Compendium of Organic Synthetic Methods

Volume 2

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Compendium of Organic Synthetic Methods

Volume 2

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PREFACE

Compendium of Organic Synthetic Methods, Volume 2 presents the early 1971 to early 1974 crop of published functional group transformations, plus the gleanings from previous years. It is in part a supplement to *Volume 1* and in addition contains a new chapter on the preparation of difunctional compounds. Previous reviewers and abstractors have tended to avoid difunctional compounds, having found the data particularly well concealed in the literature. Addition of this new chapter increases the complexity of the classification schemes, requiring more instruction in the use of the book. However, the system used is still simple enough that those who wish to just jump in will do well with no more guidance than that offered by the indexes.

The task of abstracting the approx. 90 journals covered by *Volume 1* and *2* of the *Compendium* becomes ever more difficult as chemical publications continue to appear in increasing numbers. Within a few more years it will not be possible for a team of two to continue as sole abstractors, writers, artists, typists and proofreaders for the *Compendium*. Perhaps a fully organized abstracting service, responsive to the needs of the synthetic chemist, will someday be set up. It would help, of course, if chemists would learn to write orderly, concise papers that can actually be read rather than deciphered.

Ian T. Harrison
Shuyen Harrison

Palo Alto, California
May 1974

CONTENTS

ABBREVIATIONS

Ac	acetyl
9-BBN	9-borabicyclo[3.3.1]nonane
Bu	butyl
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMA	dimethylacetamide
DMF	dimethylformamide
Et	ethyl
HMPA	hexamethylphosphoramide (hexamethylphosphoric triamide)
Me	methyl
Ms	methanesulfonyl
NBA	*N*-bromoacetamide
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
Ni	Raney nickel
NIS	*N*-iodosuccinimide
Ph	phenyl
Pr	propyl
Pyr	pyridine
THF	tetrahydrofuran
THP	tetrahydropyranyl
Ts	*p*-toluenesulfonyl

INDEX, MONOFUNCTIONAL COMPOUNDS

Sections—heavy type
Pages—light type

PREPARATION OF → / FROM ↓	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**			**91**	**106**				**166**		**196**
	1	7	28	53			92	108				155		193
Carboxylic acids, acid halides, anhydrides	**2**	**17**	**32**	**47**	**62**	**77**	**92**	**107**		**137**	**152**	**167**	**182**	**197**
	1	8	29	53	70	82	92	108		136	146	156	185	194
Alcohols, phenols		**18**	**33**	**48**	**63**	**78**	**93**	**108**	**123**	**138**	**153**	**168**		**198**
		10	30	55	71	84	92	113	127	137	146	157		195
Aldehydes	**4**	**19**	**34**	**49**	**64**	**79**	**94**	**109**	**124**		**154**	**169**	**184**	**199**
	2	11	31	57	71	84	94	115	130		148	159	186	197
Alkyls, methylenes, aryls		**20**		**50**	**65**							**170**		**200**
		12		59	72							160		199
Amides		**21**		**51**		**81**	**96**				**156**	**171**	**186**	
		13		59		85	95				149	161	187	
Amines			**37**	**52**		**82**	**97**	**112**		**142**	**157**	**172**	**187**	**202**
			32	60		86	96	117		141	149	161	188	199
Esters		**23**	**38**			**83**		**113**			**158**	**173**		**203**
		13	32			87		117			150	162		200
Ethers, epoxides		**24**	**39**	**54**	**69**		**99**	**114**	**129**	**144**	**159**	**174**		**204**
		15	34	61	73		98	118	131	141	150	162		200
Halides, sulfonates, sulfates	**10**	**25**	**40**	**55**	**70**	**85**	**100**	**115**	**130**	**145**	**160**	**175**	**190**	**205**
	3	16	36	61	73	88	99	119	132	141	151	163	188	201
Hydrides (RH)		**26**	**41**	**56**	**71**		**101**	**116**	**131**	**146**		**176**	**191**	**206**
		18	38	63	76		101	121	132	142		167	189	204
Ketones	**12**	**27**	**42**	**57**	**72**		**102**	**117**	**132**		**162**	**177**	**192**	**207**
	4	20	41	64	77		101	122	132		152	168	189	204
Nitriles				**58**		**88**	**103**	**118**			**163**	**178**	**193**	
				65		89	102	124			153	174	190	
Olefins	**14**	**29**	**44**	**59**	**74**	**89**	**104**	**119**	**134**	**149**		**179**		**209**
	5	23	45	66	79	90	103	124	133	144		175		208
Miscellaneous compounds	**15**	**30**	**45**	**60**			**105**	**120**	**135**	**150**	**165**	**180**	**195**	**210**
	5	24	46	66			104	125	135	145	154	178	191	211

PROTECTION

	Sect.	Pg.
Acetylenes	15A	5
Carboxylic acids	30A	26
Alcohols, phenols	45A	47
Aldehydes	60A	67
Amides	90A	90
Amines	105A	105
Esters	120A	126
Ketones	180A	181
Olefins	210A	211

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

INDEX, DIFUNCTIONAL COMPOUNDS

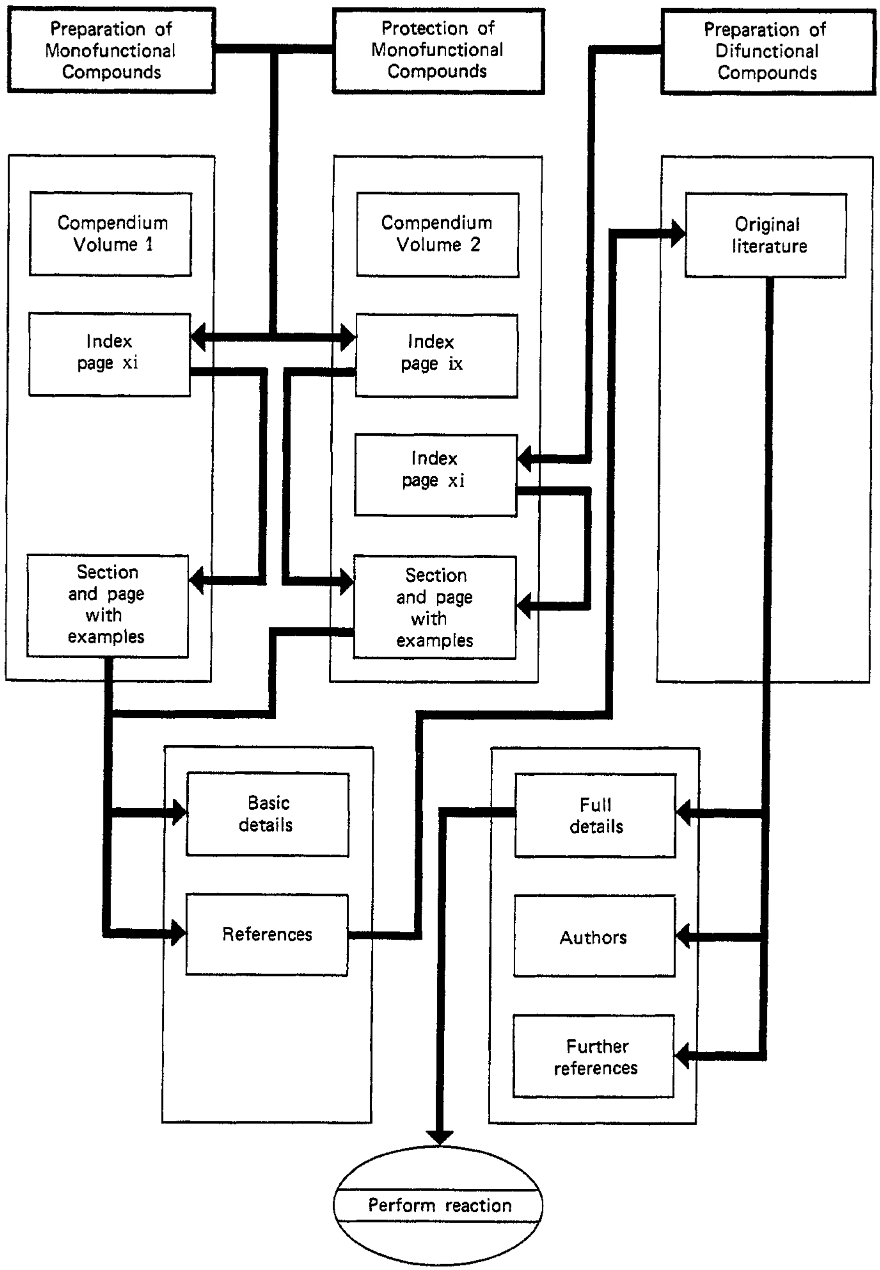
Sections—heavy type

Pages—light type

Acetylene	Carboxylic acid	Alcohol	Aldehyde	Amide	Amine	Ester	Ether, epoxide	Halide	Ketone	Nitrile	Olefin
300 214											
301 216	**312** 233										
302 218	**313** 241	**323** 276									
303 220	**314** 246	**324** 284	**333** 317								
304 222	**315** 248	**325** 287		**342** 335							
305 222	**316** 248	**326** 290	**335** 319	**343** 335	**350** 341						
306 224	**317** 255	**327** 294	**336** 320	**344** 336	**351** 343	**357** 354					
307 225	**318** 256	**328** 298	**337** 322	**345** 336	**352** 346	**358** 358	**363** 382				
308 226	**319** 257	**329** 300	**338** 322	**346** 337	**353** 347	**359** 359	**364** 383	**368** 390			
309 228	**320** 260	**330** 302	**339** 324	**347** 337	**354** 348	**360** 362	**365** 384	**369** 394	**372** 405		
310 231	**321** 269	**331** 311	**340** 327	**348** 340	**355** 352	**361** 372	**366** 387	**370** 400	**373** 414	**375** 428	
311 231	**322** 270	**332** 312	**341** 328	**349** 340	**356** 353	**362** 374	**367** 388	**371** 400	**374** 417	**376** 430	**377** 432

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

HOW TO USE THE COMPENDIUM



INTRODUCTION

Relationship Between Volume 1 and Volume 2. *Compendium of Organic Synthetic Methods, Volume 2*, presents more than 1000 examples of published methods for the preparation of monofunctional compounds, updating the 3000 or so in Volume 1. In addition Volume 2 presents a new chapter with about 1000 examples of the preparation of difunctional compounds. Methods for the protection of carboxylic acids, alcohols, phenols, aldehydes, amines, and ketones were included in Volume 1. In Volume 2 protective methods for acetylenes, amides, esters, and olefins are also covered.

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 $\rightarrow$ t-BuCOOH, $PhCH_2OH \rightarrow PhCOOH$ and $PhCH{=}CHCH_2OH \rightarrow PhCH{=}CHCOOH$ would all be considered as preparations of carboxylic acids from alcohols.

The terms hydrides, alkyls, and aryls classify compounds containing reacting hydrogens, alkyl groups, and aryl groups, respectively; for example, $RCH_2\text{-}H \rightarrow RCH_2COOH$ (carboxylic acids from hydrides), $RMe \rightarrow RCOOH$ (carboxylic acids from alkyls), $RPh \rightarrow RCOOH$ (carboxylic acids from aryls). Note the distinction between $R_2CO \rightarrow R_2CH_2$ (methylenes from ketones) and $RCOR' \rightarrow RH$ (hydrides from ketones).

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)

Yields quoted are overall; they are 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. When several references are given, the first refers to the reaction illustrated; others give further examples, related reactions, or reviews.

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.

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 Volume 1 are given again in Volume 2 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 new 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. xi 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).

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 1 PREPARATION OF ACETYLENES

Section 1 Acetylenes from Acetylenes

$$\text{t-BuC}\equiv\text{CH} \xrightarrow[\text{2 } I_2 \quad Et_2O]{\text{1 } Ph_3B \quad BuLi \quad THF} \text{t-BuC}\equiv\text{CPh} \qquad 83\%$$

JACS (1973) 95 3080

Section 2 Acetylenes from Carboxylic Acids

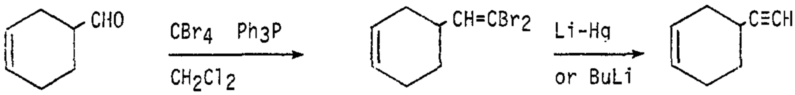
$$\underset{(CH_2)_4COOH}{\overset{COOMe}{|}} \xrightarrow[\text{electrolysis} \quad MeOH]{C_8H_{17}C\equiv C(CH_2)_3COOH} \underset{(CH_2)_7C\equiv CC_8H_{17}}{\overset{COOMe}{|}} \qquad 24\%$$

JCS (1955) 2218

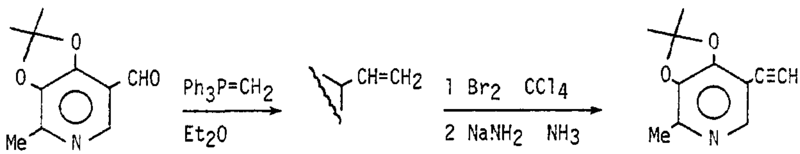
Section 3 Acetylenes from Alcohols

No additional examples

Section 4 Acetylenes from Aldehydes



Tetr Lett (1972) 3769



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J Med Chem (1972) 15 1262

Section 5 Acetylenes from Alkyls, Methylenes and Aryls

No examples

Section 6 Acetylenes from Amides

No examples

Section 7 Acetylenes from Amines

No additional examples

Section 8 Acetylenes from Esters

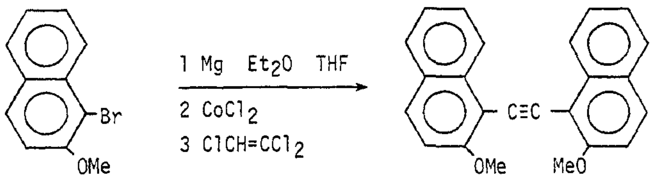
No additional examples

Section 9 Acetylenes from Ethers

No examples

Section 10 Acetylenes from Halides

Examples of the conversion of dibromides into acetylenes are included in section 14 (Acetylenes from Olefins)



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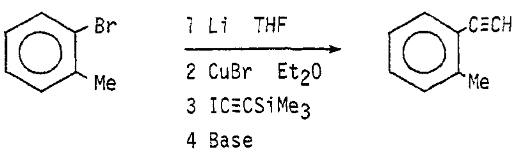
Synthesis (1972) 38



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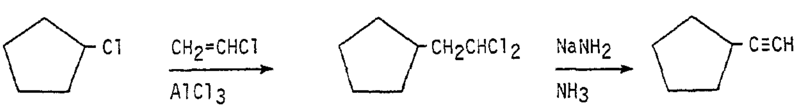
Tetr Lett (1972) 5209

$$RBr \xrightarrow[NH_3]{NaC\equiv CH} RC\equiv CH$$

Org Synth (1963) Coll Vol 4 117
Angew (1959) 71 245



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Rec Trav Chim (1965) 84 31

Section 11 Acetylenes from Hydrides

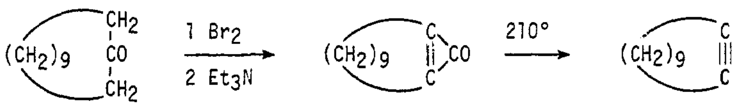
No examples

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

Section 12 Acetylenes from Ketones

$$PhCOCH_2Me \xrightarrow[\text{2 } SeO_2 \text{ HOAc; 3 } \Delta]{\text{1 } NH_2CONHNH_2} PhC\equiv CMe \qquad 49\%$$

Angew (1970) 82 484
Internat Ed 9 464
Chem Comm (1971) 1059



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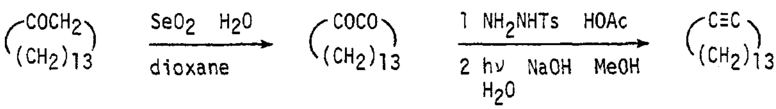
JACS (1965) 87 1326



23%

Synthesis (1971) 215

Section 13 Acetylenes from Nitriles

No examples

Section 14 Acetylenes from Olefins

$$C_7H_{15}CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} C_7H_{15}CH_2CH(Br)CH_2Br \xrightarrow[Me_2SO]{NaNH_2} C_7H_{15}CH_2C{\equiv}CH \quad >89\%$$

or

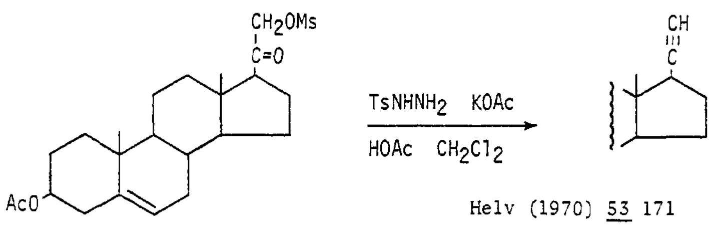
$$\longrightarrow C_7H_{15}C{\equiv}CMe \quad >89\%$$

Tetrahedron (1970) 26 2127 2637

Section 15 Acetylenes from Miscellaneous Compounds

$$PhC(Br){=}C(Br)Ph \xrightarrow[H_2O]{CrSO_4 \quad DMF} PhC{\equiv}CPh \quad 96\%$$

JACS (1964) 86 4603



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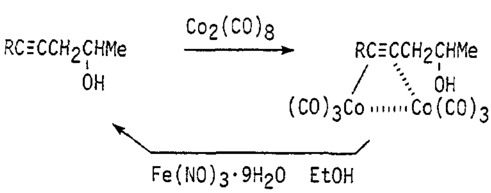
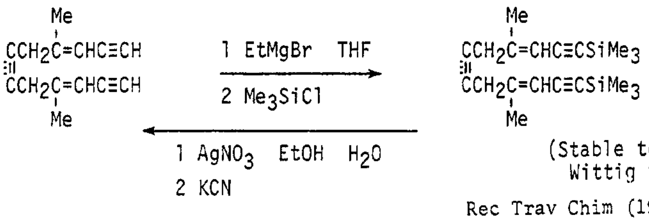
Helv (1970) 53 171

Section 15A Protection of Acetylenes



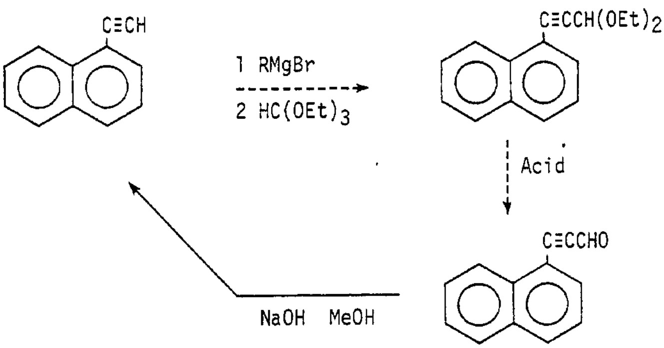
(Stable to B_2H_6, diimide and acid)

Tetr Lett (1971) 3475



(Stable to acid, NaH Wittig reagents and H_2/Pd)

Rec Trav Chim (1967) 86 1138
JCS Perkin I (1972) 361
JACS (1968) 90 5618
Tetrahedron (1972) 28 4591 4601 5221



JCS C (1969) 2173

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Chapter 2 PREPARATION OF CARBOXYLIC ACIDS ACID HALIDES AND ANHYDRIDES

Section 16 Carboxylic Acids from Acetylenes

$$C_8H_{17}C{\equiv}CH \xrightarrow[\text{2 } Br(CH_2)_5COOH \quad \text{3 } H_2 \ Pd\text{-}C \ EtOH]{\text{1 } LiNH_2 \ NH_3} C_8H_{17}(CH_2)_7COOH \qquad 92\%$$

JCS (1963) 775
(1965) 894

$$t\text{-}BuC{\equiv}CH \xrightarrow[CCl_4 \ H_2O]{RuO_2 \ NaOCl} t\text{-}BuCOOH \qquad 60\%$$

Tetr Lett (1971) 2941

$$C_6H_{13}C{\equiv}CH \xrightarrow[MeOCH_2CH_2OMe \ H_2O]{Tl(NO_3)_3 \ HClO_4} C_6H_{13}COOH \qquad 80\%$$

JACS (1973) 95 1296

Also via:

