[\substack{18\text{-crown-6} \\ CH_3CN}]{KCN} CH_3(CH_2)_5CN$$ 100%

JOC (1974) 39 3416

$$\underline{n}\text{-BuBr} \xrightarrow[Bu_3N]{NaCN} \underline{n}\text{-BuCN}$$ 100%

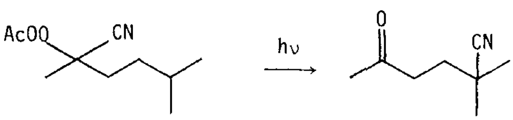
Synth Comm (1976) 6 193

$$PhI + KCN \xrightarrow{Pd(0)\ cat} PhCN$$ 93%

Chem Lett (1975) 277

Bull Chem Soc Japan (1975) 48 3298
(Pd II catalyst)

Section 191 Nitriles from Hydrides



50%

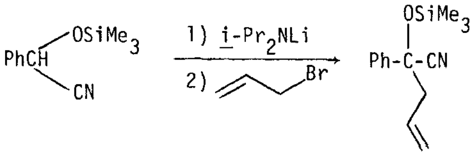
JACS (1976) 98 271

Section 192 Nitriles from Ketones

No additional examples

Section 193 Nitriles from Nitriles

Reductive alkylations of of unsaturated nitriles are found in Section 74 (Alkyls from Olefins).

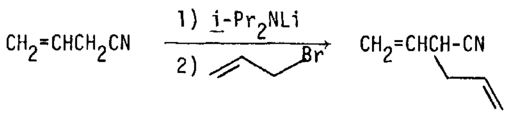


96%

Synthesis (1975) 180

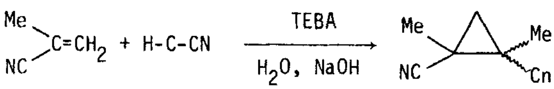
$$PhCH_2CN \xrightarrow[2)\ MeI]{1)\ MeLi,\ THF} PhC(Me)_2CN$$ 95%

Tetrahedron (1975) 31 153



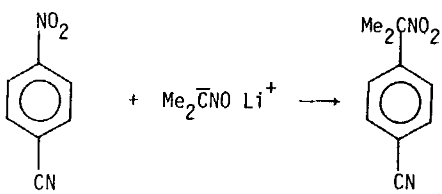
98%

Tetr Lett (1975) 4647



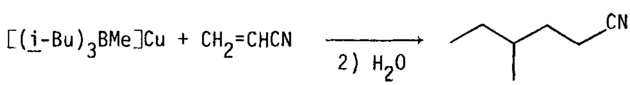
75%

Synthesis (1976) 387



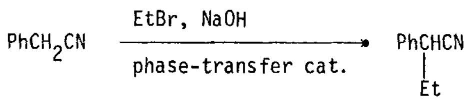
82%

JOC (1976) 41 1560



88%

Tetr Lett (1976) 255



Org Synth (1976) 55 91

Section 194 Nitriles from Olefins

$$Ph_2C{=}CHNO_2 \xrightarrow[\text{MeCN}]{Et_4NF} NCCH_2CPh_2CH_2NO_2 \qquad 45\%$$

Synthesis (1975) 162

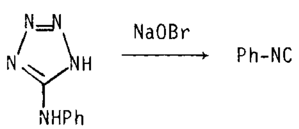
$$(n\text{-octyl})_3B \xrightarrow[\substack{CH_3CN \\ \text{electrochemical} \\ \text{rdxn}}]{Et_4N^+I^-} (n\text{-octyl})CH_2CN \qquad \sim 50\%$$

Chem Lett (1975) 523

Section 195 Nitriles from Miscellaneous Compounds

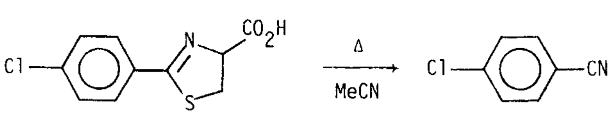
$$HOOC\text{-}CH_2\text{-}CH_2\text{-}C(=N\text{-}OH)\text{-}COOH \xrightarrow{PhNCO} HOOC\text{-}CH_2CH_2CN \qquad 93\%$$

Synthesis (1976) 418



92%

Angew Int Ed (1976) 15 113



~100%

JCS Perkin I (1976) 1901

$$\mathrm{Et\text{-}C(=NH)\text{-}NH_2} \xrightarrow[\text{phase-transfer cat}]{\mathrm{CHCl_3,\ NaOH}} \mathrm{Et\text{-}C{\equiv}N} \qquad 84\%$$

Z Chem (1975) 15 301

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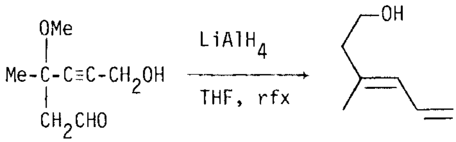
Edited by Louis S. Hegedus, Leroy Wade

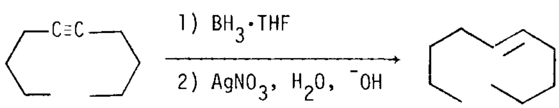
Chapter 14 PREPARATION OF OLEFINS

Section 196 Olefins from Acetylenes



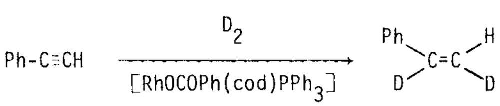
93%

Acta Chem Scand B (1975) 29 609



72%

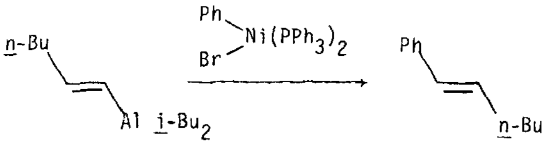
Tetr Lett (1976) 4871



>95% cis isomer

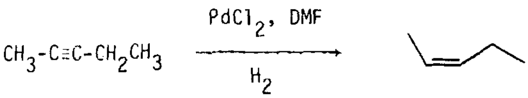
No yields, few details

JCS Chem Comm (1975) 647



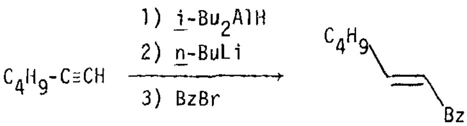
85%

JCS Chem Comm (1976) 596



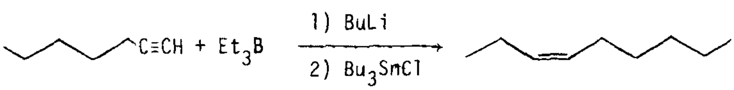
∿100%

Chem Ber (1976) 109 531



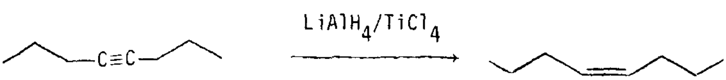
46%

Tetr Lett (1976) 1927



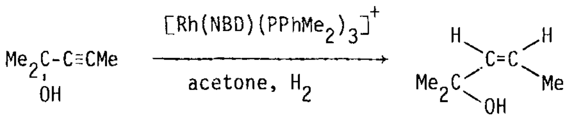
71%

Tetr Lett (1976) 805



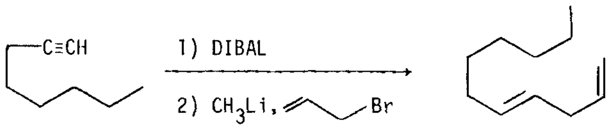
73%

Tetr Lett (1976) 15



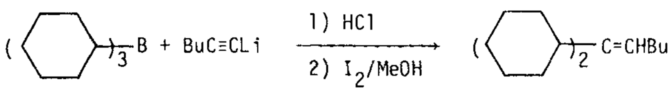
97%

JACS (1976) 98 2143



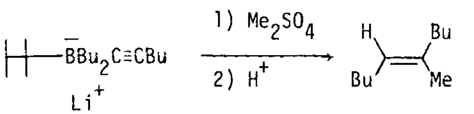
68%

JOC (1976) 41 2214



76%

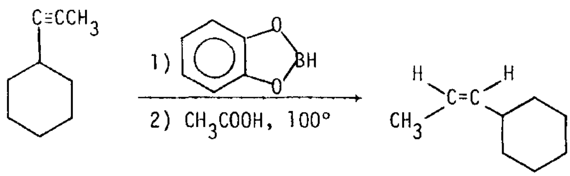
Synthesis (1975) 376



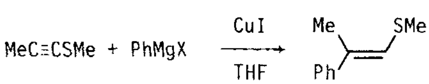
74%

(83% E isomer)

Tetr Lett (1975) 1633



JACS (1975) 97 5249



95%

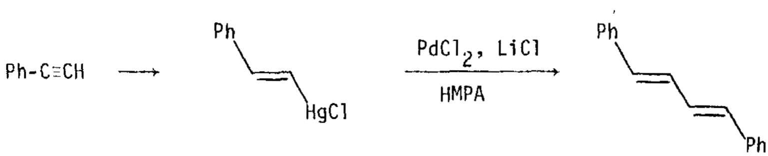
Rec Trav Chim (1974) 93 24

$$\text{Ph-C}\equiv\text{C-CH}_3 \xrightarrow[\text{2 BuLi}]{\text{CuI}} \text{Ph(H)C=C(H)CH}_3 \qquad 100\%$$

JOC (1976) 41 4089

$$\text{PhC}\equiv\text{C-H} \xrightarrow[\text{2) H}_2\text{O}]{\text{1) [PrCuBr]MgBr}} \text{Ph(Pr)C=CH}_2 \qquad 95\%$$

Rev Trav Chim (1976) 95 299, 304



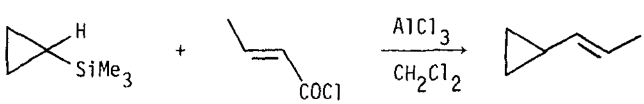
99%

JOC (1976) 41 2241

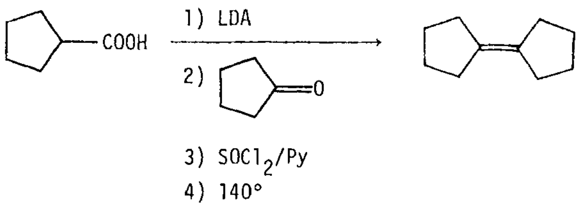
Section 197 Olefins from Carboxylic Acids and Acid Halides

$$\text{Ph}_2\text{C(OH)CH}_2\text{COOH} \xrightarrow[\text{CHCl}_3]{\text{DMF acetal}} \text{Ph}_2\text{C=CH}_2 \qquad 88\%$$

Tetr Lett (1975) 1545



Synthesis (1976) 737

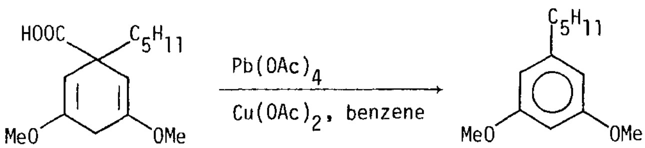


63%

JOC (1974) 39 1650

$Et_3\bar{B}C{\equiv}CPh$ + EtCOOH ⟶ EtCH=CHPh 75%

Tetr Lett (1974) 2961



80%

Tetr Lett (1976) 2079

Section 198 Olefins from Alcohols

$CH_2{=}C(-(CH_2)_2CH{=}CMe_2)-CH(OH)CH_2OH \xrightarrow[2)\ Zn]{1)\ PBr_3,\ CuBr} CH_2{=}C(-(CH_2)_2CH{=}CMe_2)-CH{=}CH_2$ 58%

JACS (1975) 97 3252

$(PhCH_2)_2C(OH)\text{-}CH_2SPh \xrightarrow[R_3N,\ PhH,\ diox]{(TiCl_4\ +\ LiAlH_4)} (PhCH_2)_2C{=}CH_2$ 96%

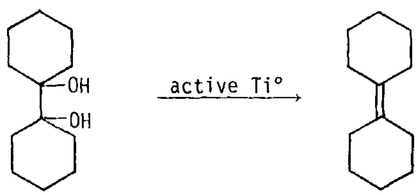
Chem Lett (1975) 871

$PhSCMe_2CHOHR \xrightarrow[dark]{p\text{-}TsOH,\ PhH} RCH(SPh)CMe{=}CH_2$ high yield

JCS Chem Comm (1975) 8211

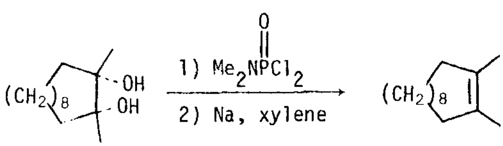
$CH_3CH(OH)\text{-}CH(NO_2)CH_3 \xrightarrow[Et_3N]{MeSO_2Cl} CH_3CH{=}C(NO_2)CH_3$ 67%

JOC (1975) 40 2138



85%

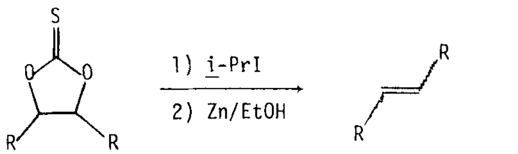
JOC (1976) 41 896



85%

90% cis

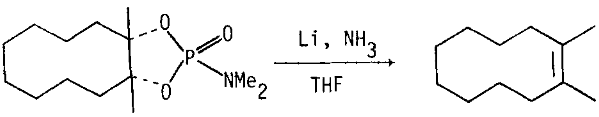
Synth Comm (1975) 5 293



40-80%

mixture of isomers

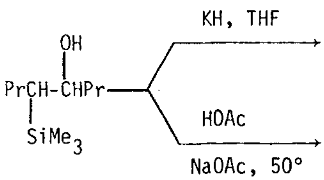
JOC (1974) 39 3641



98%

90% cis

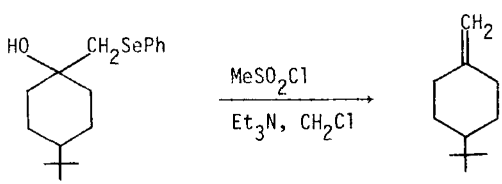
Synth Comm (1975) 5 293



PrCH=CHPr 96%
95% trans

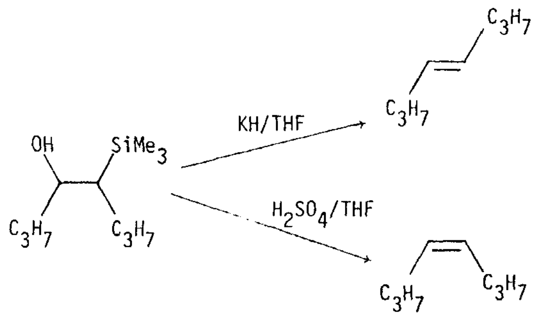
PrCH=CHPr 85%
98% cis

JACS (1975) 97 1464



98%

JCS Chem Comm (1975) 790



96%

99%

Tetr Lett (1974) 1133

Section 199 Olefins from Aldehydes

$$PhCHO + Ph_3\overset{+}{P}CH_2Ph \xrightarrow[\substack{CH_2Cl_2,\\ 18\text{-crown-6}}]{t\text{-BuOK}} PhCH{=}CHPh \qquad 96\%$$

Synthesis (1975) 784

$$(EtO)_2P(O)CH_2Ph \xrightarrow[\substack{2)\ CCl_4\\ 3)\ \underline{i}\text{-PrCHO}}]{1)\ BuLi} i\text{-PrCH}{=}\underset{\substack{|\\ Cl}}{C}\text{-Ph} \qquad 69\%$$

Synthesis (1975) 658

$$Ph_3\overset{+}{P}CH_3 + PhCHO \xrightarrow[NaOH/H_2O]{PhH} PhCH{=}CH_2 \qquad 95\%$$

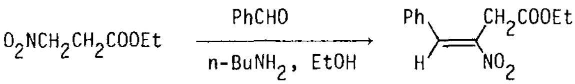
Tetr Lett (1974) 2587

94% (E)

Tetr Lett (1974) 207

$$PhSO_2CH_3 + PhCHO \xrightarrow[CH_2Cl_2,\ TEBA]{50\%\ aq\ NaOH} PhSO_2CH{=}CHPh \qquad 86\%$$

Synthesis (1975) 453

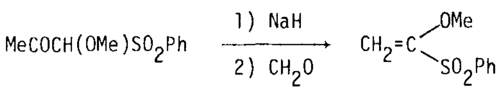


45%

J Prakt Chem (1975) 317 337

$$PhCH{=}CH_2 + PhCONHCH(OMe)COOMe \xrightarrow[2)\ NaOH]{1)\ H_2SO_4,\ PhH} PhCH{=}CHCH(NHCOPh)COOH \qquad 42\%$$

Tetr Lett (1975) 3737

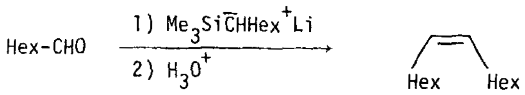


75%

Liebigs Ann Chem (1975) 1484

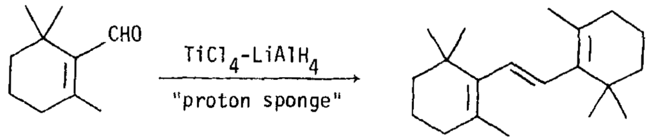
$$PhNHSO_2CH_2COOH + PhCHO \xrightarrow[PhMe,\ rfx]{Py,\ NH_4OAc} PhNHSO_2CH{=}CH\text{-}Ph \qquad 67\%$$

Synthesis (1975) 321



45%

Angew Int Ed (1976) 15 161



94%

retinal ⟶ β-carotene 90%

Chem Lett (1976) 1127

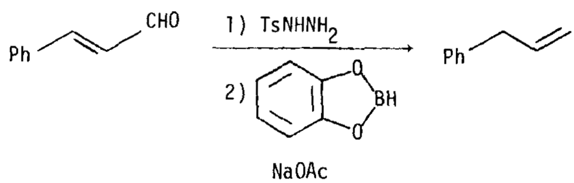
retinal + $LiAlH_4$ + $TiCl_3$ ⟶ carotene 85%

(RCHO ⟶ RCH=CHR)

JACS (1974) 96 4708

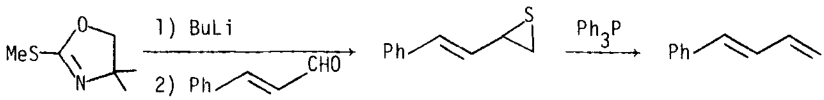
PhCHO $\xrightarrow{H_2CCa_2I_2}$ Ph(H)C=CH_2 11%

Bull Chem Soc Japan (1976) 49 1177



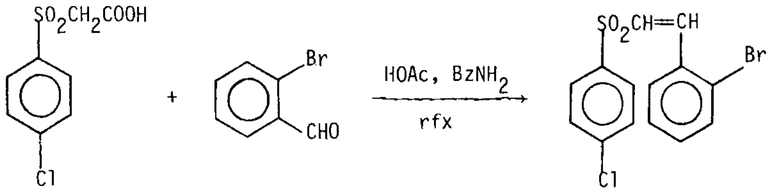
53%

JOC (1976) 41 574



46%

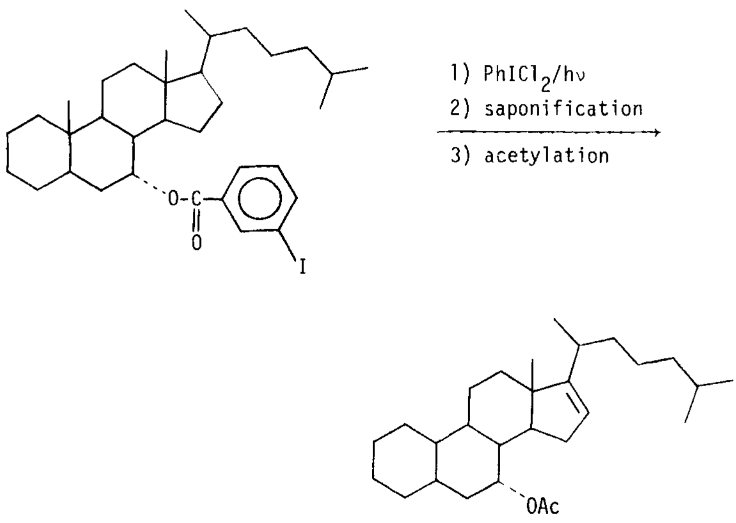
Tetr Lett (1975) 2861



60%

Bull Chem Soc Japan (1975) 48 1091

Section 200 Olefins from Aryls



54%

JACS (1975) 97 6580

Related methods: Alkyls and Aryls from Alkyls and Aryls (Section 65)

Alkyls and Aryls from Olefins (Section 74)

Section 201 Olefins from Amides

No additional examples

Section 202 Olefins from Amines

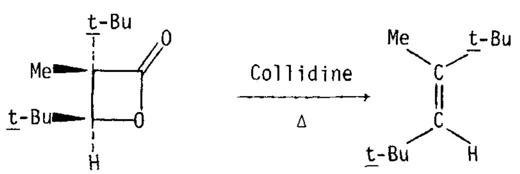
$$\underset{\displaystyle NMe_2}{CH_2}CH_2OCHPh_2 \xrightarrow[\text{3) }\Delta]{\text{1) MeI; 2) anion-exchange resin}} H_2C{=}CHOCHPh_2 \qquad \sim 80\%$$

Org Synth (1976) 55 3

Section 203 Olefins from Esters

$$PhCOOEt \xrightarrow[\text{DMSO}]{\text{xs } Ph_3P{=}CH_2} PhCMe{=}CH_2 \qquad 56\%$$

Tetr Lett (1975) 1439

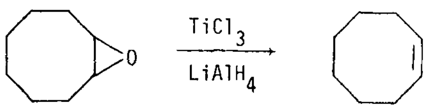


58%

JCS Perkin I (1976) 884

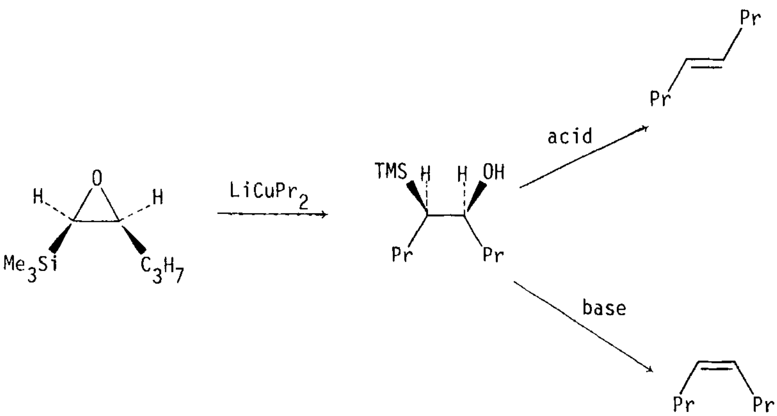
Review: Olefins via Phosphonates Chem Rev (1974) 74 87

Section 204 Olefins from Epoxides



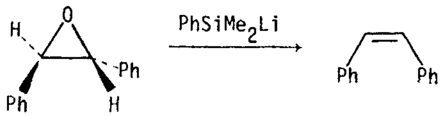
53%

JOC (1975) 40 2555



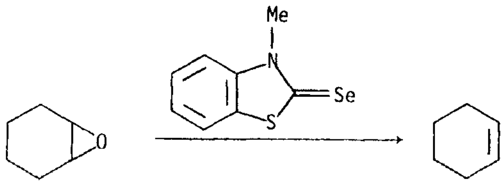
~90%

JOC (1975) 40 2263



75%

Synthesis (1976) 199



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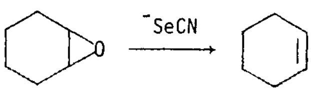
Synthesis (1976) 200



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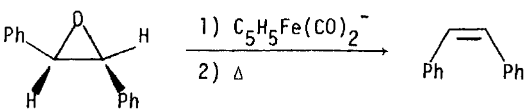
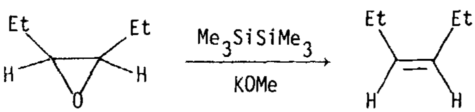
JCS Perkin I (1975) 1216

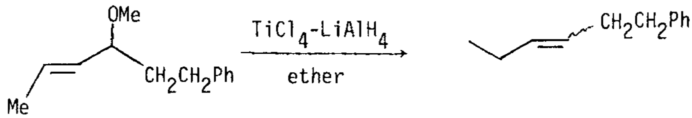


Tetr Lett (1975) 4009



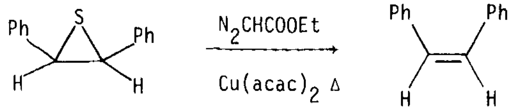
86%

JACS (1976) 98 1265



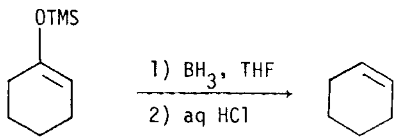
95%

Chem Lett (1976) 737



94%

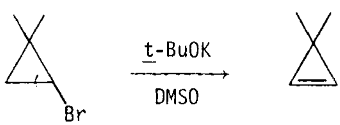
JACS (1975) 97 2553



76%

Tetr Lett (1975) 4005

Section 205 Olefins from Halides and Sulfonates

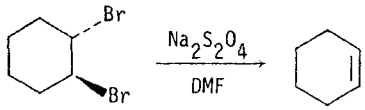


84%

Synthesis (1974) 190

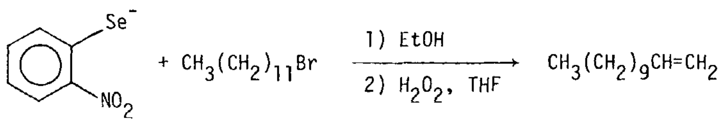
$$RCH_2CH_2Br \xrightarrow[\text{2) } H_2O_2\text{, THF}]{\text{1) o-}NO_2C_6H_4Se^-} RCH{=}CH_2$$

JOC (1975) 40 947



60%

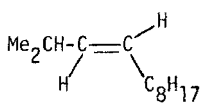
Acta Chem Scand B (1976) 30 366



~70%

JOC (1975) 40 947

$$Me_2C{=}CHCH_2PO(OEt)_2 \xrightarrow[BuLi]{Octyl\ Br} \underset{94\%}{\underset{|}{Me_2C{=}CHCH\text{-}PO(OEt)_2}\atop Octyl} \xrightarrow[Et_2O,\ 0°]{LiAlH_4}$$



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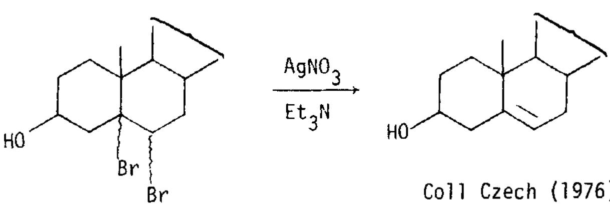
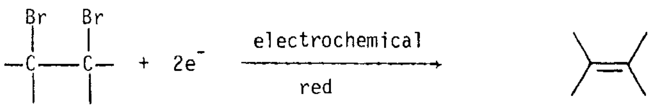
Angew Int Ed (1974) 13 407



95%

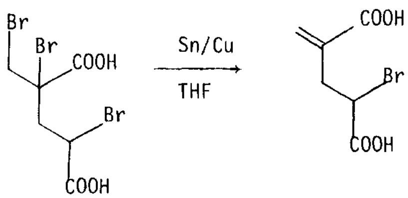
Coll Czech (1976) 41 2040



<u>trans</u> periplanar elimination

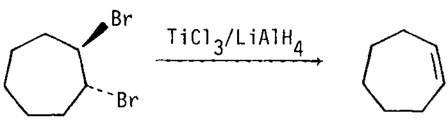
· high yield

JOC (1974) <u>39</u> 2408



81%

JOC (1976) <u>41</u> 4035



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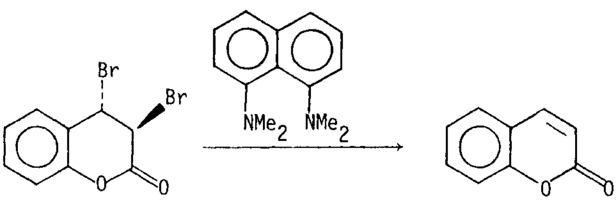
Synthesis (1976) 607



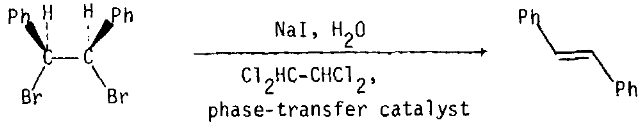
92%

Synth Comm (1975) <u>5</u> 87

$$n\text{-}C_8H_{17}CHBrCH_2(OH) \xrightarrow{TiCl_4\text{-}LiAlH_4} n\text{-}C_8H_{17}CH{=}CH_2$$

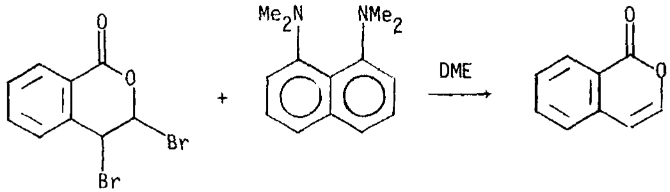
74%

JOC (1975) <u>40</u> 3797



89%

Synthesis (1975) 397



100%

Synth Comm (1975) 5 87

$$Et_2CH\text{-}\underset{\underset{\displaystyle OMe}{|}}{C}HCCl_3 \xrightarrow[Et_2O/THF]{BuLi,\ -50^\circ} Et_2CH\text{-}CH{=}CCl_2$$

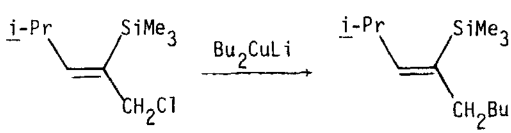
75%

J. Organometal Chem (1975) 97 355

$$PhCHBrCHBrPh \ + \ R_4P^+Br^- \xrightarrow[\substack{NaI \\ H_2O/PhMe \ \ 90\%}]{Na_2S_2O_3} PhCH{=}CHPh$$

86%

Synthesis (1975) 397

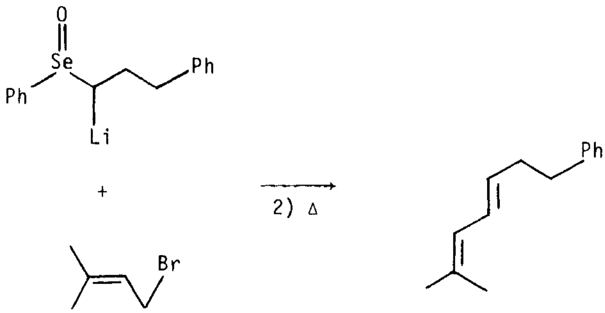


80%

Tetr Lett (1976) 4439

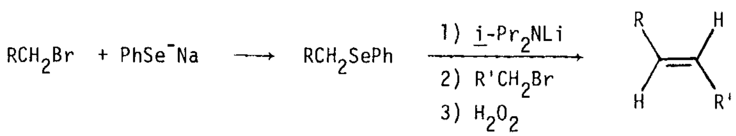
$$\overset{O}{\underset{\uparrow}{}}\!\!PhSCH_2Ph + LiICA \xrightarrow[rfx]{RCH_2X} RCH{=}CHPh$$

JOC (1975) 40 2014



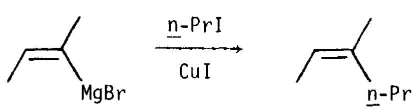
64%

JACS (1975) 97 3250



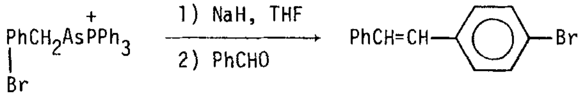
60-80%

JCS Chem Comm (1974) 990



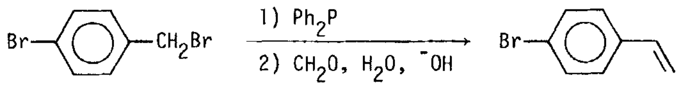
97%

Tetr Lett (1976) 3225



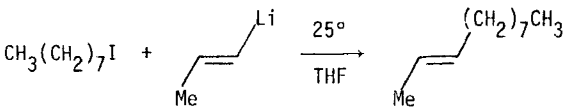
50%

J Organometal Chem (1975) 96 237



98%

Synth Comm (1976) 6 53



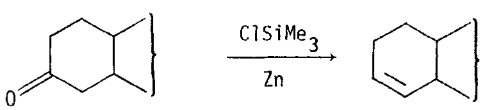
100%

Tetr Lett (1974) 3809

Section 206 Olefins from Hydrides

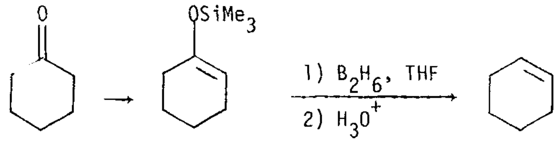
No additional examples

Section 207 Olefins from Ketones



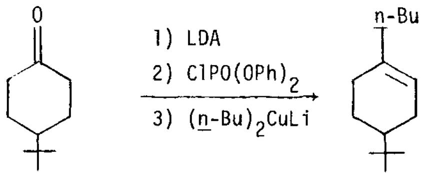
37-72%

JCS Perkin I (1975) 809



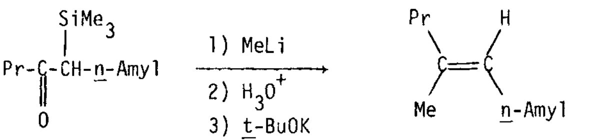
76%

Tetr Lett (1975) 4005



59%

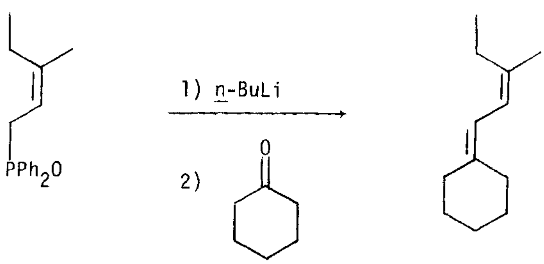
Tetr Lett (1976) 4405



59%

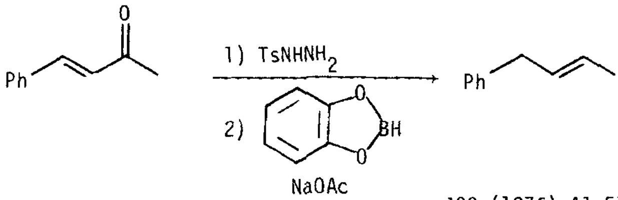
91% stereoselectivity

JOC (1976) 41 2940



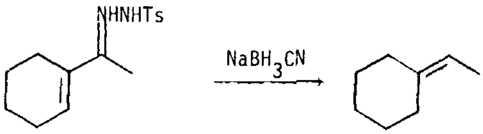
67%

JCS Perkin I (1976) 2386



72%

JOC (1976) 41 574



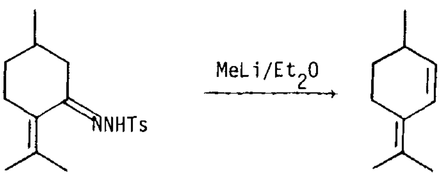
79%

JOC (1975) 40 923

$$MeCH_2\underset{\displaystyle Ph}{\underset{|}{C}}=NNHTs \xrightarrow[\text{2) MeI}]{\text{1) BuLi, TMEDA}} MeCH=\underset{\displaystyle Ph}{\underset{|}{C}}-Me$$

95%

Tetr Lett (1975) 1811



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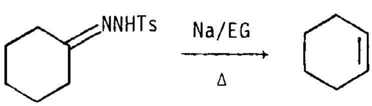
Org React (1976) 23 405



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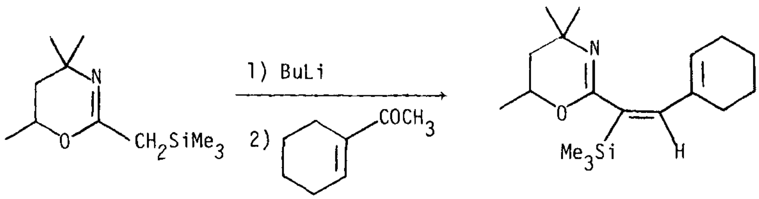
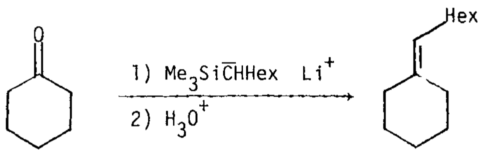
Org React (1976) 23 405



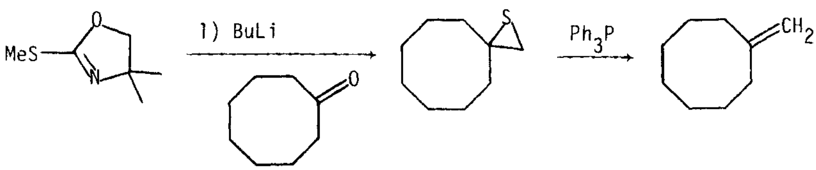
80%

Tetr Lett (1976) 4041



40%

Angew Int Ed (1976) 15 161



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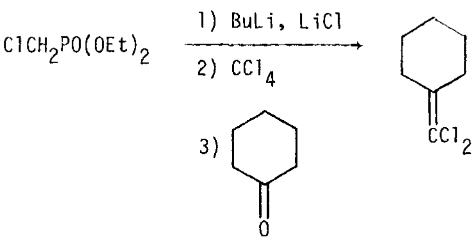
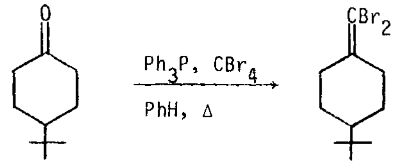


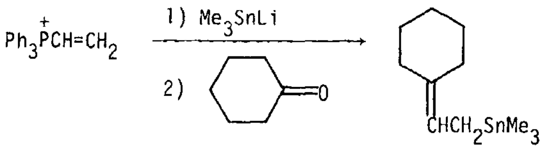
77%

Synthesis (1975) 535



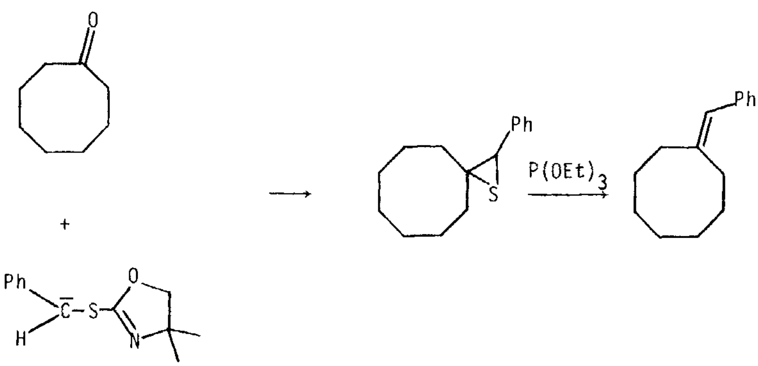
81%

Tetr Lett (1975) 1373



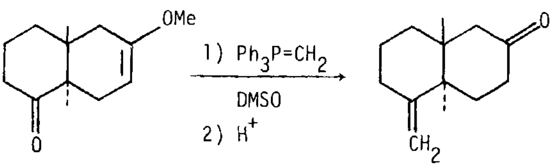
>90%

JCS Chem Comm (1975) 630



72%

JOC (1976) 41 1735



Tetrahedron (1974) 30 2961

$(EtO)_2P(O)CH_2SOMe \xrightarrow[\text{2) } Ph_2CO]{\text{1) BuLi, THF, -78°}} MeSOCH{=}CPh_2$ 84%

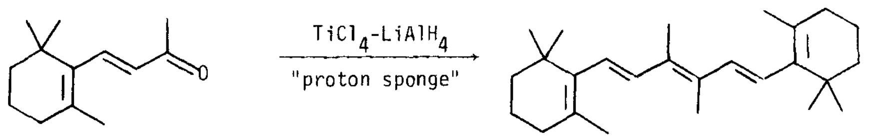
JOC (1975) 40 1979

$MeCOCH_2SiMe_3 \xrightarrow[\text{2) } H^+]{\text{1) } LiCH_2CN} MeC(CH_2CN){=}CH_2$ 75%

Synth Comm (1975) 5 15

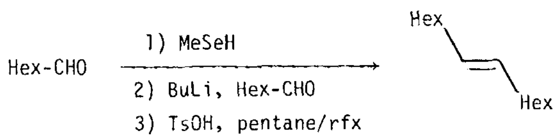
Review: Bis-Wittig Reactions in the Synthesis of Nonbenzenoid Aromatic Ring Systems

Synthesis (1975) 765



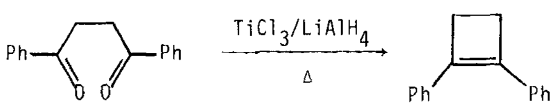
94%

Chem Lett (1976) 1127



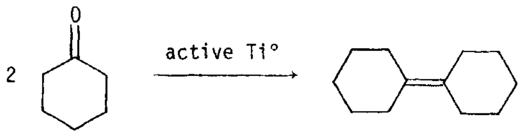
~65%

Tetr Lett (1976) 1385



~50%

Tetr Lett (1976) 3265



85%

JOC (1976) 41 896

$Ph_2CO \xrightarrow[TiCl_3]{LiAlH_4} Ph_2C{=}CPh_2$ 95%

JACS (1974) 96 4708

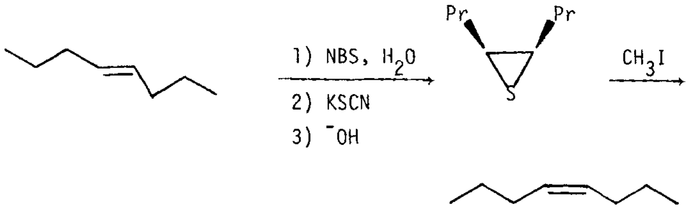
Review: Organic Chemistry of Low Valent Titanium

Accts Chem Res (1974) 7 281

Section 208 Olefins from Nitriles

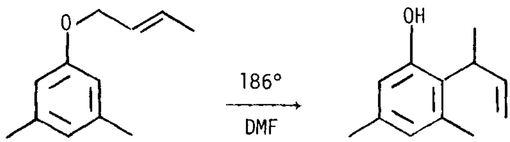
No additional examples

Section 209 Olefins from Olefins



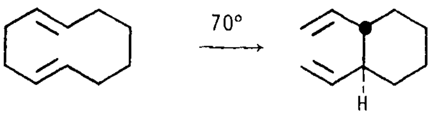
~50%

Tetr Lett (1975) 2709



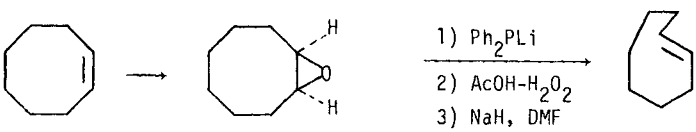
91%

Org React (1975) 22 1



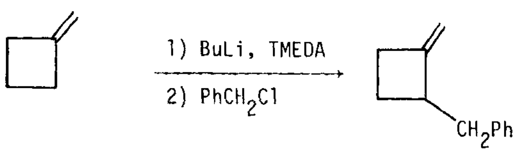
100%

Org React (1975) 22 1



76%

JCS Chem Comm (1974) 142



71%

Tetr Lett (1975) 3047

$$\mathrm{TMS{-}C(Cl){=}CH_2} \xrightarrow{\underline{t}\text{-BuLi}} \mathrm{TMS{-}CH{=}CHBu} \qquad 85\%$$

J Organometal Chem (1974) 81 C9

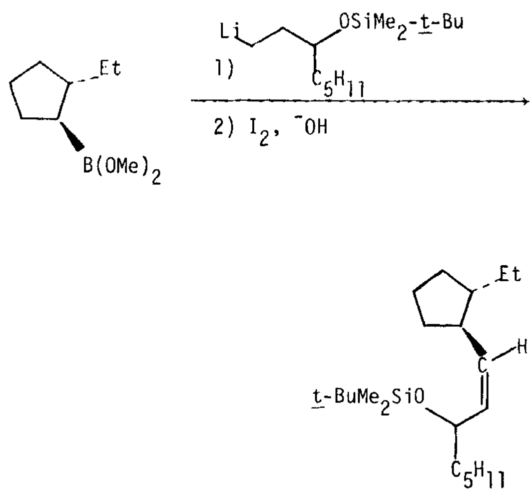
$$\mathrm{CH_2{=}CH_2} + \mathrm{CH_2{=}C(Me)CH_2MgX} \xrightarrow[\mathrm{Et_2O}]{} \mathrm{MeCH_2CH_2C(Me){=}CH_2} \qquad 75\%$$

Liebigs Ann Chem (1975) 103; 119; 1176

$$\mathrm{CH_2{=}CH_2} \xrightarrow[\text{2) HCl}]{\text{1) } \underline{t}\text{-Bu}_2\text{Zn, PhH}} \mathrm{CH_2{=}C(Me)(Bu\text{-}\underline{t})} \qquad 70\%$$

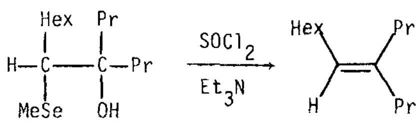
Liebigs Ann Chem (1975) 1162

Section 210 Olefins from Miscellaneous Compounds



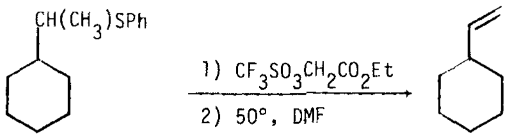
22%

JOC (1976) 41 3947



65%

Tetr Lett (1976) 3743



57%

Tetr Lett (1976) 3487

$$PhCH_2NO_2 \xrightarrow[\Delta]{\text{KOAc, 95\% EtOH}} PhCH{=}CHPh$$ 81%

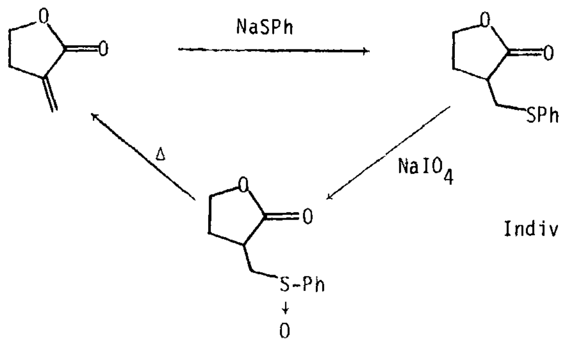
JOC (1975) 40 187

Review: Methods for the Preparation of Bridgehead Olefins

Angew Int Ed (1975) 14 528

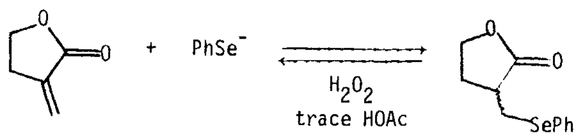
Section 210A Protection of Olefins

The protection of isolated double bonds is considered in this section.

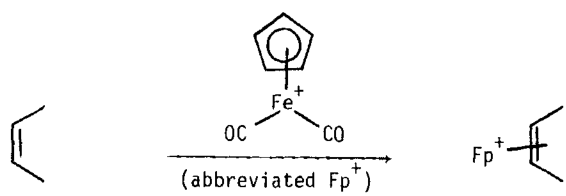


Individual yields >95%

JOC (1975) 40 1181

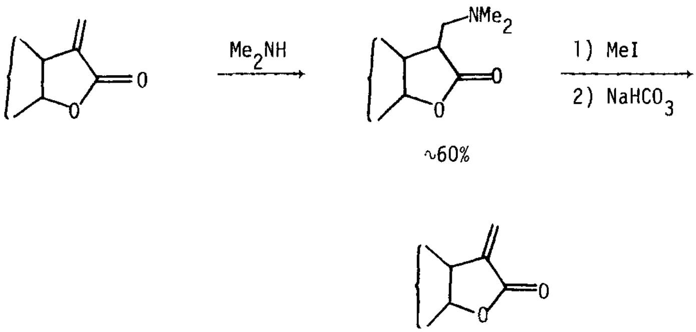


Tetr Lett (1974) 1869



Stable to halogens, $Hg(OAc)_2$, cat. H_2, etc.

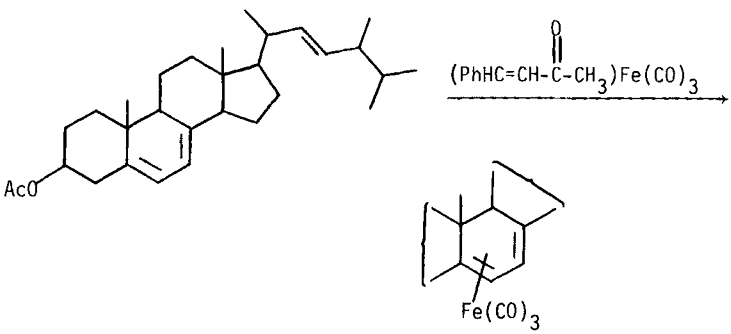
JACS (1975) 97 3254



$\sim$60%

$\sim$80%

Tetrahedron (1976) 32 765



Protects the diene system so the side chain double bond can be hydroxylated by OsO_4. Removed with $FeCl_3$.

J Organometal Chem (1975) 102 507

Sections 211 to 299 are reserved for future additions (e.g., the preparation of nitro compounds).

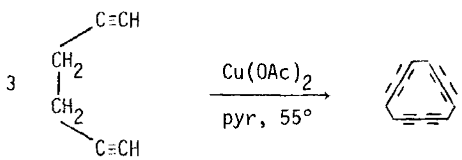
Compendium of Organic Synthetic Methods, Volume 3
Edited by Louis S. Hegedus, Leroy Wade

Chapter 15 PREPARATION OF DIFUNCTIONAL COMPOUNDS

Section 300 Acetylene - Acetylene

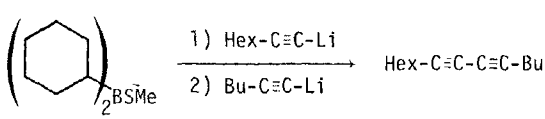
$$Thexyl_2\,BX \xrightarrow[2)\ I_2,\ -78°]{1)\ BuC{\equiv}CLi,\ THF} BuC{\equiv}C{-}C{\equiv}CBu$$ 90%

JCS Chem Comm (1975) 857



∿30%

Org Synth (1974) 54 1



61%

Tetr Lett (1976) 4385

Section 301 Acetylene - Carboxylic Acid

No additional examples

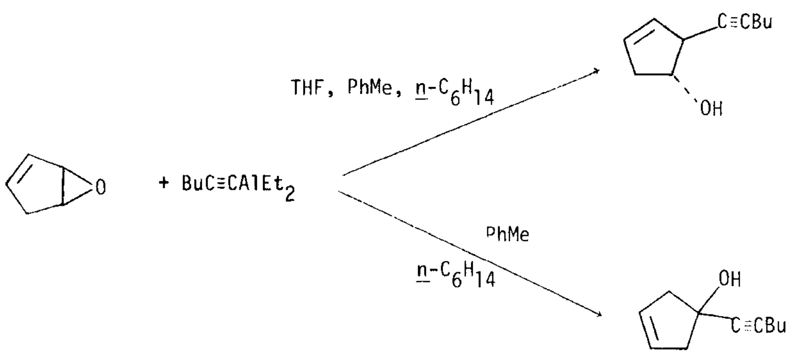
Section 302 Acetylene - Alcohol

$$HC{\equiv}CH \xrightarrow[\text{2) } Me_2CO]{\text{1) BuLi, THF, -78°}} Me_2C(OH){-}C{\equiv}CH \qquad 94\%$$

JOC (1975) 40 2250

$$MeC{\equiv}CH \xrightarrow[\text{2) BuBr, hexane; 3) } CH_2O]{\text{1) BuLi, TMEDA}} BuCH_2C{\equiv}CCH_2OH$$

JCS Chem Comm (1975) 817

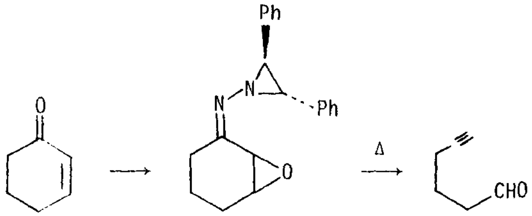


65%

63%

JCS Chem Comm (1975) 287

Section 303 Acetylene - Aldehyde



60%
(last step

Org Synth (1976) 55 52

Section 304 Acetylene - Amide

$$\text{Ph-C}\equiv\text{C-MgBr} \xrightarrow[\text{2) } H_2O]{\text{1) } Me_2SiNCO} \text{Ph-C}\equiv\text{C-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-NH}_2$$

48%

Tetr Lett (1975) 981

Section 305 Acetylene - Amine

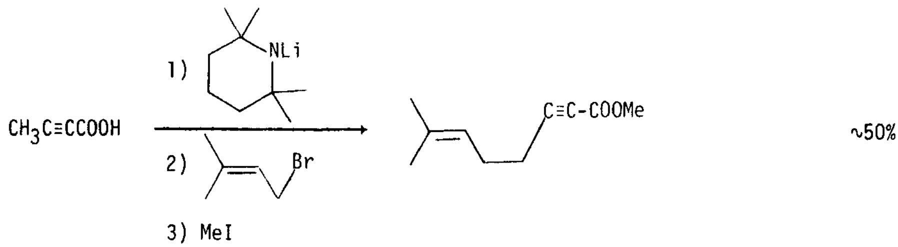
No additional examples

Section 306 Acetylene - Ester

$$HC\equiv CCH_2OH \longrightarrow HC\equiv CCH_2OTHP \xrightarrow[\substack{\text{2) } Ac_2O \\ \text{3) } H^+}]{\text{1) } NaNH_2} AcOC\equiv CCH_2OH$$

~40%

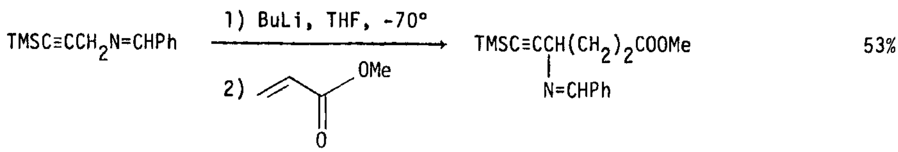
Synthesis (1974) 357



JOC (1975) 40 269

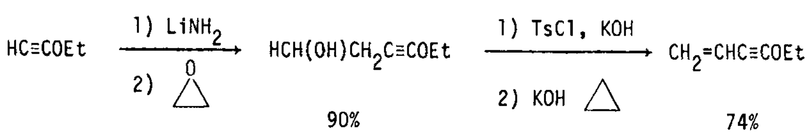
$$\mathrm{Pr{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}COOEt} \xrightarrow[\text{2) } Tl(NO_3)_3,\ MeOH]{\text{1) } H_2NNH_2} \mathrm{Pr{-}C{\equiv}CCOOCH_3} \qquad \sim 55\%$$

Org Synth (1976) 55 73



Tetr Lett (1975) 3337

Section 307 Acetylene - Ether, Epoxide

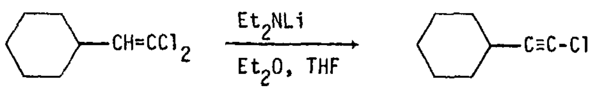


Rec Trav Chim (1974) 93 92

Section 308 Acetylene - Halide

$$(Me_2N)_2\overset{O}{\overset{\|}{P}}CH_2C\equiv CH + \underline{n}\text{-}BuI \xrightarrow[2)\ PBr_3]{1)\ NaH,\ THF} BuC\equiv CCH_2Br \qquad \sim 70\%$$

Synthesis (1974) 730



80%

Synthesis (1975) 458

$$HOCH_2\text{-}C\equiv C\text{-}CH_2OH + 2\ Ph_3PBr_2 \xrightarrow{MeCN} BrCH_2\text{-}C\equiv C\text{-}CH_2Br \qquad 92\%$$

Synthesis (1975) 255

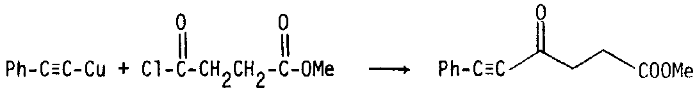
Section 309 Acetylene - Ketone

$$PhCOCN + PhC\equiv CLi \xrightarrow[-70°]{Et_2O} PhCOC\equiv CPh \qquad 61\%$$

Bull Soc Chim Fr (1975) 779

$$TMSC\equiv CH \xrightarrow[2)\ PhCOCl]{1)\ CuI,\ \underline{t}\text{-}BuOLi} TMSC\equiv CCOPh \qquad 66\%$$

JOC (1975) __40__ 131



52%

Comptes Rendus C (1976) 282 277

$$H\text{-}C{\equiv}C\text{-}\underset{}{\overset{OH}{\overset{|}{C}}}H\text{-}Ph \xrightarrow{\text{nickel peroxide}} H\text{-}C{\equiv}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph$$

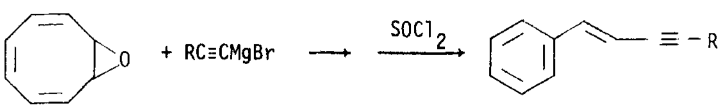
98%

JOC USSR (1974) 10 2081

Section 310 Acetylene - Nitrile

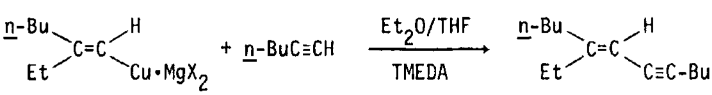
No additional examples

Section 311 Acetylene - Olefin



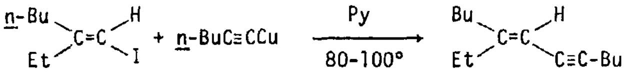
70-80%

Ber (1974) 107 2985



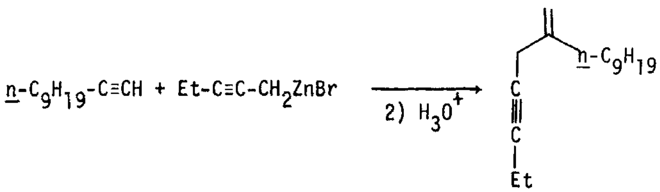
78%

Tetr Lett (1975) 1465



85%

J Organometal Chem (1975) 93 415



45%

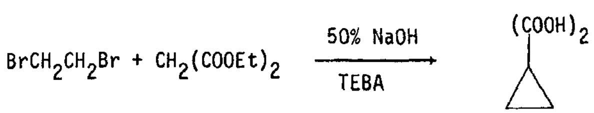
Comptes Rendus C (1976) 282 277

Section 312 Carboxylic Acid - Carboxylic Acid

$$PhCH(COOH)_2 \xrightarrow[\text{2) MeI}]{\text{1) 3 BuLi, THF, -50°}} PhC(Me)(COOH)_2$$

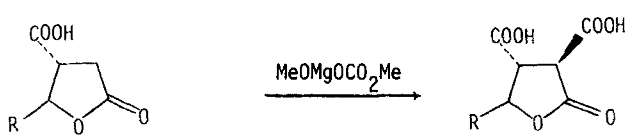
88%

Tetr Lett (1975) 707



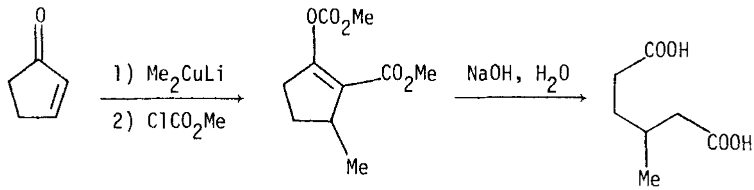
75%

J Org Chem (1975) 40 2969



93%

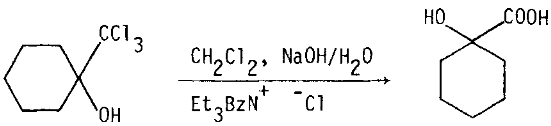
JOC (1974) 39 1676



~55%

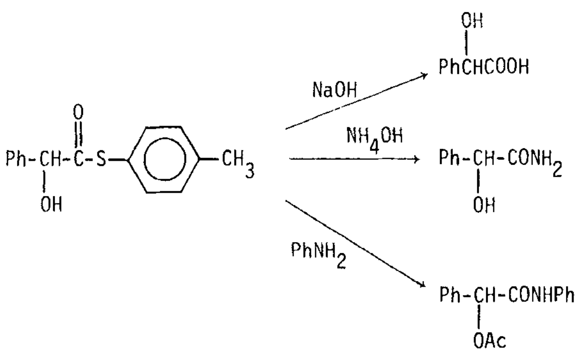
JOC (1975) 40 1488

Section 313 Carboxylic Acid - Alcohol



68%

Synthesis (1976) 825



65%

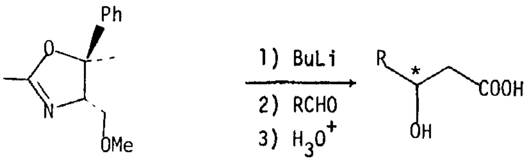
71%

55%

JACS (1975) 97 596

$$Ph_2C{=}C(OTMS)_2 \xrightarrow[2)\ H_3O^+]{1)\ MCPBA} Ph_2C(OH){-}COOH$$ 81%

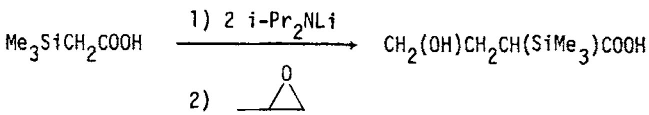
JOC (1975) <u>40</u> 3783



<77% yield

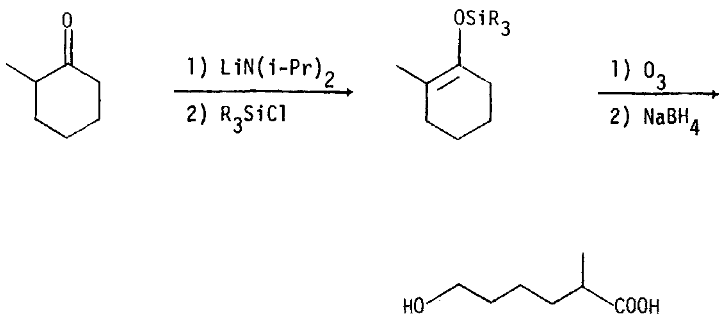
<20% optical yield

Tetr Lett (1974) 1333



94%

JCS Chem Comm (1975) 537



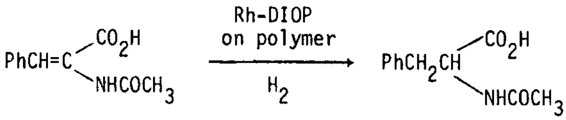
94%

Tetr Lett (1974) 2027

Section 314 Carboxylic Acid - Aldehyde

No additional examples

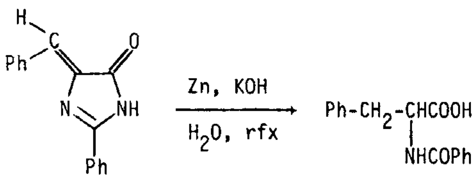
Section 315 Carboxylic Acid - Amide



~100%

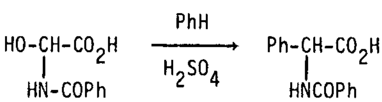
81% ee

JACS (1976) 98 5400



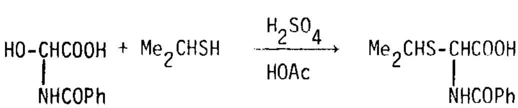
74%

Tetr Lett (1975) 4051



91%

JCS Chem Comm (1975) 349



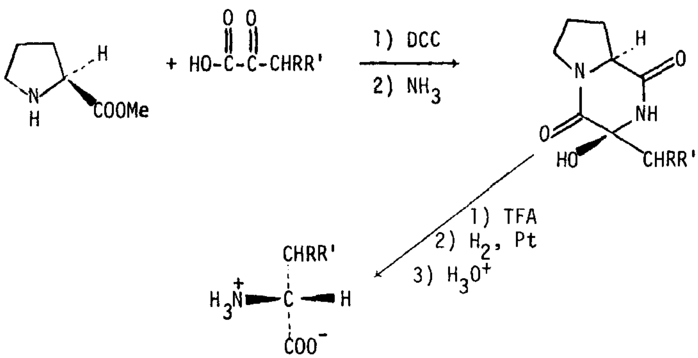
~80%

Tetrahedron (1975) 31 863

Section 316 Carboxylic Acid - Amine

Review: "Advances in the Synthesis and Manufacture of α-Aminoacids"

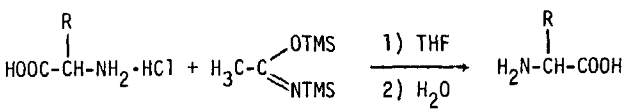
Russ Chem Rev (1974) 43 745



>90% ee

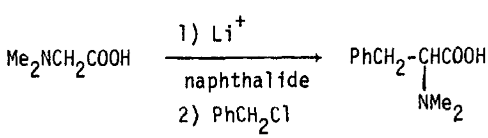
up to 60% yield

JCS Chem Comm (1975) 988



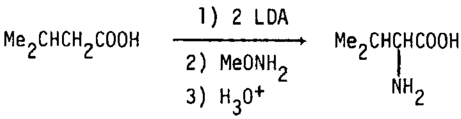
∿95%

Synthesis (1975) 113



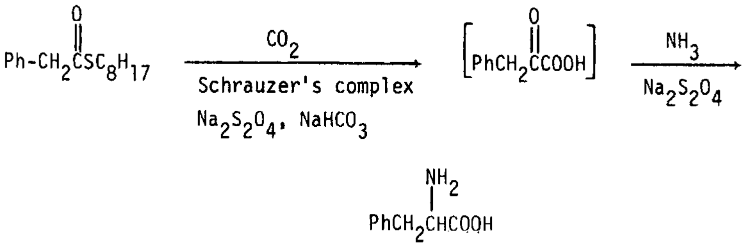
60%

Compte Rendus (1974) 287 1383



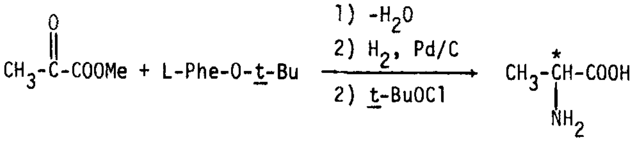
33%

Chem Pharm Bull (1975) 23 167



73%

Tetr Lett (1976) 4343

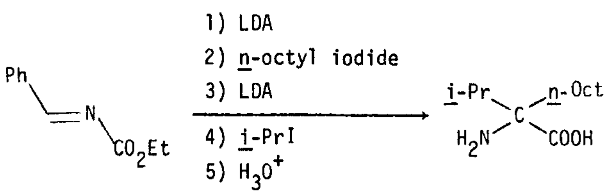


58%

70% ee

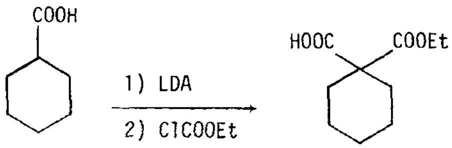
(L predominates)

Tetr Lett (1976) 997; 1001



JOC (1976) 41 3491

Section 317 Carboxylic Acid - Ester



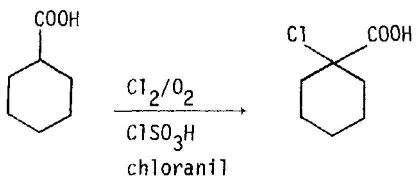
88%

Tetr Lett (1974) 2721

Section 318 Carboxylic Acid - Ether, Epoxide

No additional examples

Section 319 Carboxylic Acid - Halide

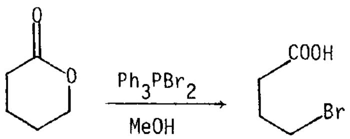


73%

JOC (1975) 40 2960

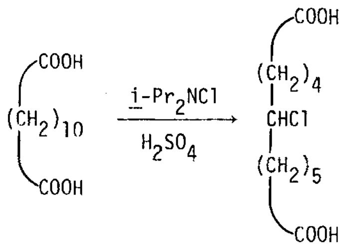
$$\underset{\displaystyle NH_2}{RCH}\text{-}COOH + NaNO_2 + (HF)_xF^-PyH^+ \longrightarrow \underset{\displaystyle F}{RCH}COOH$$

Synthesis (1974) 652



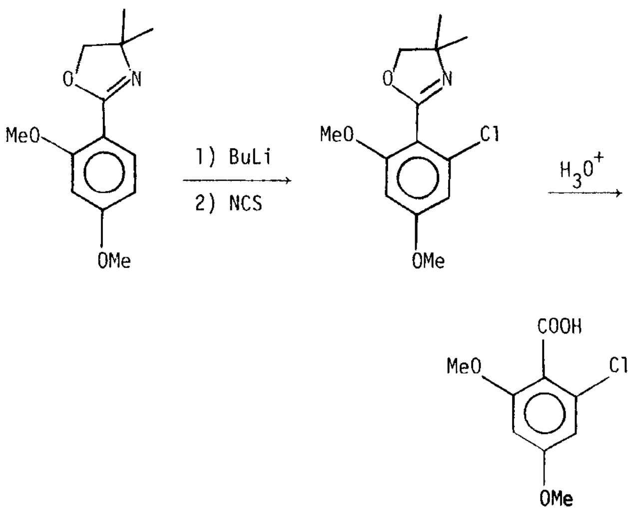
30%

JOC (1975) 40 1640



60%

Angew Int Ed (1976) 15 306



90%

JOC (1975) 40 3158

$$CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow[CCl_4,\ H^+]{SOCl_2,\ NCS} CH_3(CH_2)_3\underset{Cl}{\underset{|}{C}}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \qquad 87\%$$

JOC (1975) 40 3420

$$\underline{n}\text{-}BuCH_2COOH \xrightarrow[2)\ (CH_2CO)_2NBr,\ HBr]{1)\ SOCl_2} \underline{n}\text{-}Bu\underset{Br}{\underset{|}{C}}H\text{-}COCl \qquad \sim 70\%$$

Org Synth (1976) 55 27

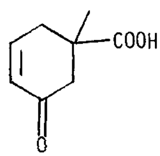
$$RCH_2COCl \xrightarrow[2)\ SOCl_2,\ HCl]{1)\ NCS} RCHClCOCl \qquad \sim 80\%$$

Tetr Lett (1974) 3225

Also via: Haloesters (Section 359)

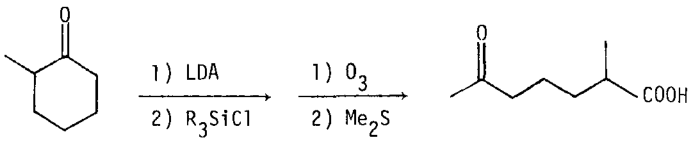
Section 320 Carboxylic Acid - Ketone

$$MeSCH{=}CH\underset{CH_2C\equiv CH}{\underset{|}{C}}MeCOOMe \xrightarrow[rfx]{HCl\text{-}HOAc}$$



93%

Tetr Lett (1975) 405



90%

Tetr Lett (1974) 2027

$MeCOCH_2COOMe$ + PhCONHCH(OH)COOH $\xrightarrow{H_2SO_4}$ MeCOCHCOMeCH(NHCOPh)COOH 71%

JCS Chem Comm (1975) 905

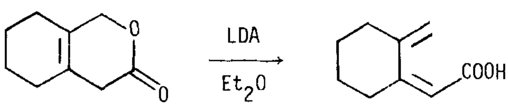
Section 321 Carboxylic Acid - Nitrile

PhCOCl + NaCN $\xrightarrow[\text{cat., } CH_2Cl_2]{\text{phase transfer}}$ PhCOCN 60%

Tetr Lett (1974) 2275

Also via: Cyanoesters (Section 361)

Section 322 Carboxylic Acid - Olefin



90%

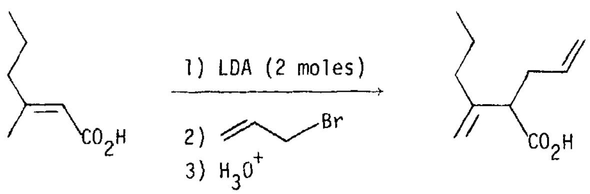
JCS Perkin I (1974) 2005

$PhCH_2COOH \xrightarrow[\text{2) } PhCH_2CH_2Br \text{ 3) } NaIO_4\text{, }120°]{\text{1) } R_2NLi} PhC(=CH_2)\text{-}COOH$ 84%

JCS Chem Comm (1974) 135

$Me_3SiCH_2COOH \xrightarrow[\text{2) } PhCHO]{\text{1) 2 LDA}} PhCH{=}CHCOOH$ 88%

JCS Chem Comm (1975) 537



80%

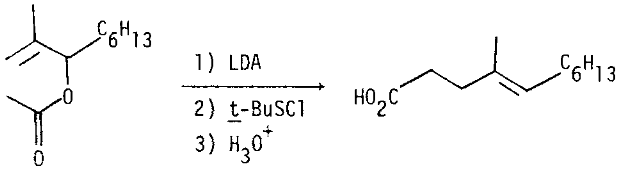
JACS (1976) 98 4925

$Me_2C{=}CHCH_2SO_2CH_2COOMe \xrightarrow[KOH,\ CCl_4]{\underline{t}\text{-BuOH}} Me_2C{=}CHCH{=}CHCOOH$ 80%