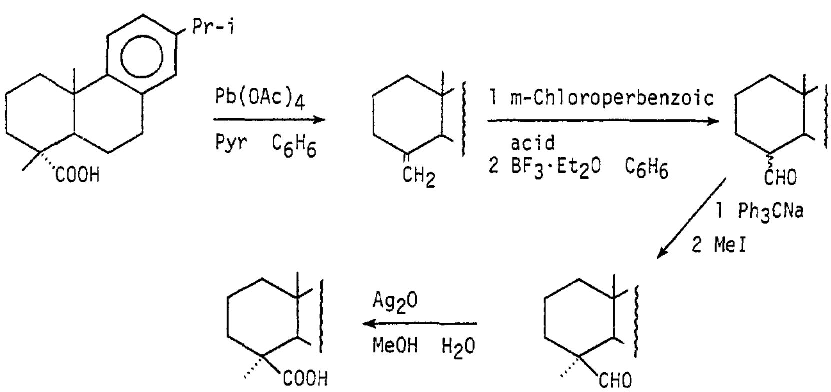
	Section
Esters	106
Amides	76
Ketoacids	320
Ketoesters	360
Olefinic acids	322
Olefinic esters	362
Acetylenic acids	301

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

$$RCH_2COOH \xrightarrow[2\ RBr]{1\ NaH\quad (i\text{-}Pr)_2NLi\quad THF} \underset{\displaystyle R}{RCHCOOH}$$

Org Synth (1970) 50 58
JOC (1972) 37 451

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)



Chem Comm (1971) 10

$$C_{14}H_{29}CH_2COOH \xrightarrow[\text{2 PhH } AlCl_3]{\text{1 } SOCl_2} C_{14}H_{29}CH_2COPh \xrightarrow[\text{HCl dioxane; 2 TsCl NaOH; 3 KOH PrOH}]{\text{1 i-}PrCH_2CH_2ONO} C_{14}H_{29}COOH \quad 63\%$$

JACS (1953) 75 2347
JOC (1961) 26 3507

$$C_7H_{15}COOH \xrightarrow[BF_3\cdot Et_2O \quad CH_2Cl_2]{MeC{\equiv}CH \quad Hg(OAc)_2} C_7H_{15}COOC(Me){=}CH_2 \xrightarrow{HF} C_7H_{15}COF \quad 35\%$$

JOC (1969) 34 2486

$$C_{17}H_{35}COOH \xrightarrow{PCl_5 \quad C_6H_6} C_{17}H_{35}COCl \quad 70\%$$

JACS (1945) 67 2239

$$RCOOK \xrightarrow[CH_2Cl_2]{SOCl_2 \quad Pyr} RCOCl$$

Can J Chem (1968) 46 2549
JACS (1963) 85 643

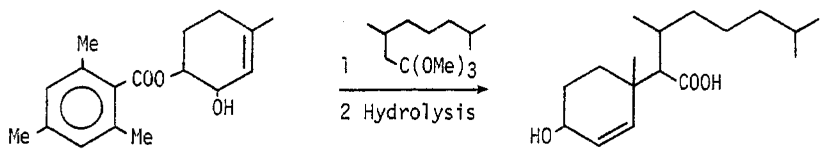
$$PhCOOH \xrightarrow{(Me_2N)_3P \quad CCl_4} (PhCO)_2O \quad 90\%$$

Bull Soc Chim Fr (1971) 3034

$$C_{17}H_{35}COOH \xrightarrow[C_6H_6 \quad Et_2O]{\text{Resin-}CH_2N{=}C{=}NPr\text{-i}} (C_{17}H_{35}CO)_2O \quad 65\%$$

Tetr Lett (1972) 3281

Section 18 Carboxylic Acids from Alcohols



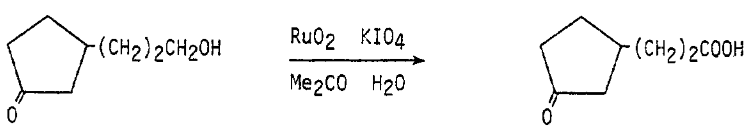
Chem Comm (1970) 1513 1512

$$PrOH \xrightarrow[Ph_3P \quad THF]{\underset{CH_2COOEt}{\overset{|}{CN}} \quad \underset{NCOOEt}{\overset{\|}{NCOOEt}}} PrCH(CN)COOEt \xrightarrow{Hydrolysis} PrCH_2COOH \qquad < 52\%$$

Tetr Lett (1972) 1279

$$C_6H_{13}CH_2OH \xrightarrow[C_6H_6]{KMnO_4 \quad \text{dicyclohexyl-18-crown-6}} C_6H_{13}COOH \qquad 70\%$$

JACS (1972) 94 4024



JOC (1972) 37 1947

$$RCH_2OH \xrightarrow{KOH \quad 245\text{-}255°} RCOOH$$

JACS (1948) 70 3485

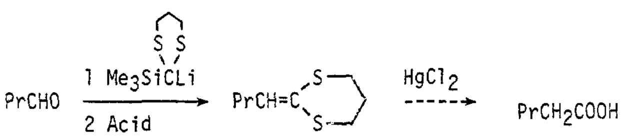
$$\text{t-BuCH(Me)CHOH(Et)}\ \xrightarrow{Br_2\quad NaOH\quad H_2O}\ \text{t-BuCHCOOH(Et)} \qquad 38\%$$

JACS (1950) 72 3701

Section 19 Carboxylic Acids and Anhydrides from Aldehydes

$$C_6H_{13}CHO \xrightarrow[\text{dibenzoyl peroxide}]{CH_2{=}CH(CH_2)_8COOEt} C_6H_{13}CO(CH_2)_{10}COOEt \xrightarrow[\text{diethylene glycol}]{N_2H_4\quad KOH} C_6H_{13}(CH_2)_{11}COOH$$

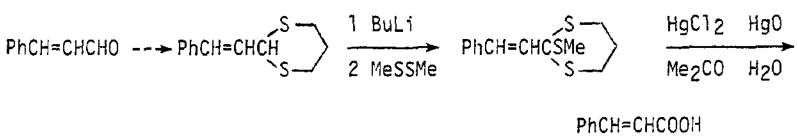
Rec Trav Chim (1953) 72 84



Chem Comm (1972) 526
Ber (1973) 106 2277

$$C_5H_{11}CHO \xrightarrow{\text{m-Chloroperbenzoic acid}\quad THF} C_5H_{11}COOH$$

JACS (1967) 89 291



< 86%

JOC (1972) 37 2757

$$PhCHO \xrightarrow[C_6H_6]{KMnO_4 \quad \text{dicyclohexyl-18-crown-6}} PhCOOH$$

JACS (1972) 94 4024

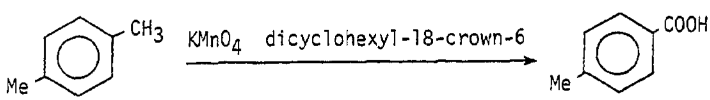
Related methods: Carboxylic Acids from Ketones (Section 27)

Also via:		Section
	Esters	109
	Amides	79
	Ketoacids	320
	Ketoesters	360
	Olefinic acids	322
	Olefinic esters	362
	Olefinic amides	349
	Acetylenic acids	301

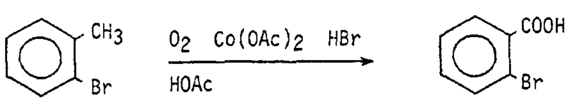
$$PhCHO \xrightarrow{PhCOO_2Bu\text{-}t \quad CuBr} (PhCO)_2O \qquad 70\%$$

JOC (1960) 25 899

Section 20 Carboxylic Acids from Alkyls

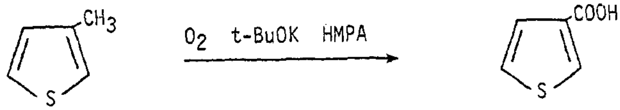


JACS (1972) 94 4024



91%

Can J Chem (1965) 43 1306
Chem Comm (1971) 1166
JOC (1972) 37 2564



80%

JOC (1965) 30 3520
JACS (1965) 87 2523

Section 21 Carboxylic Acids from Amides

$$Et_3CCONH_2 \xrightarrow{NaNO_2 \quad H_2SO_4 \quad H_2O} Et_3CCOOH$$

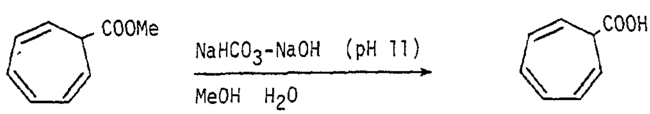
>80%

M. S. Newman, Steric Effects in Organic Chemistry (J. Wiley 1956) 228 footnote 73

Section 22 Carboxylic Acids, Acid Halides and Anhydrides from Amines

No additional examples

Section 23 Carboxylic Acids from Esters



92%

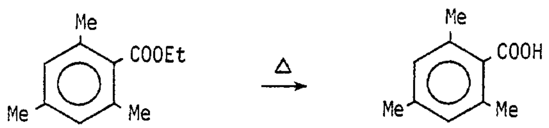
Ber (1972) 105 1778

$(i\text{-}Pr)_3CCOOMe \xrightarrow[\text{xylene}]{\text{1,5-Diazabicyclo[4.3.0]nonene}} (i\text{-}Pr)_3CCOOH$ 94%

Tetr Lett (1972) 3987
JOC (1973) 38 1223

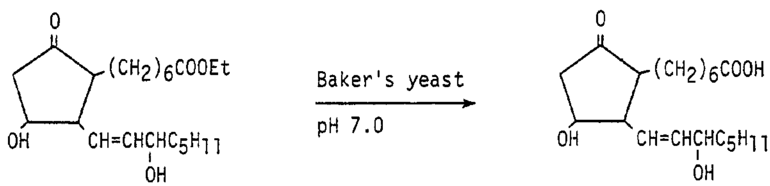
$PhCOOMe \xrightarrow{\text{LiI NaCN DMF}} PhCOOH$

Synth Comm (1972) 2 389

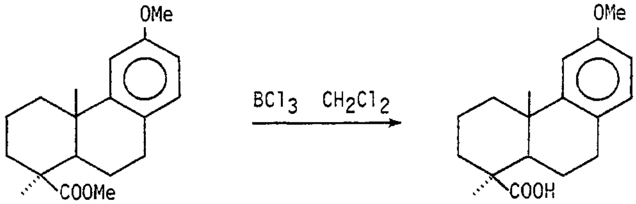


91%

J Am Oil Chem Soc (1956) 33 317
JOC (1964) 29 1252

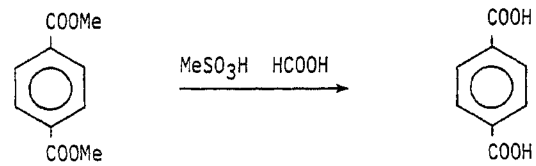


JACS (1972) 94 3643



90%

Chem Comm (1971) 667



99%

Chem Ind (1964) 193

$$C_{17}H_{35}COOMe \xrightarrow{Ph_3P\cdot HBr \quad 170\text{-}180^\circ} C_{17}H_{35}COOH$$

62%

Annalen (1967) <u>709</u> 105

$$RCH_2COOEt \xrightarrow[2\ 220\text{-}230^\circ]{1\ PhMgBr \quad Et_2O} RCH{=}CPh_2 \xrightarrow[H_2O]{CrO_3 \quad HOAc} RCOOH$$

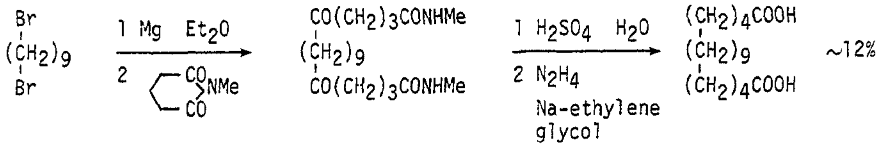
JCS (1957) 1622
(1953) 1785

Section 24 Carboxylic Acids from Ethers

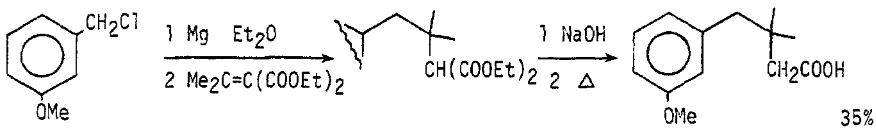
$$\overset{COOH}{(CH_2)_9}CH_2OEt \xrightarrow{KOH \quad 360^\circ} \overset{COOH}{(CH_2)_9}COOH$$

JCS <u>C</u> (1971) 1840

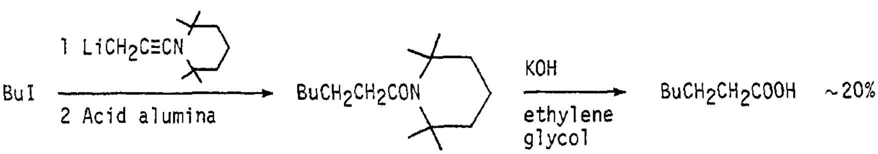
Section 25 Carboxylic Acids from Halides



Chem Listy (1958) 52 1926
(Chem Abs 53 3055)



JOC (1971) 36 3260
(1972) 37 825



JOC (1970) 35 3405

RCl (3ry) $\xrightarrow{CH_2{=}CCl_2 \quad H_2SO_4 \quad BF_3}$ RCH_2COOH

Ber (1967) 100 978

BuBr $\xrightarrow[NH_3]{NaC{\equiv}COEt}$ BuC≡COEt $\xrightarrow[2\ NaOH\quad EtOH]{1\ HgO\quad H_2SO_4\quad EtOH}$ $BuCH_2COOH$ 17%

JCS (1954) 1860
Advances in Org Chem (1960) 2 117

$$PhCH_2Cl \xrightarrow{NaCH_2COONa \quad decalin} PhCH_2CH_2COOH \qquad 34\%$$

Annalen (1966) <u>691</u> 61

$$RBr \xrightarrow[EtOH]{CH_2(COOEt)_2 \quad EtONa} RCH(COOEt)_2 \xrightarrow[2\ HCl \quad H_2O]{1\ KOH \quad EtOH} RCH_2COOH$$

JOC (1971) <u>36</u> 3944

$$PhCH{=}CHCH_2Cl \xrightarrow[EtONa \quad EtOH]{CH_2(COOEt)_2} PhCH{=}CHCH_2CH(COOEt)_2 \xrightarrow[\substack{EtONa \\ 2\ Ac_2O \\ 3\ KOH}]{1\ C_5H_{11}ONO} PhCH{=}CHCH_2COOH$$

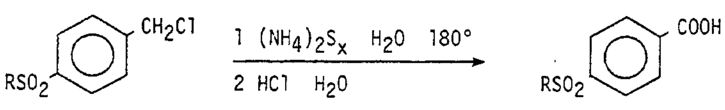
JCS (1950) 926

$$C_{12}H_{25}Br \xrightarrow[2\ O_2 \quad THF]{1\ Na_2Fe(CO)_4} C_{12}H_{25}COOH \qquad 84\%$$

JACS (1973) <u>95</u> 249

$$PhF \xrightarrow{Lithium\ dihydronaphthylide} PhLi \xrightarrow{CO_2} PhCOOH$$

Chem Comm (1972) 752



48%

Ber (1971) <u>104</u> 1697

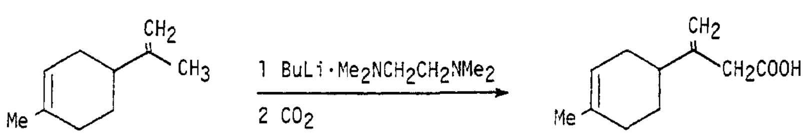
Also via:		Section
	Esters	115
	Amides	85
	Ketoacids	320
	Ketoesters	360
	Olefinic acids	322
	Olefinic esters	362
	Acetylenic acids	301
	Acetylenic esters	306

Section 26 Carboxylic Acids from Hydrides

Reactions in which a hydrogen is replaced by carboxyl or a carboxyl containing chain are included in this section. For reactions in which alkyl groups are oxidised to carboxyl see section 20 (Carboxylic Acids from Alkyls)

$$\text{i-PrC(Me)}_2\text{H} \xrightarrow[\text{2 } H_2SO_4 \text{ } H_2O \quad \text{3 NaOH } H_2O]{\text{1 } (CN)_2 \text{ dibenzoyl peroxide}} \text{i-PrC(Me)}_2\text{COOH}$$

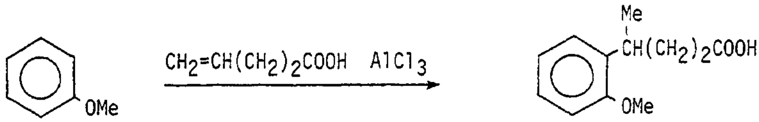
JACS (1969) 91 3028



JACS (1972) 94 4298

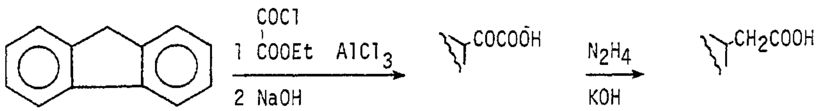
$$\text{PhH} \xrightarrow{\text{ClC(Me)=CHCOOH} \quad AlCl_3} \text{Ph}_2\text{C(Me)CH}_2\text{COOH} \qquad 36\%$$

JACS (1943) 65 59



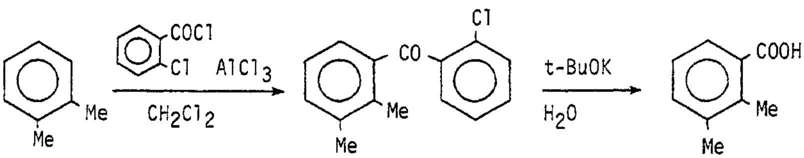
23%

Tetrahedron (1967) 23 2481



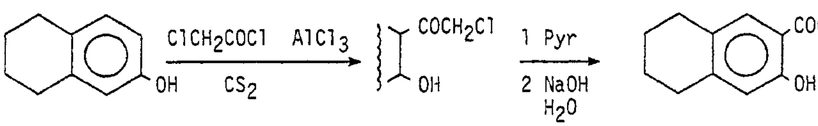
75%

J Med Chem (1972) 15 1029



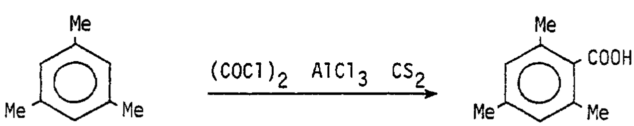
58%

Tetr Lett (1971) 3825



44%

Tetrahedron (1970) 26 201

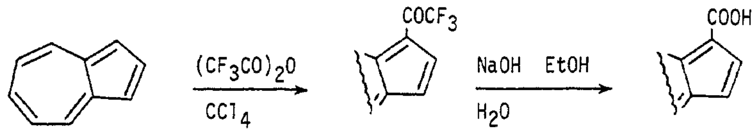


65-76%

Org Synth (1964) 44 69

$PhH \xrightarrow{ClCOSEt \quad AlCl_3} PhCOSEt \xrightarrow{Hydrolysis} PhCOOH$ ~49%

Annalen (1972) 761 77



81%

JOC (1962) 27 3578

$PhH \xrightarrow{TlCl_4 \cdot 4H_2O \quad CCl_4} PhCOOH$ 10%

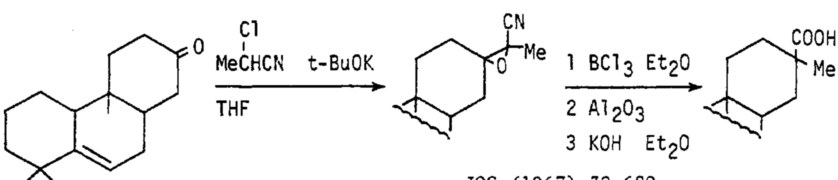
JCS Perkin I (1972) 2268

Also via: Esters (Section 116)

Section 27 Carboxylic Acids from Ketones

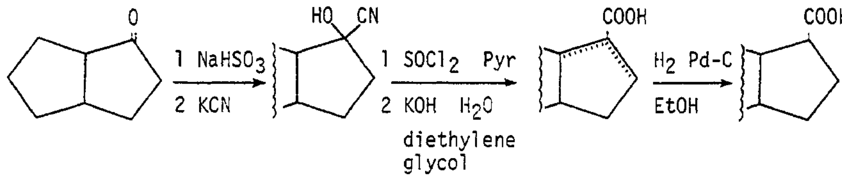
$Me_2CO \xrightarrow[\text{2 MeMgI CuCl } Et_2O]{\text{1 } CH_2(COOEt)_2 \text{ } ZnCl_2 \text{ } Ac_2O} Me_3CCH(COOEt)_2 \xrightarrow[\text{2 } \Delta]{\text{1 Hydrolysis}} Me_3CCH_2COOH$

Org Synth (1970) 50 38

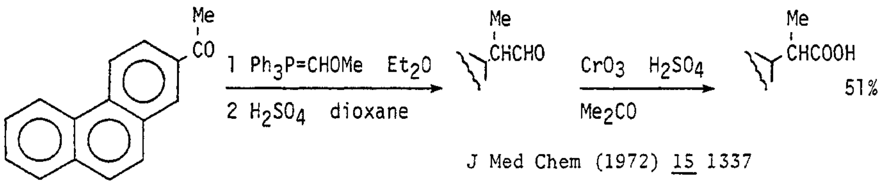


14%

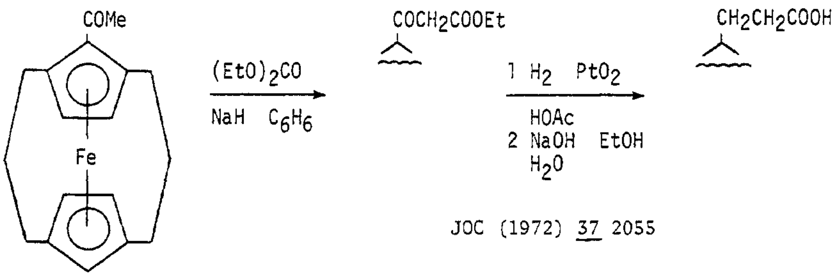
JOC (1967) 32 689



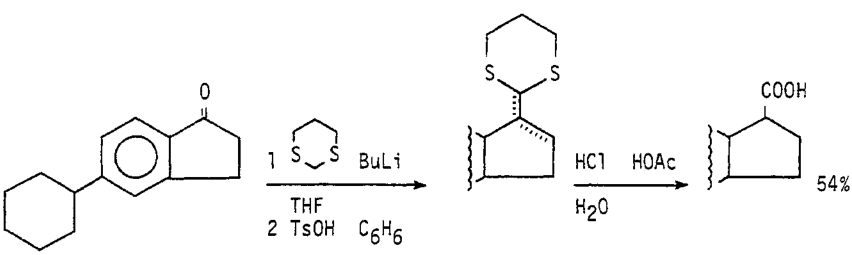
JOC (1970) 35 2376



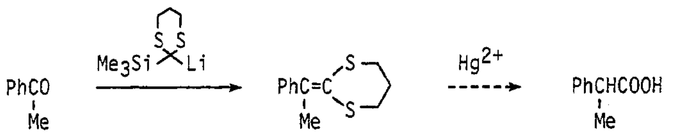
J Med Chem (1972) 15 1337



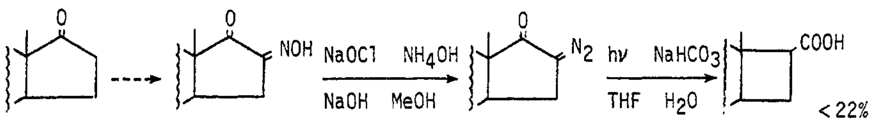
JOC (1972) 37 2055



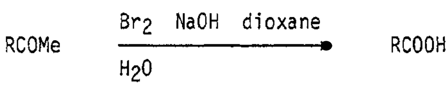
J Med Chem (1972) 15 1297



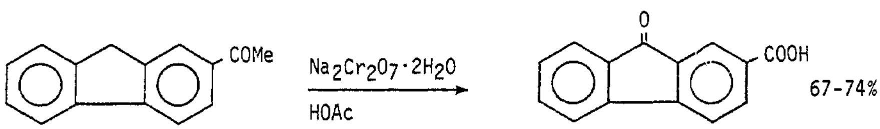
Chem Comm (1972) 526
Ber (1973) 106 2277



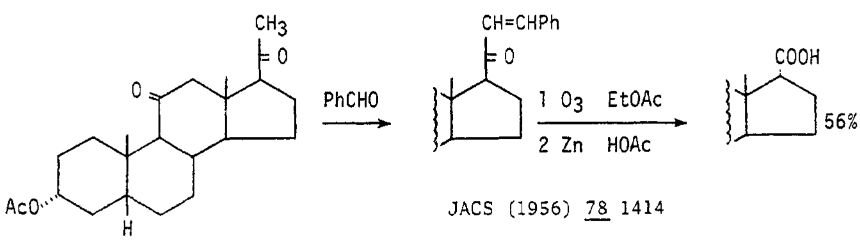
JACS (1972) 94 1282



JOC (1972) 37 25
Annalen (1971) 747 14
Tetrahedron (1972) 28 3381



Org Synth (1960) Coll Vol 3 420



JACS (1956) 78 1414

$$\mathrm{RCOPh} \xrightarrow[150°]{\text{t-BuOK}\quad H_2O\quad \text{anisole}} \mathrm{RCOOH}$$

Ber (1971) <u>104</u> 2637

$$C_{14}H_{29}CH_2COPh \xrightarrow[HCl\quad \text{dioxane}\quad H_2O]{\text{i-PrCH}_2CH_2ONO} C_{14}H_{29}\underset{\underset{NOH}{\|}}{C}COPh \xrightarrow[2\ KOH\quad PrOH]{1\ TsCl\quad NaOH\quad H_2O} C_{14}H_{29}COOH$$

JACS (1953) <u>75</u> 2347

Also via:

	Section
Esters	117
Ketoacids	320
Ketoesters	360
Ketoamides	347
Olefinic acids	322
Olefinic esters	362
Olefinic amides	349

Section 28 Carboxylic Acids from Nitriles

No additional examples

Section 29 Carboxylic Acids from Olefins

$$RCH{=}CH_2 \xrightarrow[\text{di-t-butyl peroxide}]{CH_3COOH} R(CH_2)_3COOH$$

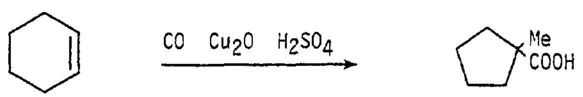
Synthesis (1970) 99
Chem Comm (1973) 694

$$R_2C{=}CH_2 \xrightarrow{CH_2{=}CCl_2\quad BF_3\quad H_2SO_4} R_2\underset{\underset{Me}{|}}{C}CH_2COOH$$

Ber (1967) <u>100</u> 978

$C_6H_{13}CH{=}CH_2 \xrightarrow[\substack{MeOCH_2CH_2OMe \quad H_2O \\ 2\ NaBH_4 \quad NaOH \quad THF \\ 3\ KMnO_4 \quad NaOH \quad H_2O}]{1\ CH(NO_2)_3 \quad Hg(NO_3)_2 \quad HClO_4} C_6H_{13}CH(Me)COOH$ 8%

Acta Chem Scand (1970) <u>24</u> 550



63%

JOC (1973) <u>38</u> 2016

$R_2C{=}CH_2 \xrightarrow[2\ H_2O_2 \quad NaOH \quad H_2O]{1\ NaBH_4 \quad AlCl_3 \quad diglyme} R_2CHCH_2OH \xrightarrow[HOAc \quad H_2O]{CrO_3 \quad H_2SO_4} R_2CHCOOH$ 53%

JACS (1960) <u>82</u> 2498

$PhCH{=}CHPh \xrightarrow[C_6H_6]{KMnO_4 \quad \text{dicyclohexyl-18-crown-6}} PhCOOH$ 100%

JACS (1972) <u>94</u> 4024

Also via:

	Section
Esters	119
Olefinic esters	362

Section 30 <u>Carboxylic Acids from Miscellaneous Compounds</u>

$MeCH{=}CHCOOH \xrightarrow{EtMgBr \quad Et_2O} MeCH(Et)CH_2COOH$ 40%

JACS (1953) <u>75</u> 6342

$$PhCH{=}CHCOOH \xrightarrow[2\ MeI]{1\ Li\quad HMPA} PhCH_2\underset{\displaystyle Me}{C}HCOOH \qquad 63\%$$

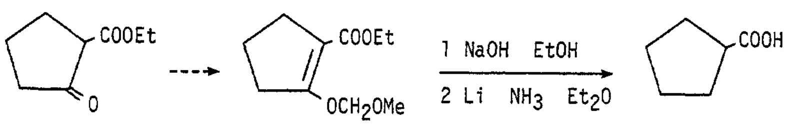
Compt Rend (1969) C 268 640

$$R_2C{=}\underset{\displaystyle R}{C}COOH \longrightarrow R_2CH\underset{\displaystyle R}{C}HCOOH$$

$Li\text{-}NH_3$	JOC (1971) 36 1151
Na-Hg	J Med Chem (1965) 8 598
$NiCl_2\text{-}KCN\text{-}NaBH_4$	Tetr Lett (1968) 1821

$$PhC{\equiv}CCOOH \xrightarrow[Me_2SO_4\quad HOAc\quad H_2O]{N_2H_4\quad NaIO_4\quad CuSO_4} PhCH_2CH_2COOH \qquad 85\%$$

Chem Comm (1971) 1245



JOC (1971) 36 1151

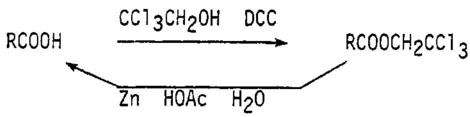
$$C_8H_{17}CH{=}CH(CH_2)_7COOH \xrightarrow{KOH\quad 360°} C_8H_{17}(CH_2)_7COOH \qquad 80\text{-}85\%$$

Tetrahedron (1960) 8 221

$$C_6H_{13}CH{=}CHCOOH \xrightarrow{KOH\quad 360°} C_6H_{13}COOH \qquad \sim 80\%$$

Tetrahedron (1960) 8 221

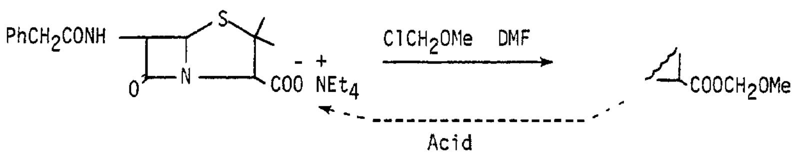
Section 30A Protection of Carboxylic Acids



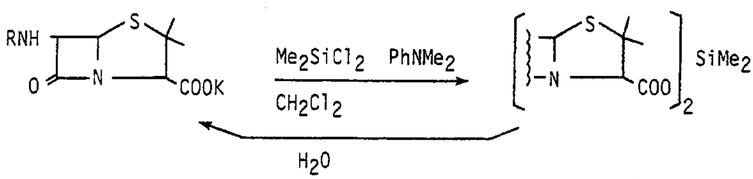
JOC (1970) 35 2430
(1971) 36 1259
J Med Chem (1971) 14 420 426

Selective removal of haloethoxy groups by electrolysis

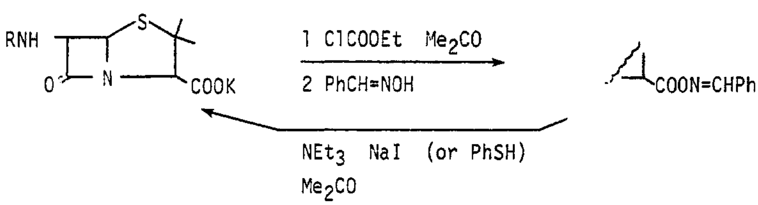
JACS (1972) 94 5139



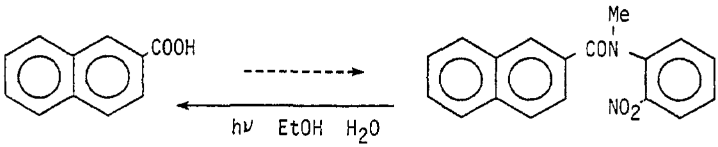
JCS (1965) 2127



Rec Trav Chim (1970) 89 1081



JCS C (1971) 1917



Tetr Lett (1973) 2205

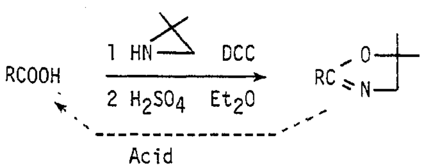
$$RCOOH \dashrightarrow RCONHNH_2 \qquad RCOOH \xleftarrow{Ce(NH_4)_2(NO_3)_6} RCONHNH_2$$

Synthesis (1972) 562

$$C_{15}H_{31}COOH \dashrightarrow C_{15}H_{31}COCl \xrightarrow[C_6H_6]{i\text{-}PrNHNHPr\text{-}i} C_{15}H_{31}CON(i\text{-}Pr)NHPr\text{-}i$$

$$C_{15}H_{31}CON(i\text{-}Pr)NHPr\text{-}i \xrightarrow{Pb(OAc)_4 \quad Pyr} C_{15}H_{31}COOH$$

JCS Perkin I (1972) 929



(Stable to RMgX and $LiAlH_4$)

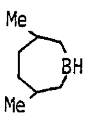
Tetr Lett (1972) 3031

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 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 3 PREPARATION OF ALCOHOLS AND PHENOLS

Section 31 Alcohols from Acetylenes



$PrC{\equiv}CH \xrightarrow[\text{2 MeLi } Et_2O \quad \text{3 } CH_2{=}CHCH_2Br \quad \text{4 NaOH } H_2O_2 \ H_2O]{\text{1 (above reagent) THF}} PrCH_2CH(OH)CH_2CH{=}CH_2$ 84%

Synthesis (1973) 37

$EtCH(Me)C{\equiv}CH \xrightarrow[\text{2 } HC{\equiv}CCH_2OH \ \ CuCl_2 \ \ NH_2OH \ \ EtNH_2]{\text{1 NaOBr}} EtCH(Me)(C{\equiv}C)_2CH_2OH \xrightarrow[\text{EtOH}]{H_2 \ \ PtO_2} EtCH(Me)(CH_2)_4CH_2OH$ 55%

JOC (1971) 36 2902

Also via:

	Section
Acetylenic alcohols	302
Olefinic alcohols	332

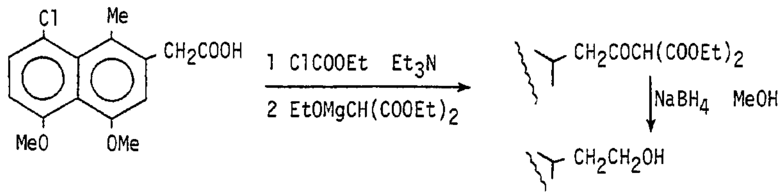
Section 32 Alcohols from Carboxylic Acids

$$BuCOOH \xrightarrow{C_5H_{11}MgBr \quad Et_2O \quad C_6H_6} BuC(C_5H_{11})_2OH$$ 40-60%

JACS (1946) 68 1382

$$Ph(CH_2)_2COOH \xrightarrow[(CF_3CO)_2O]{CF_3CH_2OH} Ph(CH_2)_2COOCH_2CF_3 \xrightarrow[MeOCH_2CH_2OMe]{NaBH_4} Ph(CH_2)_2CH_2OH$$

JOC (1970) 35 1505



66%

Ber (1965) 98 3040

$$RCOOH \xrightarrow{B_2H_6 \quad THF} RCH_2OH$$

JOC (1973) 38 2786

$$RCOOH \xrightarrow[EtOH \quad H_2O]{Electrolysis \quad H_2SO_4} RCH_2OH$$

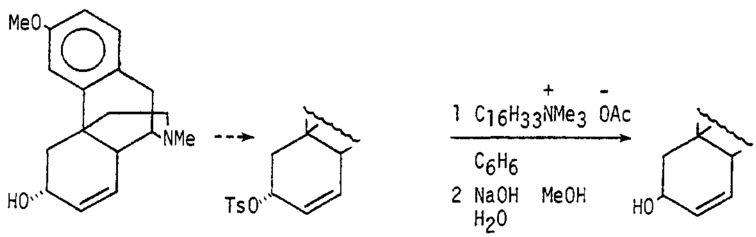
Synthesis (1971) 285

Also via: Esters (Section 38)

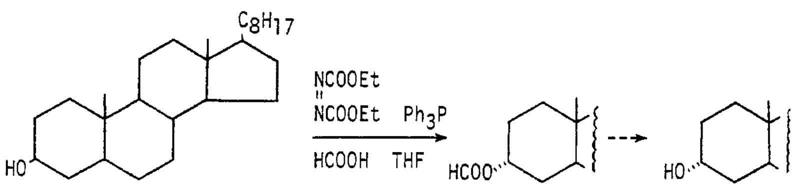
Section 33 Alcohols from Alcohols and Phenols

$C_6H_{13}CH_2CH_2OH \xrightarrow[295°]{C_8H_{17}ONa \quad \text{copper bronze}} C_6H_{13}\underset{\displaystyle CH_2CH_2C_6H_{13}}{CH}CH_2OH$ 52%

JOC (1950) 15 54
JACS (1954) 76 52



JCS C (1971) 3047



97%

Tetr Lett (1973) 1619

$PrCH_2OH \dashrightarrow PrCH_2OOH \xrightarrow[CH_2Cl_2]{H_2SO_4 \quad H_2O} PrOH$ < 60%

JOC (1970) 35 3080

$PhOH \dashrightarrow PhOPO(OEt)_2 \xrightarrow[K \quad NH_3]{MeCOCH_2K} PhCH_2\underset{\displaystyle OH}{CH}Me$ < 42%

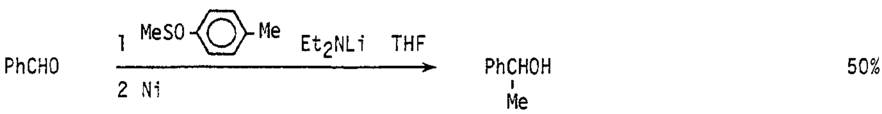
JACS (1972) 94 683

Section 34 Alcohols from Aldehydes

$$\mathrm{RCHO} \xrightarrow{\text{MeBr Li THF}} \underset{\mathrm{Me}}{\mathrm{RCHOH}}$$

(One-step procedure)

JCS Perkin I (1972) 1655



Tetr Lett (1972) 4605

$$\mathrm{C_5H_{11}CHO} \xrightarrow{\text{i-PrC(Me)}_2\text{BH}_2\ \ \text{THF}} \mathrm{C_5H_{11}CH_2OH}$$

JOC (1972) 37 2942

Related methods: Alcohols from Ketones (Section 42)

Also via:

	Section
Acetylenic alcohols	302
Olefinic alcohols	332

Section 35 Alcohols and Phenols from Alkyls, Methylenes and Aryls

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

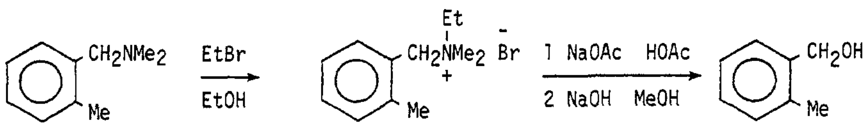
Section 36 Alcohols and Phenols from Amides

No additional examples

Section 37 Alcohols and Phenols from Amines

$$ArNH_2 \xrightarrow[\text{2 } HPF_6]{\text{1 } NaNO_2 \quad HCl \quad H_2O} ArN_2^+ \ PF_6^- \xrightarrow[\text{2 } NaOH]{\text{1 } Me_2NCONMe_2} ArOH$$

JOC (1963) 28 568



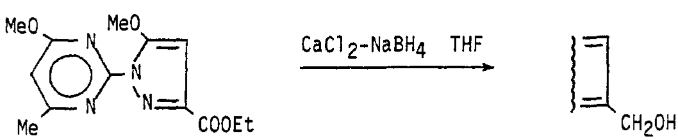
Org Synth (1963) Coll Vol 4 582 ~80%

Also via: Esters (Section 112)

Section 38 Alcohols from Esters

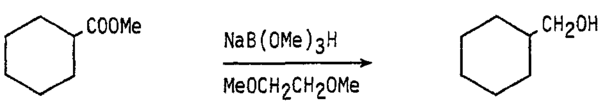
$$PhCH_2COOEt \xrightarrow{Na \quad NH_3} PhCH_2CH_2OH$$