Synth Comm (1975) 5 315

$H_2C{=}CHCH{=}CH_2 + \underline{t}\text{-BuCu, } MgBr_2 \xrightarrow{CO_2} \underline{t}\text{-}BuCH_2CH(COOH)CH{=}CH_2$ 95%

J Organometal Chem (1975) 92 C28



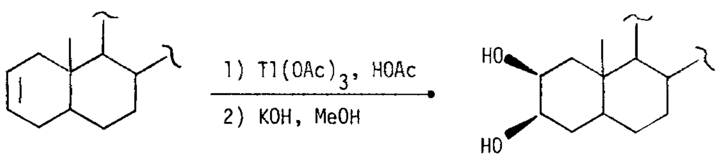
80%

>98% E

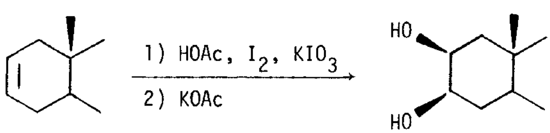
JOC (1974) 39 3315

Also via: Hydroxy acids (Section 313)
Olefinic amides (Section 349)
Olefinic esters (Section 362
Olefinic nitriles (Section 376)

Section 323 Alcohol - Alcohol

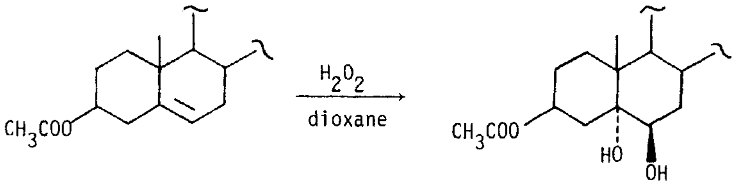


JCS Perkin I (1976) 1660



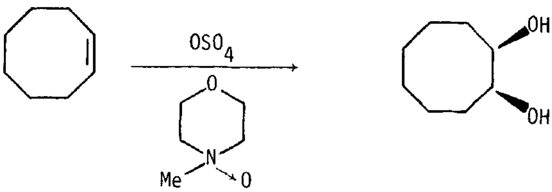
82%

Gazz Chim Ital (1975) 105 377



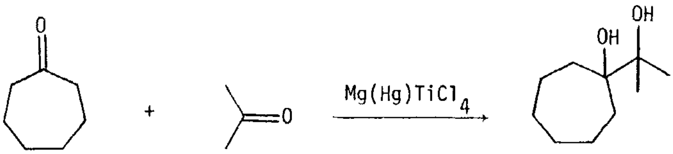
~60%

JOC USSR (1976) 12 1234



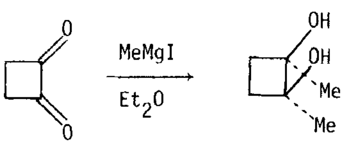
79%

Tetr Lett (1976) 1973



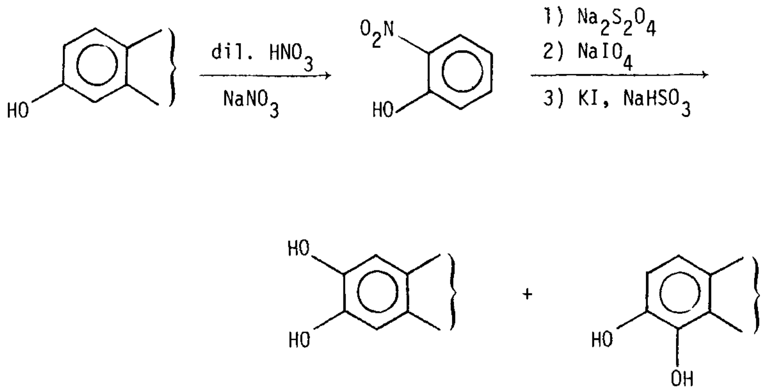
75%

JOC (1976) 41 260



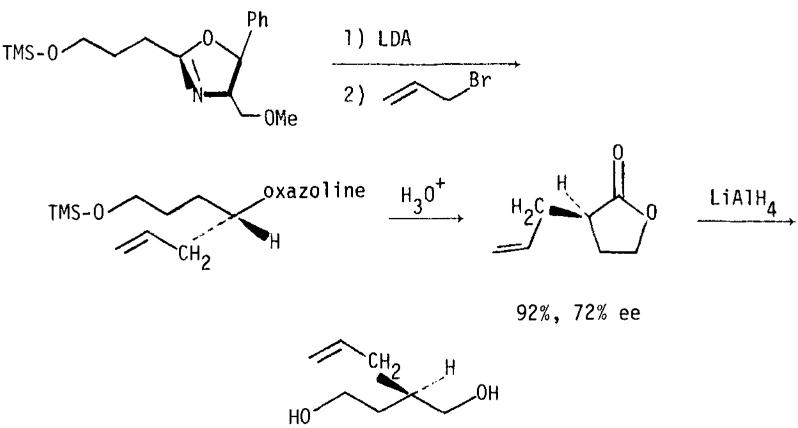
100%

Tetr Lett (1974) 30 1397



~50% total

Steroids (1976) 28 733

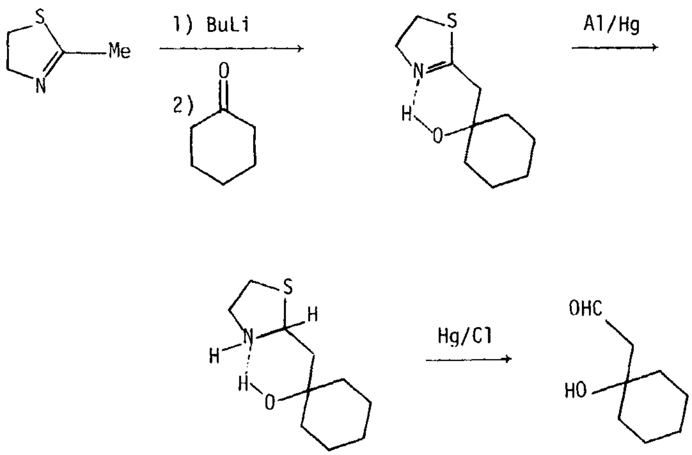


92%, 72% ee

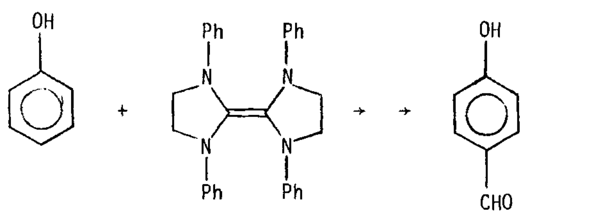
JOC (1975) 40 1186

Also via: Hydroxyesters (Section 327)
Diesters (Section 357)

Section 324 Alcohol - Aldehyde

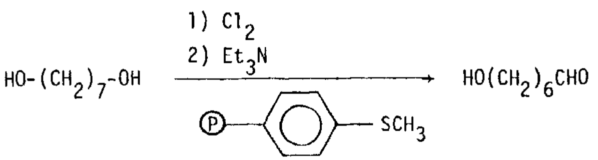


JOC (1975) 40 2025



55%

Angew Int Ed (1976) 15 169



57%

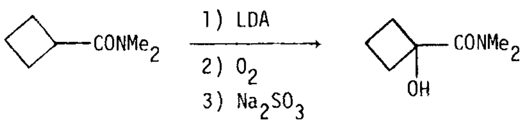
JACS (1975) 97 2232

Also via: Acetoxyladehydes (Section 336)

Section 325 Alcohol - Amide

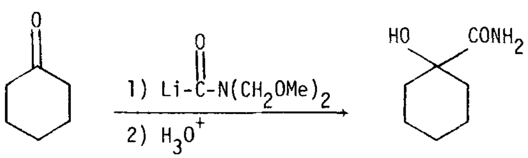
$(\underline{i}\text{-}Pr)_2NCHO \xrightarrow[\text{2) } Ph_2CO]{\text{1) LDA}} Ph_2C(OH)\text{-}CON(\underline{i}\text{-}Pr)_2$ 92%

Can J Chem (1974) 52 185



84%

Tetr Lett (1975) 1731

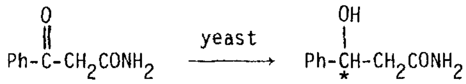


44%

Angew Int Ed (1976) 15 293

$Me_2CHCONEt_2 \xrightarrow[\text{2) PhCHO}]{\text{1) LDA}} PhC(OH)HCMe_2CONMe_2$ 85%

Comptes Rendus (1975) 281 893

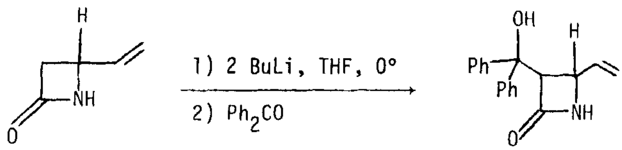


26%

high optical purity

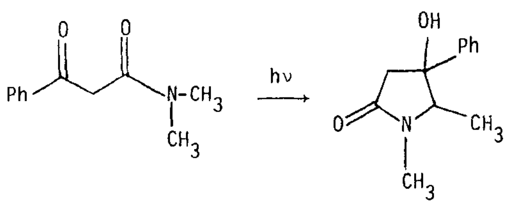
Also works with α-ketoamides

Aust J Chem (1976) 29 2459



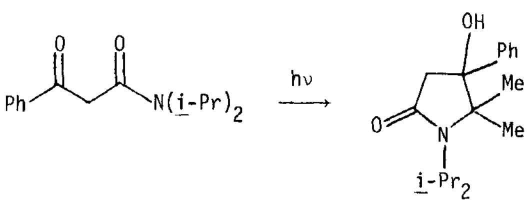
88%

Can J Chem (1974) 52 3206



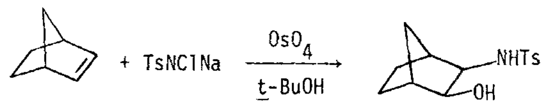
∿70%

JCS Chem Comm (1974) 743



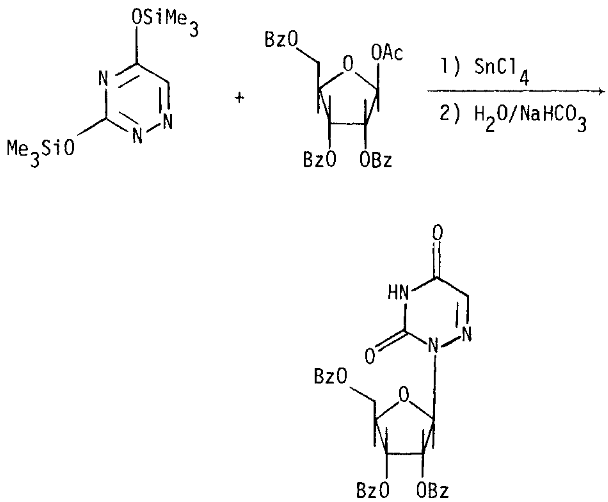
90%

JCS Perkin I (1976) 2054



64%

JOC (1976) 41 177



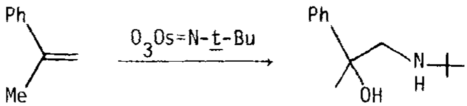
93% on 10 Kg scale

JOC (1974) 39 3654
39 3660 (uracils)
39 3664 (disaccharides)
39 3668
39 3672 (5-azacytidines)

Glycosidation of Purines using $SnCl_4/ClCH_2CH_2Cl$

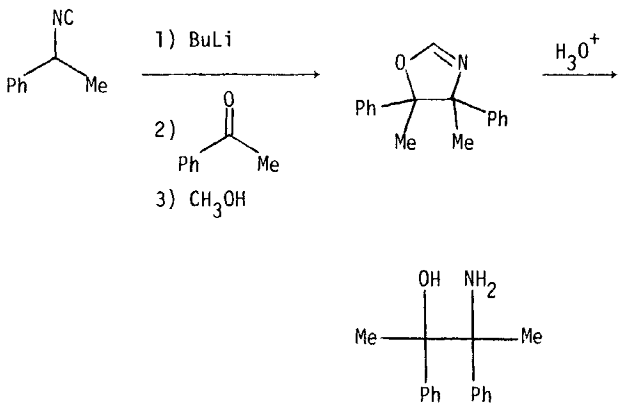
Tetr Lett (1974) 2141

Section 326 Alcohol - Amine



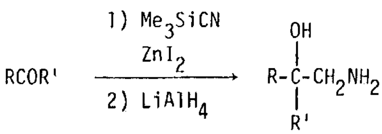
93%

JACS (1975) 97 2305

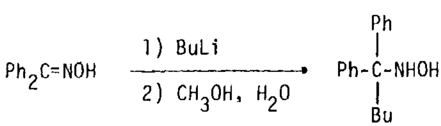


74%

Liebigs Ann Chem (1976) 183



JOC (1974) 39 914



63%

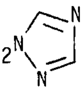
Tetr Lett (1976) 233

Review: Methods of Synthesis of Pyrimidine Nucleosides

Russ Chem Rev (1973) 494

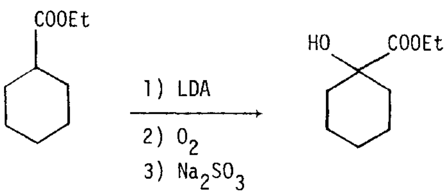
Review: The Silyl Method of Synthesis of Nucleosides and Nucleotides

Russ Chem Rev (1974) 140

Use of $ArSO_2N$  as condensing agent in polynucleotide synthesis.

JCS Chem Comm (1974) 325

Section 327 Alcohol - Ester



76%

Tetr Lett (1975) 1731

$$RCH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR' + LDA + MoO_5{\cdot}Py{\cdot}HMPA \xrightarrow[\text{2) } H_2O]{\text{1) } -70^\circ} \underset{\underset{\displaystyle OH}{|}}{RCH}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}OEt$$

50-80%

Works with lactones, ketones

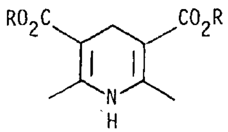
JACS (1974) 96 5944

$$\underset{\substack{|\\ OSiMe_3}}{EtC}{=}CHMe + MeCOCOOEt \xrightarrow[2)\ H_2O]{1)\ TiCl_4} EtCO\underset{\substack{|\\ Me}}{C}H{-}\underset{\substack{|\\ Me}}{C}(OH)COOEt \qquad 87\%$$

Chem Lett (1975) 741

$$Ph\underset{\substack{|\\ Cl}}{C}HCOCOOEt + MeMgBr \xrightarrow{Et_2O} Ph\underset{\substack{|\\ Cl}}{C}H{-}\overset{OH}{\underset{\substack{|\\ Me}}{C}}{-}COOEt \qquad 90\%$$

Comptes Rendus (1974) <u>279</u> 469



$$Ph{-}\overset{O}{\overset{\|}{C}}{-}COOMe \xrightarrow[R\ =\ (-)\text{-menthyl}]{} Ph{-}\overset{\substack{OH\\ |}}{\underset{*}{C}}H{-}COOMe \qquad 82\%$$

21% ee

JCS Chem Comm (1976) 101

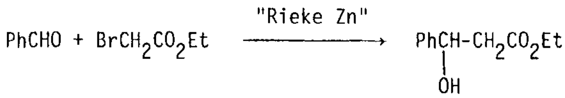
$$\underline{n}{-}C_6H_{13}CHO + CH_3CHBrCOOEt + Zn \longrightarrow \underline{n}{-}C_6H_{13}CHOH{-}\underset{\substack{|\\ CH_3}}{C}HCOOEt \qquad 73\%$$

Org React (1975) <u>22</u> 423

$$PhCHO \xrightarrow[Zn]{BrCH_2COOEt} PhCH(OH)CH_2COOEt \qquad 97\%$$

continuous flow apparatus

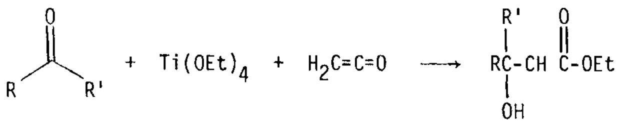
JOC (1974) <u>39</u> 269



98%

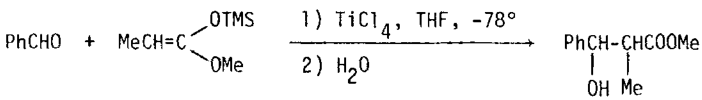
Synthesis (1975) 452

Use of activated In JOC (1975) 40 2253



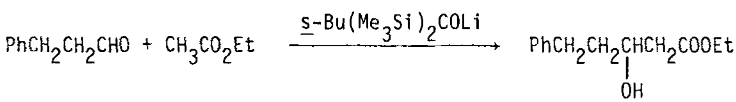
50-90%

Helv Chim Acta (1974) 57 1703



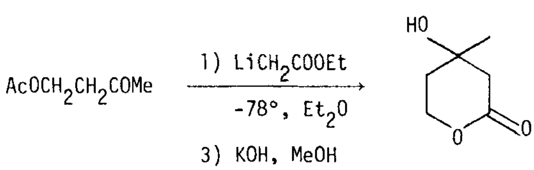
88%

Chem Lett (1975) 989



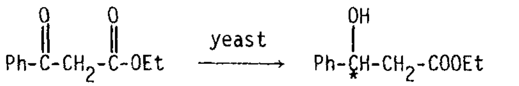
77%

Tetr Lett (1976) 2253



94%

Synthesis (1974) 719

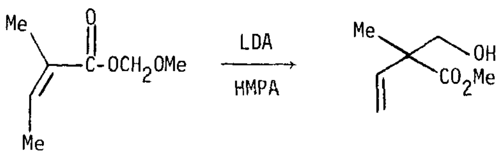


70%

high optical yield

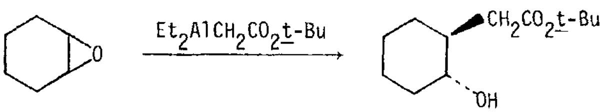
Also works with α-ketoesters

Aust J Chem (1976) 29 2459



61%

JOC (1976) 41 585

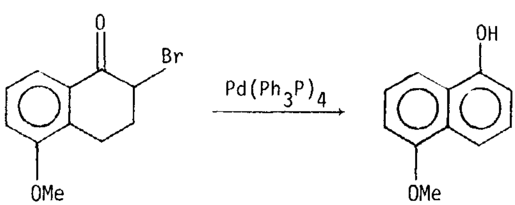


34%

JOC (1976) 41 1669

Also via: Hydroxyacids (Section 313)

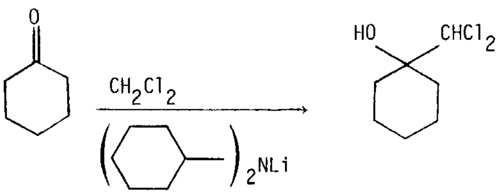
Section 328 Alcohol - Ether, Epoxide



94%

JOC (1975) 40 2976

Section 329 <u>Alcohol - Halide</u>



100%

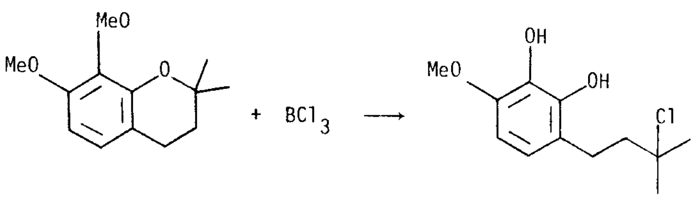
JACS (1974) <u>96</u> 3010

$$\text{R-CH=CH}_2 \xrightarrow[\text{electrolysis}]{\text{H}_2\text{O, Br}^-} \text{R-}\underset{}{\overset{\text{OH}}{\overset{|}{\text{CH}}}}\text{-CH Br}$$

~60%

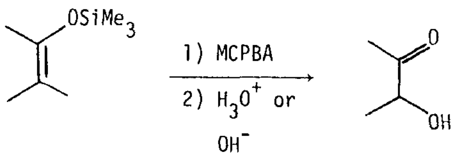
R = 1° alkyl

J Gen Chem USSR (1975) <u>45</u> 2072



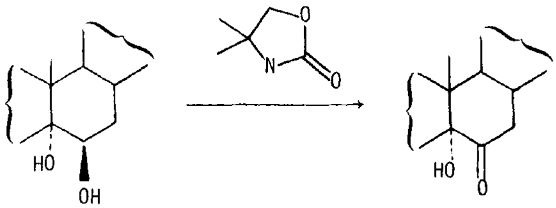
JCS Chem Comm (1974) 318

Section 330 <u>Alcohol - Ketone</u>



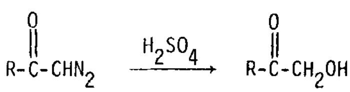
70%

Tetr Lett (1974) 4319



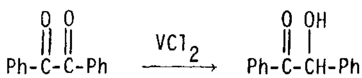
83%

Tetrahedron (1976) 32 1097



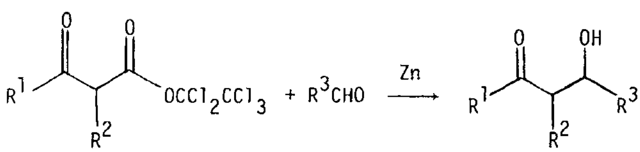
~80%

Comptes Rendus C (1976) 282 1125

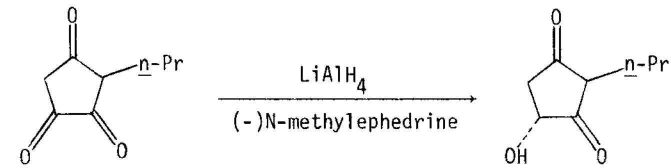


100%

Synthesis (1976) 815



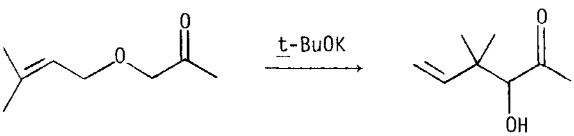
Chem Lett (1976) 95



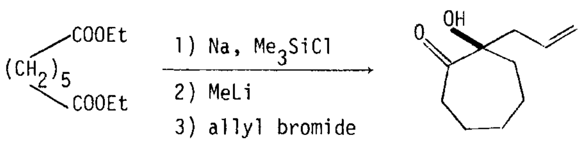
55%

58% ee

Tetr Lett (1976) 3165

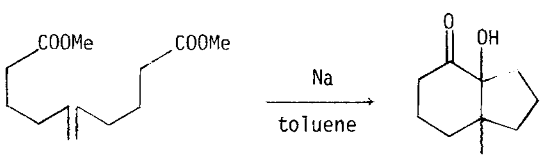


Helv Chim Acta (1974) 57 2084



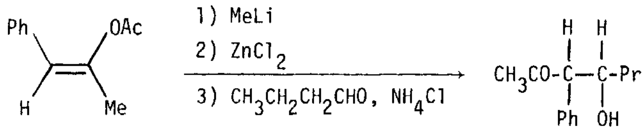
80%

Synthesis (1976) 341



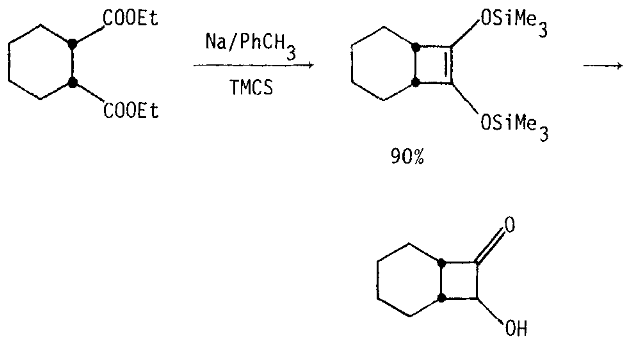
50%

JACS (1974) 96 5618



~55%

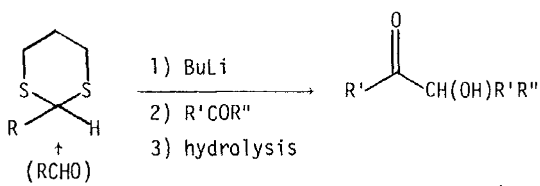
Org Synth (1974) 54 49



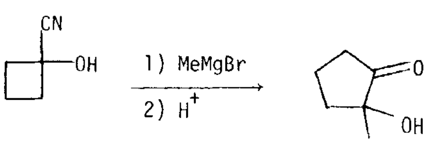
90%

77%

Org React (1976) 23 259

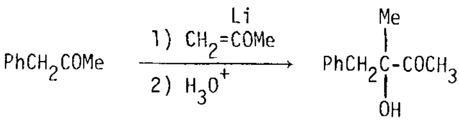


JOC (1975) 40 231 (full paper)



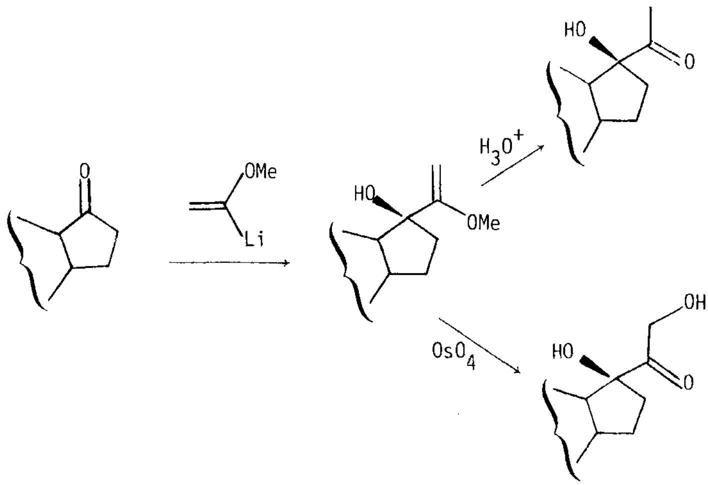
75%

Bull Soc Chim Fr (1975) 333



72%

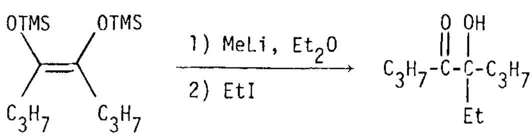
JACS (1974) 96 7125



63%

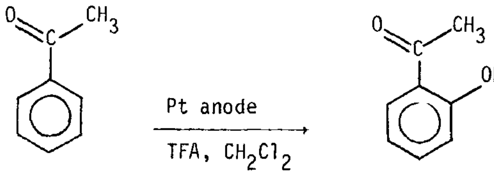
54%

JOC (1976) 41 2312



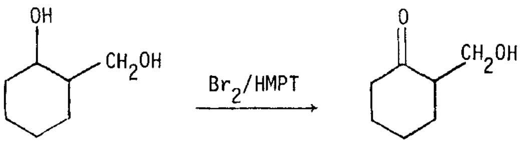
82%

Tetr Lett (1974) 3879
Tetr Lett (1974) 3883



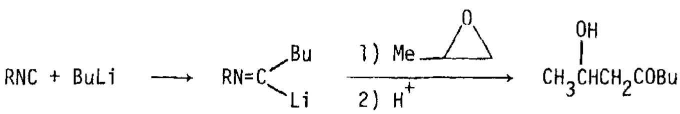
85%

JCS Chem Comm (1975) 262



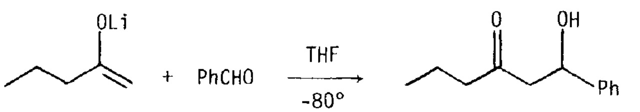
93%

Synthesis (1976) 811



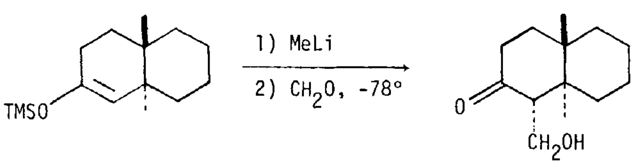
90%

JOC (1974) 39 600



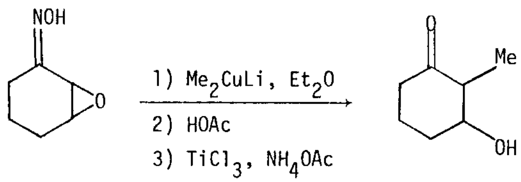
80%

JOC (1974) 39 3459



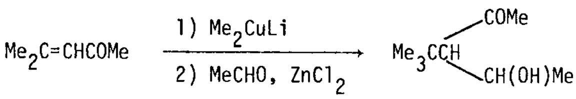
90%

JACS (1974) 96 7114



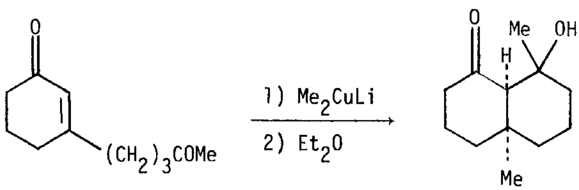
90%

Tetr Lett (1975) 3117



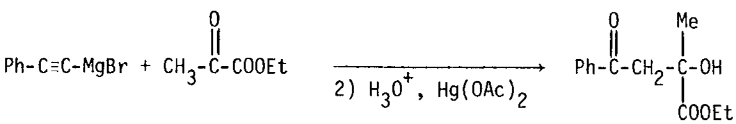
96%

Tetr Lett (1975) 589



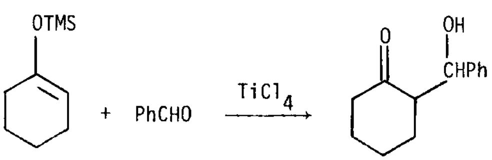
63%

Helv Chim Acta (1975) 58 1808



55%

Synthesis (1976) 832



94%

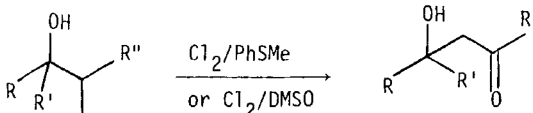
JACS (1974) 96 7503

$$PhCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 + Me_2CHCHO \xrightarrow{(Me_3Si)_2\overset{i\text{-}Bu}{\overset{|}{C}}OLi} PhCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2\underset{OH}{\underset{|}{C}H}CHMe \qquad 71\%$$

Tetr Lett (1976) 1817

$$PhSOCH_2COCH_3 \xrightarrow[3)\ Ph_2CO]{1)\ NaH \quad 2)\ BuLi} Ph_2C(OH)CH_2COCH_2SOPh \qquad 91\%$$

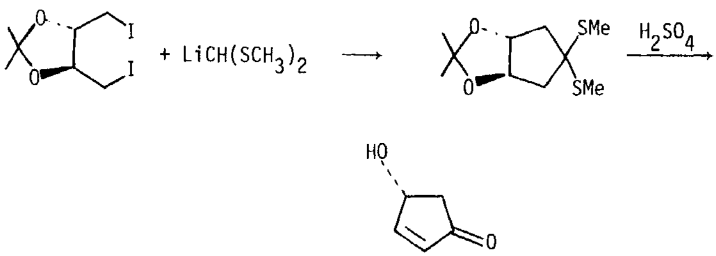
Tetr Lett (1974) 107



80%

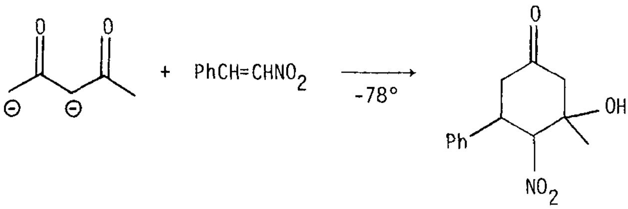
(no C-C bond cleavage)

Tetr Lett (1974) 287



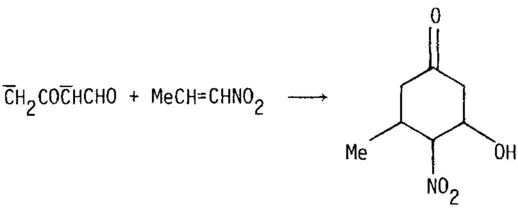
42%

Tetr Lett (1976) 759

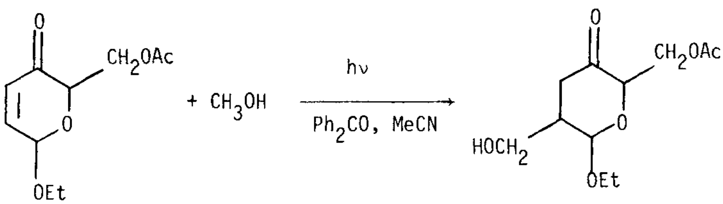


73%

Angew Int Ed (1974) 13 400

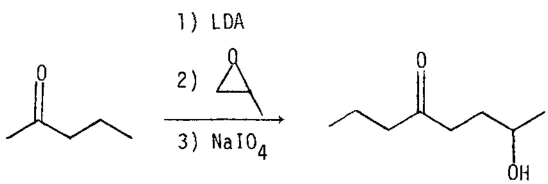


Ber (1975) 108 1961; 1924



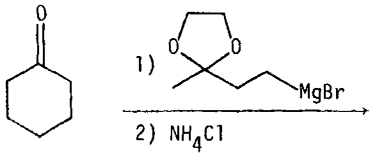
75%

Tetr Lett (1975) 297



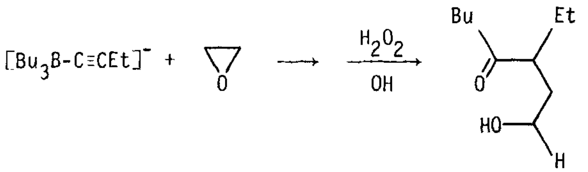
98%

Tetr Lett (1976) 11



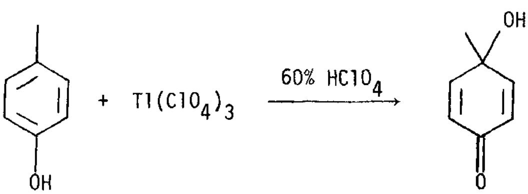
97%

Tetr Lett (1976) 3105



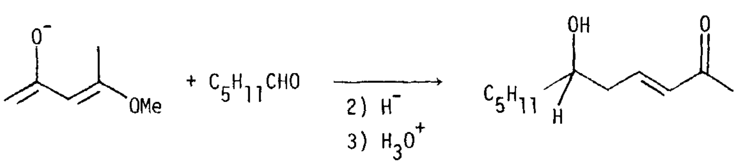
70%

Tetrahedron (1974) <u>30</u> 3037



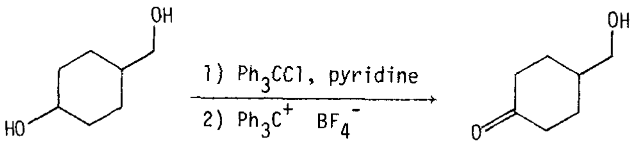
50%

Chem Comm (1974) 661



~50%

JACS (1976) <u>98</u> 2351



79%

JACS (1976) 98 7882

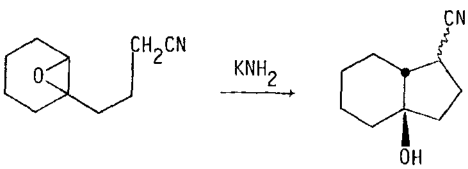
Also via: Acyloxyketones (Section 360)

Section 331 Alcohol - Nitrile

$$PhCH_2CH_2CH_2CN \xrightarrow[\text{2) } MoO_5\cdot Py\cdot HMPA]{\text{1) LDA}} PhCH_2CH_2CH(OH)CN$$

57%

JOC (1976) 41 740



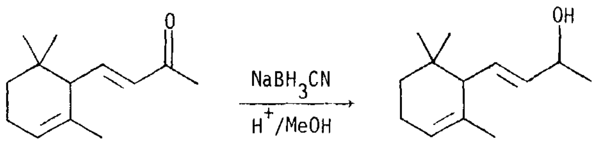
75%

JACS (1974) 96 5268

Also via: Cyanohydrin trimethylsilyl ethers (Section 366)
Cyanohydrin esters (Section 361)

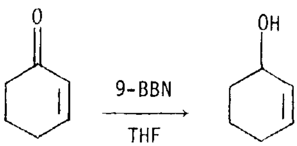
Section 332 Alcohol - Olefin

Allylic and benzylic hydroxylation (C=C-CH → C=C-C-OH, etc.) is listed in Section 41 (Alcohols and Phenols from Hydrides)



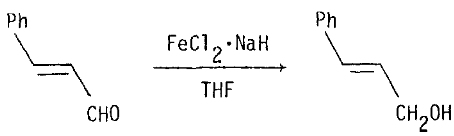
88%

JOC (1975) 40 2530



85%

JOC (1975) 40 1864



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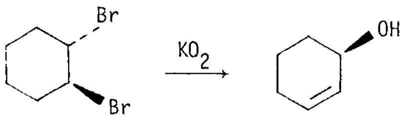
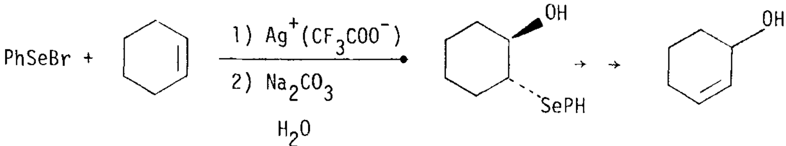
Chem Lett (1976) 581