Compt Rend (1913) 156 1020



76%

Chem Pharm Bull (1970) 18 1908



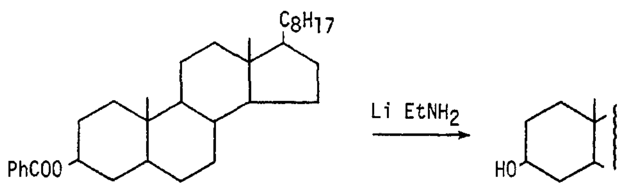
Can J Chem (1969) 47 2099

$$\underset{\mid \atop Me}{PrC}{=}CHCOOEt \xrightarrow{AlH_3 \quad THF} \underset{\mid \atop Me}{PrC}{=}CHCH_2OH \qquad 74\%$$

Tetr Lett (1973) 1277

$$C_8H_{17}COOEt \xrightarrow[C_6H_6]{NaAl(OCH_2CH_2OMe)_2H_2} C_8H_{17}CH_2OH \qquad 92\%$$

Coll Czech (1969) 34 1025



62%

Synthesis (1972) 391

$$HCOOC_8H_{17} \xrightarrow{Pd\text{-}C \quad 200^\circ} C_8H_{17}OH \qquad 94\%$$

JOC (1970) 35 1694
(1973) 38 3954

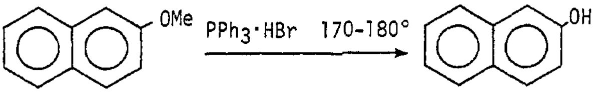
$$ROAc \xrightarrow{HCl \quad MeOH} ROH$$

Acta Chem Scand (1952) 6 1127

Related methods:

	Section
Carboxylic Acids from Esters	23
Protection of Alcohols	45A

Section 39 Alcohols and Phenols from Ethers and Epoxides

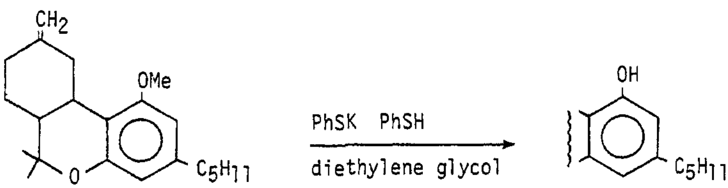


74%

Annalen (1967) 709 105

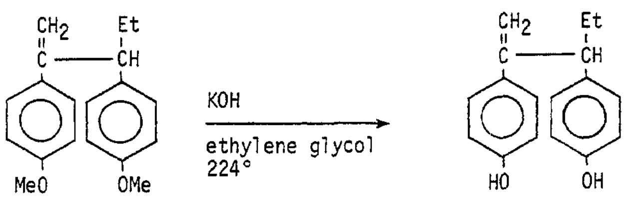
$$\text{ArOMe} \xrightarrow{\text{EtSNa} \quad \text{DMF}} \text{ArOH}$$

Tetr Lett (1972) 241



(Applicable to compounds with labile double bonds)

JOC (1971) 36 721



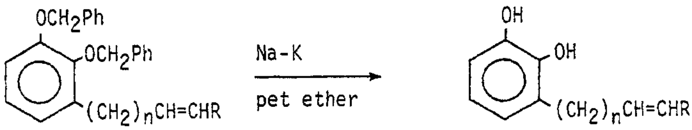
<55%

JACS (1943) 65 11

$$\underset{\text{COOH}}{\vert}(CH_2)_9CH_2OEt \xrightarrow{\text{KOH} \quad 200°} \underset{\text{COOH}}{\vert}(CH_2)_9CH_2OH$$

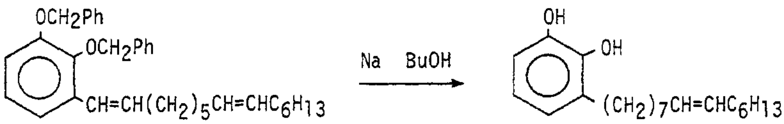
26%

JCS C (1971) 1840

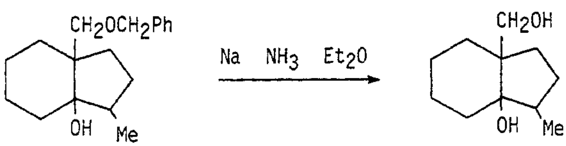


75%

JOC (1965) 30 1610



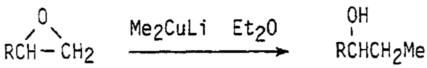
JOC (1959) 24 980



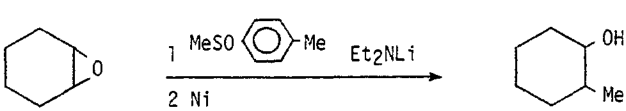
70%

JOC (1971) 36 2035

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

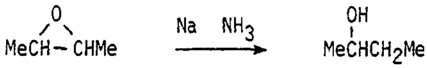


JACS (1970) 92 3813
JOC (1973) 38 4263 4346



~44%

Tetr Lett (1972) 4605



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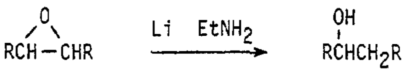
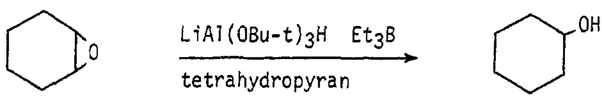
JOC (1971) 36 330



Synthesis (1972) 391



100%

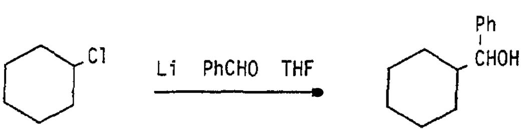
JACS (1972) 94 1750

Section 40 Alcohols and Phenols from Halides and Sulfonates

$$C_5H_{11}Br \xrightarrow{Mg} C_5H_{11}MgBr \xrightarrow[C_6H_6]{PrCOOH \quad Et_2O} PrC(OH)(C_5H_{11})_2$$

40-60%

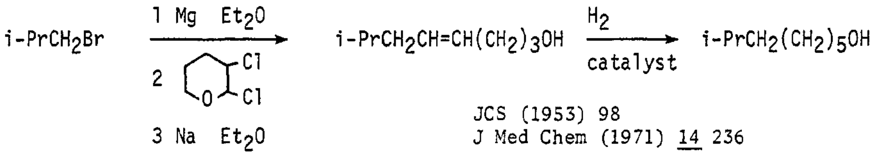
JACS (1946) 68 1382



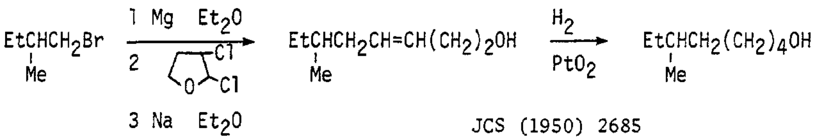
60%

(One-step procedure)

JCS Perkin I (1972) 1655



JCS (1953) 98
J Med Chem (1971) 14 236

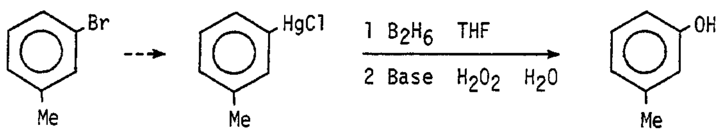


36%

JCS (1950) 2685

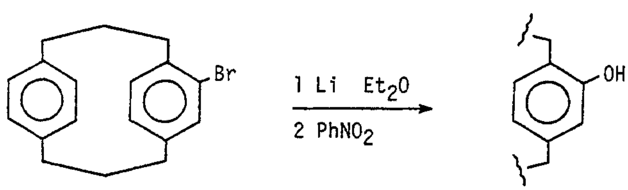
$C_7H_{15}Br \xrightarrow[\text{2 } CO_2 \quad \text{3 } NaAl(OCH_2CH_2OMe)_2H_2]{\text{1 Mg} \quad Et_2O} C_7H_{15}CH_2OH$ 85%

Coll Czech (1971) 36 2394



70%

Chem Comm (1971) 1475



51%

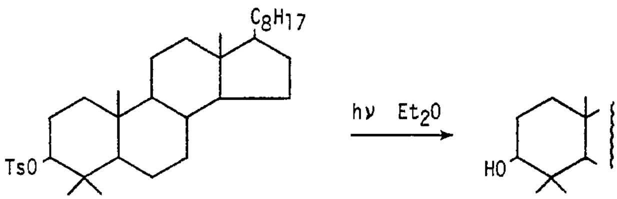
JACS (1969) 91 3544

$ArCH_2Cl \xrightarrow{AgNO_3 \quad Me_2CO \quad H_2O} ArCH_2OH$ 79%

JOC (1971) 36 1765

$C_5H_{11}CH(Br)\text{-}CH(Br)CH_2CH(Br)\text{-}CH(Br)(CH_2)_7Br \xrightarrow[PhBr \quad EtOH]{CF_3COONa} C_5H_{11}CH(Br)\text{-}CH(Br)CH_2CH(Br)\text{-}CH(Br)(CH_2)_7OH$ 39%

Acta Chem Scand (1953) 7 1001

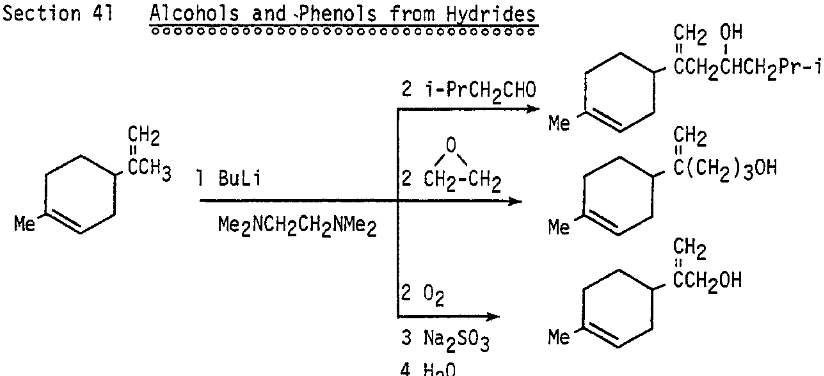


78%

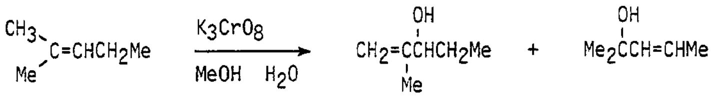
Tetr Lett (1971) 4555 4559
Bull Chem Soc Jap (1968) 41 3025

Also via: Section
Olefinic alcohols 332
Acetylenic alcohols 302

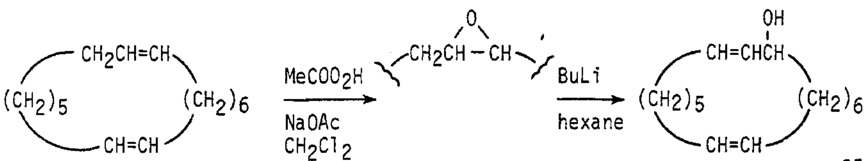
Section 41 Alcohols and Phenols from Hydrides



JACS (1972) 94 4298
JOC (1972) 37 3543

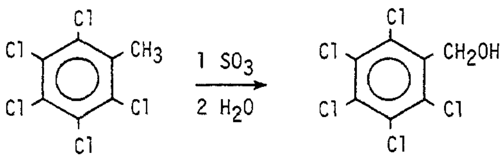


JACS (1972) 94 4348



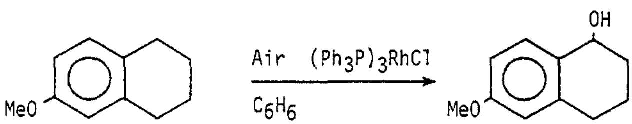
35%

JOC (1971) 36 3266
Synthesis (1972) 194



~91%

JACS (1971) 93 3538



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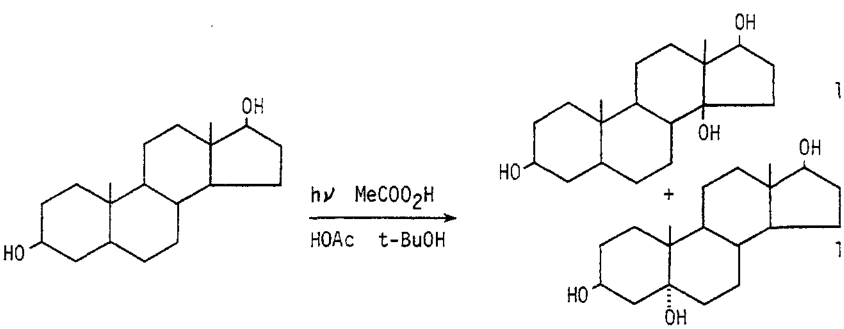
Tetr Lett (1968) 2917



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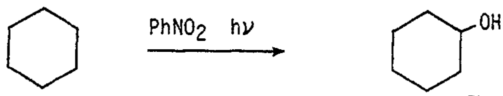
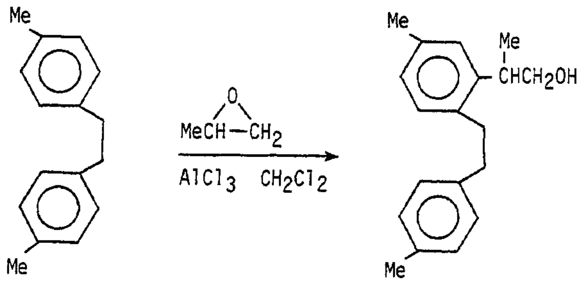
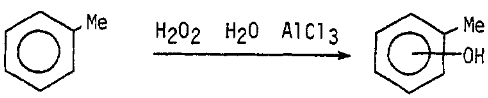
JACS (1972) 94 6228



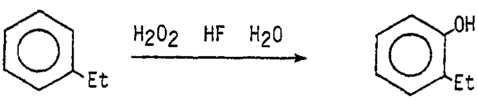
Chem Comm (1970) 1390



JACS (1972) 94 4241



JOC (1971) 36 3184



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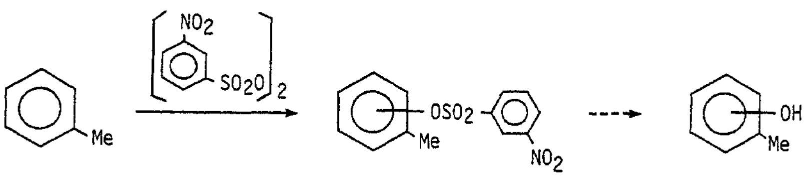
JOC (1970) 35 4028



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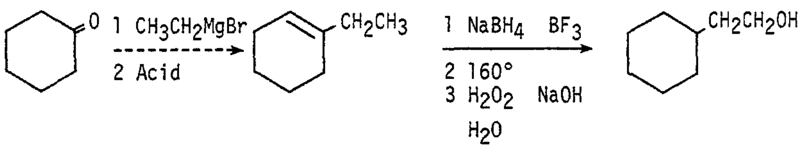
JOC (1966) 31 153

Also via: Esters (Section 116)

Section 42 Alcohols from Ketones

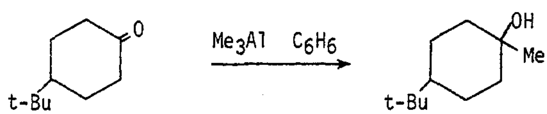


JACS (1967) 89 561

$$R_2CO \xrightarrow{\text{BuBr Li THF}} R_2C(OH)Bu$$

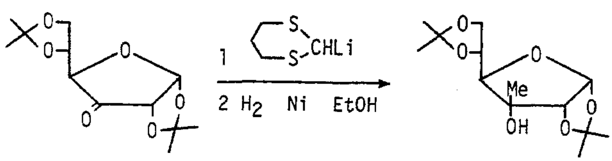
(One-step procedure)

JCS Perkin I (1972) 1655



87%

Chem Comm (1971) 351



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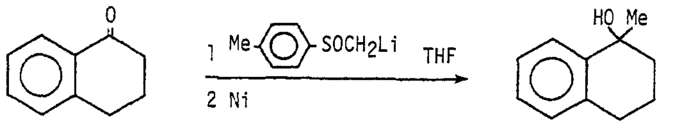
Ber (1972) 105 1978



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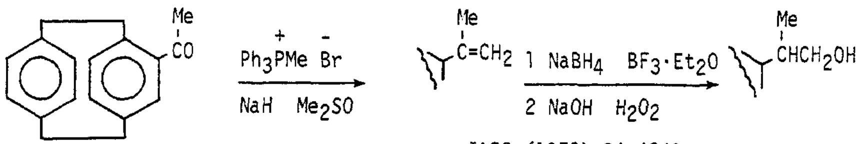
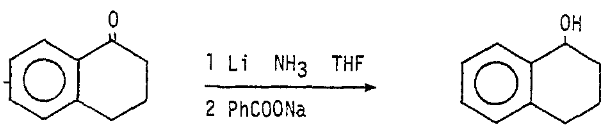
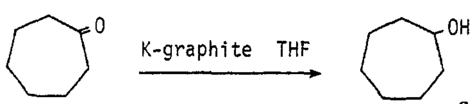
Tetr Lett (1972) 4605



JACS (1972) 94 4241

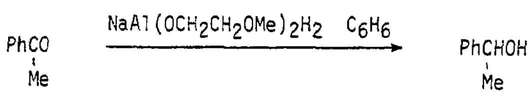


Tetr Lett (1971) 1853



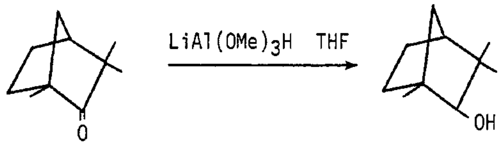
92%

Can J Chem (1972) 50 3058



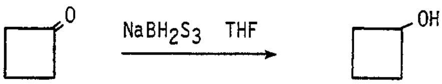
90%

Coll Czech (1969) 34 118



80%

Synthesis (1972) 217



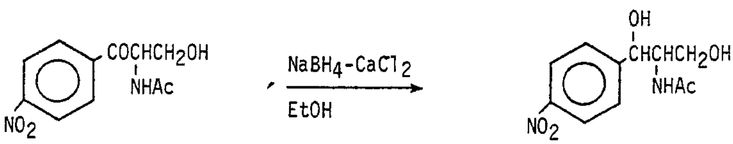
90%

Can J Chem (1970) 48 2366
Synthesis (1972) 526

$$\underset{\displaystyle Me}{PhCO} \xrightarrow[\text{pH 4}]{NaBH_3CN\quad MeOH} \underset{\displaystyle Me}{PhCHOH}$$

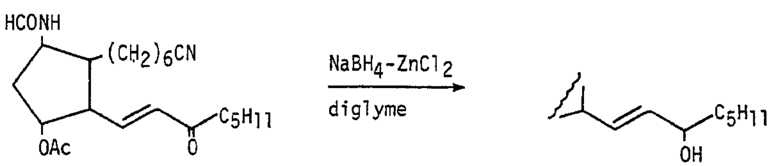
93%

JACS (1971) 93 2897

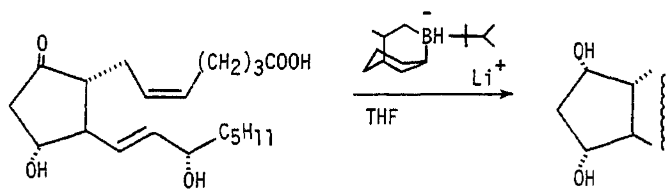


70%

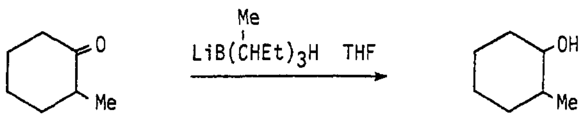
Ber (1960) 93 387



JACS (1968) 90 3245
(1960) 82 6074



JACS (1971) 93 7319

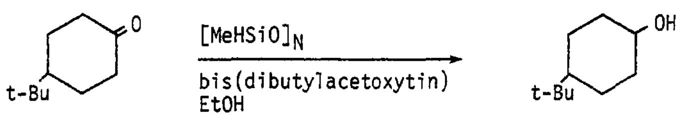


100% (99% cis)

JACS (1972) 94 7159

$R_2CO \xrightarrow{R'_2SnH_2 \text{ or } R'_3SnH} R_2CHOH$

Synthesis (1970) 499



65%

JOC (1973) 38 162

$R_2CO \xrightarrow[\text{i-PrOH} \quad H_2O]{IrCl_4 \quad (MeO)_3P \quad HCl} R_2CHOH$