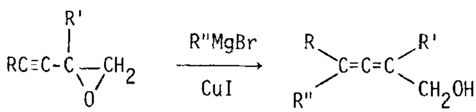
100%

Tetr Lett (1975) 3183



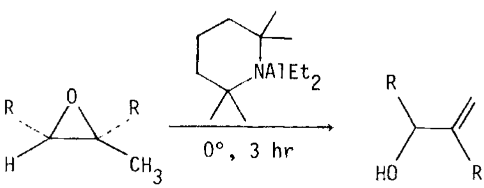
76%

JCS Chem Comm (1974) 100



>90%

Rec Trav Chim (1974) 93 47



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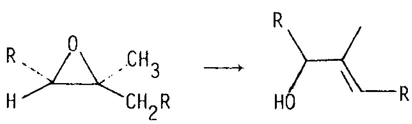
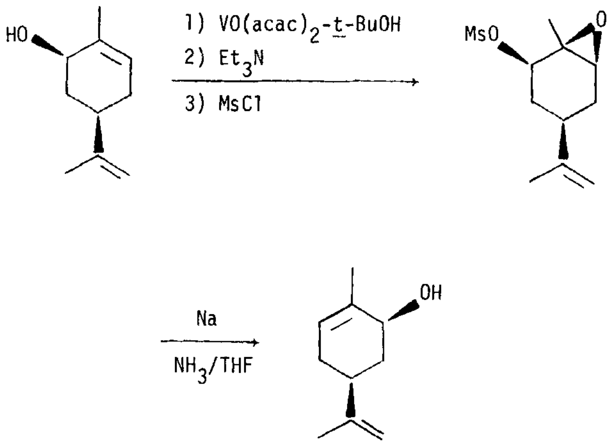


78%

JACS (1974) 96 6513



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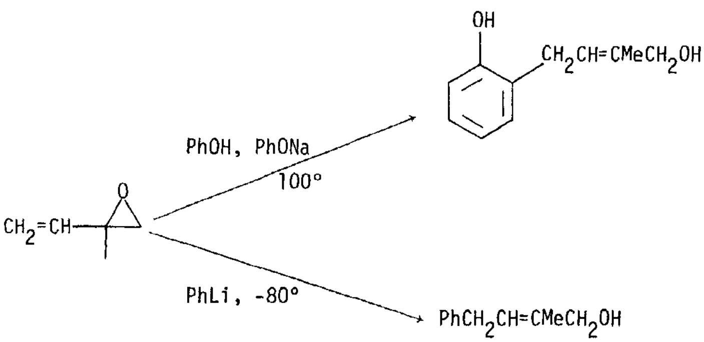
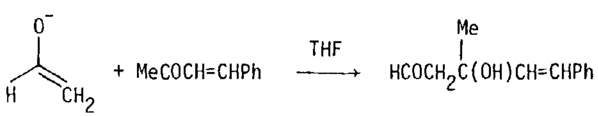
Tetr Lett (1976) 2621

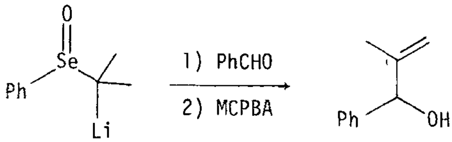


Tetr Lett (1975) 4419



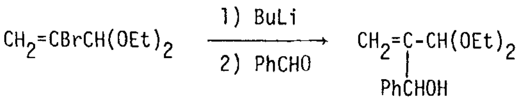
98%

Comptes Rendus (1974) <u>278</u> 533
<u>279</u> 961



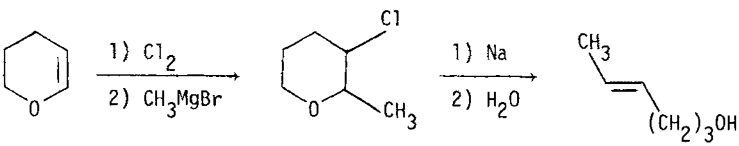
81%

JACS (1975) 97 3250



82%

Tetr Lett (1974) 2751; 2755



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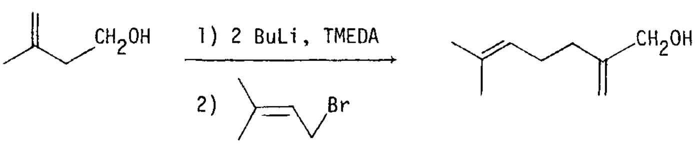
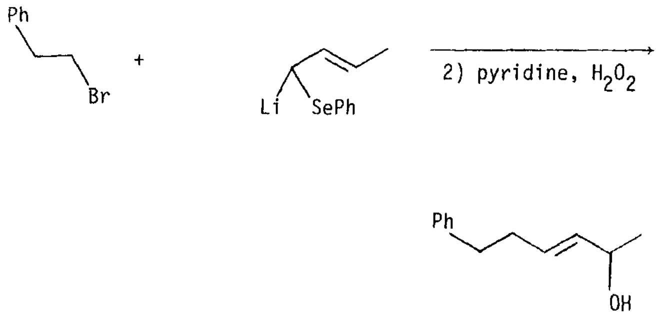
Org Synth (1976) 55 62



70%

Tetr Lett (1974) 2215



80%

JOC (1975) 40 2570

$$\underset{\substack{|\\ CH_3}}{PhSe(O)CHCH_3} \xrightarrow[\substack{2)\ PhCHO\\ 3)\ H^+,\ rfx}]{1)\ LDA,\ THF} CH_2{=}\underset{\substack{|\\ Me}}{C}{-}\overset{\substack{OH\\ |}}{C}HPh$$

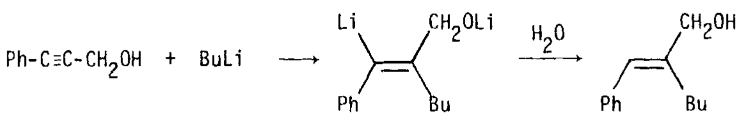
81%

JACS (1975) 97 3250

$$HC{\equiv}CCH_2OH \;+\; MeCH{=}CHCH_2ZnBr \longrightarrow H_2C{=}C\begin{matrix} \diagup CH_2OH \\ \diagdown \underset{\substack{|\\ Me}}{CH}{-}CH{=}CH_2 \end{matrix}$$

93%

Comptes Rendus C (1975) 280 1473

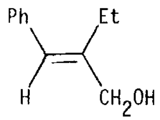


90%

Acta Chem Scand B (1976) 30 521

$$\underset{\text{OTHP}}{Me_2C}\text{-}C{\equiv}CCH_2CH_2OH \xrightarrow[Cu^+]{MeMgX} Me_2C{=}C{=}CMeCH_2OH \qquad 56\%$$

Tetr Lett (1975) 1509

$$PhC{\equiv}CCH_2OH \xrightarrow[CuI,\ Et_2O]{EtMgBr}$$  70%

J Organometal Chem (1975) 91 Cl

$$F_2C{=}CFCl \xrightarrow[2)\ PhCOMe]{1)\ BuLi,\ THF,\ Et_2O,\ pentane,\ -135°} PhC(OH)(Me)\text{-}CF{=}CF_2 \qquad 83\%$$

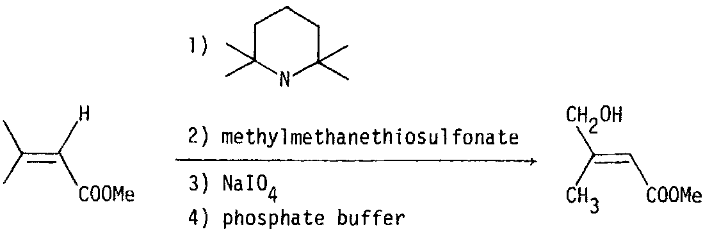
Synthesis (1975) 122

$$CH_2{=}CBrCH_2OH \xrightarrow[2)\ RCOR']{1)\ t\text{-}BuLi,\ Et_2O} RR'C(OH)C(CH_2OH){=}CH_2 \qquad 65\text{-}75\%$$

JOC (1975) 40 2975

$$Ph_2\bar{C}C{\equiv}C^-(Na)_2^+ \xrightarrow[2)\ H_3O^+]{1)\ Ph_2CO} Ph_2C{=}C{=}CHC(OH)Ph_2 \qquad 70\%$$

JOC USSR (1975) 11 1691



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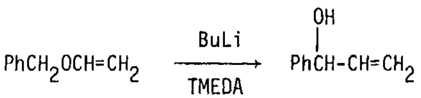
Tetr Lett (1976) 4215



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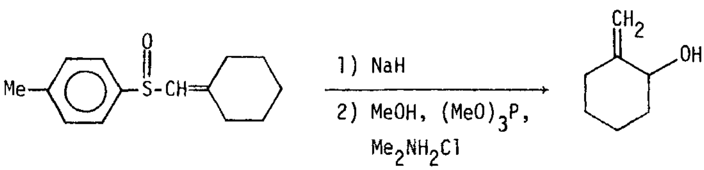
JACS (1974) 96 2576



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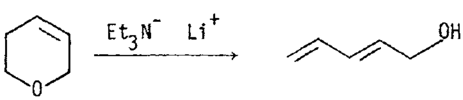
Tetr Lett (1976) 2237



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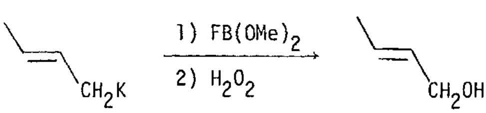
Comptes Rendus C (1976) 282 391

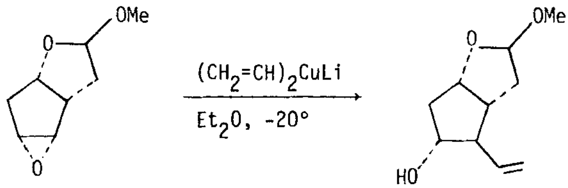


58%

Helv Chim Acta (1975) 58 1094

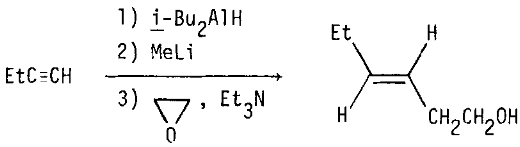
Review: Preparation of α-Allenic Alcohols

Bull Soc Chim Fr (1975) 2369



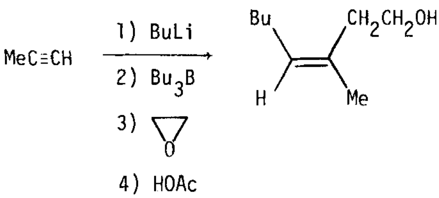
72%

Tetr Lett (1974) 2439



84%

Synthesis (1975) 632

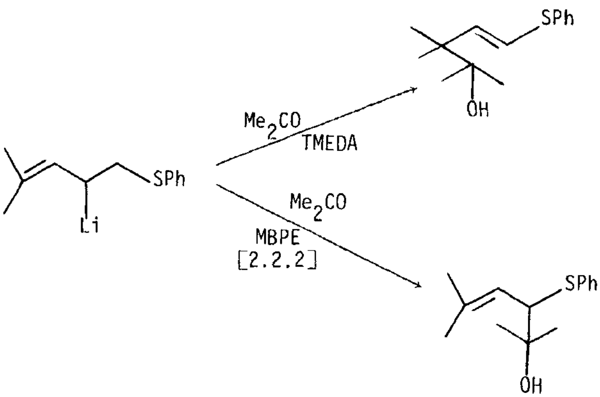


62%

Chem Lett (1975) 397

$H_2C{=}CHCH{=}CH_2$ + t-BuCu, $MgBr_2$ $\xrightarrow{Me_2CO}$ t-$BuCH_2CHCH{=}CH_2$ (with Me_2COH on the CH) 62%

J Organometal Chem (1975) 92 C28



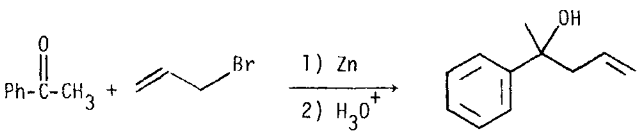
100%

60%

Tetr Lett (1974) 2665

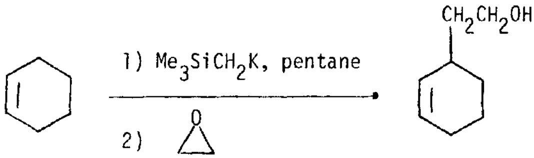
$$PhCH_2CHO + CH_2{=}CH\text{-}CH_2SiMe_3 \xrightarrow[CH_2Cl_2]{AlCl_3} PhCH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2CH{=}CH$$

Tetr Lett (1976) 2449



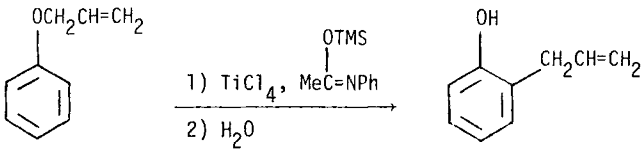
97%

JOC (1976) 41 550



83%

Synthesis (1975) 328



88%

Chem Lett (1975) 1041

Also via: Acetylenes - Alcohols (Section 302)

Section 333 Aldehyde - Aldehyde

No additional examples

Section 334 Aldehyde - Amide

No additional examples

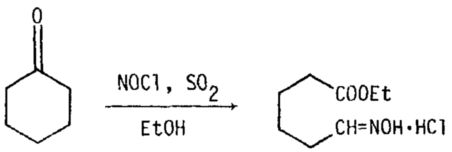
Section 335 Aldehyde - Amine

No additional examples

Section 336 Aldehyde - Ester

$$\underline{n}\text{-}C_3H_7CH_2CHO \xrightarrow[\text{2) } BrCH_2COOEt \text{ 3) } H_3O^+]{\text{1) } (\underline{i}\text{-}Bu)_2NH} \underline{n}\text{-}C_3H_7\underset{\displaystyle CH_2COOEt}{\underset{|}{C}}HCHO$$ 70%

Synth Comm (1974) 4 147



95%

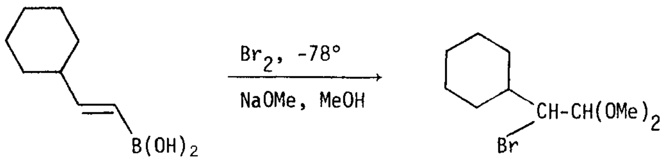
JACS (1975) 97 3848

Also via: Carboxyaldehydes (Section 314)

Section 337 Aldehyde - Ether, Epoxide

$$PhCH_2CH_2CHO + CH_2{=}CHOEt \xrightarrow[\text{2) EtOH}]{\text{1) } (\underline{i}\text{-}PrO)_4Ti,\ TiCl_4} PhCH_2CH_2\underset{\displaystyle O\text{-}\underline{i}\text{-}Pr}{\underset{|}{C}}HCH_2CH(OEt)_2$$ 100%

Chem Lett (1975) 569



~70%

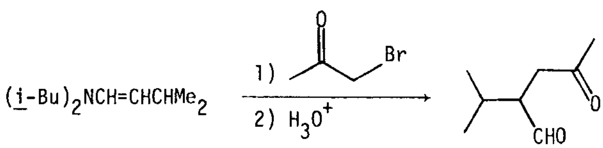
JOC (1975) 40 1189

$$\mathrm{Pr{-}CH_2{-}CH{=}N{-}\underline{t}{-}Bu} \xrightarrow[\text{2) } H_3O^+]{\text{1) NBS}} \mathrm{Pr{-}CBr_2{-}CHO}$$

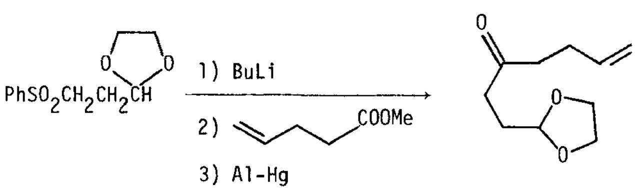
58%

Synthesis (1975) 455

Section 339 Aldehyde - Ketone



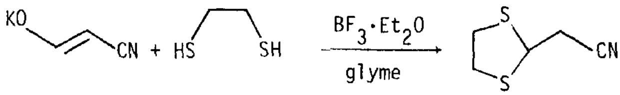
Tetr Lett (1974) 3253



~70%

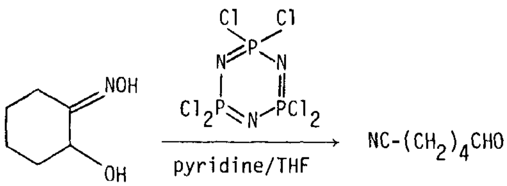
Tetr Lett (1975) 1397

Section 340 Aldehyde - Nitrile



66%

Synth Comm (1974) 4 331

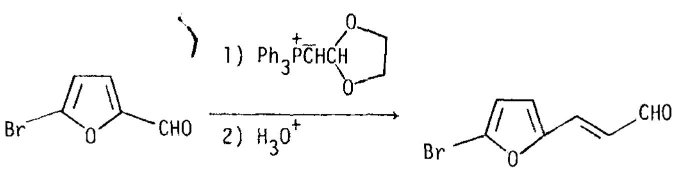


85%

Synthesis (1975) 665

Section 341 Aldehyde - Olefin

For the oxidation of allylic alcohols to olefinic aldehydes see Section 48, Vol. 1 (Aldehydes from Alcohols)



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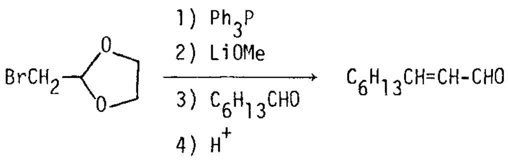
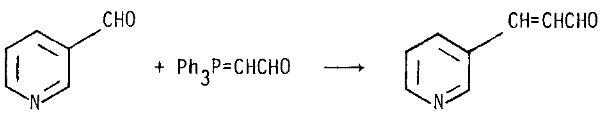
JCS Perkin I (1974) 37



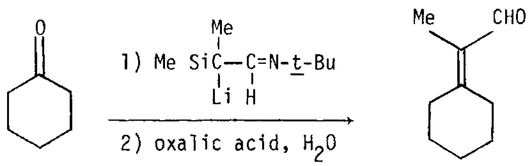
96%

JCS Perkin I (1974) 37



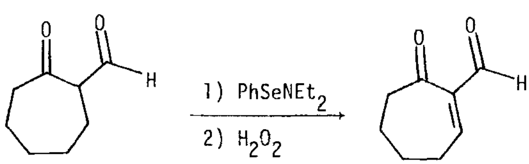
56%

Angew Int Ed (1975) 14 1486



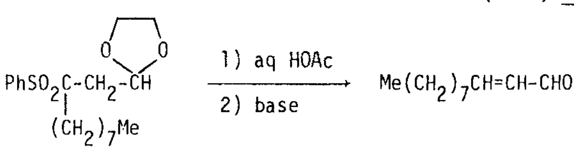
90%

Tetr Lett (1976) 7



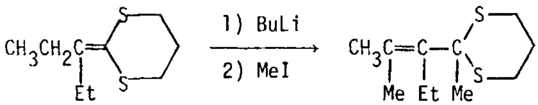
67%

JOC (1975) 40 3313



85%

Tetr Lett (1975) 1007



87%

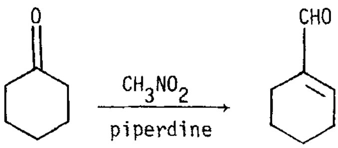
Tetr Lett (1974) 3171

$$\text{MeCH=CH-CH(OMe)}_2 + \text{CH}_2\text{=CHCH=CHOSiMe}_3 \xrightarrow[\text{2) H}_2\text{O}]{\text{1) TiCl}_4\text{, THF}}$$

86%

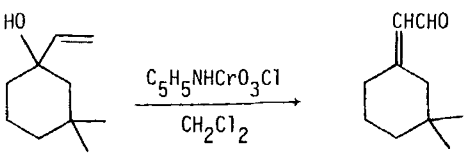
$$\text{MeCH=CHCH(OMe)CH}_2\text{CH=CHCHO}$$

Chem Lett (1975) 319



55%

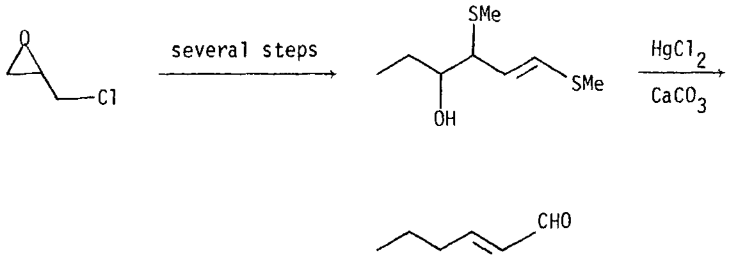
Synthesis (1974) 196



(mixture of E
and Z)

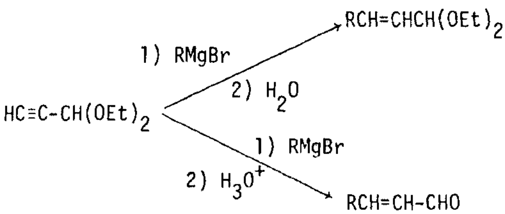
85%

Synth Comm (1976) 6 469



58%

Org Synth (1974) 54 19

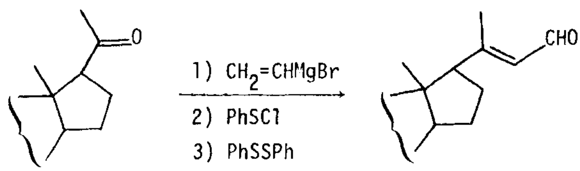


~80%

R = Ph, t-Bu, n-Bu, cyclopentyl

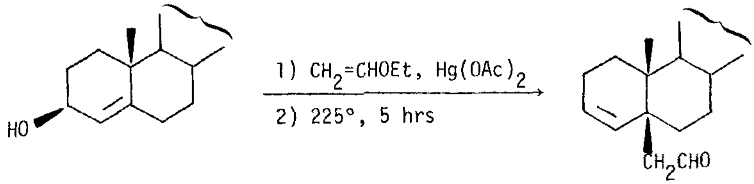
Rec Trav Chim (1976) 95 66

A 1,3-alkylative carbonyl transposition, e.g.:



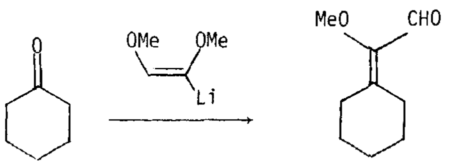
44%

JACS (1975) 97 4018



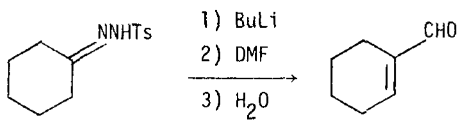
50%

Org Synth (1974) 54 71



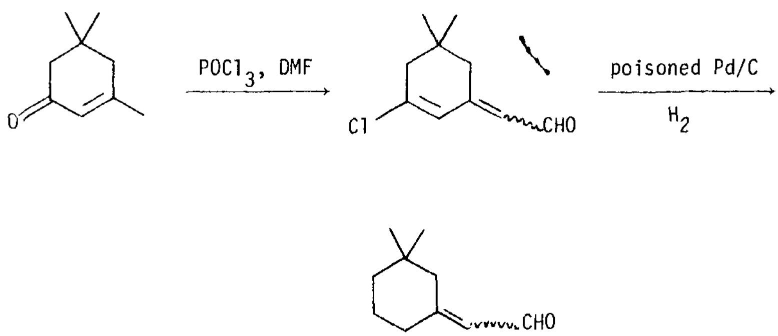
68%

Synth Comm (1976) 6 119



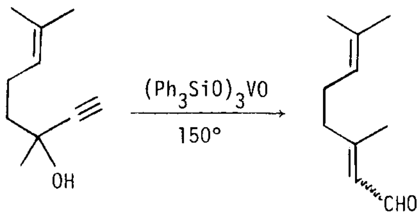
54%

Tetr Lett (1976) 2287



80%

Rec Trav Chim (1976) 95 308



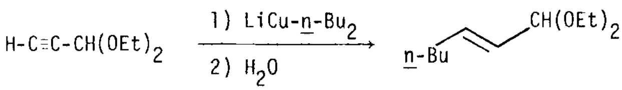
~90%

Helv Chim Acta (1976) 59 1233

$$\underline{t}\text{-BuOCH}_2\text{CH=CH}_2 \xrightarrow[\text{2) MeSSMe}]{\text{1) } \underline{\text{sec}}\text{-BuLi}} \underline{t}\text{-BuO}\underset{\displaystyle \text{SMe}}{\underset{|}{\text{C}}}\text{HCH=CH}_2$$

72%

JACS (1974) 96 5560



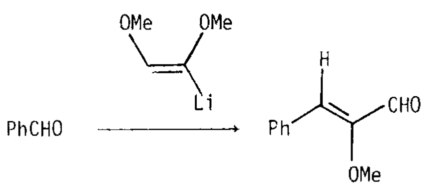
94%

Tetr Lett (1976) 2313

$$\text{PhCOCH}_3 + \text{H}\overset{\displaystyle \text{O}}{\overset{\|}{\text{C}}}\text{-CH=N-NHPh} \xrightarrow[\text{2) hydrolysis}]{\text{1) EtOK, EtOH}} \text{PhCOCH=CH-}\overset{\displaystyle \text{O}}{\overset{\|}{\text{C}}}\text{-H}$$

~80%

Chem Ber (1975) 108 88; 1756

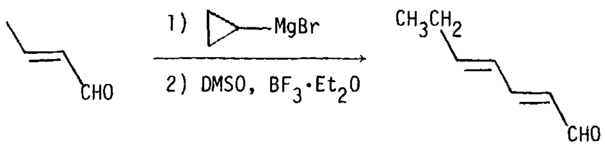


76%

Synth Comm (1976) 6 119

$$OHC\text{-}CHO \xrightarrow[\text{DMF, } 80°]{Ph_3P\text{=}CHCHO} OHC\text{-}(CH\text{=}CH)_2CHO \qquad 77\%$$

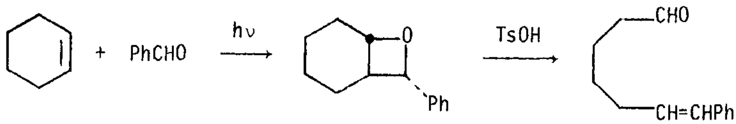
Chem Ber (1974) <u>107</u> 710



Chem Lett (1976) 1297

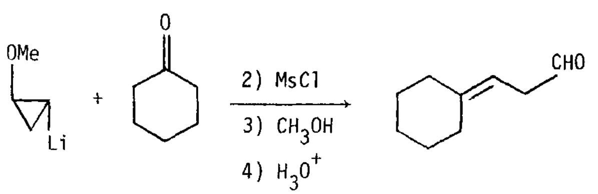
$$\underset{\displaystyle \overset{|}{OEt}}{PhCH}CH_2CH\text{=}CHCHO \xrightarrow[CH_2Cl_2]{\text{DBU}} PhCH\text{=}CH\text{-}CH\text{=}CHCHO \qquad 79\%$$

Chem Lett (1975) 1167



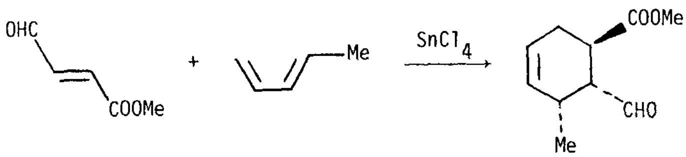
35% 94%

JCS Chem Comm (1975) 206



95%

Tetr Lett (1975) 3685

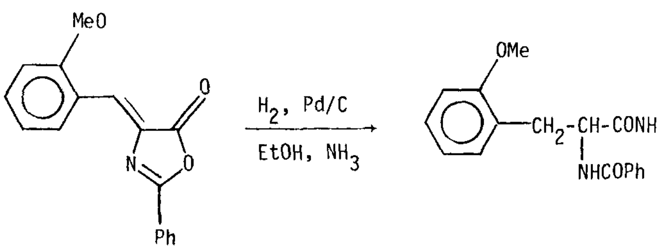


75%

Can J Chem (1976) 54 3304

Also via: β-Hydroxyaldehydes (Section 324)

Section 342 Amide - Amide



61%

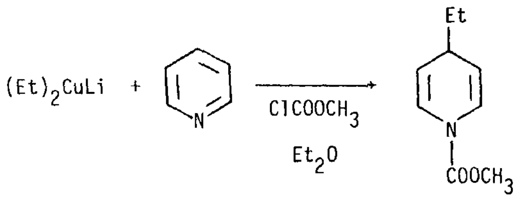
Synth Comm (1976) 6 227

Also via: Dicarboxylic acids (Section 312)
Diamines (Section 350)

Section 343 Amide - Amine

No additional examples

Section 344 Amide - Ester



Can J Chem (1975) 52 3563

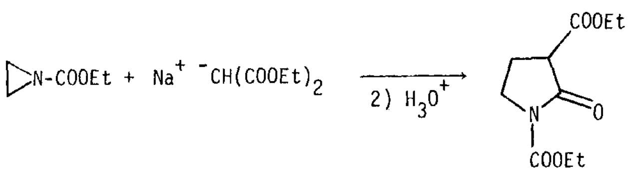
$$Cl_3CCH{=}NCOOEt \; + \; MeMgX \xrightarrow{Et_2O} Cl_3C\underset{\displaystyle Me}{\underset{|}{C}}HNHCOOEt$$ 56%

JCS Perkin I (1975) 2511

$$CH_3CH_2(CH_2)n\text{-}COOR \; + \; e^- \xrightarrow{CH_3CN} CH_3\underset{\displaystyle NHCOCH_3}{\underset{|}{C}}H\text{-}(CH_2)nCOOR$$ 40-70%

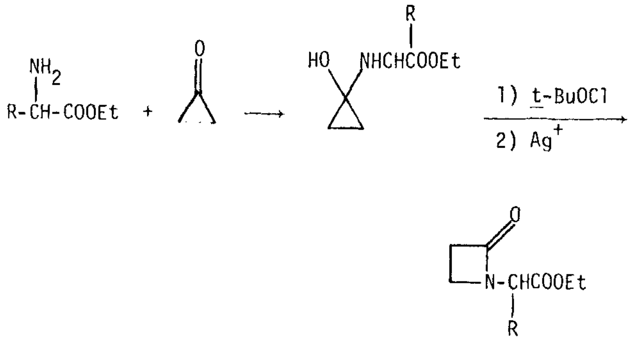
Electrolytic ω-1 oxidation

JOC (1974) 39 369



53%

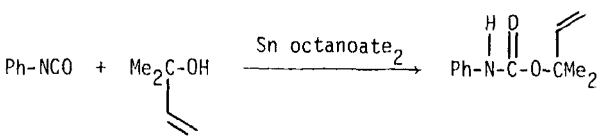
Chem Ber (1975) 108 500



47-70%

R = alkyl, benzyl

JOC (1975) 40 1505



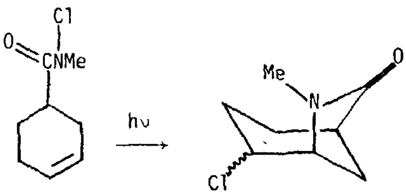
90%

Can J Chem (1976) 54 24

Section 345 Amide - Epoxide

No additional examples

Section 346 Amide - Halide



69%

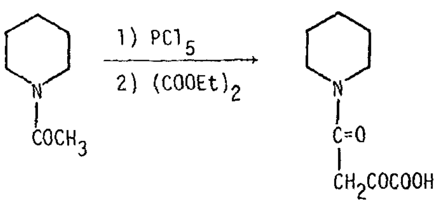
JOC (1975) 40 1287

$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow[\text{(DBI)}]{\text{dibromoisocyanuric acid}} CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHBr$$

83%

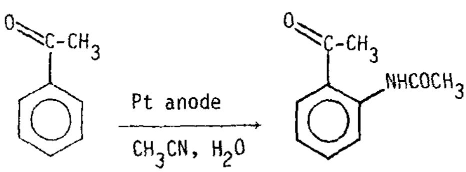
Monatshefte (1975) 106 611

Section 347 Amide - Ketone



45%

Experientia (1976) 32 1491



70%

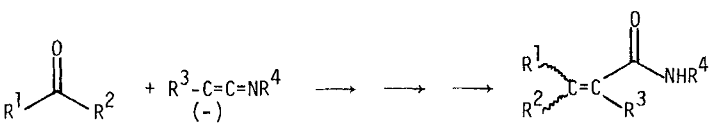
JCS Chem Comm (1975) 262

Also via: Ketoacids (Section 320)

Section 348 Amide - Nitrile

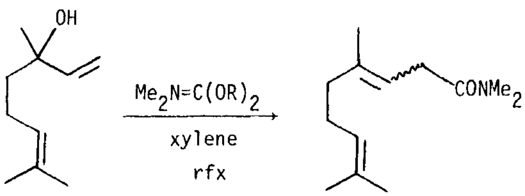
No additional examples

Section 349 Amide - Olefin



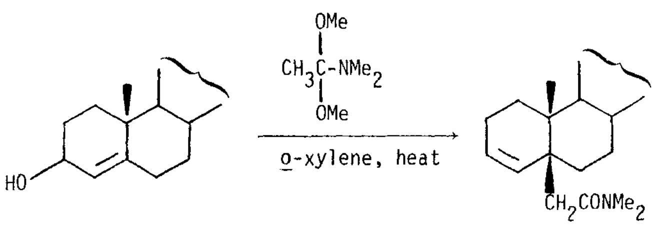
60-70%

Liebigs Ann Chem (1974) 1655



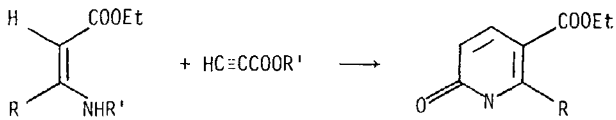
75%

JACS (1974) 96 5563



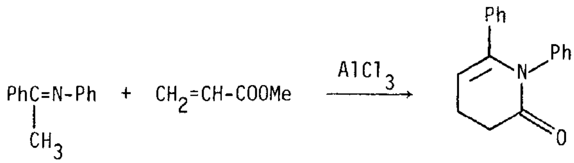
65%

Org Synth (1974) 54 77



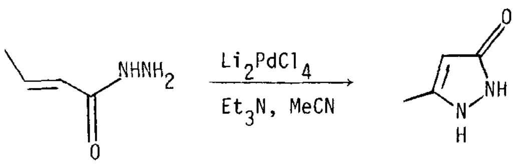
60-85%

Tetr Lett (1974) 30 623



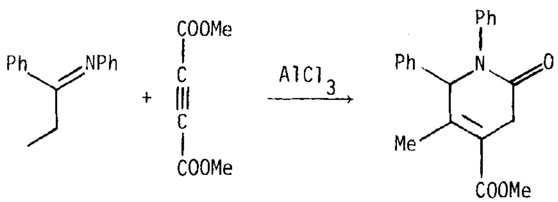
85%

Tetr Lett (1974) 977



40%

Chem and Ind(1976) 1032

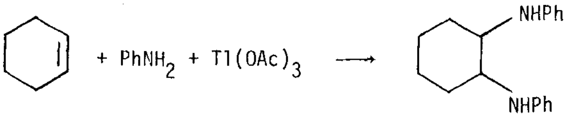


81%

Synthesis (1975) 643

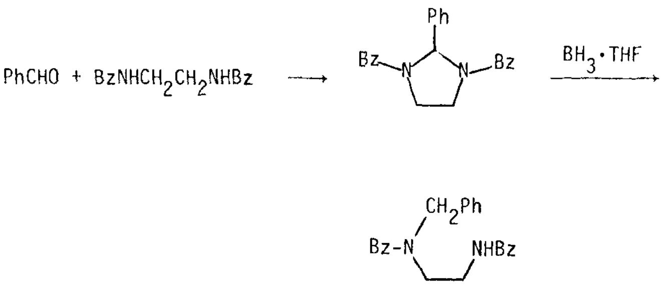
Also via: Olefinic acids (Section 322)

Section 350 Amine - Amine



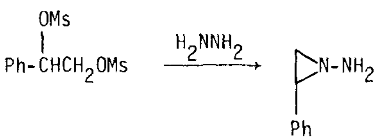
~70%

Synthesis (1974) 504



57%

JOC (1975) 40 558

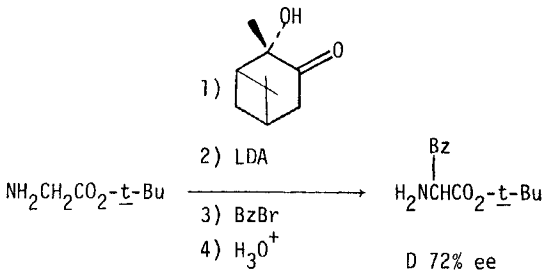


~80%

Org Synth (1976) 55 114

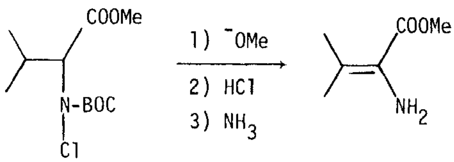
Section 351 Amine - Ester

Direct esterification of aminoacids and aminoacid halides. Other preparations of esters of aminoacids. Esters of aminoalcohols.



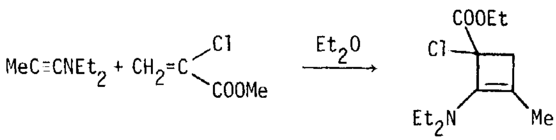
79%

JCS Chem Comm (1976) 136



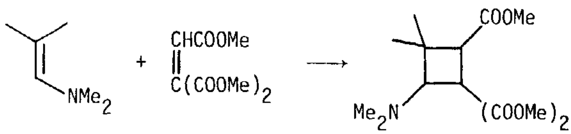
~60%

Angew Int Ed (1976) 15 294



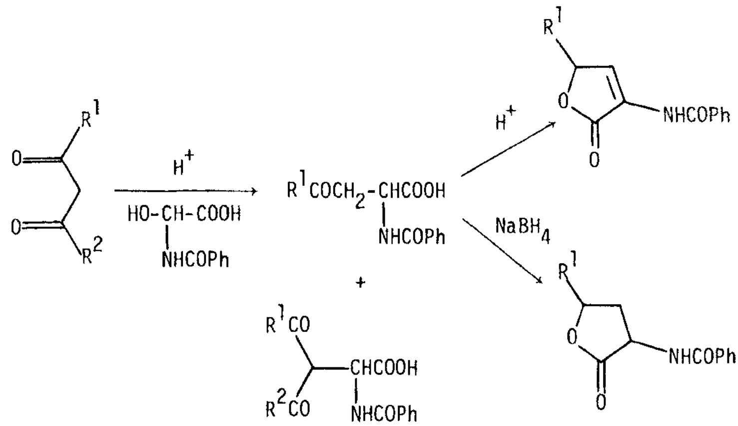
89%

Tetrahedron (1974) 30 3481
Tetr Lett (1974) 1447 with cyclohexenone



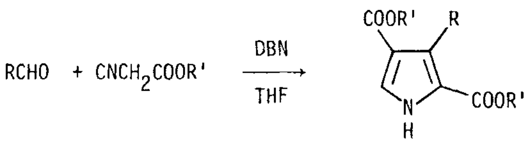
84%

Chem Comm (1974) 587



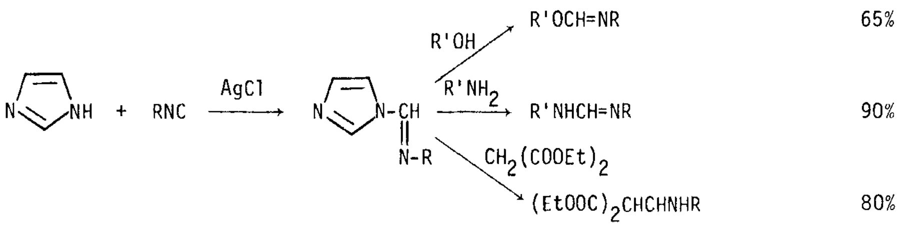
R's = Me, Ph, OMe

JCS Chem Comm (1975) 905

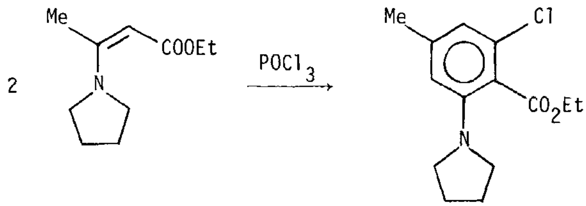


50-71%

JOC (1974) 39 1980



Tetr Lett (1974) 1283



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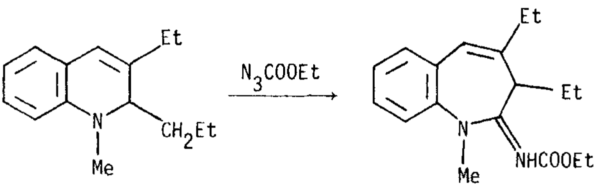
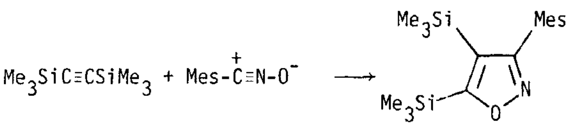
Angew Int Ed (1976) 15 498



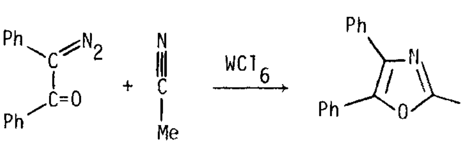
83%

JOC (1976) 41 195

Section 352 Amine - Ether



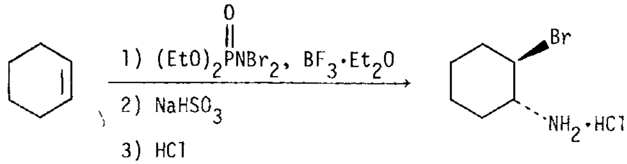
Chem Ber (1974) 107 3717



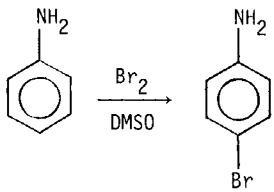
65%

Tetr Lett (1974) 1531

Section 353 Amine - Halide



Angew Int Ed (1976) 15 302



74%
(+6% ortho)

JOC (1975) 40 1867

$$ArNH_2 \xrightarrow{Cl_2O} ArNHCl$$

Aust J Chem (1976) 29 367

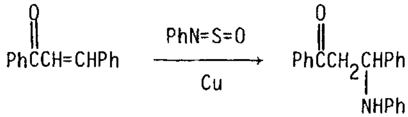
Section 354 Amine - Ketone

$$Me_2\overset{+}{N}{=}CH_2 \quad CF_3COO^- \xrightarrow{TFA} Me_2NCH_2\overset{|}{\underset{|}{C}}\text{-}COMe$$

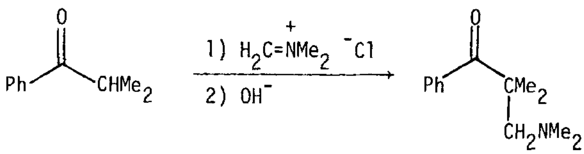
RCOMe +

$$\underline{i}\text{-}Pr_2\overset{+}{N}{=}CH_2ClO_4^- \xrightarrow{CH_3CN} \rangle CHCOCH_2CH_2NR_2$$

JCS Chem Comm (1974) 253

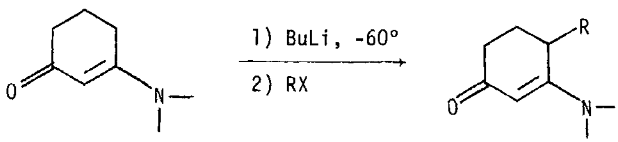


JOC (1976) 41 3811

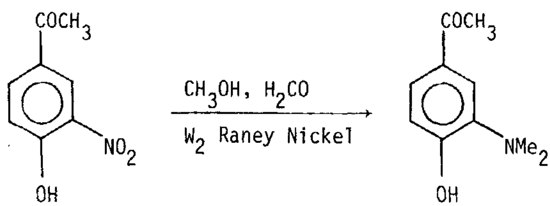


78%

Angew Int Ed (1976) 15 239

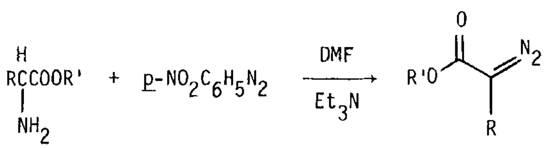


Tetr Lett (1974) 3963



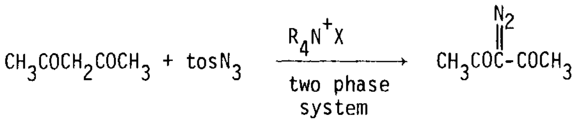
~70%

Indian J Chem (1975) 13 33



40-90%

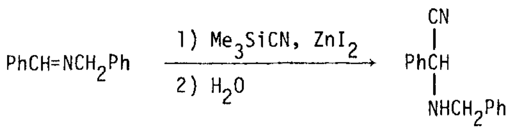
JCS Chem Comm (1974) 558



80%

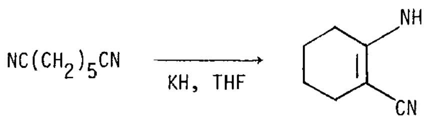
Synthesis (1974) 347
Tetr Lett (1974) 1391 for polymer bound TsN_3

Section 355 Amine - Nitrile



98%

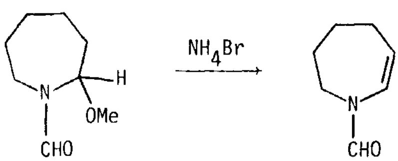
Chem Lett (1975) 331



83%

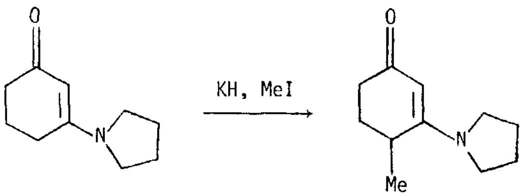
Synthesis (1975) 326

Section 356 Amine - Olefin



89%

Synthesis (1976) 545



~50%

Synthesis (1976) 401

$MeC(O)CH(Cl)CN \xrightarrow{ArNH_2} MeC(NHAr)=C(Cl)CN$ ~60%

Chem Ber (1976) 109 2908

$RC(O)CHClCHO \xrightarrow{HNR'_2} RC(O)CCl=CHNR'_2$ 35-48%

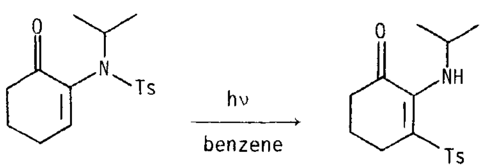
R = Ph, OEt

R'_2 = Me_2, Et_2, $(CH_2)_5$

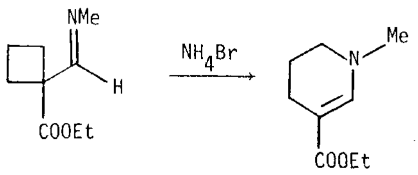
Comptes Rendus C (1976) 282 935

$PhN(Me)CH_2CH=CH_2 \xrightarrow[\text{2) MeI}]{\text{1) BuLi}} PhN(Me)-CH=CHCH_3$ 75%

Synthesis (1974) 672

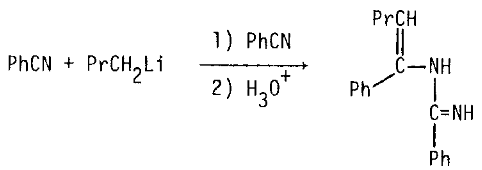


Tetr Lett (1976) 3919



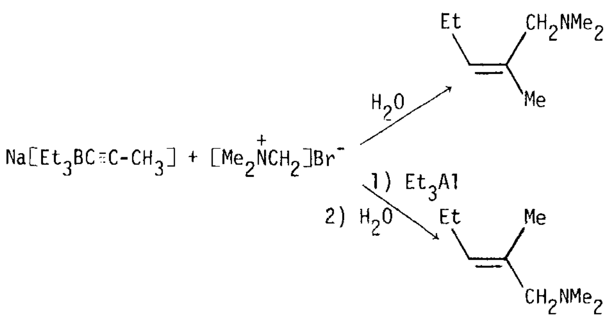
66%

JCS Chem Comm (1975) 682

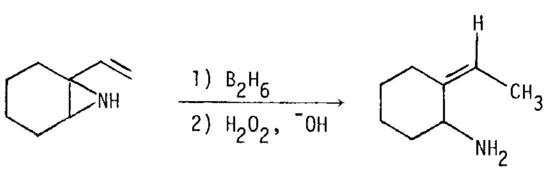


63%

Tetr Lett (1976) 147

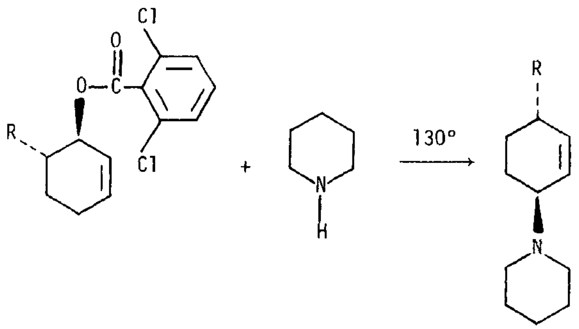


Chem Ber (1975) 108 395



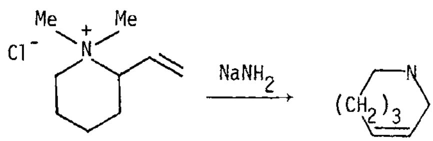
51%

Tetr Lett (1976) 757



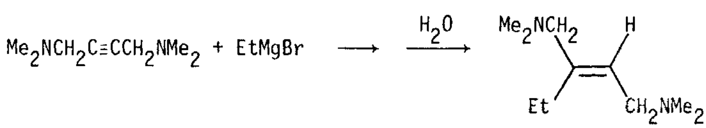
60-73%

JACS (1976) 98 2901



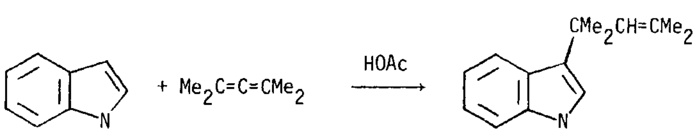
94%

Comptes Rendus C (1976) 282 1003



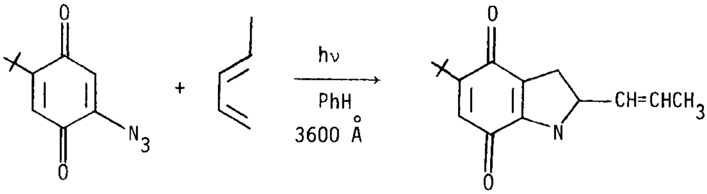
73%

J Organometal Chem (1975) 86 297



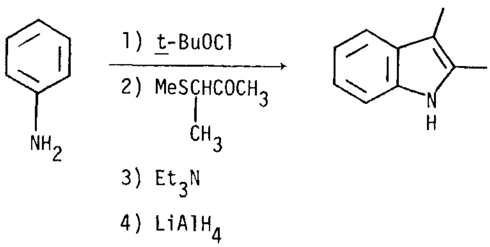
100%

Indian J Chem (1975) 13 1124



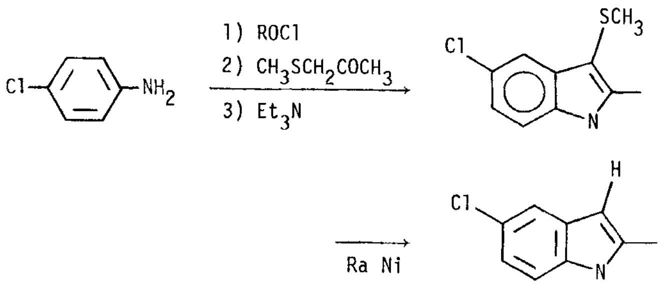
96%

JOC (1974) <u>39</u> 781



85%

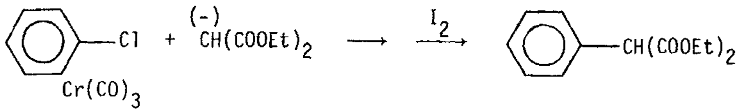
JCS Chem Comm (1974) 201



75%

JACS (1974) <u>96</u> 5495
<u>96</u> 5508 (oxindole)
<u>96</u> 5512

Section 357 Ester - Ester



50-90%

JACS (1974) 96 7091

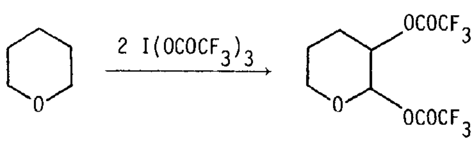
$$Me_2CHCO_2Et \xrightarrow[\text{2) } I_2\text{, THF}]{\text{1) LDA, THF}} \begin{array}{l} Me_2CCOOEt \\ \quad | \\ Me_2C\text{-}COOEt \end{array}$$

85%

Synthesis (1975) 396
Chem Lett (1975) 621 (electrolytic coupling)

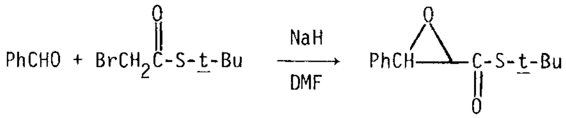
Also via: Dicarboxylic acids (Section 312)
Hydroxyesters (Section 327)
Diols (Section 323)

Section 358 Ester - Ether, Epoxide



42%

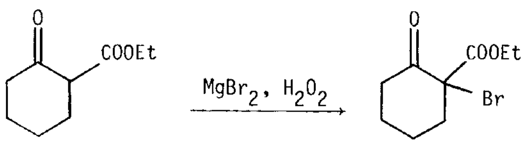
Angew Int Ed (1976) 15 436



67%

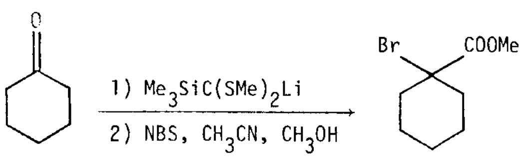
JOC (1974) 39 2938

Section 359 Ester - Halide



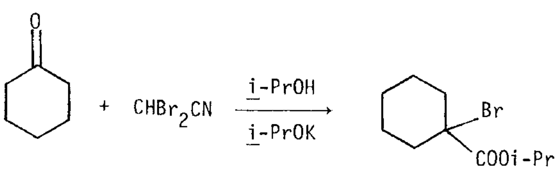
100%

Chem Pharm Bull (1976) 24 820



76%

Synthesis (1976) 121

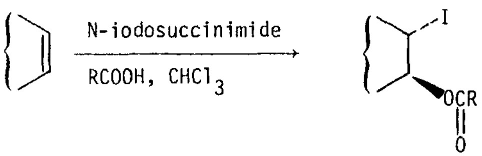


74%

Comptes Rendus (1974) 278 77

$$\text{Me-CH=C(Me)-COOMe} \xrightarrow[\text{2) PhHgCBrCl}_2]{\text{1) Et}_3\text{SiH, Rh(I)}} \text{Me-CH}_2\text{-C(Me)=C(Cl)COOMe} \qquad 92\%$$

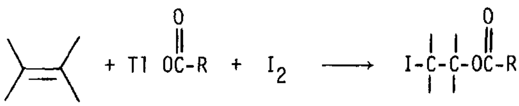
Chem Pharm Bull (1976) 24 1957



70-95%

R = Me, Ar, CF_3, H

Tetr Lett (1976) 3661



high yield

JCS Perkin I (1974) 1858
JCS Perkin I (1974) 1864
(Iodolactonization)

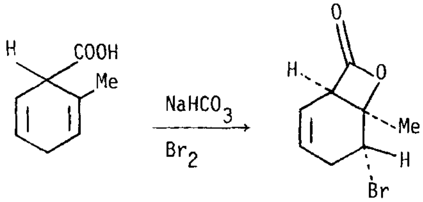
$$\text{RCH(OH)-(CH}_2)_n\text{CH}_2\text{OH} + \text{Ph}_3\text{PBr}_2 \xrightarrow[-20°]{\text{DMF}} \text{RCH(OCHO)-(CH}_2)_n\text{-CH}_2\text{Br} \qquad 50\text{-}90\%$$

Differentiation between OH's in diols

1° → Br

2° → formate ester

Tetr Lett (1974) 913



52%

JOC (1975) 40 2843

Also via: Haloacids (Section 319)
Halohydrins (Section 329)

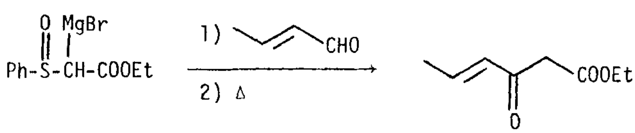
Section 360 Ester - Ketone

$RCOCH_2COR' \xrightarrow{SeO_2}$

or

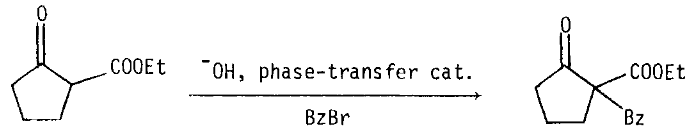
$\xrightarrow[\text{2) DMSO}]{\text{1) } Br_2/Py}$ RCOCOCOR' 70%

Helv Chim Acta (1974) 57 2201



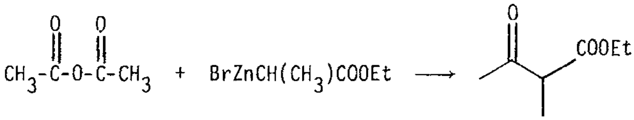
90%

Tetr Lett (1975) 2841



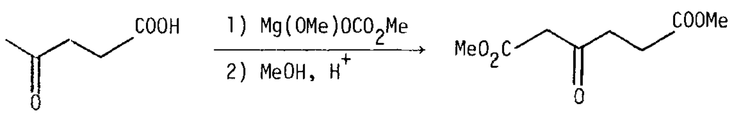
95%

Chem Lett (1976) 1259



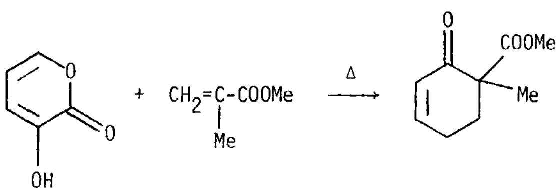
87%

JOC USSR (1975) 11 2360



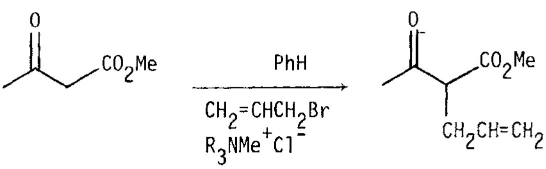
92%

JOC (1974) 39 3144



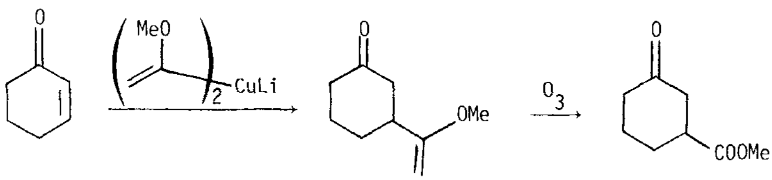
85%

Tetr Lett (1975) 2389

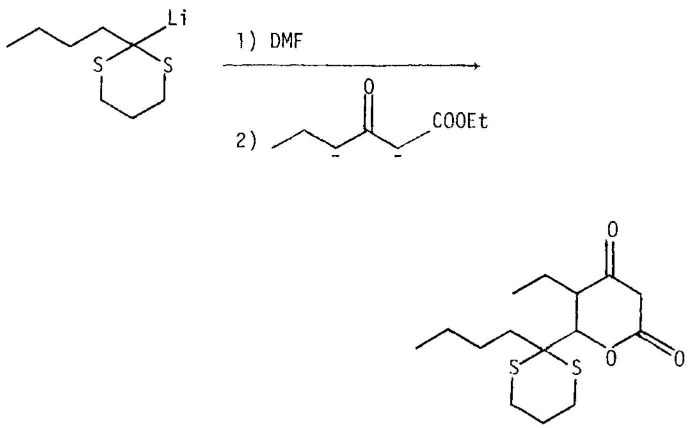


85%

JOC (1974) 39 3271

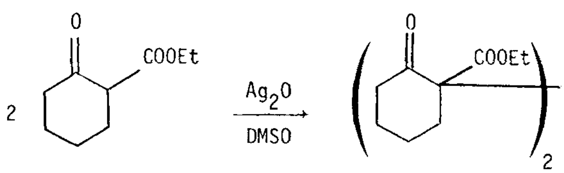


JACS (1975) 97 3822



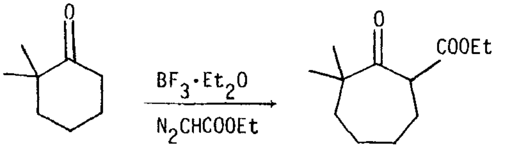
74%

Angew Int Ed (1974) 13 77



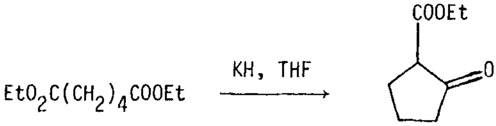
90%

Synth Comm (1976) 6 429



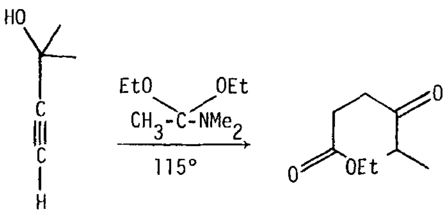
96%

Synth Comm (1975) 5 125



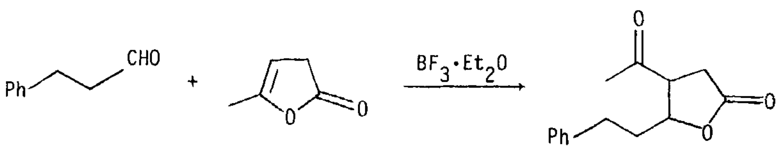
95%

Synthesis (1975) 326



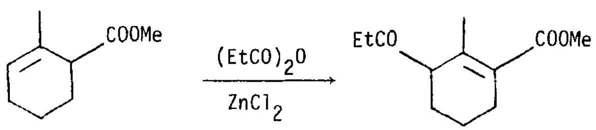
73%

Tetr Lett (1976) 341



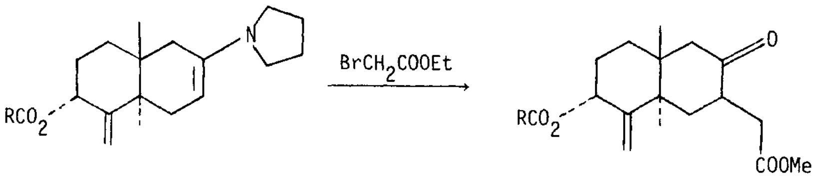
83%

Bull Chem Soc Japan (1976) 49 1055

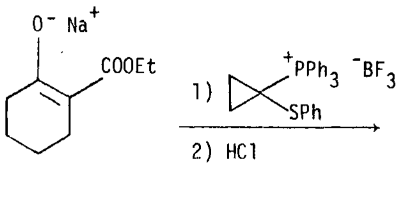


55%

Bull Soc Chim Fr (1975) 274

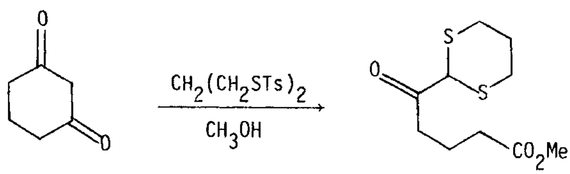


JACS (1974) 96 8102
JOC (1974) 39 1873



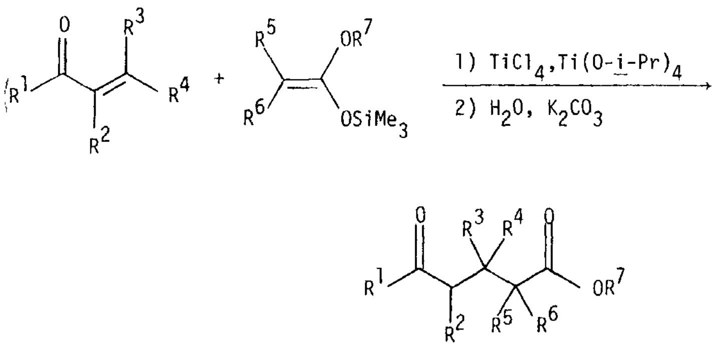
~70%

Tetr Lett (1975) 4531



93%

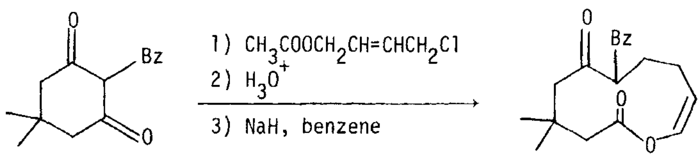
Tetr Lett (1975) 3841



70-98%

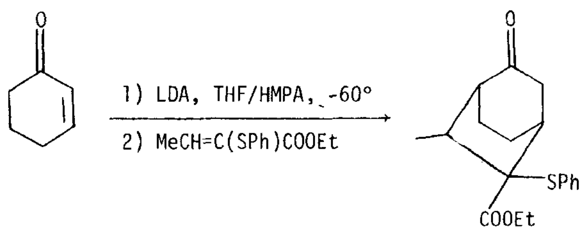
R's = alkyl, Ph

Chem Lett (1976) 163



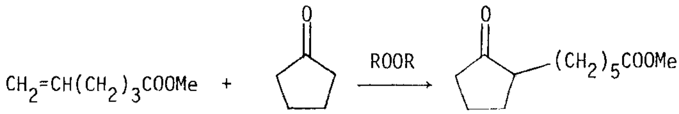
50%

Synthesis (1976) 110



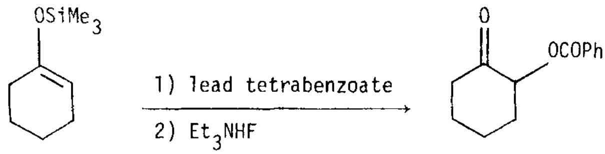
70%

Bull Chem Soc Japan (1975) 48 3769



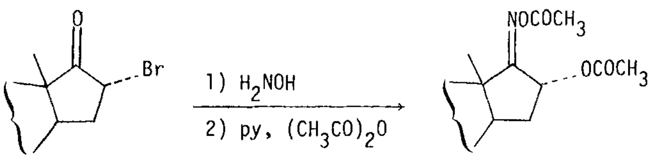
70%

Coll Czech (1976) 41 1698



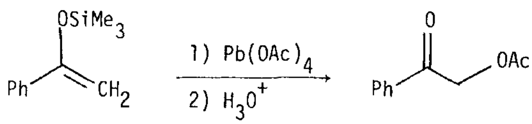
91%

JOC (1976) 41 1673



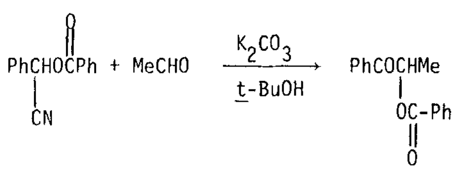
~80%

Bull Soc Chim France (1976) 642



95%

Synth Comm (1976) 6 59



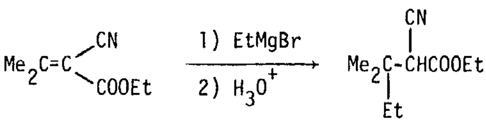
59%

Tetr Lett (1975) 903

Also via: Ketoacids (Section 320)
Hydroxyketones (Section 330)

Section 361 Ester - Nitrile

α, β and higher cyanoesters. Esters of cyanohydrins



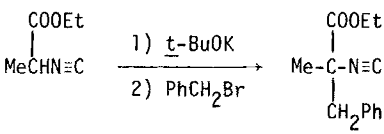
62%

Angew Int Ed (1975) 14 629

$$NCCH_2COOEt + PhCH_2Br \xrightarrow[160°]{LiCl,\ HMPA} NCCH(CH_2Ph)COOEt + NCC(CH_2Ph)_2COOEt$$

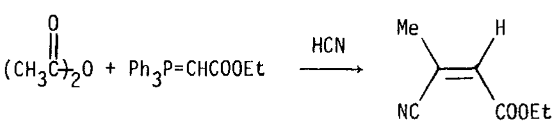
30% 64%

Chem Lett (1975) 1149



79%

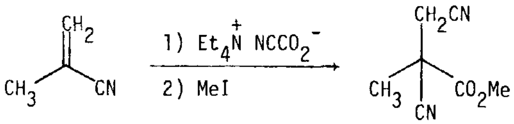
Chem Ber (1975) 108 1580



58%

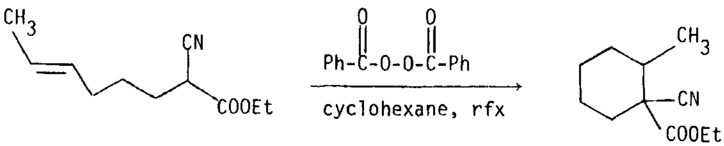
cis-trans mixture

Coll Czech (1976) 41 2040



85%

JCS Perkin I (1976) 1926



75%

Org Synth (1976) 55 57

Also via: Cyanoacids (Section 321)
Hydroxynitriles (Section 331)

Section 362 Ester - Olefin

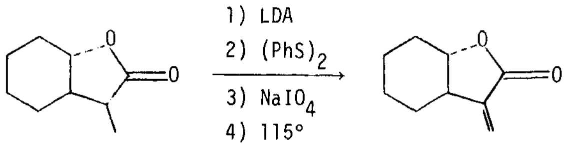
For allylic acetoxylation see section 116, Vol. 1 and 2 (Esters from Hydrides)

Review: "Methods for the Synthesis of α-Methylene Lactones"

Synthesis (1975) 67

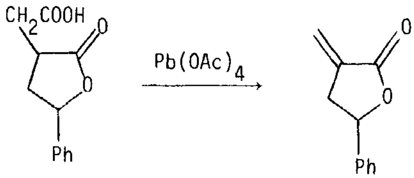
Review: "Synthesis of α-Methylene-γ-Butyrolactones"