Org Synth (1970) 50 13

$C_9H_{19}C(O)Me \xrightarrow[\text{EtOH} \quad H_2O]{\overset{+}{N}H_2{=}C(NH_2)SO_2^- \quad NaOH} C_9H_{19}CH(OH)Me$

74%

Tetr Lett (1972) 343
JCS Perkin I (1973) 2633

Related methods: Alcohols from Aldehydes (section 34)

		Section
Also via:	Olefinic alcohols	332
	Acetylenic alcohols	302

Section 43 Alcohols and Phenols from Nitriles

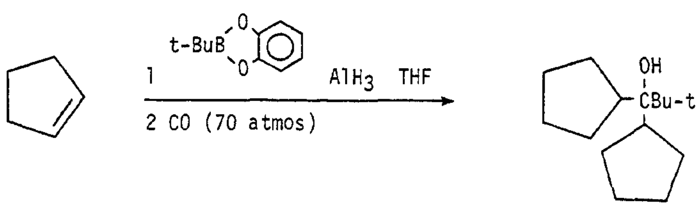
No examples

Section 44 Alcohols from Olefins

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

$$C_6H_{13}CH{=}CH_2 \xrightarrow[\substack{2\ NaCN \\ 3\ (CF_3CO)_2O \\ 4\ H_2O_2\ \ NaOH\ \ H_2O}]{1\ B_2H_6\ \ THF} (C_6H_{13}CH_2CH_2)_3COH \quad 75\%$$

Chem Comm (1971) 1048
JACS (1971) 93 2070
JOC (1973) 38 3968



60%

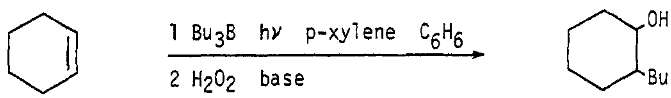
Synthesis (1972) 197

$$EtCH{=}CH_2 \xrightarrow[\substack{2\ Br_2\ \ h\nu\ \ CH_2Cl_2\ \ H_2O \\ 3\ H_2O_2\ \ NaOH\ \ H_2O}]{1\ B_2H_6\ \ THF} (EtCH_2CH_2)_2C(OH)CH_2Et \quad 76\%$$

JACS (1971) 93 1025
Synthesis (1972) 699

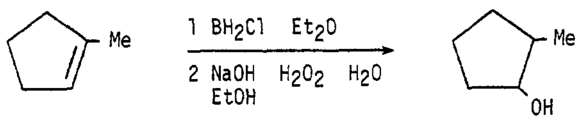
$Me_2C{=}CHMe \xrightarrow[\substack{2\ MeOH \\ 3\ Br_2\ \ h\nu\ \ CH_2Cl_2\ \ H_2O \\ 4\ H_2O_2\ \ NaOH\ \ EtOH\ \ H_2O}]{1\ B_2H_6\ \ THF}$ $Me_2CHC(Me)(OH)$–$CHMeCHMe_2$ (Me / Me_2CHCOH / $Me_2CHCHMe$) 82%

Synthesis (1972) 303 304 699

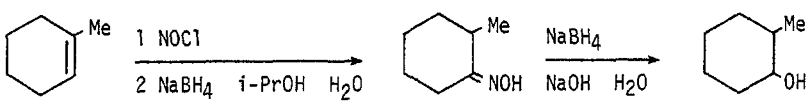


80%

Tetrahedron (1973) 29 2365



JOC (1973) 38 182



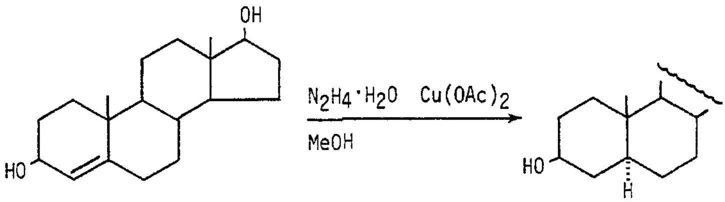
74%

Aust J Chem (1971) 24 1089

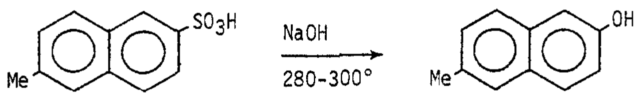
Section 45 Alcohols from Miscellaneous Compounds

$PhCH{=}CHCH_2OH \xrightarrow{H_2\ \ nickel\ boride\ \ EtOH} Ph(CH_2)_3OH$ 100%

JOC (1971) 36 2018



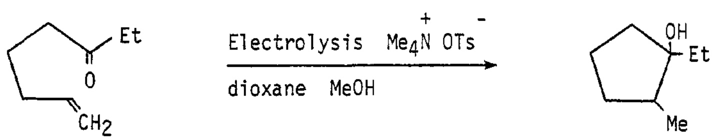
JOC (1971) 36 2730



Ber (1925) 58B 1211
JACS (1949) 71 3889

$Ph_2S \xrightarrow{MeCOCH_2K \quad K \quad NH_3} PhCH_2\underset{|\;\;\;\;}{C}HOH$ (Me) 71%

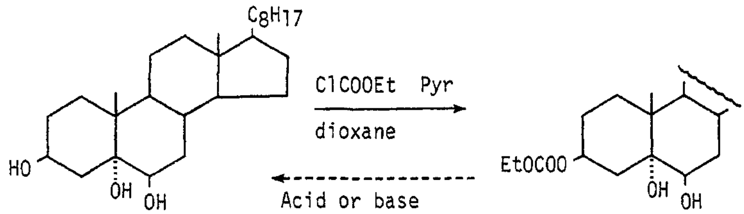
JACS (1972) 94 683



47%

JACS (1971) 93 5284

Section 45A Protection of Alcohols and Phenols



JACS (1952) 74 3309

$$\mathrm{ROH} \; \underset{\text{Electrolysis}}{\overset{\mathrm{ClCOOCH_2CCl_3}\quad\mathrm{Pyr}}{\rightleftarrows}} \; \mathrm{ROCOOCH_2CCl_3}$$

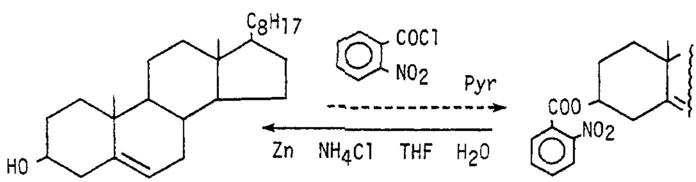
JACS (1972) 94 5139

$$\mathrm{C_{10}H_{21}OH} \; \underset{\mathrm{Ni(CO)_4}\quad \mathrm{Me_2NCH_2CH_2NMe_2}\quad \mathrm{DMF}}{\overset{\mathrm{ClCOOCH_2CH{=}CH_2}\quad\mathrm{Pyr}}{\rightleftarrows}} \; \mathrm{C_{10}H_{21}OCOOCH_2CH{=}CH_2}$$

JOC (1973) 38 3223 3575

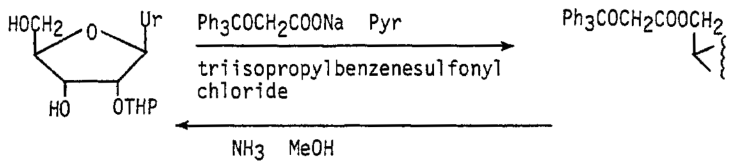
$$\begin{array}{l}\mathrm{Ur}\\ \mathrm{CH_2}\\ \mathrm{HOCH}\\ \mathrm{HOCH_2}\end{array} \; \underset{\alpha\text{-Chymotrypsin}\quad \mathrm{pH}\ 7.8}{\overset{\mathrm{(PhCH_2CH_2CO)_2O}\quad\mathrm{Pyr}}{\rightleftarrows}} \; \begin{array}{r}\mathrm{Ur}\\ \mathrm{CH_2}\\ \mathrm{PhCH_2CH_2COOCH}\\ \mathrm{PhCH_2CH_2COOCH_2}\end{array}$$

JOC (1973) 38 977

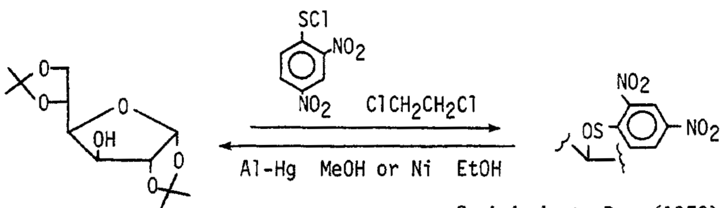


(Applicable to phenols)

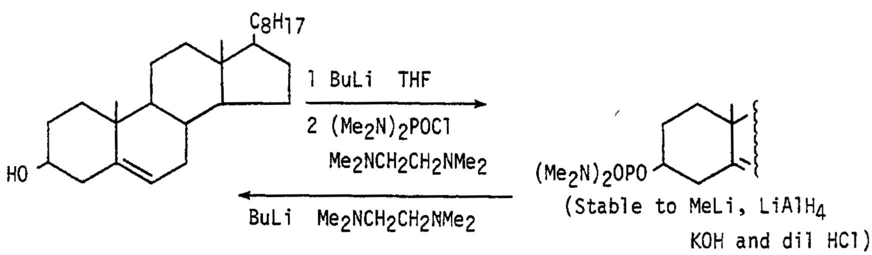
JCS Perkin I (1973) 599



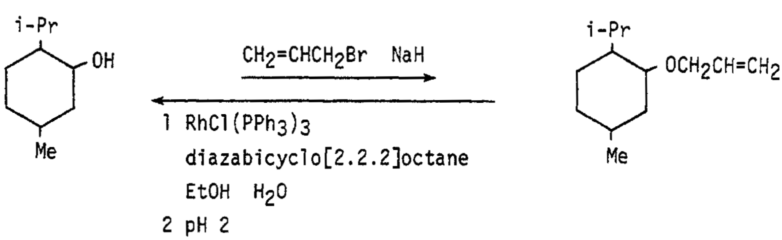
Can J Chem (1972) 50 1283



Carbohydrate Res (1972) 21 301



JACS (1972) 94 5098



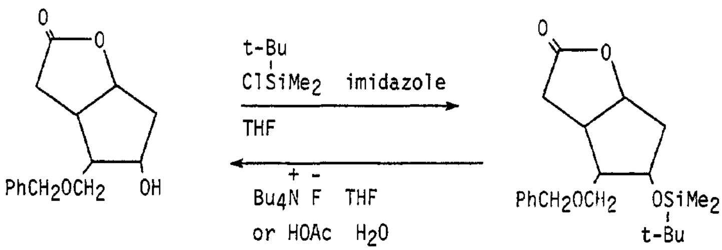
JOC (1973) 38 3224

$$\mathrm{ROH} \underset{\mathrm{H_2\ \ Pd\text{-}C\ \ EtOH}}{\overset{\mathrm{NaH\ \ PhCH_2Br\ \ C_6H_6}}{\rightleftarrows}} \mathrm{ROCH_2Ph}$$

JACS (1971) 93 1746

Cleavage of benzyl ethers with $Ph_3\overset{+}{C}\ \overset{-}{B}F_3$ JCS Perkin I (1972) 542

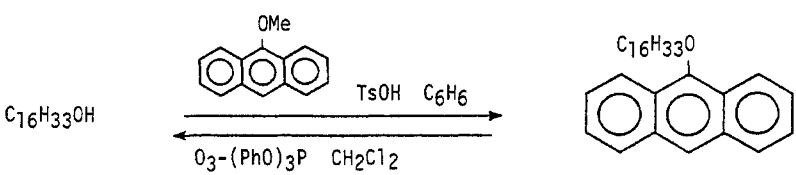
Further examples of the cleavage of benzyl ethers are included in Section 39 (Alcohols and Phenols from Ethers and Epoxides)



(More stable than $OSiMe_3$. Stable to base, Wittig reagents, $(i\text{-}Bu)_2AlH$ and H_2/Pd)

JACS (1972) 94 6190
Tetr Lett (1973) 317

Preparation of $ROSiMe_3$ using Me_3SiNEt_2		JACS (1972) 94 3651
" " " " Me_3SiCl		Synth Comm (1971) 1 81
" " " " $MeCON(SiMe_3)_2$		J Med Chem (1973) 16 54
" " $ROSi(Me_2)Pr\text{-}i$ using $i\text{-}Pr(Me_2)SiCl$		JACS (1971) 93 7319
Cleavage of silyl ethers with H_2/Pd		JACS (1972) 94 6190 footnote 4

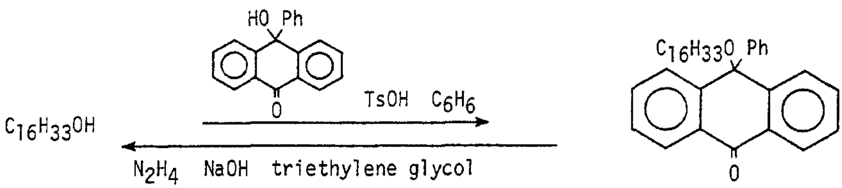


JOC (1971) 36 4134

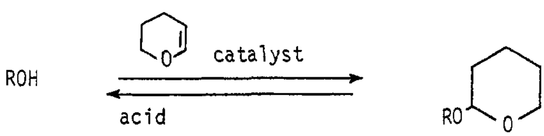
$$ROH \underset{H_2 \quad Pd\text{-}C \quad EtOH}{\overset{Ph_3CCl,\ Pyr \quad C_6H_6}{\rightleftharpoons}} ROCPh_3$$

JOC (1972) <u>37</u> 2877

Cleavage of trityl ethers with Na/NH_3 Tetr Lett (1972) 2349
Preparation of substituted trityl ethers JOC (1972) <u>37</u> 956
Polymer-bound trityl ethers Annalen (1972) <u>766</u> 6



Tetrahedron (1972) <u>28</u> 419



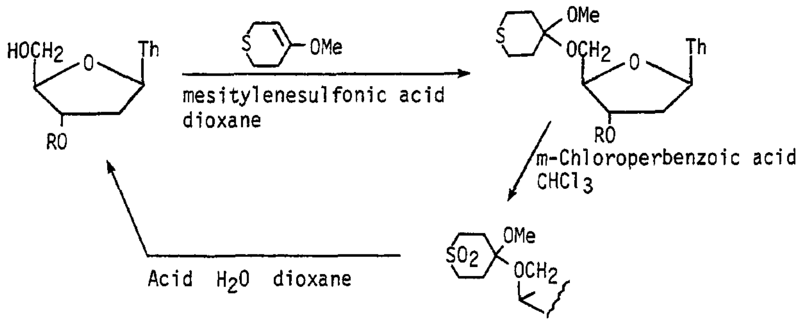
Catalyst: TsOH	Synthesis (1973) 169 Steroids (1964) <u>4</u> 229
Conc HCl	JCS Perkin I (1973) 720
$POCl_3$	JCS (1950) 3646
$BF_3 \cdot Et_2O$	Synthesis (1972) 81
Picric acid	Tetr Lett (1972) 3333
Ion exch resin (Acid)	JCS (1956) 4665

Cleavage of tetrahydropyranyl ethers with $Ph_3\overset{+}{C}\ \overset{-}{B}F_4$ Chem Comm (1971) 1109

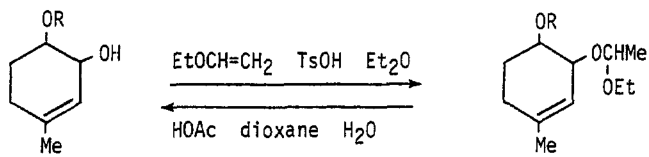
$$ROH \xrightarrow[CHCl_3]{MeOCH_2Cl\ (2\ equiv) \quad PhNEt_2\ (2\ equiv)} ROCH_2OMe$$

$$ROCH_2OMe \xrightarrow{Acid} ROH$$

V. Fletcher (Columbia Univ), unpublished



Chem Comm (1972) 766



(Stable to $LiAlH_4$ and base)

JCS C (1971) 2944

$$PhOH \underset{\text{Acid}}{\overset{HC(OEt)_3 \quad HCl \quad EtOH}{\rightleftarrows}} PhOCH(OEt)_2$$

Ber (1970) 103 643

Related methods:

	Section
Alcohols and Phenols from Ethers and Epoxides	39
Ethers from Alcohols and Phenols	123

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 4 PREPARATION OF ALDEHYDES

Section 46 Aldehydes from Acetylenes

$$EtC{\equiv}CH \xrightarrow[\text{toluene}]{CO \quad H_2 \quad HRh(CO)(Ph_3P)_3} EtCH(CHO)Me \qquad <75\%$$

Tetr Lett (1972) 3455

$$C_6H_{13}C{\equiv}CH \xrightarrow[\substack{\text{2 m-Chloroperbenzoic acid} \\ 3\ H_2SO_4 \quad MeOH \\ 4\ HOAc \quad H_2O}]{1\ Et_3SiH \quad H_2PtCl_6} C_6H_{13}CH_2CHO \qquad \sim 60\%$$

JACS (1971) 93 2080

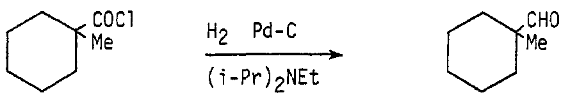
Section 47 Aldehydes from Carboxylic Acids and Acid Halides

$$C_5H_{11}COOH \xrightarrow{i\text{-}PrC(Me)_2BH_2 \quad THF} C_5H_{11}CHO \qquad 98\%$$

JOC (1972) 37 2942

$$PhCH_2COCl \xrightarrow[\text{2 HOAc EtOH } H_2O]{\text{1 } Na_2Fe(CO)_4} PhCH_2CHO \qquad \sim 59\%$$

JACS (1972) 94 2516
Bull Chem Soc Jap (1971) 44 2569
Tetr Lett (1973) 3535



78%

Rec Trav Chim (1971) 90 1323

$$C_7H_{15}COCl \xrightarrow{Et_3SiH \text{ Pd-C}} C_7H_{15}CHO \qquad 51\%$$

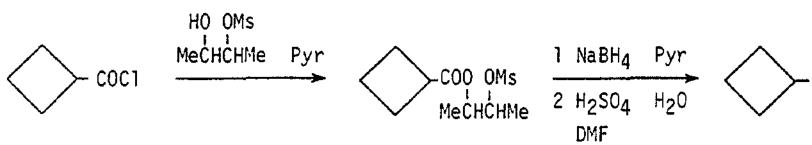
JOC (1969) 34 1977
Chem Comm (1970) 1703

$$RCOCl \xrightarrow{LiAl(OBu\text{-}t)_3H \text{ diglyme}} RCHO$$

Synthesis (1972) 217

$$PhCH{=}CHCOCl \xrightarrow[\text{2 } NaBH_4 \text{ MeOH; 3 NaOH}]{\text{1 } (EtO)_3P} PhCH{=}CHCHO \qquad 100\%$$

Ber (1970) 103 2984



~25%

Org Synth (1971) 51 11

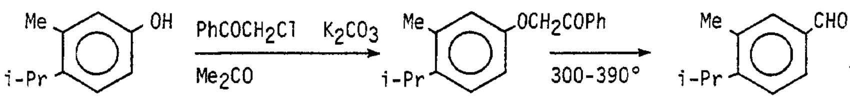
$PrCH_2COOH \dashrightarrow PrCH(Br)COOH \xrightarrow[\text{xylene}]{\text{Pyridine N-oxide}} PrCHO$ <67%

JOC (1966) 31 3058

$PhCH_2COOH \xrightarrow{Na_2S_2O_8 \quad AgNO_3 \quad H_2O} PhCHO$ 48%

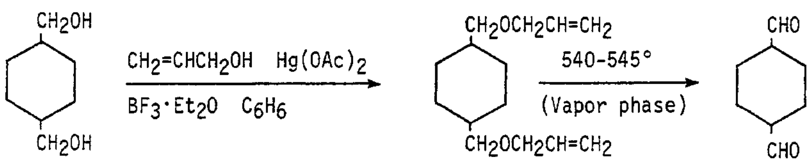
JCS (1960) 1332

Section 48 Aldehydes from Alcohols and Phenols



17%

Bull Soc Chim Fr (1960) 278
JOC (1961) 26 4308



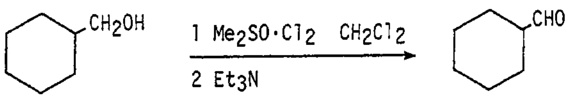
JCS C (1971) 2730

$C_7H_{15}CH_2OH \dashrightarrow C_7H_{15}CH_2OCPh_3 \xrightarrow[CH_2Cl_2]{Ph_3\overset{+}{C}\ \overset{-}{As}F_6} C_7H_{15}CHO$ <56%