Synth Comm (1975) 5 245



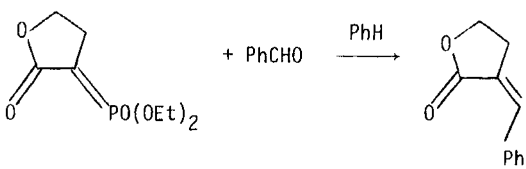
72%

Tetr Lett (1974) 1100
JCS Chem Comm (1974) 135



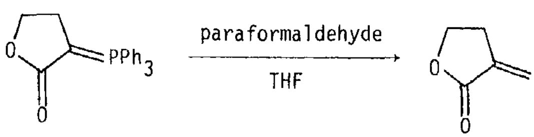
50%

Tetr Lett (1974) 339
Synth Comm (1974) 4 133



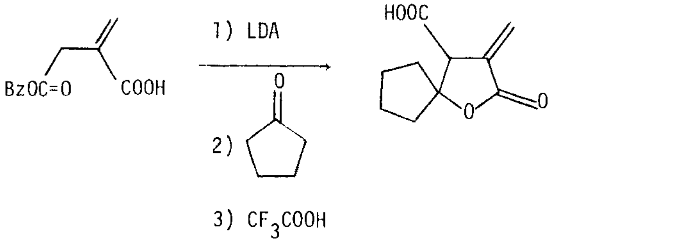
100%

JOC (1974) 39 3236



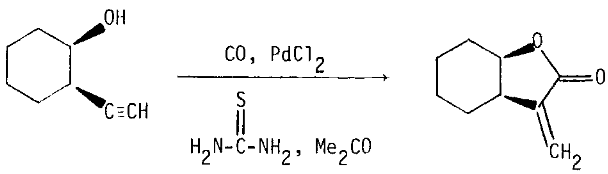
98%

JOC (1974) 39 1958



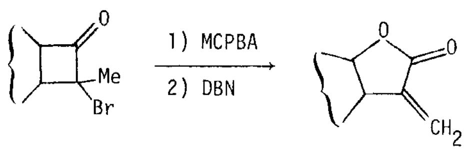
∿50%

Tetr Lett (1975) 4099



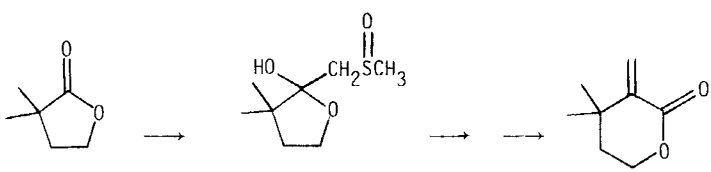
62%

JCS Chem Comm (1976) 907

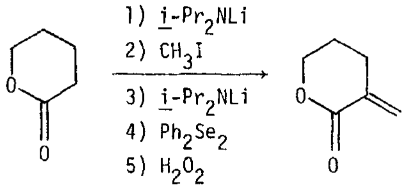


60-80%

JCS Chem Comm (1975) 887

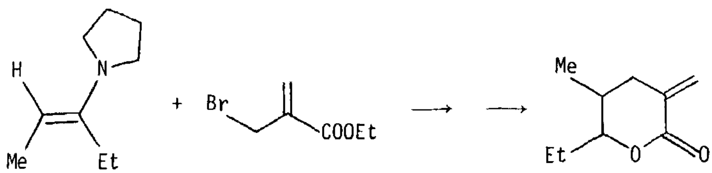


JACS (1975) <u>97</u> 7182

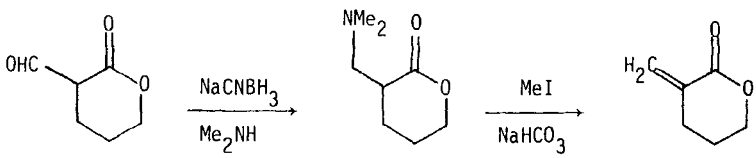


~60%

JOC (1974) 39 121

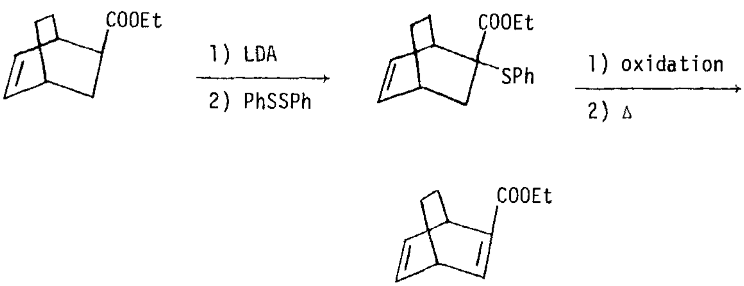


Chem Ber (1974) 107 2853



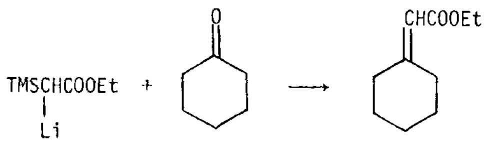
52%

JOC (1975) 40 3474



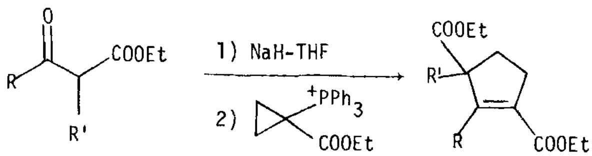
76%

JACS (1976) 98 4887



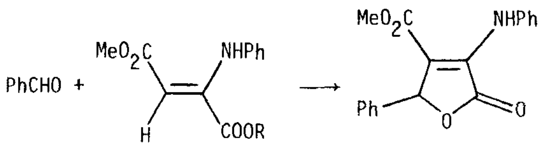
95%

JACS (1974) 96 1620
Tetr Lett (1974) 1403



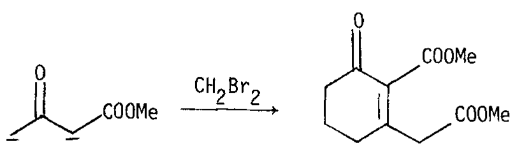
50-90%

JACS (1974) 96 1607



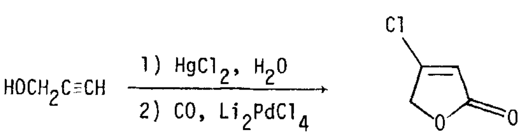
60%

Z Chem (1976) 16 13



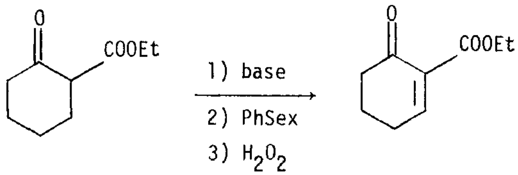
62%

JACS (1974) 96 1082

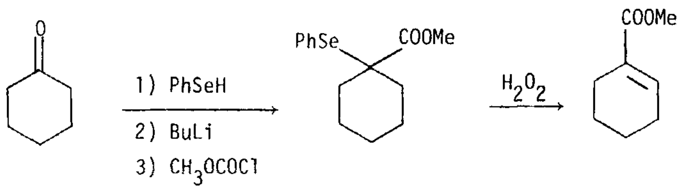


96%

Tetr Lett (1976) 4661



JOC (1974) <u>39</u> 2135
<u>39</u> 120
Tetr Lett (1974) 2279



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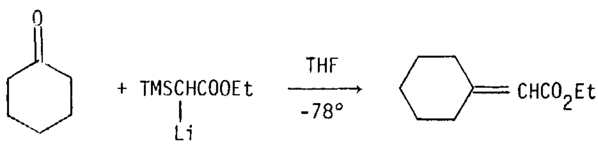
Tetr Lett (1976) 453



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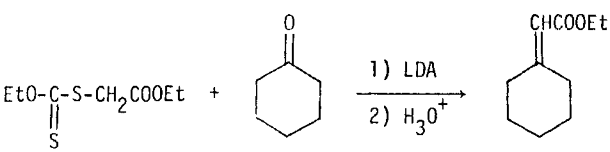
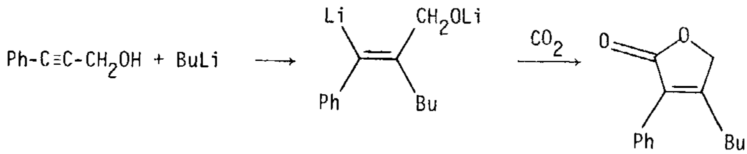
Bull Chem Soc Jap (1974) <u>47</u> 2529



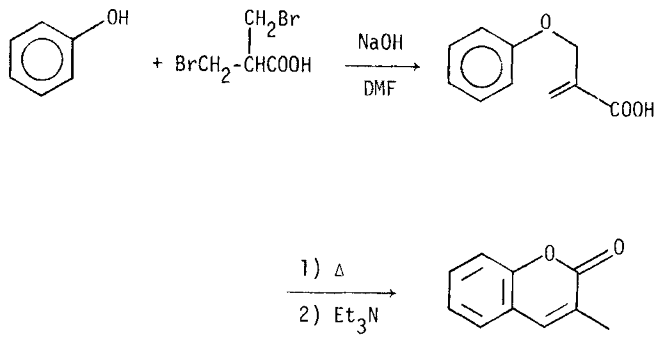
78%

Chem Lett (1976) 917



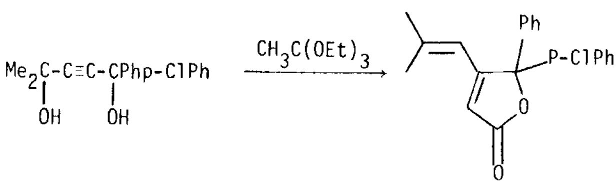
77%

Acta Chem Scand B (1976) 30 521



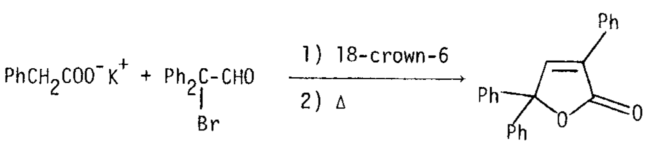
37%

Synthesis (1975) 599



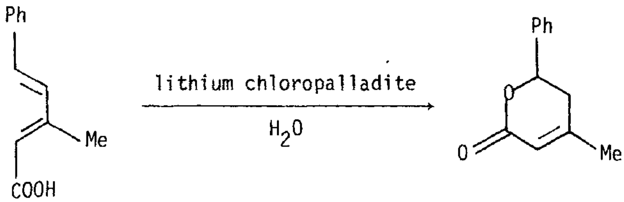
70%

Chem Lett (1975) 939



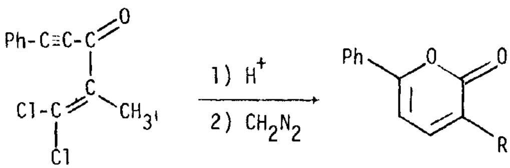
90%

JOC (1975) 40 3139



67%

Bull Chem Soc Japan (1975) 48 1673



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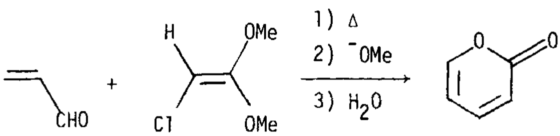
Bull Soc Chim France (1975) 751



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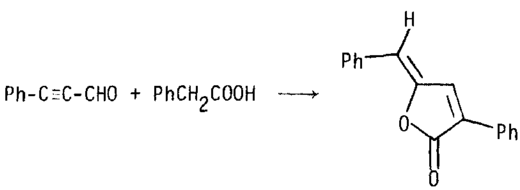
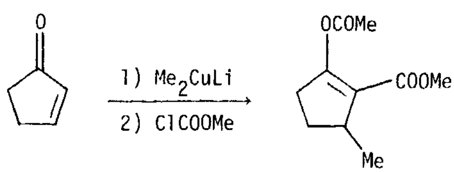
Can J Chem (1975) 53 195



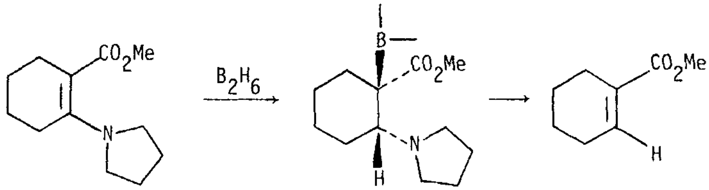
80%

Tetr Lett (1975) 1457



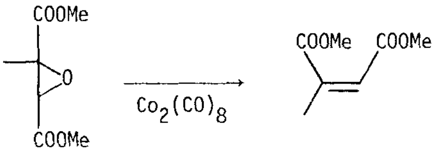
46%

JOC (1975) 40 1488



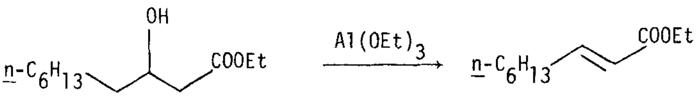
72%

Tetr Lett (1975) 1621

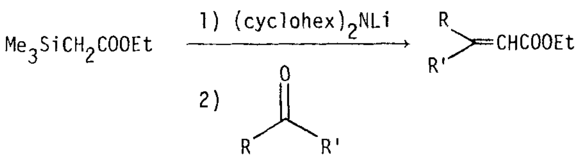


95%

JCS Chem Comm (1974) 384



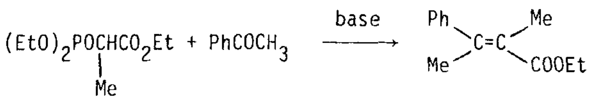
JACS (1974) 96 6153



JACS (1974) 96 1620

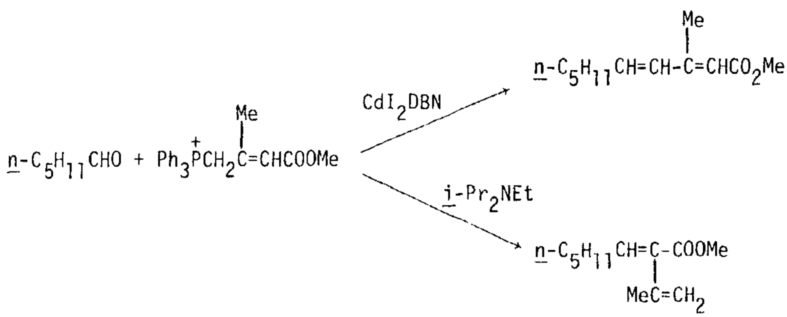
$TMSCH_2CO_2$t-Bu $\xrightarrow[\text{3) } H_3O^+]{\text{1) LDA; 2) PhCHO}}$ PhCH=CHCOOtBu 75%

Tetr Lett (1974) 1403



65%

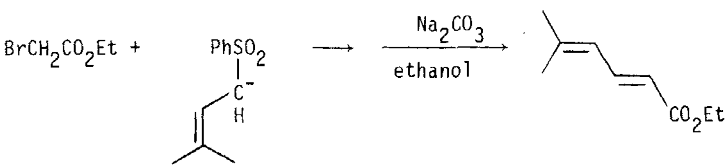
Synthesis (1974) 122
(1974) 869
Tetr Lett (1974) 711



68%

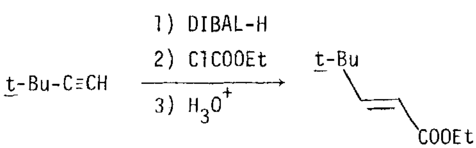
74%

JOC (1974) 39 821



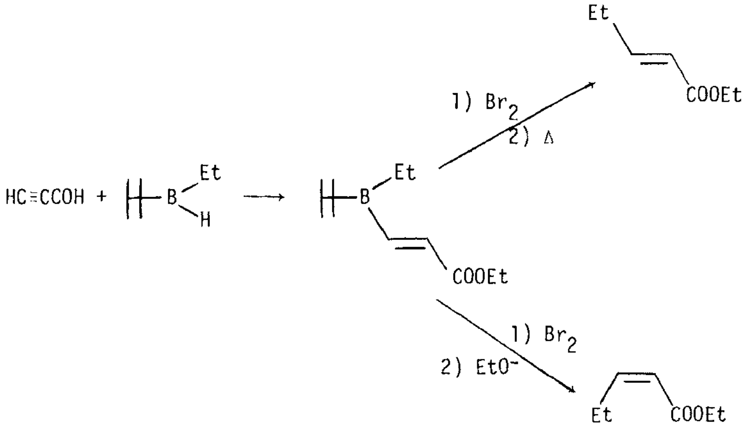
98%

Bull Soc Chim France (1976) 525



72%

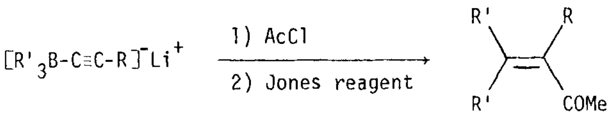
Synthesis (1976) 625



70%

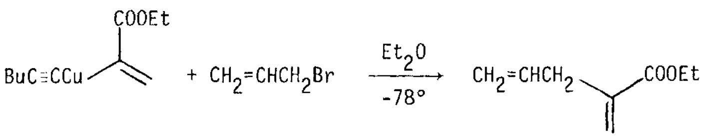
76%

JOC (1974) 39 2321



28-42%

Tetrahedron (1974) 30 835

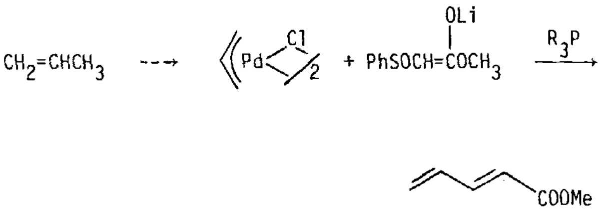


70%

JACS (1974) 96 7138

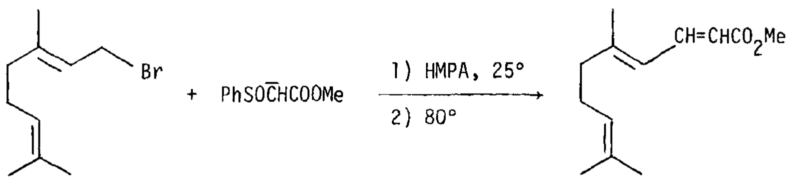
$(EtCO)_2O$ + BrZnCH(Me)COOEt ⟶ EtC(OCOEt)=CMeCOOEt 76%

JOC (USSR) (1975) 11 2360



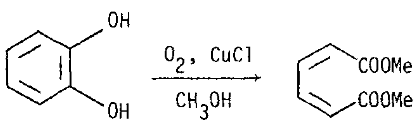
40-90%

JACS (1974) 96 7165
JOC (1974) 39 737

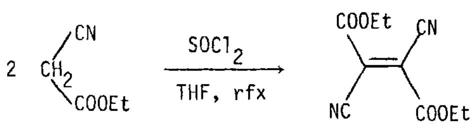


86%

JACS (1974) 96 7165

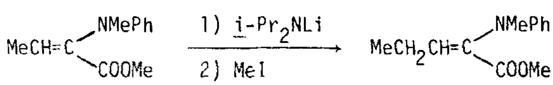


JACS (1974) 96 7349



64%

Synth Comm (1976) 6 185

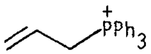


80%

Synthesis (1975) 512

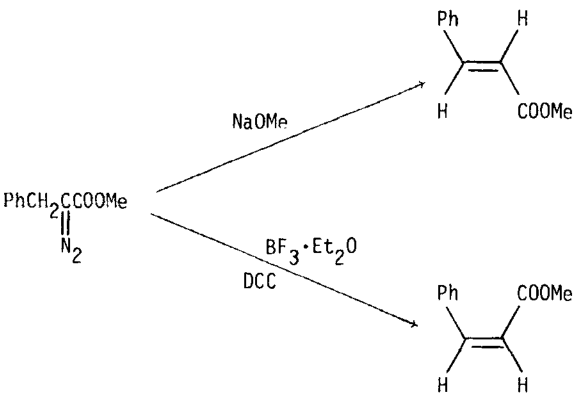
$PhTl(TFA)_2 + HC{\equiv}CCOOMe \xrightarrow[Li_2PdCl_4,\ CuCl_2,\ MeOH]{} PhCH{=}CHCOOMe$ 88%

J Organometal Chem (1975) 98 C8



$\xrightarrow[\text{2) } CH{=}CHCOOMe\ (Cl)\ \text{3) } PhCHO]{\text{1) LDA}}$ $PhCH{=}CHCH{=}CH{-}CH{=}CHCOOEt$ 84%

Tetr Lett (1975) 1359



72%

80%

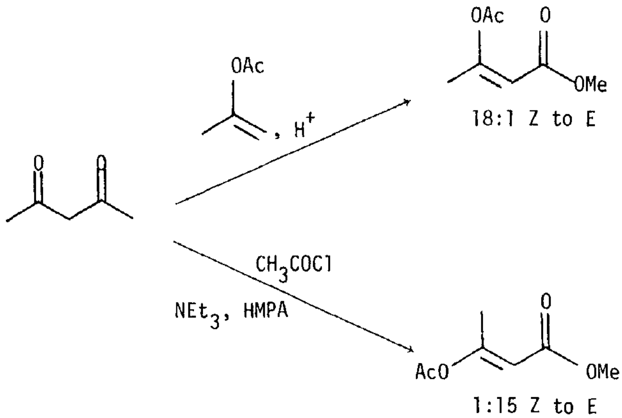
Chem Pharm Bull (1975) 23 229

$CH_2(COMe)_2 + t\text{-}BuNC \xrightarrow[PhH]{Cu_2O} (MeOC)_2C{=}CHN\,t\text{-}Bu$ 34%

J Organometal Chem (1975) 85 395

$PhCH{=}CHHgCl \xrightarrow[PdCl_2]{CO,\ MeOH} PhCH{=}CHCOOMe$ 100%

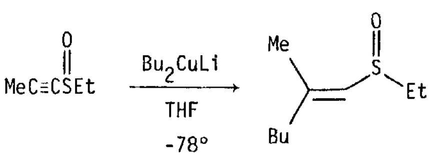
JOC (1975) 40 3237



Tetr Lett (1974) 925

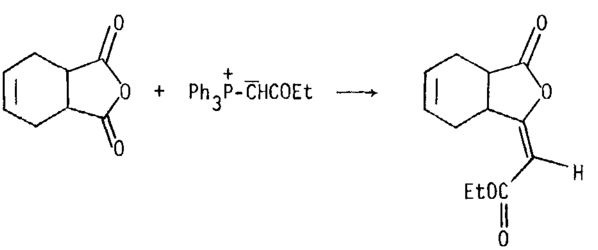
$$EtCOOH + HgOAc_2 + \text{vinyl versate 10} \xrightarrow{H^+} EtCOOCHCH_2$$

Tetrahedron (1974) 30 4205



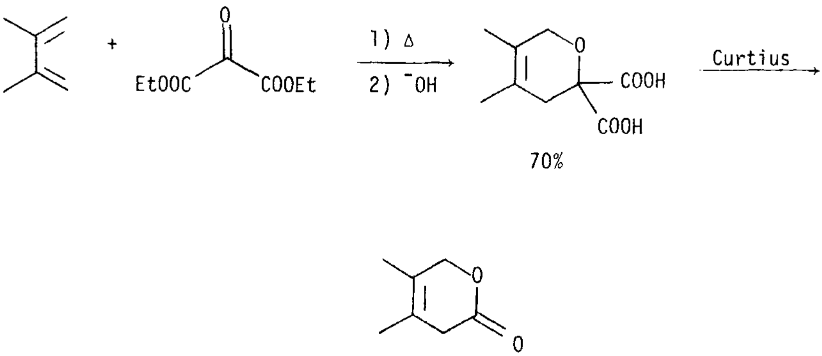
100%

JOC (1974) 39 3174



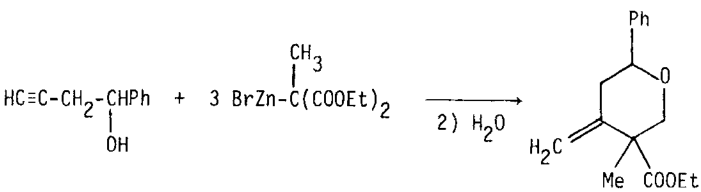
60%

Aust J Chem (1975) 28 2499



72%

JACS (1975) 97 6892



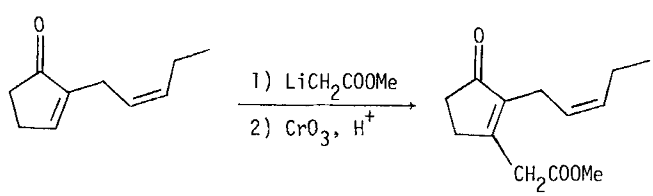
70%

Comptes Rendus C (1975) 280 999

$$MeCH{=}CHCH_2ZnBr + ClCO_2Et \xrightarrow[-15^\circ]{Et_2O} MeCH{=}CHCH_2COOEt$$

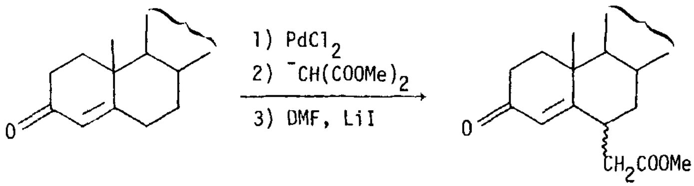
70%

J Organometal Chem (1975) 96 163



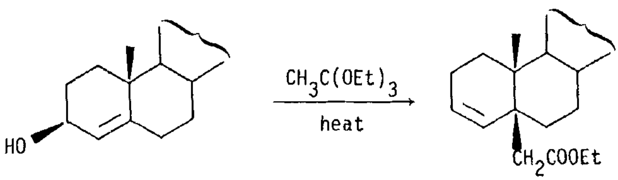
80%

JOC (1974) 39 2637



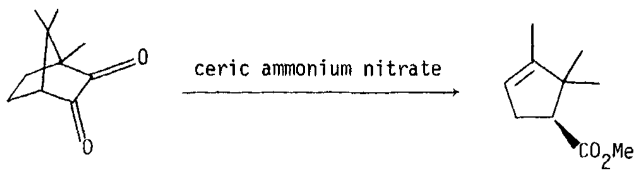
~50%

Tetr Lett (1976) 495



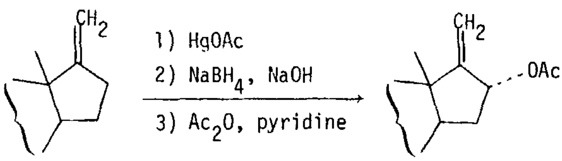
~50%

Org Synth (1974) 54 74



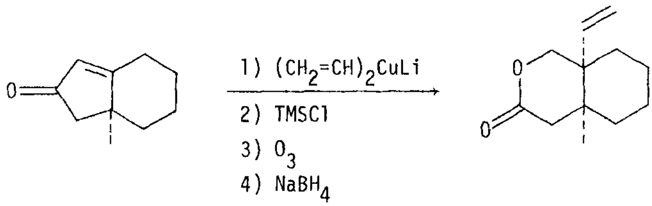
65%

Chem and Ind (1976) 565



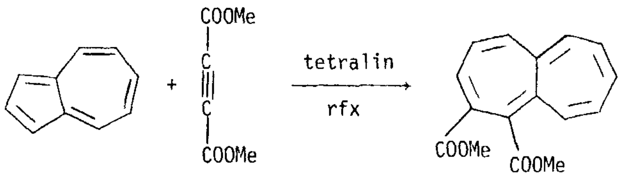
57%

Steroids (1976) 27 197



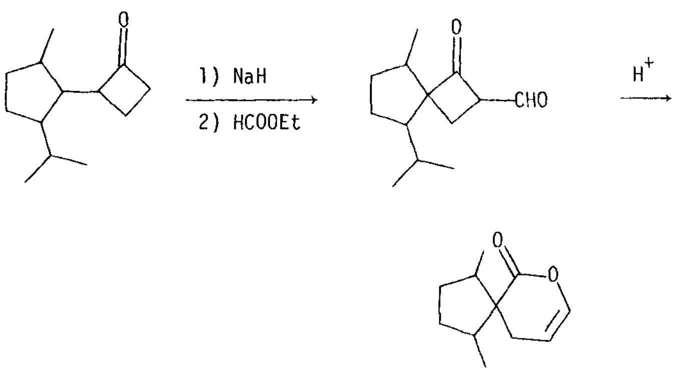
65%

Tetr Lett (1974) 1713



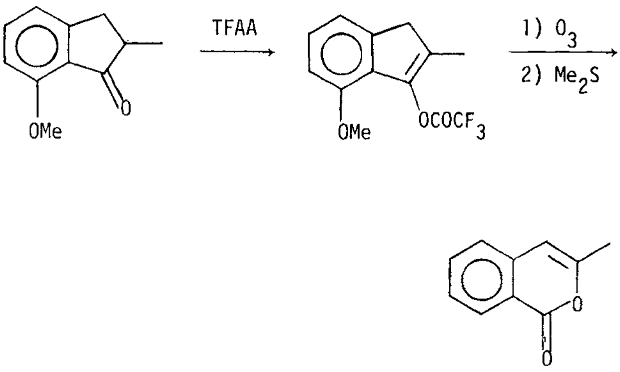
15%

Angew Int Ed (1976) 15 104



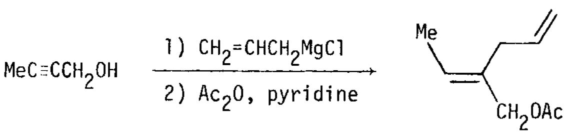
62%

JACS (1975) 97 5873



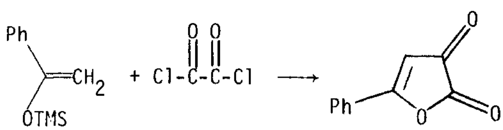
~40%

JCS Perkin I (1976) 1438



75%

Synth Comm (1976) 6 319

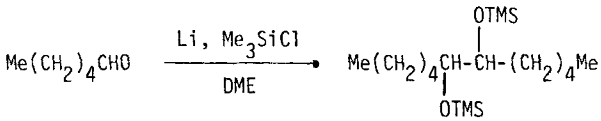


95%

Angew Int Ed (1975) 14 636

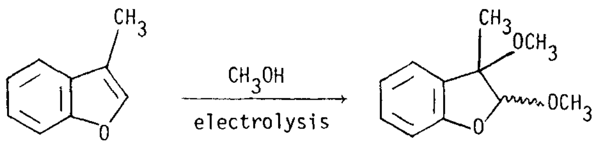
Also via: Acetylenic esters (Section 306)
Olefinic acids (Section 322)
β-Hydroxyesters (Section 327)

Section 363 Ether - Ether



60%

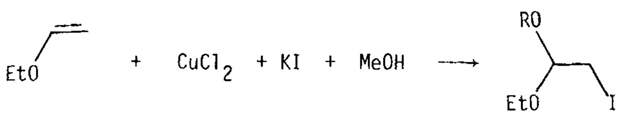
Synthesis (1975) 787



71%

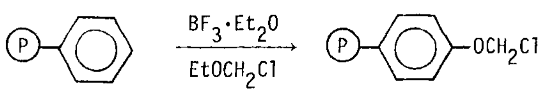
Synthesis (1975) 717

Section 364 Ether - Halide

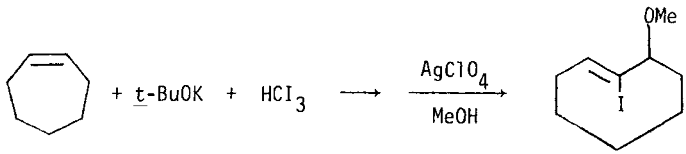


moderate yield

Bull Chem Soc Jap (1974) 47 2818



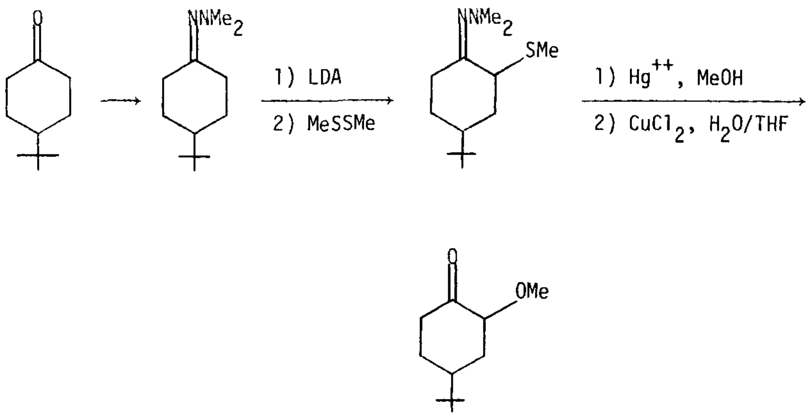
Tetr Lett (1975) 4637



55%

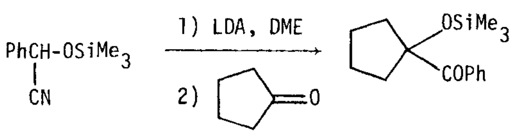
JCS Chem Comm (1974) 196

Section 365 Ether, Epoxide - Ketone



Individual yields >90%

Tetr Lett (1976) 4687

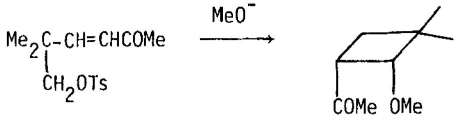


98%

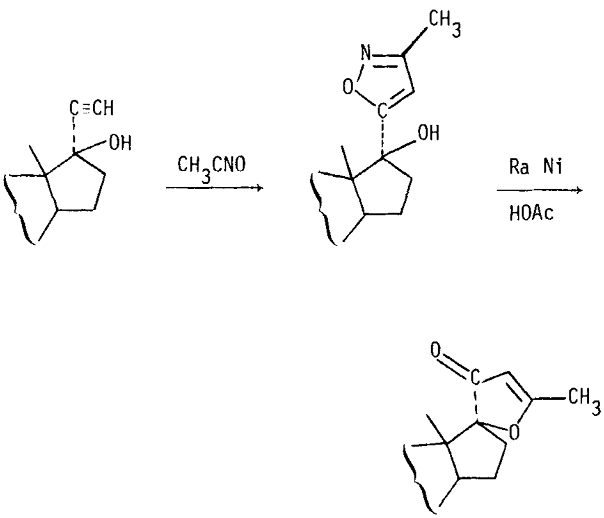
Synthesis (1975) 391

$$RC{\equiv}CCH(OEt)_2 + 2R'_2BH \xrightarrow{NaOH/H_2O} RCH_2\overset{O}{\overset{\|}{C}}CH_2OEt$$

JACS (1974) 96 316

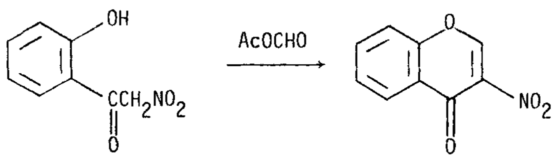


Chem Ber (1974) 107 887



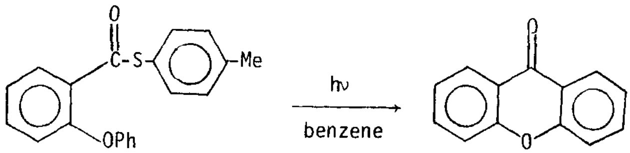
74%

J Gen Chem USSR (1975) 45 2534



∿100%

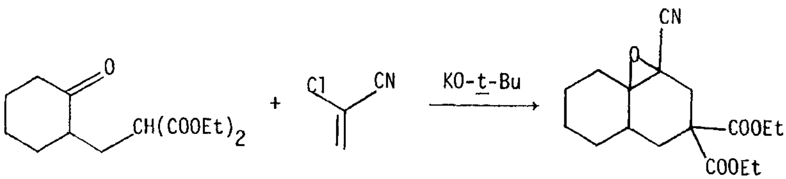
Tetr Lett (1976) 719



84%

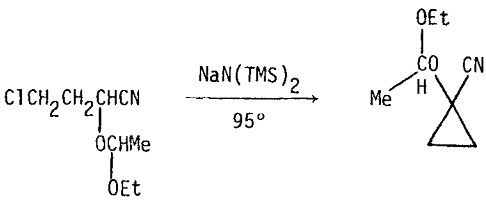
Synthesis (1976) 532

Section 366 Ether, Epoxide - Nitrile



54%

JCS Chem Comm (1975) 95



62%

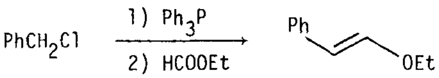
Tetr Lett (1975) 389

Section 367 Ether - Olefin

$$R'\overset{O}{\overset{\|}{C}}CH_2R^2 + EtO_3CH \xrightarrow[\text{cat}]{\text{Amberlyst 15}} R'-\overset{OEt}{\overset{|}{C}}=CHR^2$$

70-100%

Synthesis (1974) 348



90%

JOC (1976) 41 1272

$$PhOH + Ph_3\overset{+}{P}\text{-}CH{=}CH\text{-}\overset{+}{P}Ph_3\ (2Br^-) \xrightarrow[2)\ NaOH/H_2O]{1)\ Et_3N} Ph\text{-}O\text{-}CH{=}CH_2$$

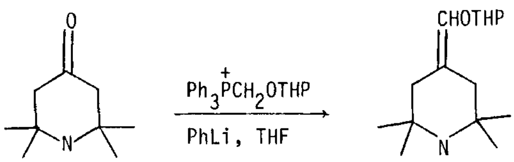
76%

Synthesis (1975) 736

$$CH_2{=}CH\text{-}CH_2OTHP \xrightarrow[\underline{sec}\text{-}BuLi;\ 2)\ MeI]{1)\ \underline{t}\text{-}BuOK} CH_3CH{=}C(OTHP)Me$$

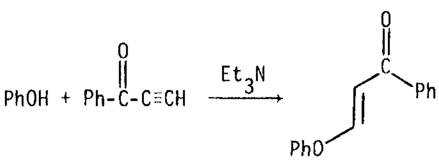
83%

Synthesis (1974) 888



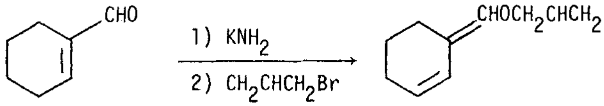
85%

Tetrahedron (1975) 31 89



75%

Indian J Chem (1975) 13 852

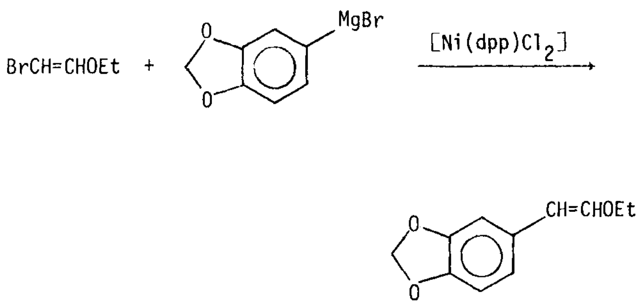


90%

Tetr Lett (1974) 1653

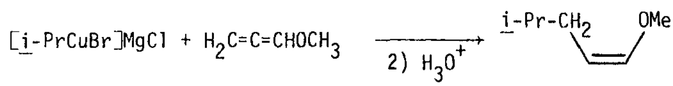
$MeSC{\equiv}CCH_2OMe \xrightarrow[\text{2) EtBr}]{\text{1) } \underline{i}\text{-}Pr_2NLi} MeSC(Et){=}C{=}CHOMe$ 93%

Tetr Lett (1975) 1741



77%

Chem Lett (1976) 1237

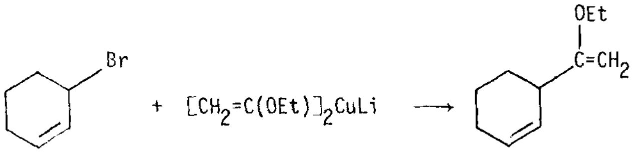


no yield

Tetr Lett (1976) 947

$\underline{i}\text{-}PrCOC(Me)_2CO_2TMS \xrightarrow{250^\circ} \underline{i}\text{-}PrC(OTMS){=}CMe_2$ 80%

JACS (1975) 97 1619



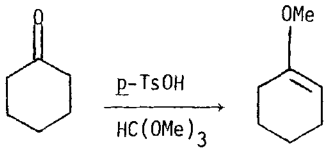
74%

JCS Chem Comm (1975) 519

$$CH_2{=}CHCH(OEt)_2 \xrightarrow[Et_2O]{\underline{n}\text{-BuMgX, CuBr}} \underline{n}\text{-BuCH}_2CH{=}CHOEt$$

83%

Tetr Lett (1975) 3833



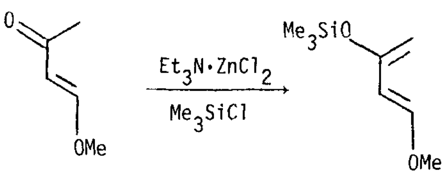
95%

Synthesis (1974) 38

$$CH_2{=}CH\text{-}CH_2OSiEt_3 \xrightarrow[\text{2) MeI}]{\text{1) }\underline{\text{sec}}\text{-BuLi}} Me\text{-}CH_2CH{=}CHOSiEt_3$$

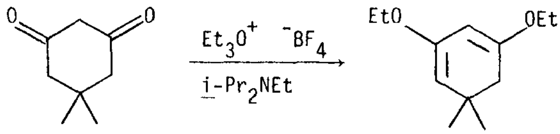
95%

JACS (1974) 96 5561

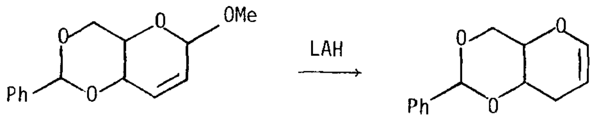


68%

JACS (1974) 96 7807

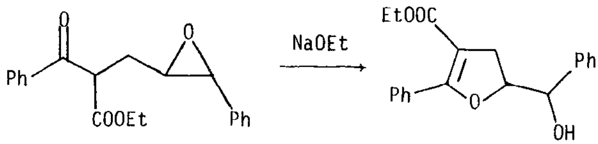


JCS Chem Comm (1975) 644



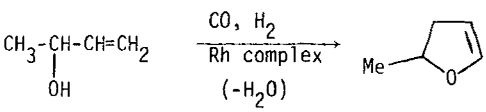
95%

Can J Chem (1975) 53 2005



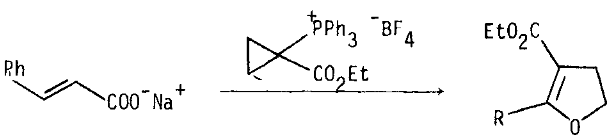
70%

Indian J Chem (1976) 14B 47



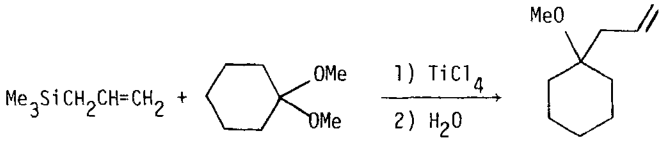
~50%

Gazz Chim Ital (1975) 105 233



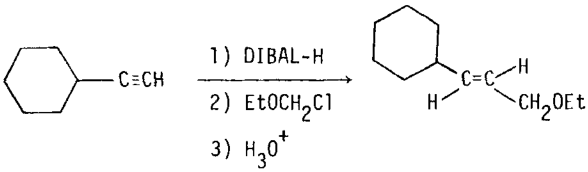
93%

Tetr Lett (1975) 4353



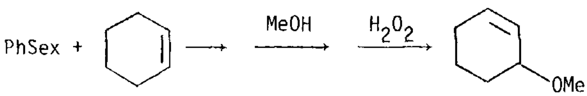
71%

Chem Lett (1976) 941



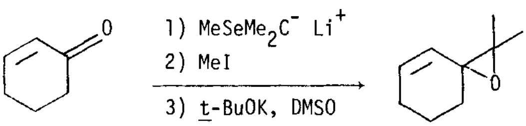
72%

Synthesis (1976) 816



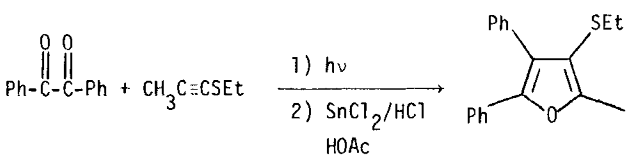
78%

JOC (1974) 39 429



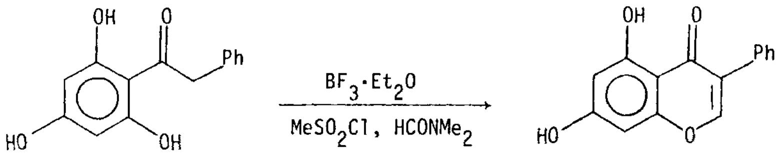
55%

Tetr Lett (1976) 457



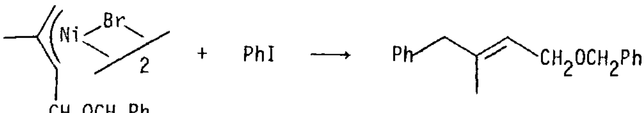
85%

Tetr Lett (1974) 4179



82%

JCS Chem Comm (1976) 78



81%

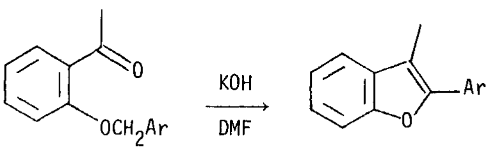
(86:14 E:Z)

Chem Lett (1975) 747

$$\underset{\displaystyle NMe_2}{\overset{}{CH_2CH_2OCHPh_2}} \xrightarrow[\text{3) }\Delta]{\text{1) MeI; 2) anion-exchange resin}} H_2C{=}CHOCHPh_2$$

~80%

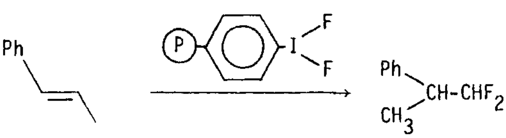
Org Synth (1976) 55 3



90%

Liebig's Ann Chem (1974) 523

Section 368 Halide - Halide



90%

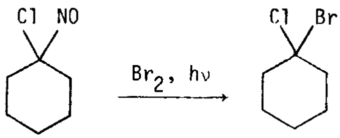
JCS Chem Comm (1975) 715

$PhCH_2CH_2NH_2 \xrightarrow[CuBr_2]{\underline{t}\text{-BuOND}} PhCH_2CHBr_2$ 70%

JCS Chem Comm (1976) 433

$PhCH_2NH_2 \xrightarrow[\text{2) } (CuBr_2 \cdot NO)_2,\ CH_3CN]{\text{1) } CuBr_2} RCHBr_2$

JACS (1976) <u>98</u> 1627



89%

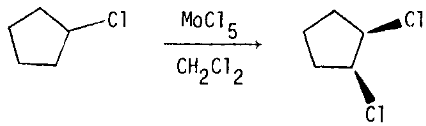
Tetr Lett (1976) 943

$PhN_2Cl + CH_2{=}CCl_2 \xrightarrow[\text{acetone}]{CuCl_2} PhCH_2CCl_3$ 79%

Org React (1976) <u>24</u> 225

$RCH_2CH(Br)CH_3 + SbCl_5 \xrightarrow{CCl_4} RCH(Cl)\text{-}CH(Br)\text{-}CH_3$ 70-90%

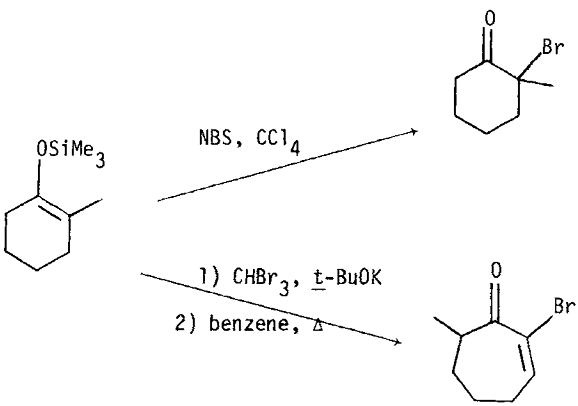
Tetr Lett (1974) 759



88%

JOC (1975) 40 3463

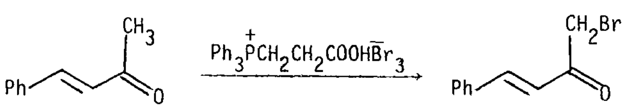
Section 369 Halide - Ketone



70%

16% overall

Synthesis (1976) 194 and 196

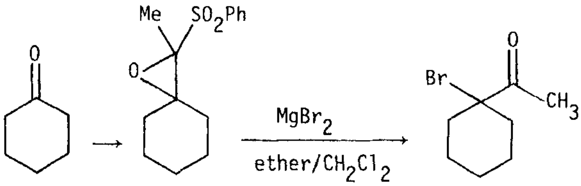


∿60%

Tetr Lett (1975) 373

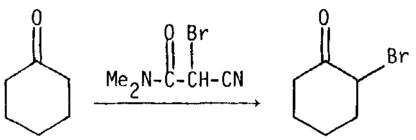
$$Me_2CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow[CH_3OH]{Br_2} Me_2CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2Br$$ ~70%

Org Synth (1976) 55 24



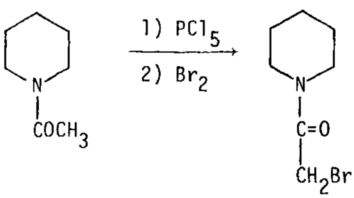
60%

Tetr Lett (1976) 3677



62%

Tetrahedron (1975) 31 231

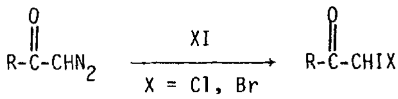


80%

Experientia (1976) 32 1491

$$R'CH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow[\substack{2)\ \underline{t}\text{-}BuOOH \\ 3)\ Br_2}]{1)\ Hg(OAc)_2} RCH(OO\text{-}\underline{t}\text{-}Bu)CHBrCOR'$$ 50-80%

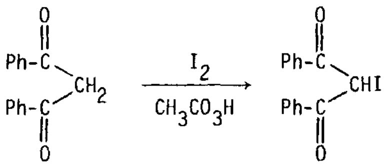
JCS Perkin I (1974) 688



~70%

R = alkyl, aryl

JOC USSR (1976) 12 228



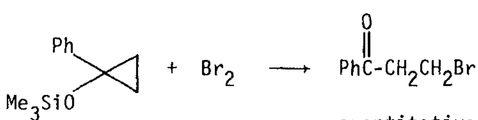
92%

JCS Perkin I (1975) 1285

$$RCOOEt + HCCl_2Li \longrightarrow \xrightarrow{H_3O^+} RCOCHCl_2$$

moderate to high yield

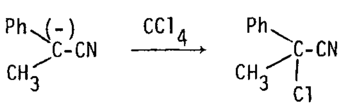
Comptes Rendus (1974) 278 929



quantitative

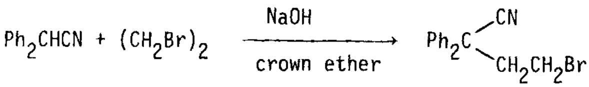
JCS Chem Comm (1974) 1032

Section 370 Halide - Nitrile



80%

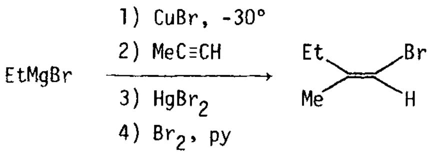
Tetrahedron (1975) 31 1335



75%

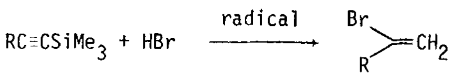
Angew Int Ed (1974) 13 665

Section 371 Halide - Olefin



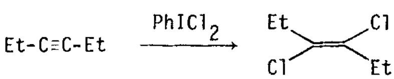
77%

Synthesis (1974) 803



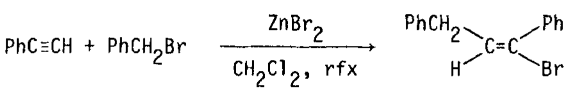
60-95%

JOC (1974) 39 3307



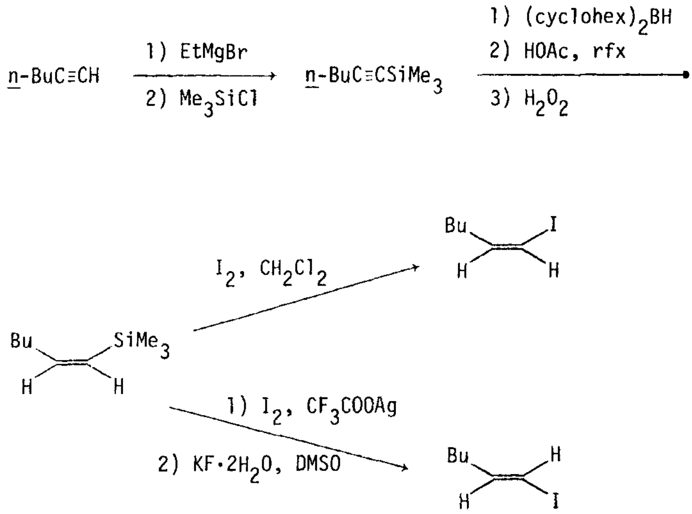
96%

Bull Soc Chim France (1975) 2493



90%

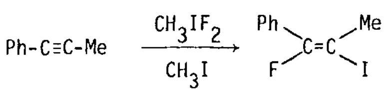
Gazz Chim Ital (1975) 105 495



60%

60%

Tetr Lett (1974) 543

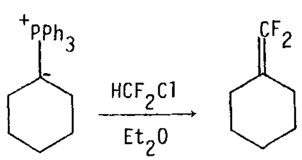


70%

Synthesis (1976) 473

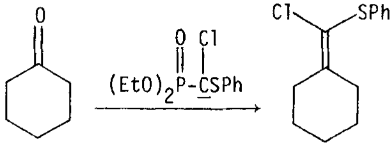
$$\text{polymer-PCl}_2 \xrightarrow{\text{PhCOCH}_3} \text{PhCCl=CH}_2$$

JACS (1974) **96** 6469



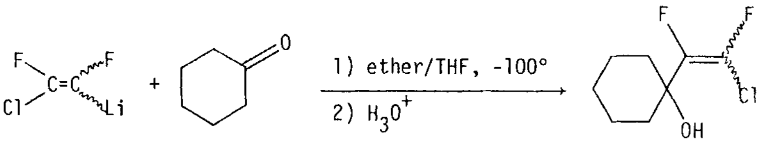
~100%

Tetr Lett (1976) 895



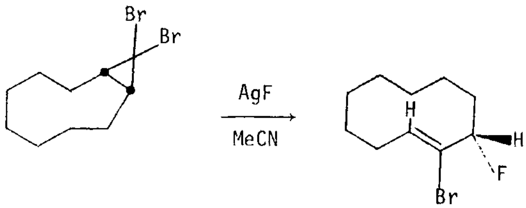
60%

Synthesis (1976) 107



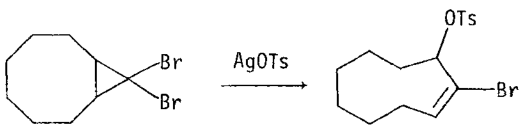
85%

Synthesis (1976) 761



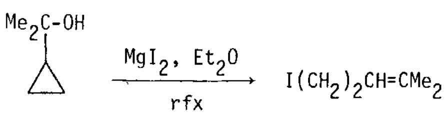
30%

Rec Trav Chim (1976) 95 248



93%

JOC (1976) 41 384

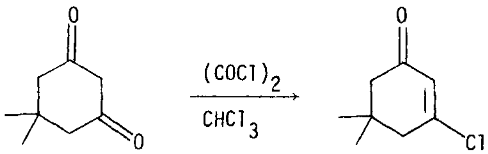


100%

JCS Chem Comm (1975) 303

$PhCOCH_2COOEt + PCl_5 \xrightarrow{PhH} PhCCl{=}CHCOOH$ 50%

JCS Chem Comm (1974) 288



91%

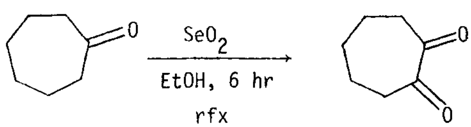
JOC (1976) 41 636

$Me_2CHCOCH_3 \xrightarrow[\text{pyridine}]{(CF_3SO_2)_2O} Me_2C{=}C(OSO_2CF_3)Me + Me_2CHC(OSO_2CF_3){=}CH_2$ 45% total

Org Synth (1974) 54 79

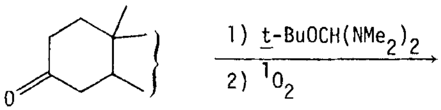
Also via: Acetylenic halides (Section 308)

Section 372 Ketone - Ketone



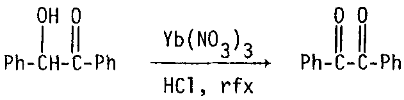
90%

Org React (1976) 24 261



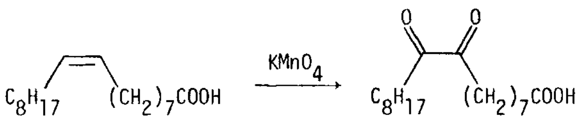
87%

JACS (1976) 98 7868



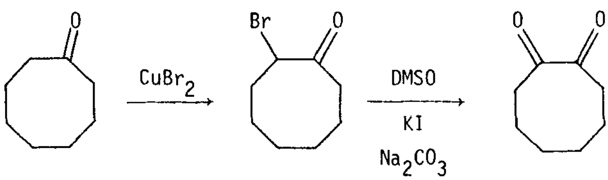
95%

Tetr Lett (1975) 4513



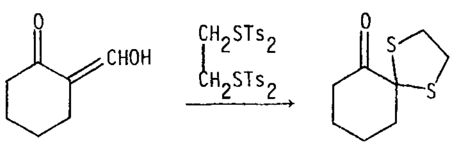
46%

JOC (1974) 39 2314



59%

JOC (1975) 40 1990



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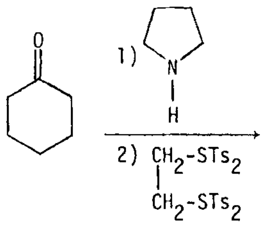
Org Synth (1974) 54 37



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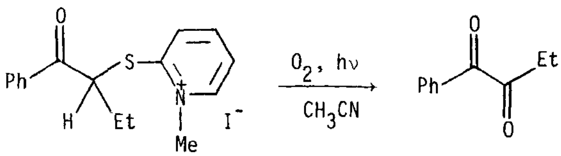
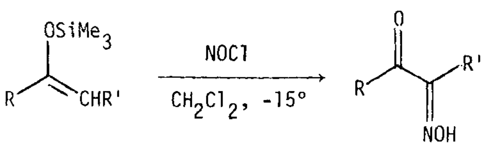
Org Synth (1974) 54 39



80%

Chem Lett (1975) 1033



66-84%

JOC (1974) 39 2558

$$CH_3CH_2COCH_3 + LiNO_2 \xrightarrow[HCl]{EtOH} CH_3\underset{\underset{NOH}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

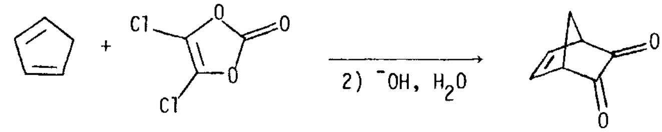
65%

Can J Chem (1974) 52 1760

$$Me_2C{=}\underset{\underset{CN}{|}}{C}-NMe_2 \xrightarrow[2)\ 10\%\ H_2SO_4]{1)\ PhLi} Me_2CHCOCOPh$$

90%

JACS (1975) 97 2276



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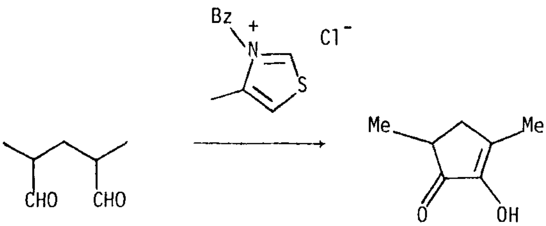
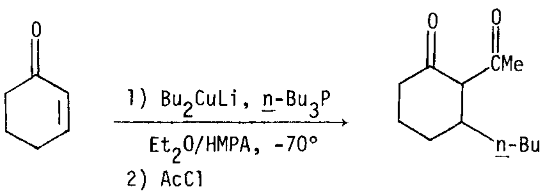
Synthesis (1976) 256



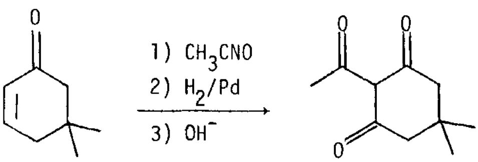
88%

JCS Chem Comm (1976) 804



92%

Tetr Lett (1975) 1535



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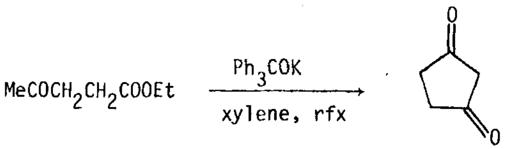
Dokl Chem (1974) 216 404



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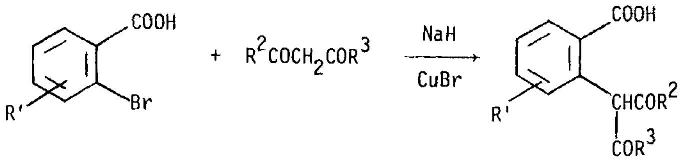
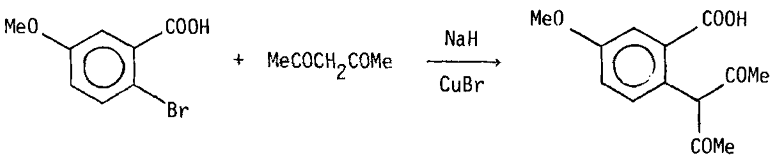
Z Chem (1975) 15 190



(Improved Hurtley reaction)

Tetrahedron (1975) 31 2607
JCS Perkin I (1975) 1267

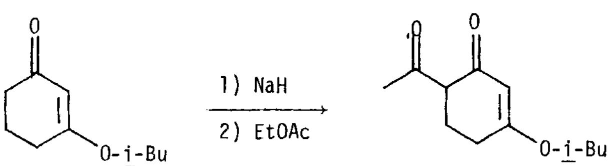


98%

Angew Int Chem (1974) 13 340

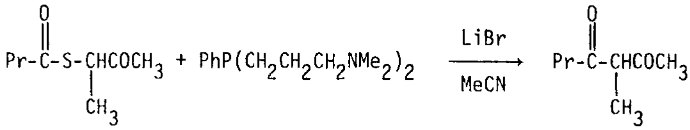
$PhCH_2Br + Ni(acac)_2 \xrightarrow{DMF} MeCOCH(CH_2Ph)COMe$ 69%

Tetr Lett (1975) 1727



78%

Rec Trav Chim (1976) 95 81



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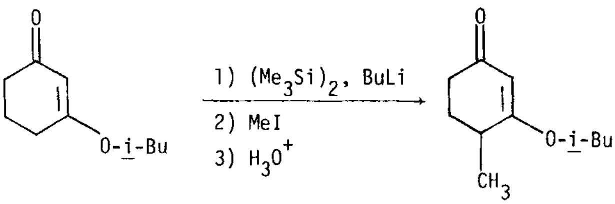
Org Synth (1976) 55 127



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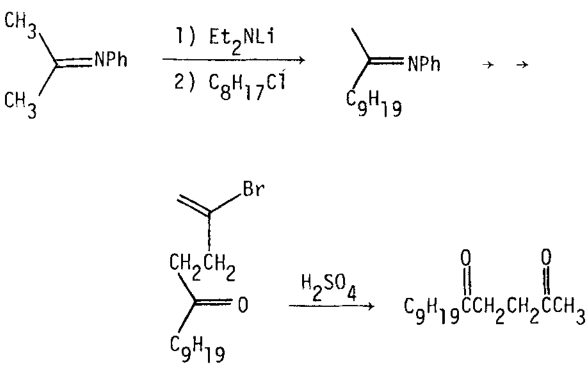
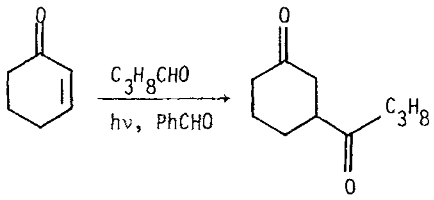
Review: "The Synthesis of 1,4-Diketones"

Aust J Chem (1976) 29 339



Liebigs Ann Chem (1975) 719



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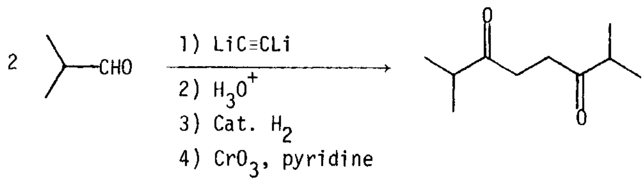
Synth Comm (1976) 6 417



62%

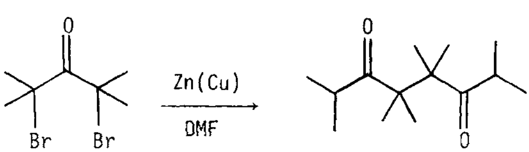
JOC (1975) 40 1131

$PhCHO + H_2C{=}CHCOCH_3 \xrightarrow[DMF,\ \Delta]{NaCN} PhCOCH_2CH_2COCH_3$ 82%

Chem Ber (1974) 107 2453

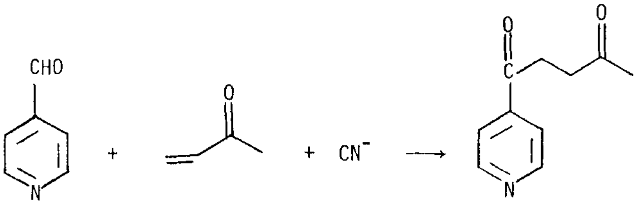
$Et\text{-}\overset{O}{\overset{\|}{C}}H + CH_2{=}CH\overset{O}{\overset{\|}{C}}Me \xrightarrow[\text{thiazolium salt}]{Et_3N} Et\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}\text{-}Me$ 66%

Tetr Lett (1974) 4505



71%

JACS (1974) 96 606

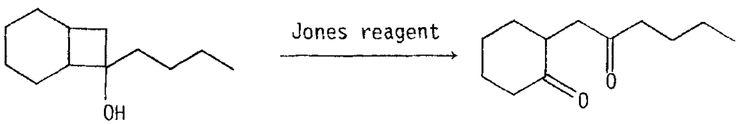


∿75%

Chem Ber (1974) 107 2453

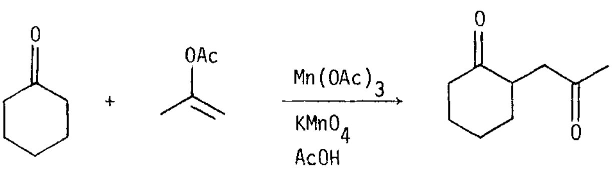
$MeSO_2\overline{C}HCOPh + BrCH_2COPh \longrightarrow \xrightarrow{Zn/HOAc} PhCOCH_2CH_2COPh$ 76%

Coll Czech Chem Comm (1974) 39 192



82%

Can J Chem (1976) 54 3113



22%

JOC (1974) 39 3457

$PhCOCH_2COMe \xrightarrow[\text{2) } \underline{n}\text{-BuLi; 3) CuCl cat, } I_2]{\text{1) NaH, THF, 0°}} (PhCOCH_2COCH_2)_2$ 75%

JOC (1975) 40 3887

$\underline{t}\text{-BuCOCH}_3 \xrightarrow[\text{2) CuCl}_2\text{, DMF}]{\text{1) LDA, THF}} \underline{t}\text{-BuCOCH}_2\text{CH}_2\text{CO-}\underline{t}\text{-Bu}$ 95%

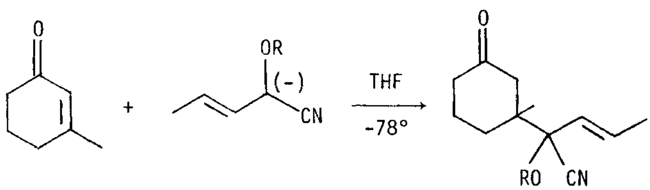
JACS (1975) 97 2912

$\text{H}_2\text{C=C(OTMS)-Ph} \xrightarrow[\text{DMSO, }\Delta]{\text{Ag}_2\text{O}} \text{PhCOCH}_2\text{CH}_2\text{COPh}$ 73%

JACS (1975) 97 649

$\text{Et(Me)C=NR} \xrightarrow[\text{2) I}_2\text{, THF; 3) H}_3\text{O}^+]{\text{1) LDA, THF}} \text{EtCOCH}_2\text{CH}_2\text{COEt}$ 80%

Synthesis (1975) 256



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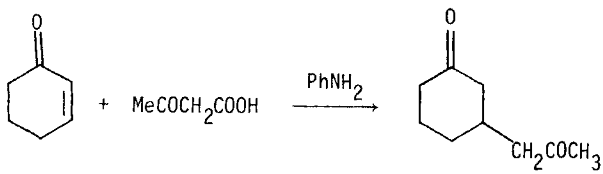

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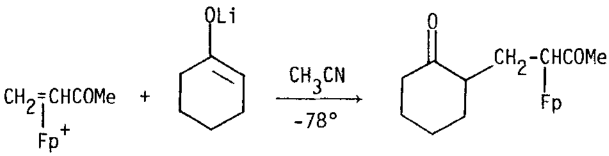
Chem Lett (1975) 89



Fp = $\pi\text{-}C_5H_5Fe(CO)_2$

JOC (1975) 40 3621

$$\mathrm{Cl\overset{O}{\overset{\|}{C}}(CH_2)_8COCl} \xrightarrow[\substack{Cu^+ \\ -78°}]{\underline{t}\text{-BuMgCl}} \underline{t}\text{-}\mathrm{BuCO(CH_2)_8CO}\underline{t}\mathrm{Bu} \qquad 84\%$$

Aust J Chem (1974) 27 2525

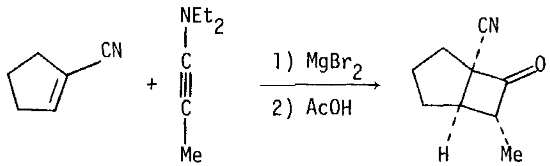
Review: "Acylation of Enamines"

Chem and Ind (1974) 731

Section 373 Ketone - Nitrile

$$\mathrm{PhCH_2CN} \xrightarrow[\text{2) } H_2O]{\text{1) } Me_2AlCl} \mathrm{PhCH_2CO\underset{\substack{| \\ CN}}{C}H\text{-}Ph}$$

Liebigs Ann Chem (1975) 636



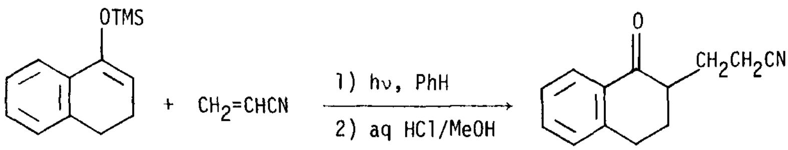
70%

Tetr Lett (1976) 683

$$PhCHO + H_2C{=}CCN \xrightarrow{CN^-} PhCOCH_2CH_2CN$$

80%

Chem Ber (1974) 107 210



86%

Chem Lett (1975) 237

Section 374 Ketone - Olefin

For the oxidation of allylic alcohols to olefinic ketones, see Section 168. Vol. 1 (Ketones from Alcohols and Phenols).

For the oxidation of allylic methylene groups ($C{=}C{-}CH_2 \rightarrow C{=}C{-}CO$), see Section 170, Vol. 1 and 2 (Ketones from Alkyls and Methylenes).

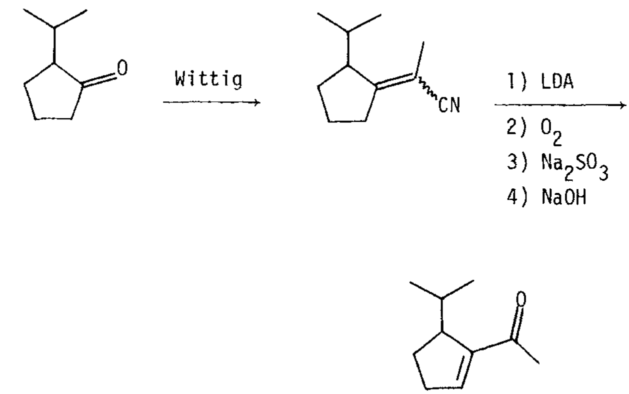
For the alkylation of olefinic ketones, see also Section 177, Vol. 1 and 2 (Ketones from Ketones) and Section 74 (Alkyls from Olefins), Vol. 3, for conjugate alkylations.