JOC (1973) 38 625

$$C_7H_{15}CH_2OH \xrightarrow[Et_3N \quad \text{toluene}]{(CH_2CO)_2\overset{+}{N}\text{-}SMe_2\ \overset{-}{Cl}} C_7H_{15}CHO \qquad 96\%$$

JACS (1972) 94 7586

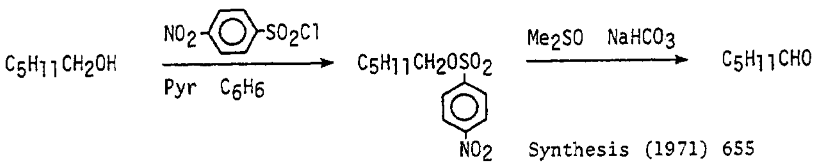


\> 95%

Tetr Lett (1973) 919

$$C_6H_{13}CH_2OH \xrightarrow[H_3PO_4 \quad Me_2SO \quad C_6H_6]{\text{Resin-}CH_2N{=}C{=}NPr\text{-}i} C_6H_{13}CHO$$

Tetr Lett (1972) 3285



33%

Synthesis (1971) 655

$$RCH_2OH \xrightarrow{\text{Argentic picolinate} \quad H_2O} RCHO$$

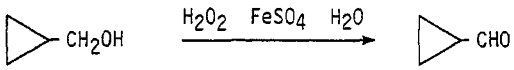
Tetrahedron (1973) 29 751

$$C_{15}H_{31}CH_2OH \xrightarrow[\text{toluene}]{CrO_3\text{-graphite}} C_{15}H_{31}CHO \qquad 95\%$$

Can J Chem (1972) 50 3058

$$C_7H_{15}CH_2OH \xrightarrow[\text{(vapor phase)}]{Cu_2O \quad 250\text{-}300°} C_7H_{15}CHO \qquad 98\%$$

Tetr Lett (1972) 257



37%

Can J Chem (1965) 43 2924

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

Section 49 Aldehydes from Aldehydes

$$C_{10}H_{21}CH_2CHO \xrightarrow[KOH \quad EtOH]{Fe(CO)_5 \quad HCHO} C_{10}H_{21}\underset{\substack{|\\ Me}}{CH}CHO \qquad 55\%$$

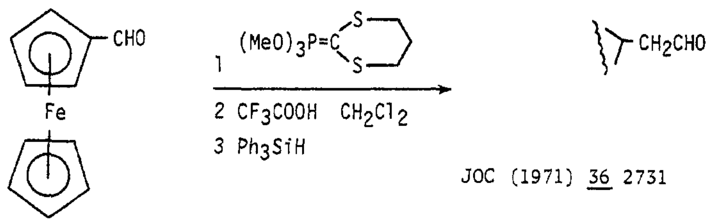
Tetr Lett (1973) 2491

$$Me_2CHCHO \xrightarrow[C_6H_6 \quad H_2O]{PhCH_2Cl \quad NaOH \quad Bu_4\overset{+}{N}\ \overset{-}{I}} Me_2\underset{\substack{|\\ PhCH_2}}{C}CHO \qquad 75\%$$

Tetr Lett (1973) 1273

$$PhCHO \xrightarrow[\substack{THF \quad MeOH \\ 2\ LiAlH_4}]{1\ MeSOCH_2SMe \quad PhCH_2\overset{+}{N}Me_3\ \overset{-}{O}H} PhCH_2CH(SMe)_2 \dashrightarrow PhCH_2CHO$$

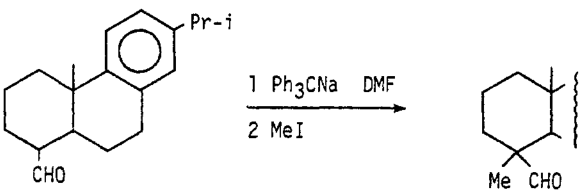
Tetr Lett (1972) 1383



JOC (1971) 36 2731

$$EtCHO \xrightarrow[THF]{BrCH_2COOEt \quad (Me_3Si)_2NLi} EtCH\overset{O}{-}CHCOOEt \xrightarrow[2\ \Delta]{1\ Base} EtCH_2CHO$$

Tetr Lett (1972) 3761



66%

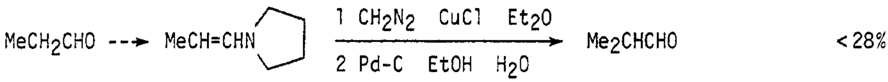
Chem Comm (1971) 10

$$Et_2CHCHO \dashrightarrow Et_2C{=}CHOAc \xrightarrow[2\ MeI]{1\ Bu_3SnOMe \quad MeCOOMe} Et_2\underset{Me}{C}CHO \qquad <82\%$$

Compt Rend (1970) C 270 100

$$C_5H_{11}CH_2CHO \xrightarrow[DMF \quad 2\ CH_2I_2 \quad Zn\text{-}Ag]{1\ ClSiMe_3 \quad Et_3N} C_5H_{11}\overset{\wedge}{CH\text{-}CH}OSiMe_3 \xrightarrow[H_2O]{NaOH \quad EtOH} C_5H_{11}\underset{Me}{CH}CHO \qquad >53\%$$

Tetr Lett (1973) 2767

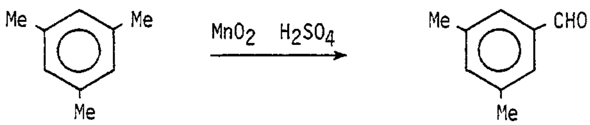


JOC (1973) 38 304

Related methods: Aldehydes from Ketones (Section 57)

Also via: Olefinic aldehydes (Section 341)

Section 50 Aldehydes from Alkyls



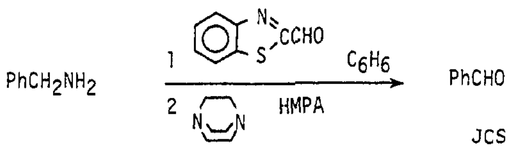
JACS (1946) 68 1085

Section 51 Aldehydes from Amides

$$RCONMe_2 \xrightarrow{LiAl(OEt)_3H \quad Et_2O} RCHO$$

Synthesis (1972) 217

Section 52 Aldehydes from Amines



69%

JCS Perkin I (1972) 1652

$$PrCH_2NH_2 \xrightarrow[H_2O]{[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+ \ PF_6^-} PrCHO$$

Chem Comm (1971) 1274

$$C_5H_{11}CH_2NH_2 \xrightarrow{h\nu \quad \text{cyclohexane}} C_5H_{11}CH{=}NCH_2C_5H_{11} \dashrightarrow C_5H_{11}CHO$$

Chem Comm (1971) 1430

$$PrCH_2NH_2 \xrightarrow{PhCOCH_2Br} PrCH_2NHCH_2COPh \xrightarrow{h\nu \quad MeOH \quad H_2O} PrCHO \qquad <57\%$$

JOC (1972) 37 1254

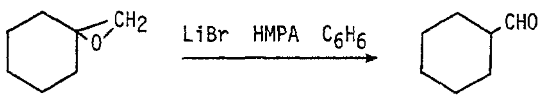
Section 53 Aldehydes from Esters

No additional examples

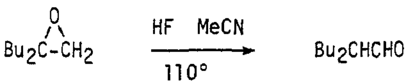
Section 54 Aldehydes from Ethers and Epoxides

$$PhCH_2OMe \xrightarrow{Ph_3\overset{+}{C}\ \overset{-}{BF_4}} PhCHO$$ 75%

Chem Comm (1971) 1109

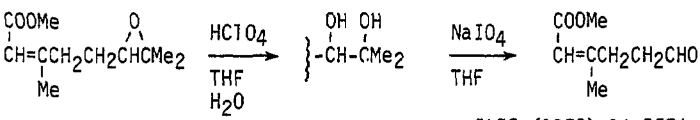


JACS (1971) 93 1693



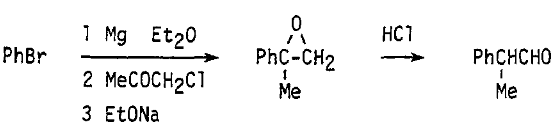
74%

Z Chem (1967) 7 229

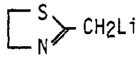


JACS (1972) 94 5374 5379

Section 55 Aldehydes from Halides

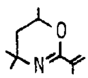


JACS (1939) 61 2383
(1946) 68 2339

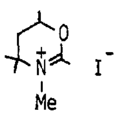
$PhCH_2Cl$ → 1  THF; 2 Al-Hg Et_2O H_2O; 3 $HgCl_2$ MeCN H_2O → $PhCH_2CH_2CHO$ 60%

2 BuLi; 3 EtI; 4 Al-Hg Et_2O H_2O; 5 $HgCl_2$ MeCN H_2O → $PhCH_2CH(Et)CHO$ 50%

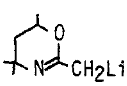
Tetr Lett (1972) 3929

t-BuCl --→ t-BuLi → 1  THF; 2 $NaBH_4$ EtOH THF; 3 $(COOH)_2$ H_2O → $t\text{-}BuCH_2CH(Me)CHO$

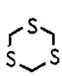
JOC (1973) 38 2136

$Ph(CH_2)_3I$ → 1  NaH DMF; 2 $NaBH_4$ EtOH; 3 Acid → $Ph(CH_2)_3CH_2CHO$ 51%

JACS (1972) 94 3243

RCl → 1  THF; 2 $NaBH_4$ THF EtOH; 3 $(COOH)_2$ H_2O → RCH_2CHO

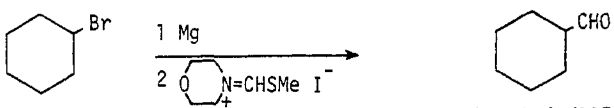
Tetrahedron (1971) 27 5979
JOC (1973) 38 36

$C_{14}H_{29}Br$ → 1  BuLi THF hexane; 2 $HgCl_2$ HgO MeOH; 3 TsOH THF H_2O → $C_{14}H_{29}CHO$ 47-55%

Org Synth (1971) 51 39

$$BuI \xrightarrow[NaH \quad THF]{MeSOCH_2SMe} \underset{\substack{| \\ SMe}}{BuCHSOMe} \xrightarrow[THF]{HCl \quad H_2O} BuCHO \qquad 66\%$$

Tetr Lett (1971) 3151
(1973) 3267



75%

Chem Ind (1972) 380

$$RBr \xrightarrow[hexane]{Li \quad Et_2O} RLi \xrightarrow{t\text{-}BuC(Me)_2NC} RCHO$$

Org Synth (1971) 51 31

$$C_7H_{15}Br \xrightarrow[THF]{HCON(Me)Ph \quad Li} C_7H_{15}CHO \qquad 73\%$$

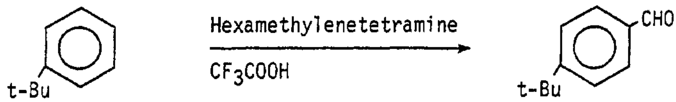
(One-step procedure)
Synthesis (1973) 160

Also via: Olefinic aldehydes (Section 341)

Section 56 Aldehydes from Hydrides

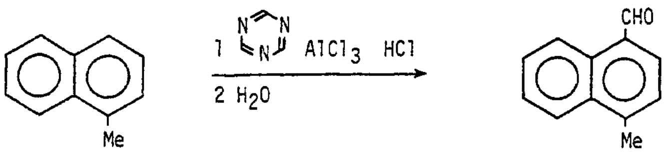
$$ArH \xrightarrow{Cl_2CHOMe \quad TiCl_4 \quad CH_2Cl_2} ArCHO$$

Org Synth (1967) 47 1

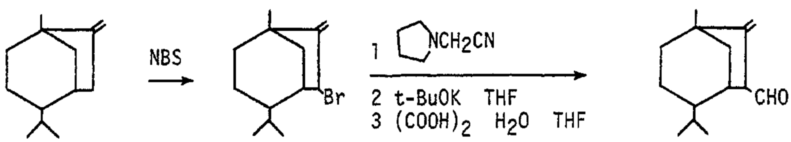


75%

JOC (1972) 37 3972



Arch Pharm (1971) 304 362



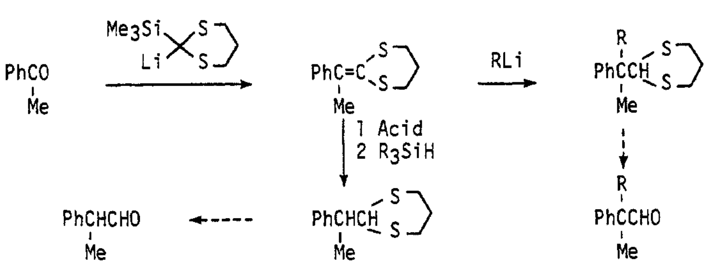
JOC (1973) 38 2915

$$\mathrm{PhC{\equiv}CH} \xrightarrow{\mathrm{HC(OEt)_3}\quad \mathrm{ZnI_2}} \mathrm{PhC{\equiv}CCH(OEt)_2} \dashrightarrow \mathrm{PhC{\equiv}CCHO}$$

~75%

Org Synth (1963) Coll Vol 4 801

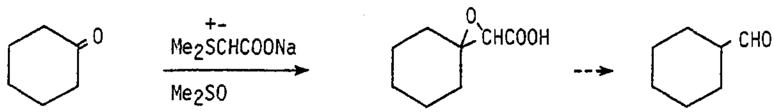
Section 57 Aldehydes from Ketones



Chem Comm (1972) 526

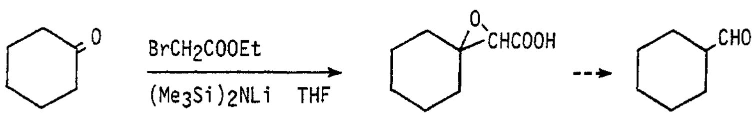
$$Ph_2CO \xrightarrow[2\ H_2SO_4\quad H_2O]{1\ Ph_2P(O)CH(Li)NMe_2\quad Et_2O} Ph_2CHCHO \qquad 44\%$$

JACS (1971) 93 4027



<60%

JOC (1970) 35 1600



<83%

Tetr Lett (1972) 3761

Further methods for the preparation of glycidic esters are included in section 358 (Ester — Ether, Epoxide)

Also via: Olefinic aldehydes (Section 341)

Section 58 Aldehydes from Nitriles

$$ArCN \xrightarrow{Ni\text{-}Al\quad HCOOH\quad H_2O} ArCHO$$

Org Synth (1971) 51 20

$$RCN \xrightarrow{LiAl(OEt)_3H\quad Et_2O} RCHO$$

Synthesis (1972) 217

Section 59 Aldehydes from Olefins

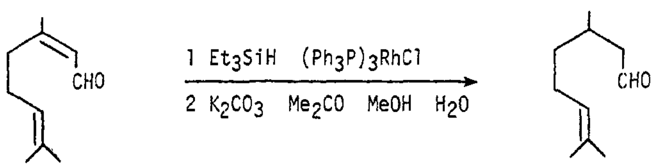
$EtCH{=}CH_2 \xrightarrow{B_2H_6} (EtCH_2CH_2)_3B \xrightarrow{N_2CHCHO} Et(CH_2)_3CHO$ ~77%

Can J Chem (1970) 48 868

$R_2C{=}CH_2 \xrightarrow[2\ Zn\ \ H_2O]{1\ CrO_2Cl_2\ \ CH_2Cl_2} R_2CHCHO$

Org Synth (1971) 51 4

Section 60 Aldehydes from Miscellaneous Compounds



Tetr Lett (1972) 5035

$EtCH_2NO_2 \xrightarrow[2\ H_2SO_4\ \ H_2O]{1\ Zn\ \ HOAc} EtCHO$ 43%

JACS (1939) 61 3194

$MeONa,\ O_3$ JOC (1974) 39 259

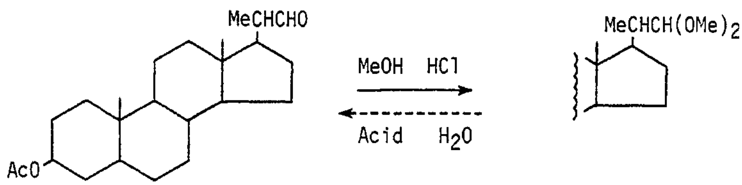
$C_6H_{13}CH(NH_2)COOH \xrightarrow[H_2O]{\text{Argentic picolinate}} C_6H_{13}CHO$ 75%

JCS C (1970) 815

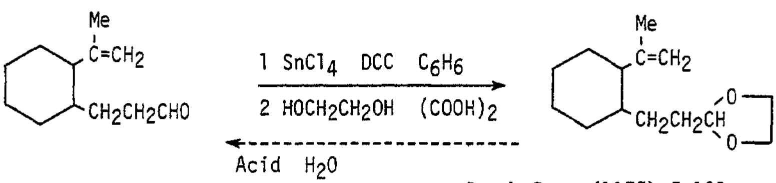
$$C_6H_{13}\underset{OH}{CH}CO(CH_2)_8COOH \xrightarrow{Pb(OAc)_4 \quad HOAc \quad H_2O} C_6H_{13}CHO$$

JCS (1957) 1622

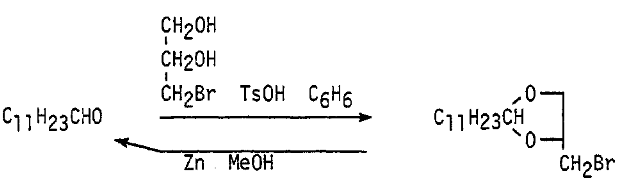
Section 60A Protection of Aldehydes



JCS (1953) 3864



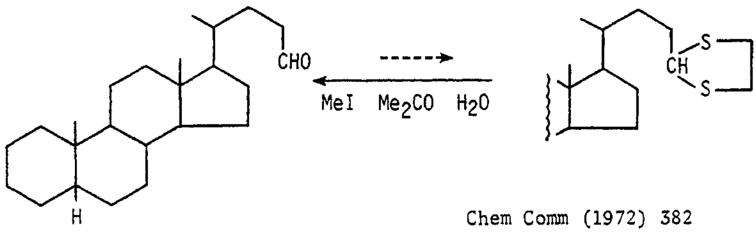
Synth Comm (1973) 3 125



(Stable to NH_3, $NaBH_4$, peracids, MeLi and CrO_3-H_2SO_4)

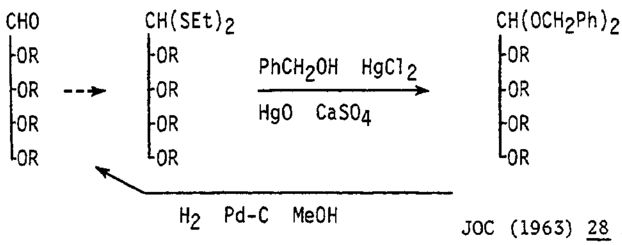
JOC (1973) 38 834

Trichloroethyl acetals JOC (1973) 38 554



Chem Comm (1972) 382

Thioacetal cleavage with NBS	Synthesis (1969) 17
chloramine-T	Tetr Lett (1971) 3445 3449
HgO, $BF_3 \cdot Et_2O$	JOC (1971) 36 366
$CuCl_2$, CuO	Bull Chem Soc Jap (1972) 45 3724
I_2, Me_2SO	Tetr Lett (1973) 3735



JOC (1963) 28 1395

$$\mathrm{PhCHO} \underset{\dashleftarrow}{\xrightarrow{(EtS)_3B \quad \text{Pet ether}}} \mathrm{PhCH(SEt)_2}$$

(Neutral conditions)

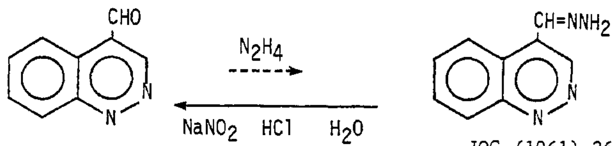
Can J Chem (1965) 43 307
(1969) 47 859

$$\mathrm{PhCHO} \underset{\text{TiCl}_3 \quad NH_4OAc \quad HOAc \quad \text{dioxane} \quad H_2O}{\overset{NH_2OH}{\rightleftarrows}} \mathrm{PhCH{=}NOH}$$

Tetr Lett (1971) 195

$$\mathrm{PhCHO} \underset{\dashleftarrow}{\xrightarrow{Ph_3CONH_2}} \mathrm{PhCH{=}NOCPh_3}$$

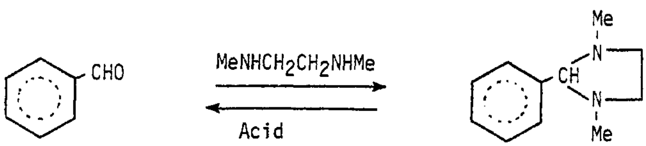
JOC (1971) 36 3835



JOC (1961) 26 4465

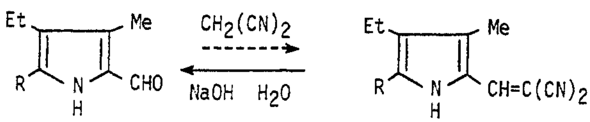
$$PhCHO \underset{MeCO_2H\quad CHCl_3}{\overset{NH_2NEt_2}{\rightleftarrows}} PhCH{=}NNEt_2$$

Ber (1961) 94 712

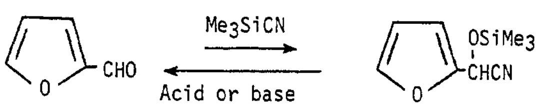


(Stable to $Na\text{-}NH_3$)

Aust J Chem (1955) 8 512



Angew (1960) 72 651



Chem Comm (1973) 55
Tetr Lett (1973) 4929

Related methods:		Section
	Protection of Ketones	180A
	Enol ethers	367
	Acetals	363

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 5 PREPARATION OF ALKYLS METHYLENES AND ARYLS

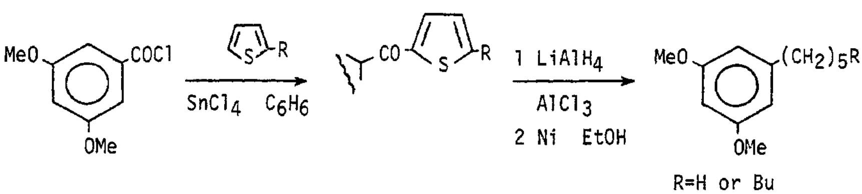
This chapter lists the conversion of functional groups into Me, Et···, CH_2, Ph etc.

Section 61 Alkyls, Methylenes and Aryls from Acetylenes

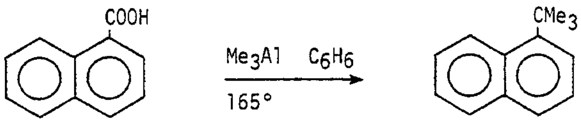
No additional examples

Section 62 Alkyls and Aryls from Carboxylic Acids

Reactions in which carboxyl groups are converted into alkyl or aryl, e.g. RCOOH → RR' are included in this section. For the conversion RCOOH → RH see section 152 (Hydrides from Carboxylic Acids)



Aust J Chem (1971) 24 2655



75%

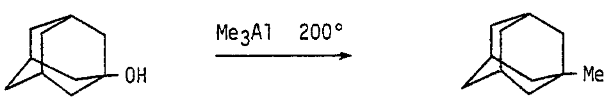
Chem Comm (1972) 595

PhCOOH ⇢ PhCONHNHCOPh $\xrightarrow{AgO\ \ C_6H_6}$ Ph-Ph <37%

JOC (1972) 37 2748

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)

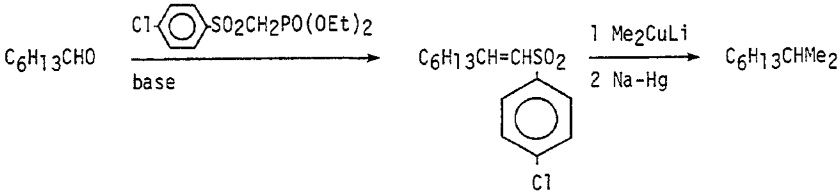


83%

Chem Comm (1972) 595

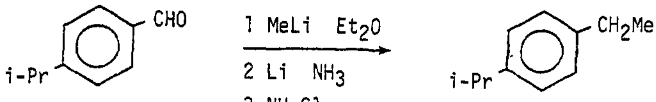
Section 64 Alkyls from Aldehydes

Reactions which convert the group CHO into CH_3 or larger alkyl groups are included in this section. For the conversion RCHO → RH see section 154 (Hydrides from Aldehydes)



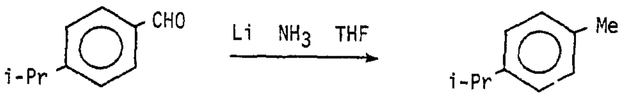
82%

Tetr Lett (1973) 935
(1972) 293



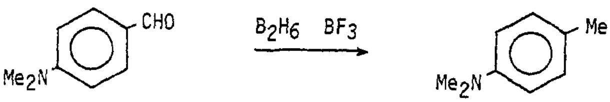
96%

Chem Comm (1971) 1242



90%

JOC (1972) 37 760



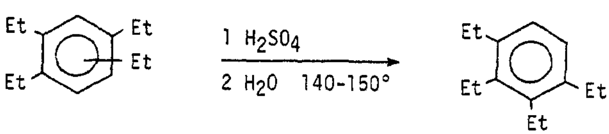
Tetr Lett (1967) 1849

$$\mathrm{RCHO} \xrightarrow[\text{sulfolane} \quad 2\ NaBH_3CN]{1\ TsNHNH_2 \quad TsOH \quad DMF} \mathrm{RMe}$$

JACS (1971) 93 1793

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

Section 65 Alkyls from Alkyls



91%

Org React (1942) 1 370

Section 66 Alkyls, Methylenes and Aryls from Amides

No additional examples

Section 67 Alkyls, Methylenes and Aryls from Amines

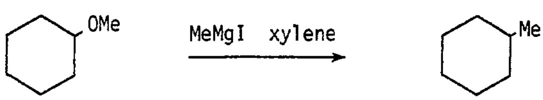
No additional examples

Section 68 Alkyls, Methylenes and Aryls from Esters

No additional examples

Section 69 Alkyls from Ethers

The conversion ROR ⟶ RR' (R'=alkyl) is included in this section. For the hydrogenolysis of ethers (ROR ⟶ RH) see section 159 (Hydrides from Ethers)

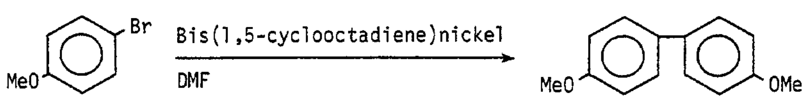


16%

Gazz (1970) 100 939

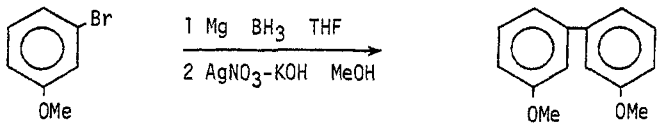
Section 70 Alkyls and Aryls from Halides

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)



83%

JACS (1971) 93 5908



52%

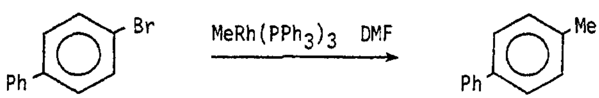
Tetr Lett (1972) 2193

PhI $\xrightarrow[\text{DMF}]{\pi\text{-allyl nickel bromide}}$ $PhCH_2CH{=}CH_2$ 82%

JOC (1972) 37 462
Org React (1972) 19 115

$PhCH_2I$ $\xrightarrow{CH_2{=}CHCH_2I \quad Et_3B \quad O_2}$ $PhCH_2CH_2CH{=}CH_2$ 64%

JACS (1971) 93 1508



65%

Tetr Lett (1973) 2967

$C_{16}H_{33}I$ $\xrightarrow{Zn\text{-}Ag \quad H_2O}$ $C_{16}H_{33}\text{-}C_{16}H_{33}$ Coll Czech (1964) 29 597 70%

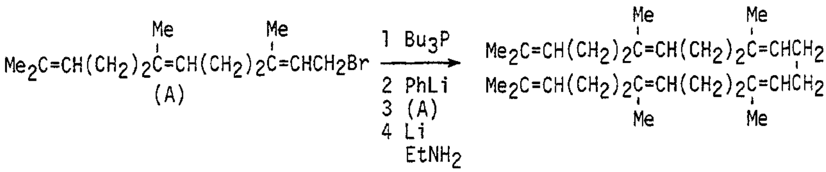
BuBr $\xrightarrow{BuMgBr \quad Ag \quad THF}$ Bu-Bu 79%

BuBr $\xrightarrow{C_6H_{13}MgBr \quad LiCl \quad CuCl_2}$ $Bu\text{-}C_6H_{13}$ 78%

Synthesis (1971) 303

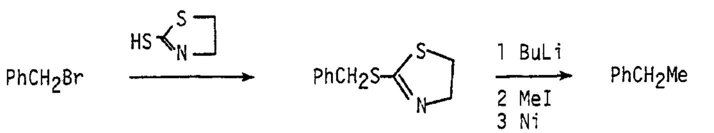
$$C_8H_{17}Br \xrightarrow[2\ AgNO_3\text{-}KOH\quad MeOH]{1\ Mg\quad BH_3\quad THF} C_8H_{17}\text{-}C_8H_{17}$$ 90%

Tetr Lett (1972) 2193
JACS (1938) 60 105



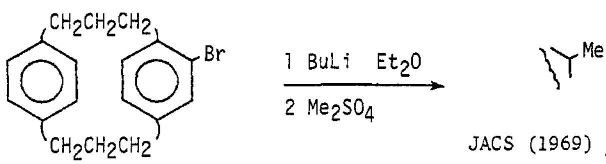
76%

JACS (1970) 92 2139



<60%

Tetr Lett (1971) 4359



58%

JACS (1969) 91 3544

$$PhCl \xrightarrow{BuMgBr\quad [NiCl_2(dpe)]\quad Et_2O} PhBu$$ 76%

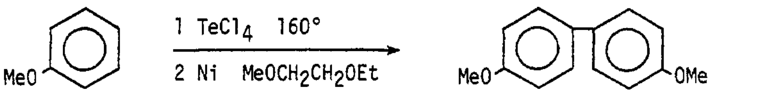
JACS (1972) 94 4374

Also via:

	Section
Acetylenes	10
Olefins	205

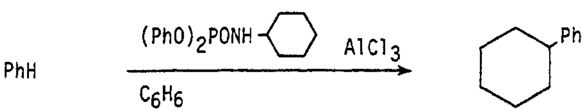
Section 71 Alkyls and Aryls from Hydrides

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)



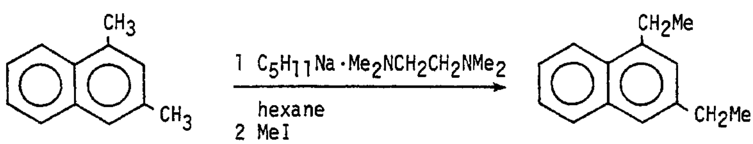
74%

Tetrahedron (1972) 28 3323

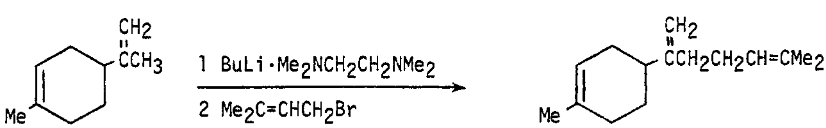


27%

Synthesis (1971) 203



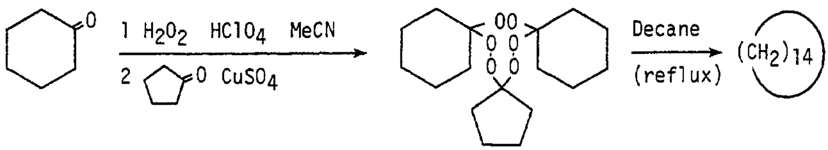
JACS (1972) 94 2152



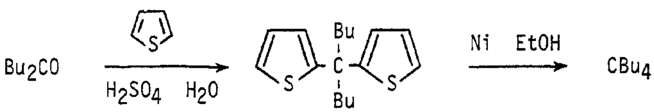
JACS (1972) 94 4298

Section 72 Alkyls and Methylenes from Ketones

The conversions $R_2CO \rightarrow RR$, R_2CH_2, R_2CHR, etc. are listed in this section.
For the conversion $R_2CO \rightarrow RH$ see section 162 (Hydrides from Ketones)



Synthesis (1970) 181
Advances in Org Chem (1972) 8 67



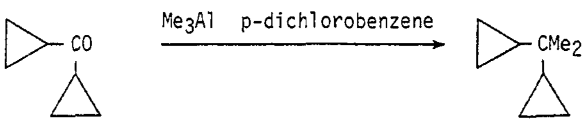
24%

Bull Soc Chim Fr (1966) 2253

$$Ph_2CO \xrightarrow[162°]{NaAlH_2(OCH_2CH_2OMe)_2\ \ PhPr} Ph_2CMe_2$$

71%

Tetr Lett (1972) 691



43%

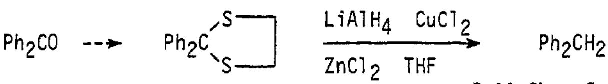
Chem Comm (1972) 595

$$R_2CO \xrightarrow[2\ BuLi\ \ C_6H_6]{1\ TsNHNH_2} R_2CHBu$$

JCS C (1971) 2294

$$Ph_2CO \xrightarrow[\substack{2\ Li\quad NH_3 \\ 3\ NH_4Cl}]{1\ MeLi\quad Et_2O} Ph_2CHMe \qquad 95\%$$

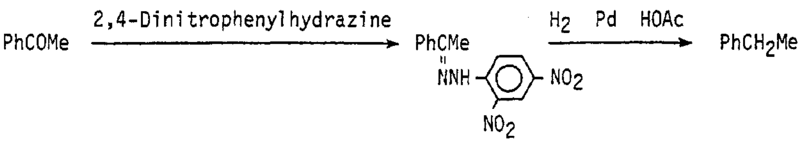
JOC (1973) 38 1735 1738



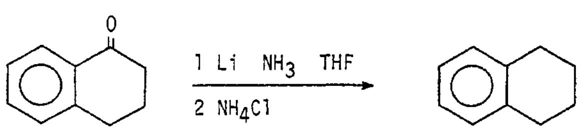
Bull Chem Soc Jap (1971) 44 2285

$$C_9H_{19}COMe \xrightarrow[2\ NaBH_3CN]{1\ TsNHNH_2\quad TsOH\quad sulfolane\quad DMF} C_9H_{19}CH_2Me$$

JACS (1971) 93 1793

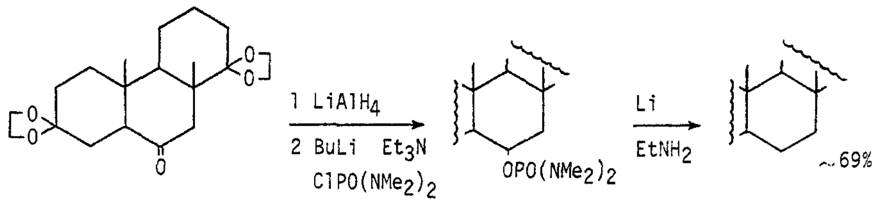


JOC (1971) 36 737



96%

JOC (1971) 36 2588



JACS (1972) 94 5098

Related methods: Alkyls from Aldehydes (Section 64)

Also via: Olefins (Section 207)

Section 73 Alkyls, Methylenes and Aryls from Nitriles

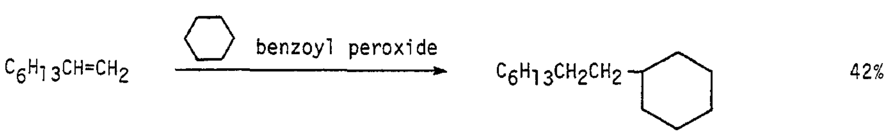
No additional examples

Section 74 Alkyls, Methylenes and Aryls from Olefins

The hydrogenation, alkylation and arylation of olefins forming alkanes or aryl-substituted alkanes, are included in this section.

$$BuCH{=}CH_2 \xrightarrow[2\ Ph_3\overset{+}{As}\overset{-}{C}HPh]{1\ B_2H_6\quad THF} Bu(CH_2)_3Ph$$

JACS (1967) 89 6804

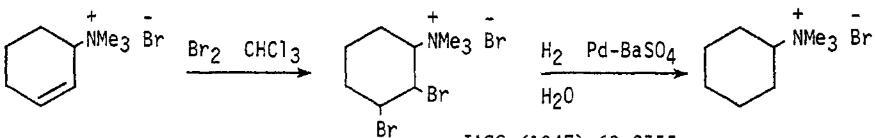


JCS (1965) 1939

Chem Comm (1968) 569

$$C_8H_{17}CH{=}CH(CH_2)_7COOH \xrightarrow[\text{MeOH}]{\text{NaBH}_4\ \ \text{NiCl}_2} C_8H_{17}(CH_2)_9COOH \qquad 92\%$$

Chem Pharm Bull (1971) 19 817
JOC (1971) 36 2018



JACS (1947) 69 2555
(1948) 70 2517

$$C_6H_{13}CH{=}CH_2 \xrightarrow[\text{EtOH}]{[\text{MeHSiO}]_N\ \ \text{Pd-C}} C_6H_{13}CH_2Me$$

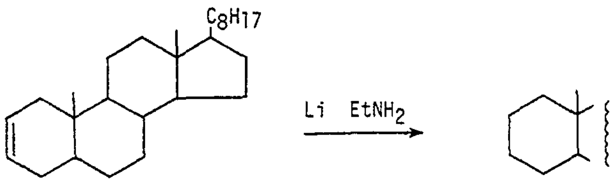
JOC (1973) 38 162

$$EtCH{=}CMe_2 \xrightarrow[\text{cyclohexane}]{H_2\ \ \text{BuLi-cobalt 2-ethylhexanoate}} EtCH_2CHMe_2 \qquad 92\%$$

JOC (1971) 36 1445

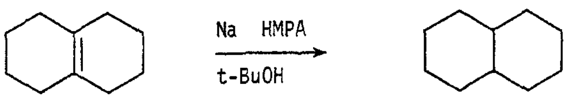
Polymer-supported Rh(I) catalyst JACS (1971) 93 3062

"Hydrogenation of Organic Compounds using Homogeneous Catalysts" Chem Rev (1973) 73 21



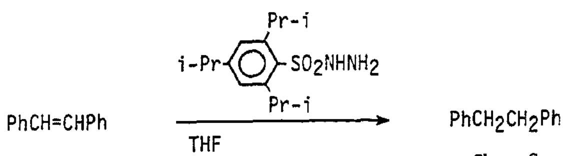
JCS (1957) 1969

77%



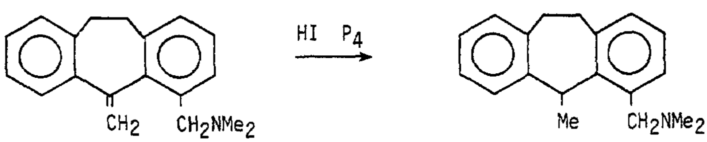
JOC (1970) 35 3565

91%



Chem Comm (1972) 1132

~60%



J Med Chem (1971) 14 982

94%

Section 75 Alkyls, Methylenes and Aryls from Miscellaneous Compounds

No additional examples

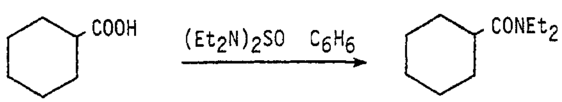
Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 6 PREPARATION OF AMIDES

Section 76 Amides from Acetylenes

No additional examples

Section 77 Amides from Carboxylic acids and Acid Halides



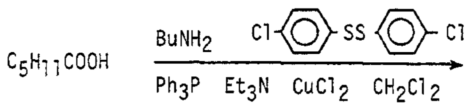
Il Farmaco Ed Sc (1971) 26 153
(Chem Abs 75 4874)

$$PhCOOH \xrightarrow[2\ BuNH_2]{1\ Ph_3P\quad CCl_4\quad THF} PhCONHBu \qquad 85\%$$

JOC (1971) 36 1305

$$PhCOOH \xrightarrow[2\ Et_2NH]{1\ (Me_2N)_3P\quad CCl_4\quad Et_2O} PhCONEt_2$$