$Ph_2C(Br)-C(=O)-Br \xrightarrow{Zn,\ THF} Ph_2C{=}C{=}O$ 95%

JCS Perkin I (1975) 1600

$Ac_2O + Bu_3Al \cdot NBu_3 \xrightarrow[xylene]{130°} CH_2{=}C{=}O$ 80%

J Organometal Chem (1975) 97 21



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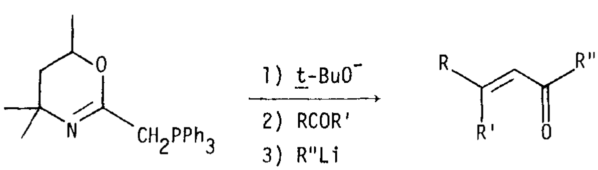
JOC (1976) 41 2939



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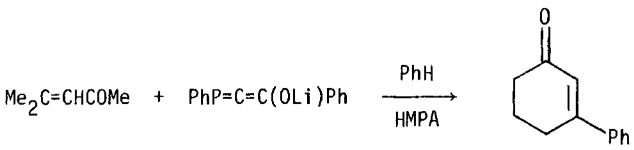
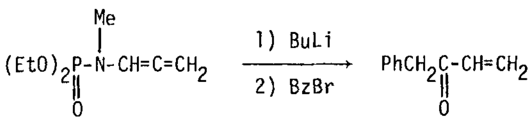
JOC (1974) 39 629



35%

Tetrahedron (1975) 31 1331



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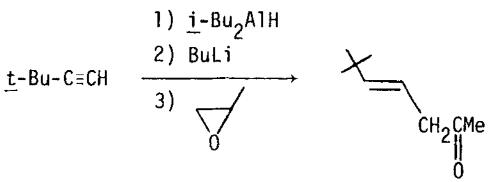
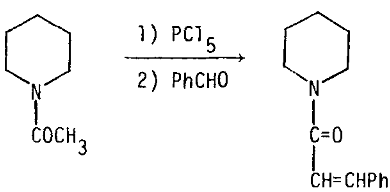
Tetr Lett (1976) 835



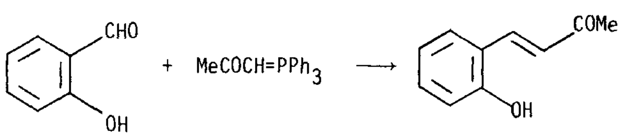
68%

JCS Chem Comm (1976) 17



80%

Experientia (1976) 32 1491

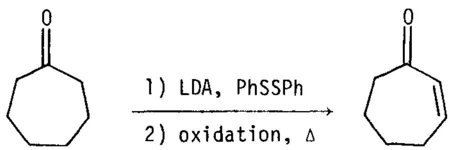


92%

Gazz Chim Ital (1975) 105 109

$Me_2NCH{=}CH{-}CH(OEt)_2 + PhCOCH_3 \longrightarrow Me_2NCH{=}CHCH{=}CHCOPh$ 74%

Liebigs Ann Chem (1975) 874



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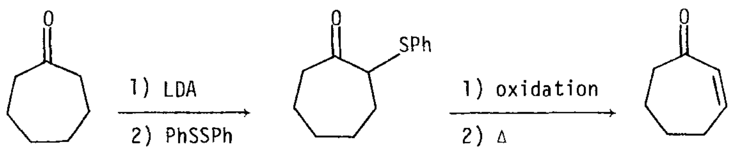
JACS (1976) 98 4887



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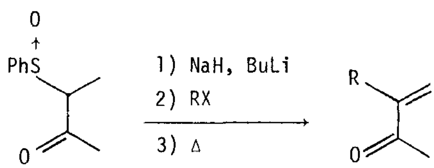
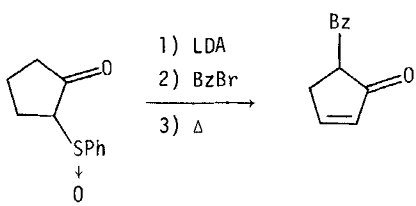
JACS (1976) 98 4887



JCS Chem Comm (1974) 497



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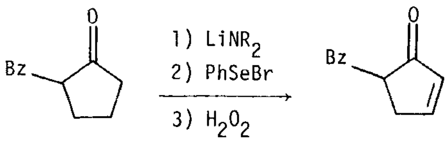
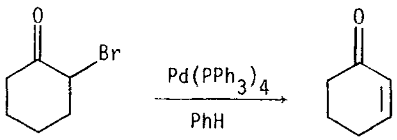


66%

JACS (1975) 97 5434



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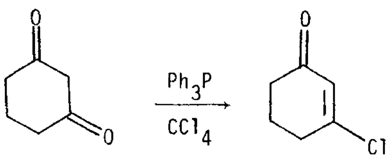
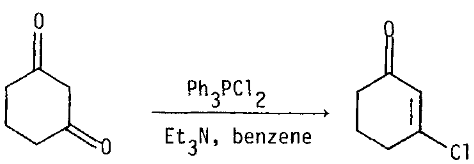
JOC (1975) 40 2976



Synthesis (1975) 708



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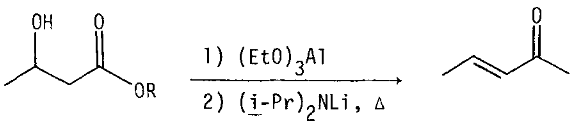
Synth Comm (1975) 5 193



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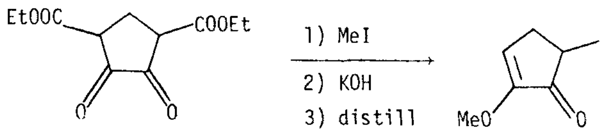
JACS (1974) 96 6153



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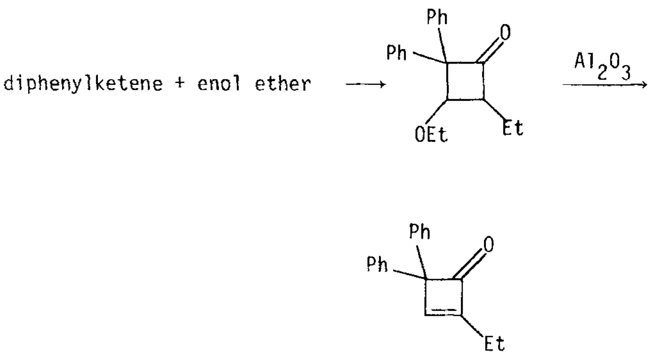
Synthesis (1974) 33



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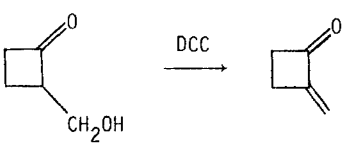

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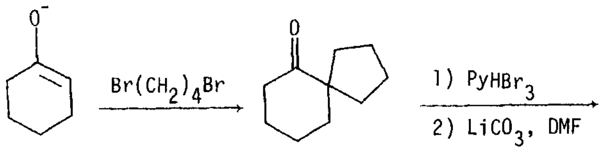
Bull Soc Chim Fr (1974) 1015



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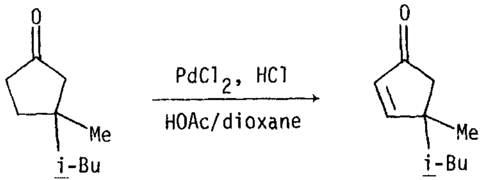

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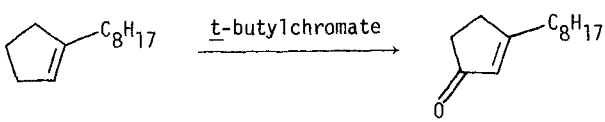
Synthesis (1976) 240



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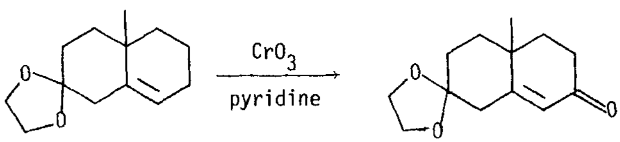

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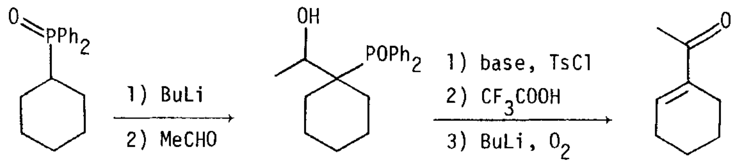
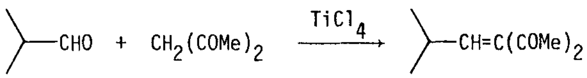
Synth Comm (1976) 6 217



JCS Chem Comm (1975) 148



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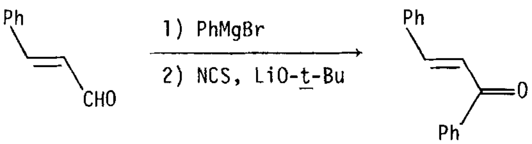
Synthesis (1974) 667



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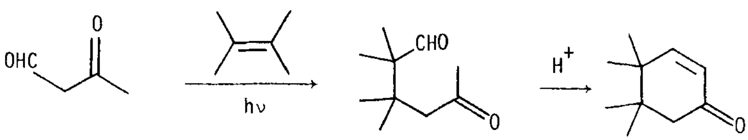
Chem Lett (1976) 771



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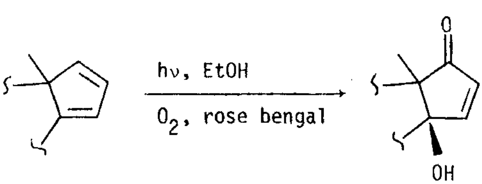
JOC (1975) 40 1865



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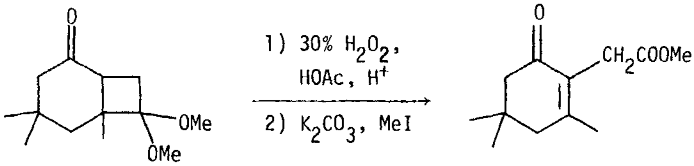

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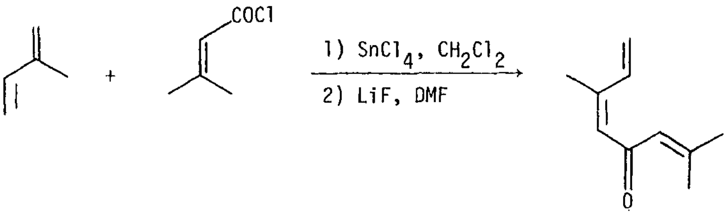

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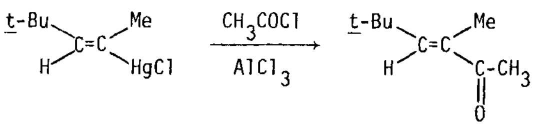
Tetr Lett (1974) 3197



99%

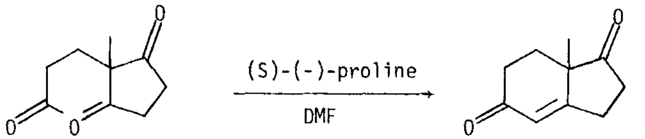
Tetr Lett (1976) 3097

TMSCH=CHTMS + PhCOCl $\xrightarrow[-20°]{AlCl_3}$ TMSCH=CHCOPh 80%

Bull Soc Chim Fr (1975) 2143

$PhCH{=}CHSiMe_3$ + $PhCH_2COCl$ $\longrightarrow$ $PhCH{=}CHCOCH_2Ph$ 86%

JCS Chem Comm (1975) 633

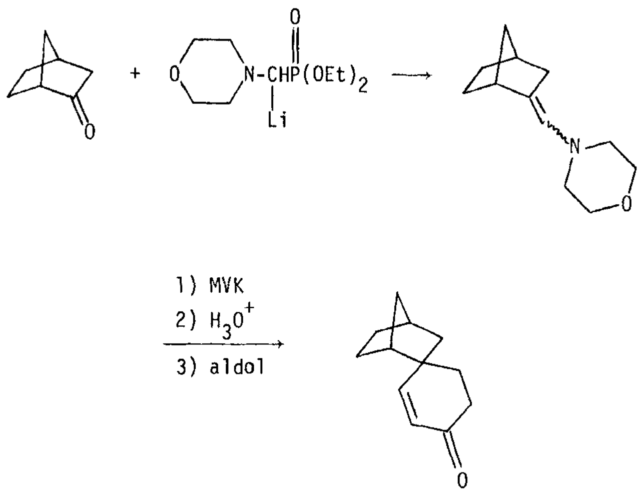


(prochiral)

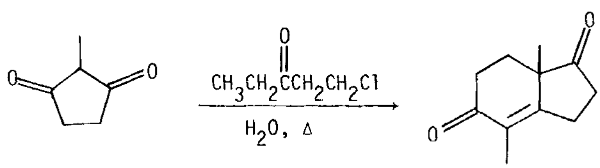
97% optical purity

97%

JOC (1974) 39 1615

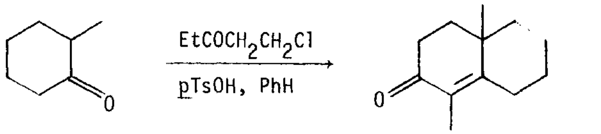


JOC (1976) 41 3337

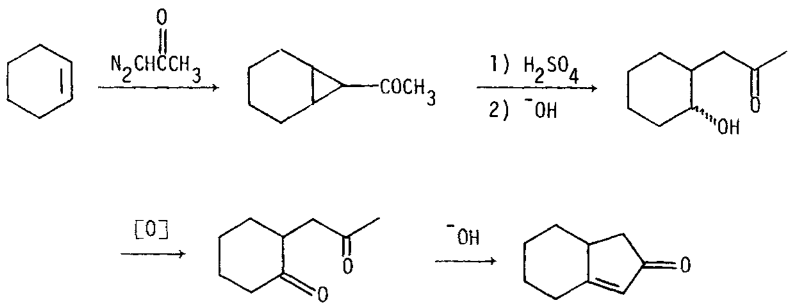


78%

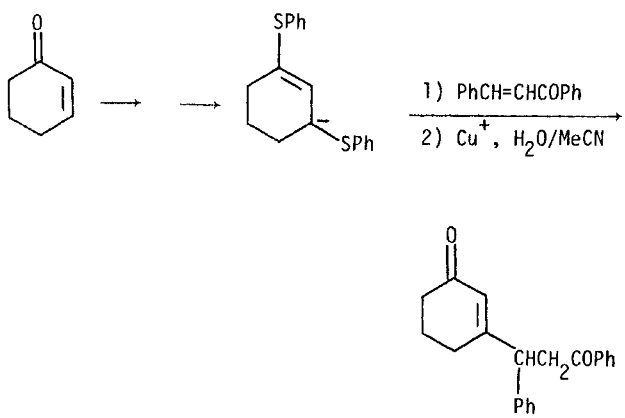
JOC (1976) 41 3767



Tetr Lett (1975) 527

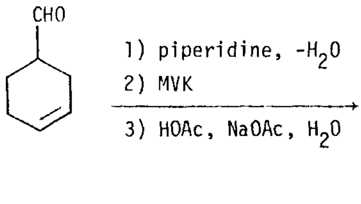


Chem Lett (1976) 1025



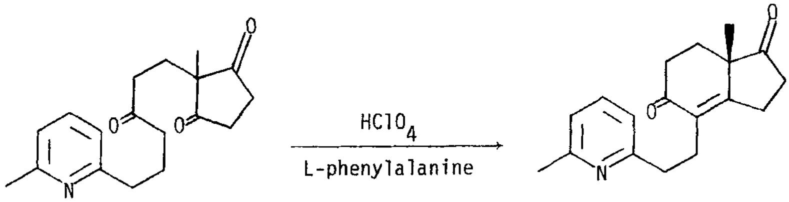
59%

JOC (1976) 41 2506



45%

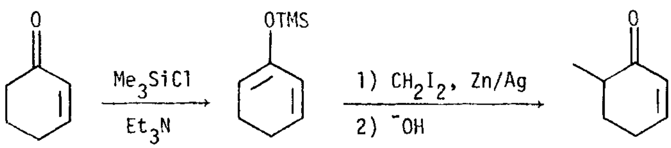
Synth Comm (1976) <u>6</u> 237



82% yield
82% ee

→ estrone

JACS (1975) <u>97</u> 5282

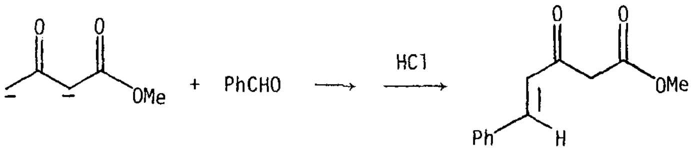


~80% overall

Pure and Appl Chem (1975) <u>48</u> 317

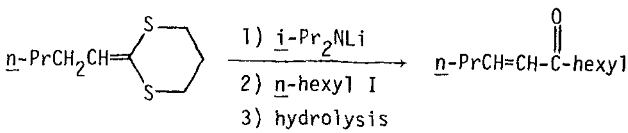
$$CH_3CH_2COOH \xrightarrow[\text{2) } H_2O]{\text{1) } CH_2=CHLi} CH_3CH_2COCH=CH_2$$ 92%

Tetr Lett (1974) 2877



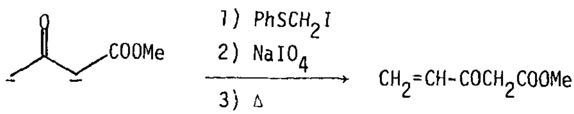
89%

Can J Chem (1974) 52 2157



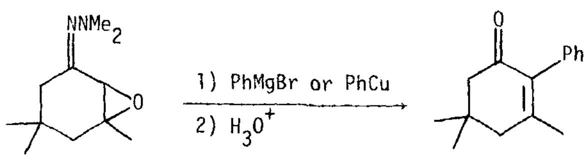
81%

Tetr Lett (1975) 925



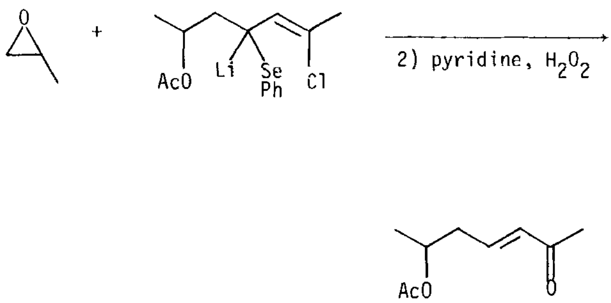
72%

JOC (1974) 39 2648



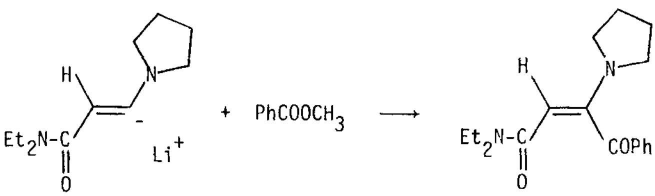
77%

JOC (1976) 41 2935; 2937



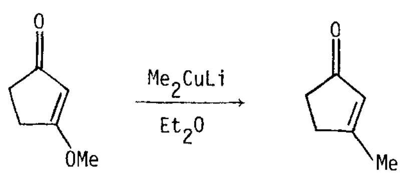
80%

JOC (1975) 40 2570



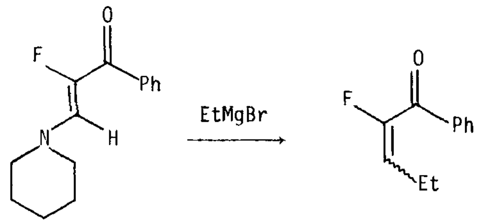
95%

Angew Int Ed (1976) 15 171



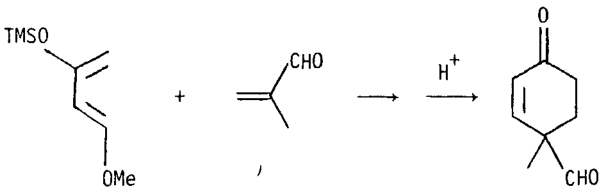
70%

Indian J Chem (1974) 12 325
Chem Comm (1974) 1005



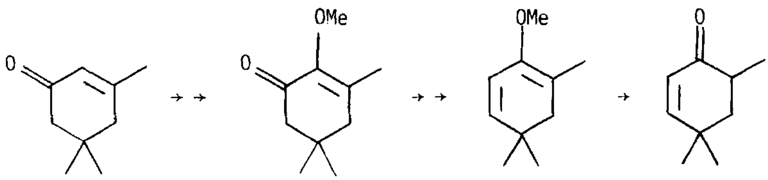
61%

Bull Soc Chim France (1976) 439



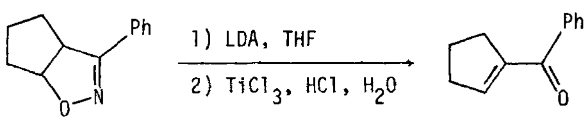
72%

JACS (1974) 96 7807



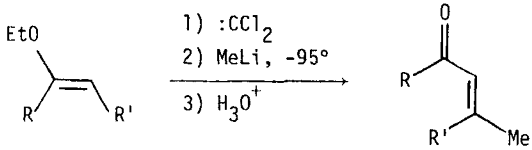
~50%

Synth Comm (1975) 5 27



61%

Angew Int Ed (1976) 15 50



40-50%

Tetr Lett (1974) 3297

$$MeCOCH_2Me \xrightarrow[\text{NaH} \quad \text{2) Si gel}]{\text{1) } Me_2NCH{=}C(NO_2)Me} MeCOC(Me){=}CHCOMe$$

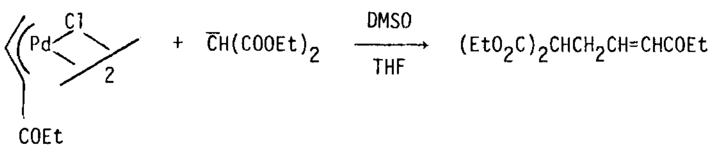
high yields

Chem Ber (1974) 107 1499

$$PhCH_2COPh + PhN{=}CHOEt \xrightarrow{190°} PhC(=CHNHPh)COPh$$

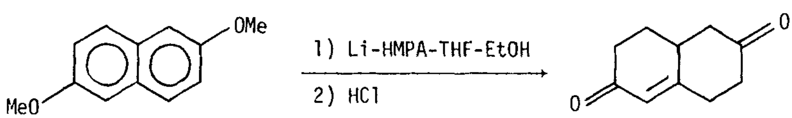
61%

Z Chem (1975) 15 15



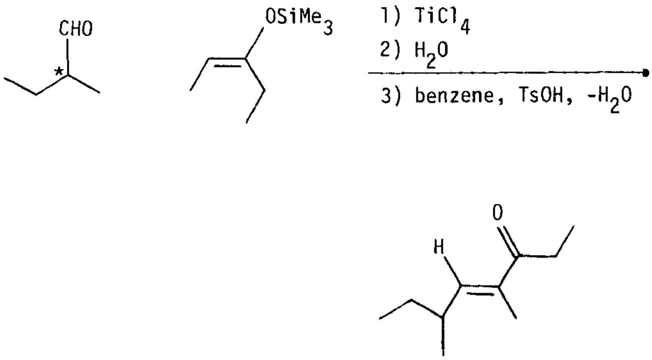
100%

Tetr Lett (1975) 2591



60%

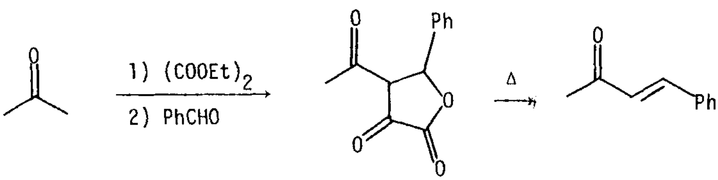
JOC (1975) 40 2841



83%

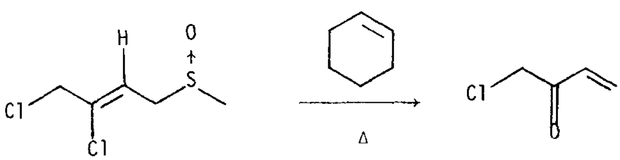
97% ee

Chem Lett (1976) 279



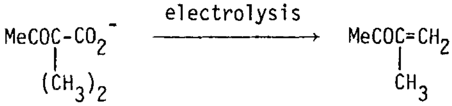
90%

Tetr Lett (1976) 4691



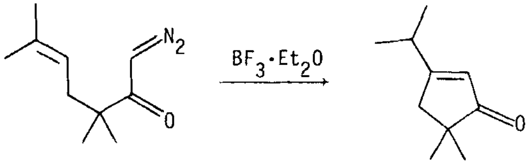
90%

JACS (1976) 98 4577



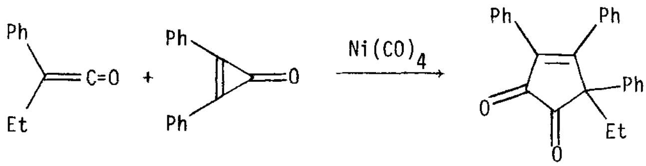
90%

Comptes Rendus C (1975) 280 731



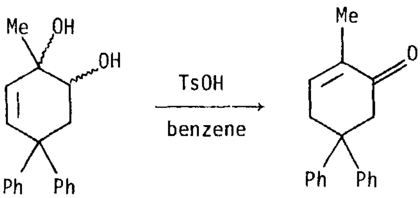
~50%

Comptes Rendus C (1976) 282 761



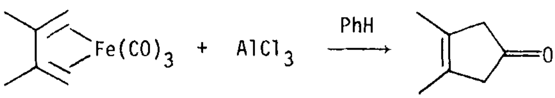
85%

J Organometal Chem (1976) 110 121



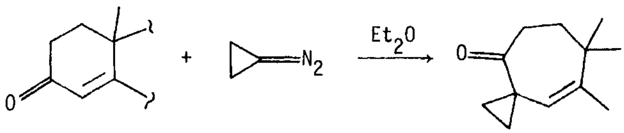
90%

Helv Chim Acta (1976) 59 2012



moderate yield

Tetr Lett (1974) 3789



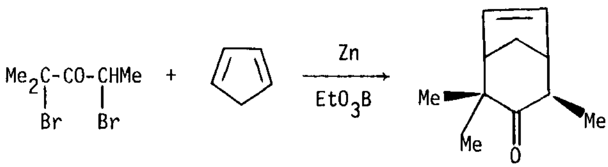
30%

JCS Perkin I (1974) 2240

$$TMSCH_2CH{=}CH_2 \quad + \quad PhCOCl \xrightarrow{AlCl_3} PhCOCH_2CH{=}CH_2$$

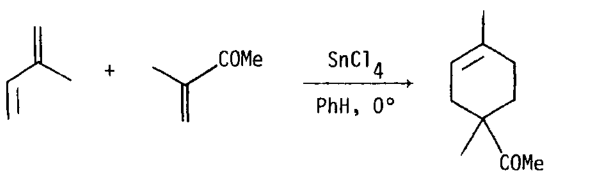
90%

J Organometal Chem (1975) 85 149



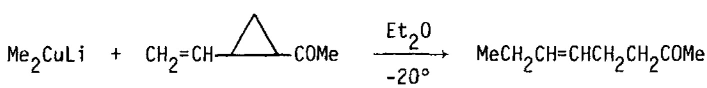
78%

Tetr Lett (1975) 4487



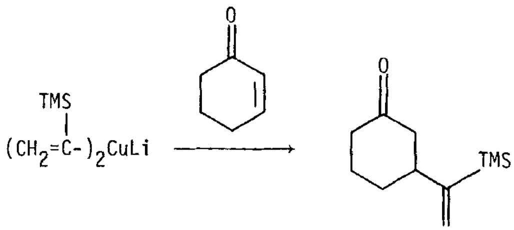
70%

Helv Chim Acta (1974) 57 164



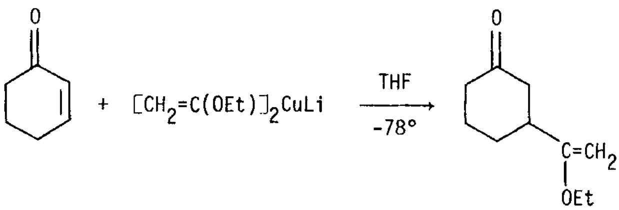
81%

Synthesis (1975) 317



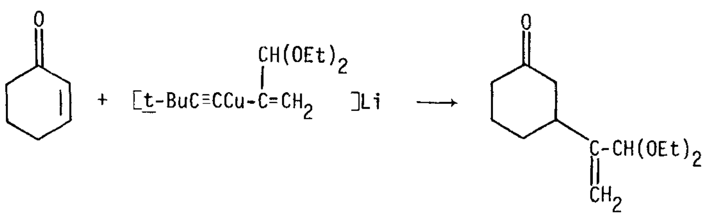
90%

Tetr Lett (1974) 3365



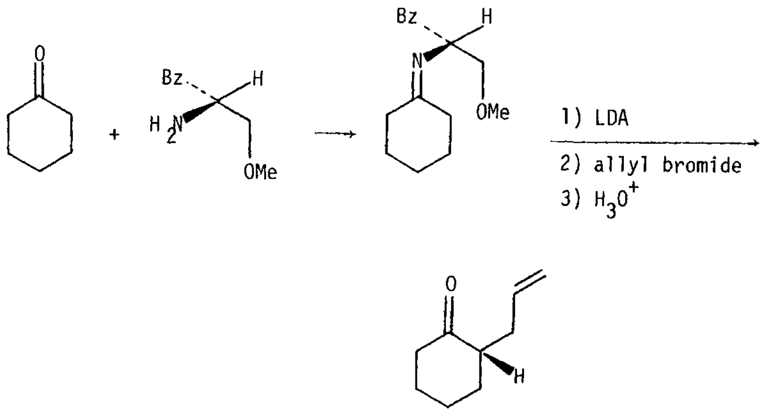
84%

JCS Chem Comm (1975) 519
JACS (1975) 97 3822



96%

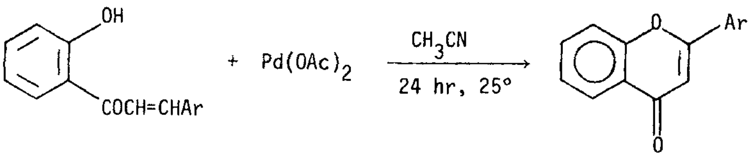
Tetr Lett (1975) 3901



80%

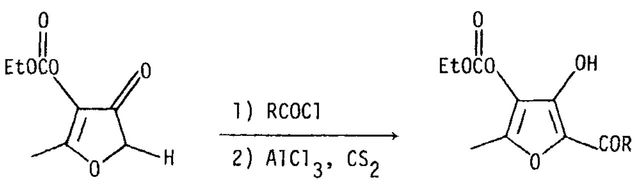
>90% ee

JACS (1976) 98 3032



80%

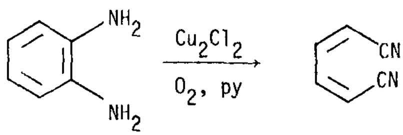
Bull Chem Soc Jap (1974) 47 2526



Comptes Rendus (1974) 278 267

Also via: Acetylenic ketones (Section 309)
β-Hydroxyketones (Section 330)

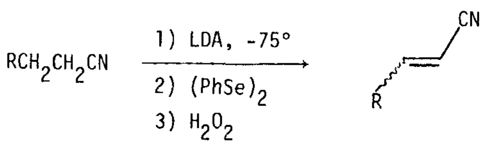
Section 375 Nitrile - Nitrile



90%

Chem Lett (1976) 147

Section 376 Nitrile - Olefin

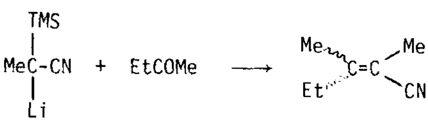


90%

Tetr Lett (1974) 2279

$H_2C{=}C{=}O$ + TMSCN $\longrightarrow$ $H_2C{=}C(OTMS)CN$ 96%

Angew Int Ed (1975) 14 179

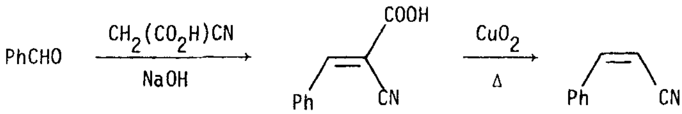


95%

Tetr Lett (1974) 4005

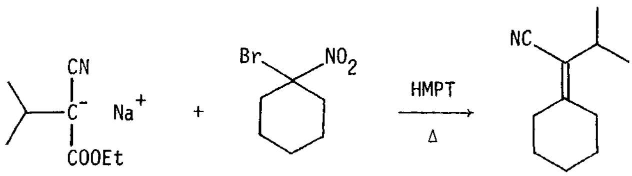
PhCHO + CH_3CN $\xrightarrow[\text{crown ether}]{\text{KOH}}$ PhCH=CHCN 82%

Tetr Lett (1976) 3495



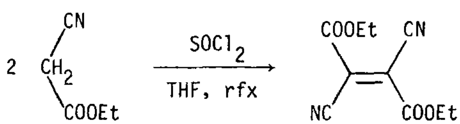
~40%

Tetr Lett (1975) 3843



63%

Chem Lett (1976) 757



64%

Synth Comm (1976) 6 185

$$PhC{\equiv}CH \xrightarrow[\text{2) HCl}]{\text{1) } [Ni_2(CN)_2(DPB)_3]} PhCH{=}CHCN$$

70%

Gazz Chim Ital (1974) 104 1279

$$\underset{\displaystyle Et}{PhCHCN} \xrightarrow[\text{phase-transfer cat}]{HC{\equiv}CH,\ KOH,\ DMSO} Ph\text{-}\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle Et}{C}}\text{-}CN$$

60%

Org Synth (1976) 55 99

Section 377 Olefin - Olefin

$$Me_2C{=}C(OTf)CH_3 \xrightarrow[100^\circ]{\text{quinoline}} Me_2C{=}C{=}CH_2 \qquad 70\%$$

JOC (1975) 40 647

$$R'C{\equiv}CCH(R^2){-}OTs \xrightarrow[\text{THF}]{R^3MgX,\ CuBr} R^3R'C{=}C{=}CHR^2 \qquad 90\%$$

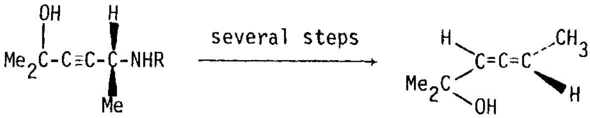
Rec Trav Chim (1975) 94 112

$$RC{\equiv}CSMe \xrightarrow[2)\ MeI,\ 0^\circ]{1)\ R'_2CuLi} (R)(R')C{=}C{=}C{=}C(R)(R') \qquad 20\text{-}50\%$$

Tetr Lett (1975) 2923

$$Ph_2C{=}C{=}C(Ph)Br \xrightarrow[\text{DMF}]{\text{CuCl}} Ph_2C{=}C{=}C(Ph){-}C(Ph){=}C{=}CPh_2 \qquad 72\%$$

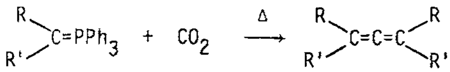
JCS Chem Comm (1975) 174



~30%

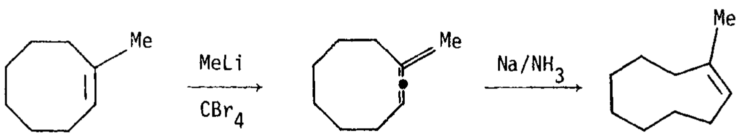
33% ee

JACS (1975) 97 2919



~30%

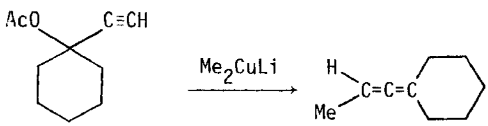
Tetr Lett (1974) 1275



95%

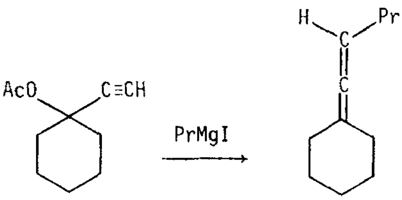
65%

Synthesis (1975) 194



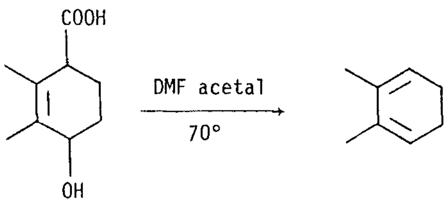
80%

JCS Chem Comm (1976) 183



72%

Angew Int Ed (1976) 15 496

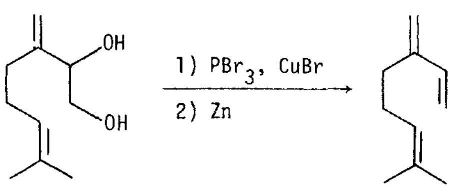


94%

Helv Chim Acta (1975) 58 1450

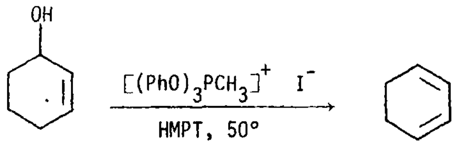
$Me_2C{=}CHCH_2SCHMeS(O)Me \xrightarrow[\text{2) MeI}]{\text{1) LDA, -10°}} CH_2{=}CHCMe_2C(SMe){=}CH_2$ 54%

Comptes Rendus (1975) 280 1231;1327



58%

JACS (1975) 97 3252



78%

Synthesis (1976) 108

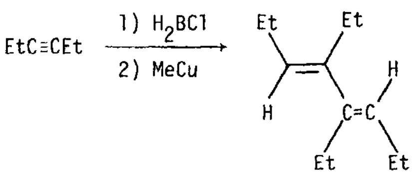
$$R'R^2C{=}CHBr + R^3CH{=}CHR^4 \xrightarrow[L_2Pd(OAc)_2,\ 100°]{Et_3N} R'R^2C{=}CHCR^3{=}CHR^4$$

JOC (1975) 40 1083

$$CH_2{=}CHCH{=}CH_2 \xrightarrow[NaBH_4,\ THF\text{-}EtOH,\ 100°]{(Ph_3P)_2NiBr_2} CH_2{=}CHCH{=}CHCH_2CH{=}CHMe$$

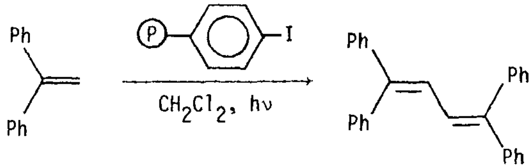
95%

JACS (1975) 97 341



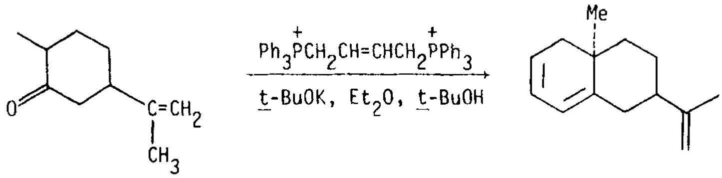
100%

JACS (1975) 97 5606



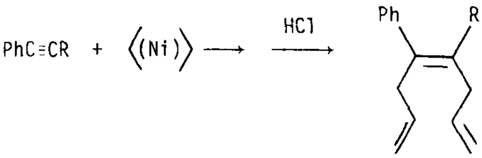
80%

Synth Comm (1976) 6 309



85%

JOC (1975) 40 100



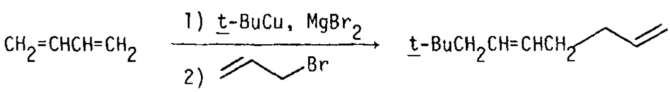
50%

J Organometal Chem (1975) 96 C19

$PhSe(O)CH_3$ → $PhCH{=}CHCH_2CH{=}CHPh$ 75%

1) LDA, THF, -78°
2) $PhCH{=}CHCH_2Br$
3) HOAc
4) CH_2Cl_2, rfx

JACS (1975) 97 3250



90%

J Organometal Chem (1975) 92 C28

i-$PrSCH_2CH{=}CH_2$ → i-$PrSCH{=}CHCH_2CH_2CH{=}CH_2$ 88%

1) s-BuLi, -25°
2) CuI, -78°
3) $CH_2{=}CHCH_2Br$

Bull Chem Soc Japan (1975) 48 1567