Bull Soc Chim Fr (1971) 3034



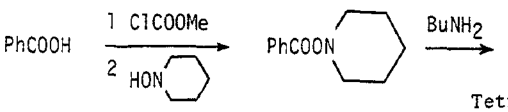
62%

Bull Chem Soc Jap (1971) 44 1373

$$PhCOOH \xrightarrow[Et_3N \quad DMF]{BuNH_2 \quad NCP(O)(OEt)_2} PhCONHBu$$

94%

Tetr Lett (1973) 1595



Tetr Lett (1971) 2697

$$RCOOH \xrightarrow[2\ t\text{-}BuNH_2]{1\ ClCOOEt \quad Et_3N \quad CH_2Cl_2} RCONHBu\text{-}t$$

JCS C (1971) 3540

$$(t\text{-}Bu)_2CHCOCl \xrightarrow{NH_3 \quad NaNH_2 \quad Et_2O} (t\text{-}Bu)_2CHCONH_2$$

81%

JACS (1960) 82 2498

$$\begin{matrix} COOMe \\ (CH_2)_4COOH \end{matrix} \xrightarrow[MeONa \quad MeOH]{\begin{matrix} COOH \\ (CH_2)_5NHAc \end{matrix} \quad electrolysis} \begin{matrix} COOMe \\ (CH_2)_9NHAc \end{matrix}$$

Z Naturforsch (1947) 2b 185

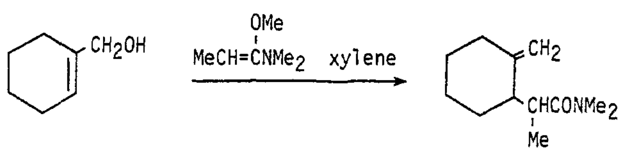
$t\text{-BuCOOK} \xrightarrow{\text{Electrolysis MeCN } H_2O} t\text{-BuNHAc}$ 40%

Acta Chem Scand (1964) 18 1567
Bull Soc Chim Fr (1968) 3657
Angew (1971) 83 579
(Internat Ed 10 557)

Related methods: Amides from Amines (Section 82)

Also via: Esters (Section 83)

Section 78 Amides from Alcohols



88%

JCS C (1971) 2950
Ber (1971) 104 3689

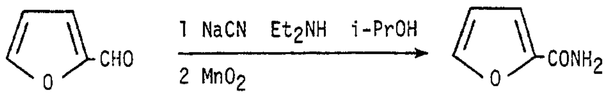
$Ph_2CHOH \dashrightarrow Ph_2CHN_3 \xrightarrow{\overset{+}{NO}\ \overset{-}{BF_4}\ \ MeCN} Ph_2CHNHAc$ ~53%

JACS (1970) 92 4999

Section 79 Amides from Aldehydes

$PhCHO \xrightarrow{Li[Me_2NCONi(CO)_3]\ \ Et_2O} PhCONMe_2$ < 84%

JOC (1971) 36 2721



98%

(Ar and $\alpha\beta$-unsaturated only)

Chem Comm (1971) 733

PhCHO $\xrightarrow{PhNH_2}$ PhCH=NPh $\xrightarrow{CrO_2Cl_2 \quad CCl_4}$ PhCONHPh 80%

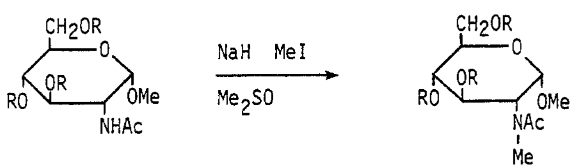
Chem Ind (1970) 1297

Also via: Olefinic amides (Section 349)

Section 80 Amides from Alkyls, Methylenes and Aryls

No additional examples

Section 81 Amides from Amides



89%

Carbohydrate Res (1972) 23 251

$MeCON(Me)CH_3 \xrightarrow[\text{cupric 2-ethylhexanoate} \quad C_6H_6]{MeCOO_2Bu\text{-}t \quad h\nu} MeCON(Me)CH_2OAc \dashrightarrow MeCONHMe$ < 67%

Synthesis (1972) 1

Related methods: Amides from Halides (Section 85)

Section 82 Amides from Amines

$BuNH_2 \xrightarrow[CCl_4 \quad THF]{HOAc \quad Ph_3P} BuNHAc$ 91%

JOC (1971) 36 1305

$PhNH_2 \xrightarrow[toluene]{Resin\text{-}CO\text{-}O\text{-}COPh} PhCONHPh$

Tetr Lett (1973) 1627

$PhNH_2 \xrightarrow{C_{17}H_{35}COOH \quad SiCl_4 \quad Pyr} PhNHCOC_{17}H_{35}$ 70%

JOC (1969) 34 2766

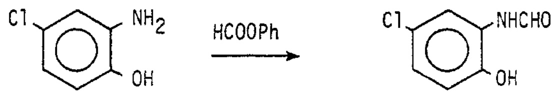
Further examples of the reaction $RNH_2 + R'COOH \rightarrow RNHCOR'$ are included in section 77 (Amides from Carboxylic Acids and Acid Halides)

$PhNH_2 \xrightarrow{MeCOOEt \quad NaH \quad Me_2SO} PhNHAc$ 85%

Tetr Lett (1971) 321

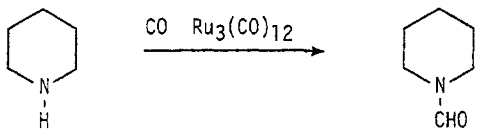
$PhNH_2 \xrightarrow{PhCOSCSNMe_2} PhCONHPh$ 80%

Tetr Lett (1972) 4785



95%

JOC (1971) 36 3238

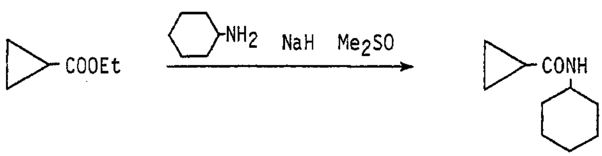


45%

Chem Comm (1971) 1482

Related methods: Protection of Amines (Section 105A)

Section 83 Amides from Esters



68%

Tetr Lett (1971) 321

$$(EtO)_2CHCH_2COOEt \xrightarrow{NH_3 \quad H_2O} (EtO)_2CHCH_2CONH_2$$

58%

J Med Chem (1973) 16 1

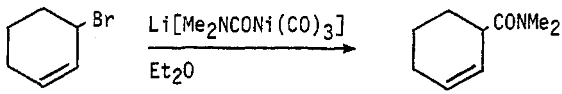
Section 84 Amides from Ethers and Epoxides

No additional examples

Section 85 Amides from Halides

$C_5H_{11}Br \xrightarrow[\text{2 } I_2 \quad Et_2NH \quad THF]{\text{1 } Na_2Fe(CO)_4} C_5H_{11}CONEt_2$ 80%

JACS (1973) 95 249



99%

(Applicable to aromatic and vinyl halides)

JOC (1971) 36 2721

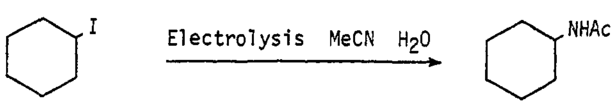
$C_7H_{15}Br \xrightarrow[THF]{Et_2NCOOEt \quad Li} C_7H_{15}CONEt_2$ 70%

(One-step procedure)

Synthesis (1973) 160

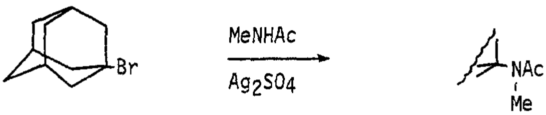
$C_{18}H_{37}Cl \xrightarrow{PhNHAc \quad KOH \quad Me_2SO} C_{18}H_{37}N(Ac)Ph$ 90%

Synthesis (1971) 266



85%

Compt Rend (1970) C 271 324



J Med Chem (1971) <u>14</u> 535

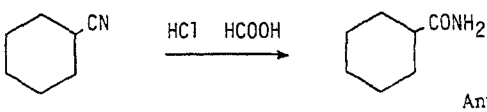
Section 86 Amides from Hydrides

No additional examples

Section 87 Amides from Ketones

No additional examples

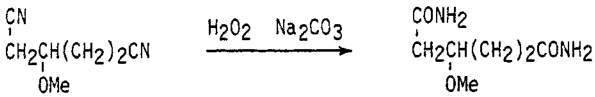
Section 88 Amides from Nitriles



92%

Annalen (1971) <u>749</u> 198

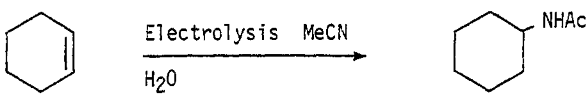
PhCN $\xrightarrow[2\ H_2O]{1\ BBr_3}$ $PhCONH_2$ JCS <u>C</u> (1969) 739



Helv (1956) 39 1233
Chem Ind (1961) 987

Also via: Amines (Section 103)

Section 89 Amides from Olefins



80%

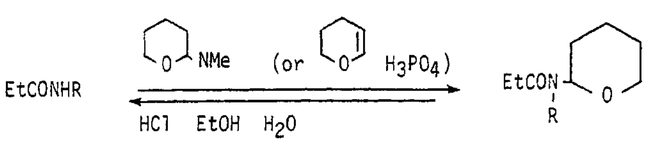
Compt Rend (1970) C 271 324

Also via: Amines (Section 104)

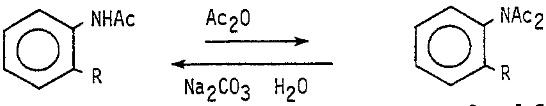
Section 90 Amides from Miscellaneous Compounds

No additional examples

Section 90A Protection of Amides

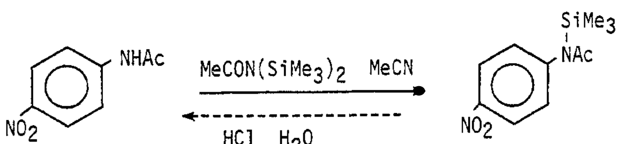


Bull Soc Chim Fr (1964) 292

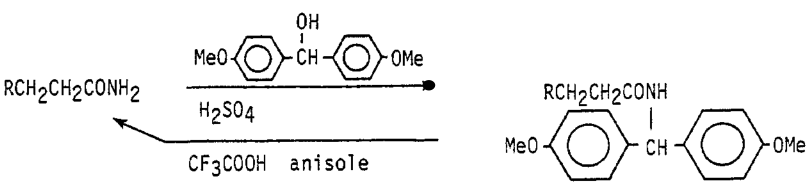


(Stable to NBS)

Can J Chem (1955) 33 1819



JACS (1966) 88 3390



(Stable to H_2/Pd)

Ber (1970) 103 2041

$$RCH_2CONH_2 \underset{Na_2CO_3 \;\; H_2O_2 \;\; Me_2CO \;\; H_2O \;\; \text{or HBr} \;\; HOAc}{\overset{POCl_3 \;\; Pyr \;\; CH_2Cl_2}{\rightleftarrows}} RCH_2CN$$

Chem Ind (1961) 987

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Chapter 7 PREPARATION OF AMINES

Section 91 Amines from Acetylenes

$$PhC{\equiv}CC_6H_{13} \xrightarrow[2\ H_2\ \ Ni\ \ NaOH\ \ MeOH]{1\ NaNHNH_2\ \ N_2H_4\ \ Et_2O} PhCH_2\underset{NH_2}{\underset{|}{C}}HC_6H_{13} \qquad 71\%$$

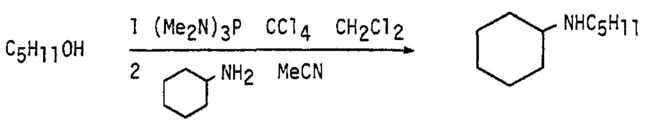
Ber (1966) 99 1843

Section 92 Amines from Carboxylic Acids

$$C_7H_{15}COOH \xrightarrow[2\ t\text{-}BuOH]{1\ N_3PO(OPh)_2\ \ Et_3N\ \ DMF} C_7H_{15}NHCOOBu\text{-}t \dashrightarrow C_7H_{15}NH_2 \qquad \sim67\%$$

JACS (1972) 94 6203

Section 93 Amines from Alcohols and Phenols



58%

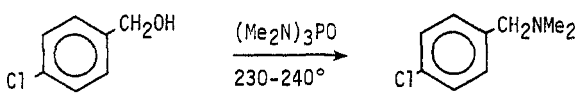
Bull Soc Chim Fr (1971) 4368

$PhCH(Me)OH \xrightarrow[\text{2 } NH_2NHCOOBu\text{-}t \quad \text{3 } Pb(OAc)_4 \quad CH_2Cl_2]{\text{1 } ClSO_2NCO \quad \text{hexane}} PhCH(Me)NH_2$ 52%

JACS (1973) 95 4083

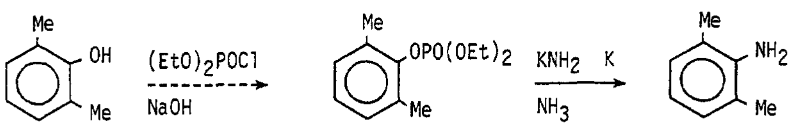
$C_6H_{13}CH(Me)OH \xrightarrow[\text{2 } N_2H_4 \quad EtOH]{\text{1 Phthalimide} \quad Ph_3P \quad EtOOCN{=}NCOOEt \quad THF} C_6H_{13}CH(Me)NH_2$

JACS (1972) 94 679
Carbohydrate Res (1972) 23 460



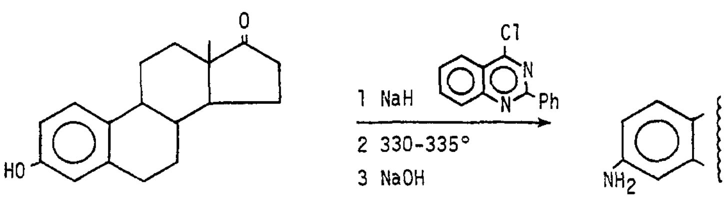
68%

Chem Comm (1971) 1018



~78%

JOC (1972) 37 3570



58%

J Med Chem (1966) 9 249
Steroids (1968) 11 151

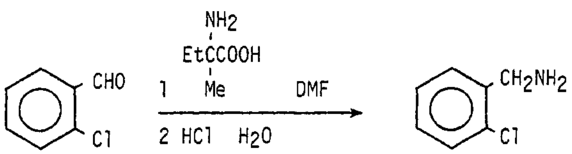
Section 94 Amines from Aldehydes

$$RCHO \xrightarrow[HOAc]{CH_3NO_2 \quad NH_4OAc} RCH{=}CHNO_2 \xrightarrow{LiAlH_4 \quad THF} RCH_2CH_2NH_2$$

Ber (1971) 104 2517
JCS (1965) 3645
(1957) 2926

$$RCHO \xrightarrow[MeOH \quad pH\ 6\text{-}8]{R'NH_2 \quad NaBH_3CN} RCH_2NHR'$$

JACS (1971) 93 2897



70%

(Ar aldehydes only)

JOC (1971) 36 1710

$$C_6H_{13}CHO \xrightarrow{NH_2OH} C_6H_{13}CH{=}NOH \xrightarrow[CHCl_3]{H_2 \quad PtO_2 \quad EtOH} C_6H_{13}CH_2NH_2$$

JOC (1972) 37 335

Related methods: Amines from Ketones (Section 102)

Section 95 Amines from Alkyls, Methylenes and Aryls

No examples

Section 96 Amines from Amides

$$C_5H_{11}CONR_2 \xrightarrow{B_2H_6 \quad THF} C_5H_{11}CH_2NR_2$$

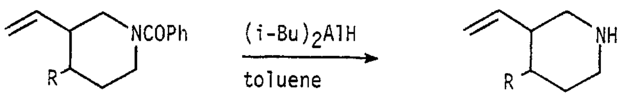
87% R=H
95% R=Me

JOC (1973) 38 912

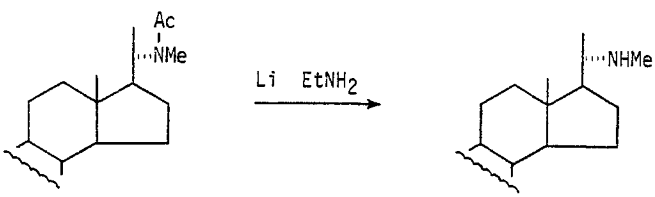
$$PhCONH_2 \xrightarrow{NaBH_2S_3 \quad THF} PhCH_2NH_2$$

46%

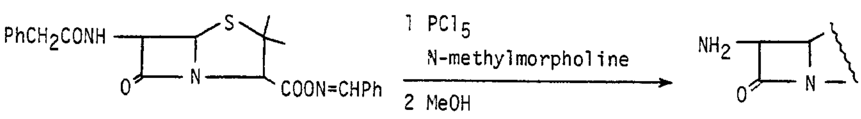
Can J Chem (1971) 49 2990



JACS (1970) 92 204



Tetr Lett (1971) 1935



JCS C (1971) 1917
Rec Trav Chim (1970) 89 1081
JOC (1971) 36 1259

Section 97 Amines from Amines

$$\mathrm{PhCH(Me)NH_2} \xrightarrow{\mathrm{BuLi}} \mathrm{PhC(Me)(Bu)NH_2}$$

25%

Tetr Lett (1971) 2187

$$\mathrm{t\text{-}BuN(Me)CH_3} \xrightarrow[\text{2 PhMgBr} \quad \mathrm{Et_2O}]{\text{1 } \mathrm{Ph_3\overset{+}{C}\ \overset{-}{ClO_4}} \quad \mathrm{CH_2Cl_2}} \mathrm{t\text{-}BuN(Me)CH_2Ph}$$

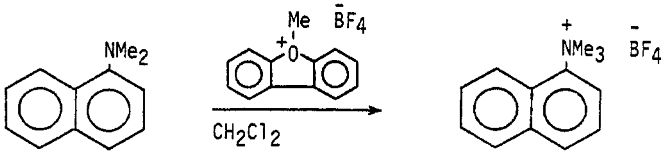
75%

Annalen (1971) 752 86

$$\mathrm{BuNH_2} \xrightarrow{\mathrm{MeI} \quad \mathrm{Bu_3N} \quad \mathrm{DMF}} \mathrm{Bu\overset{+}{N}Me_3\ \overset{-}{I}}$$

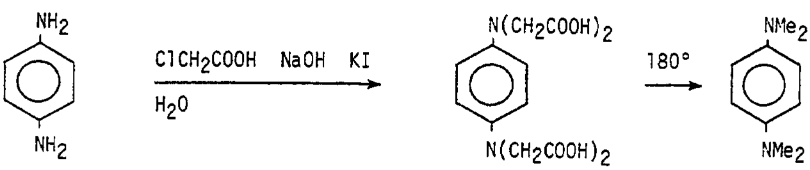
92%

JOC (1971) 36 824

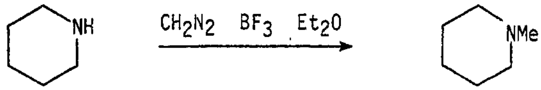


100%

Chem Comm (1972) 315



JOC (1964) 29 488



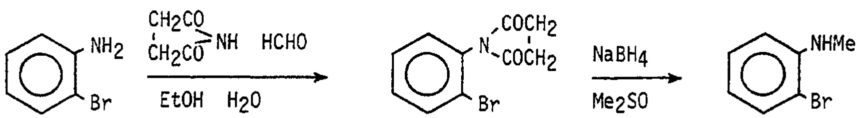
30%

Annalen (1959) <u>623</u> 34

$$PhCH_2NH(Et) \xrightarrow[MeCN \quad H_2O]{HCHO \quad NaBH_3CN} PhCH_2NMe(Et)$$

98%

JOC (1972) <u>37</u> 1673

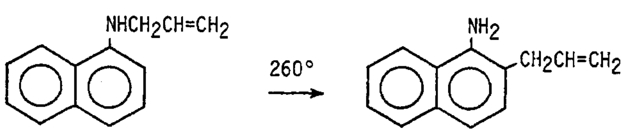


JOC (1973) <u>38</u> 1348

72%

$$BuNH_2 \xrightarrow{PhBr \quad NaNH_2} BuNHPh$$

JOC (1971) <u>36</u> 1841

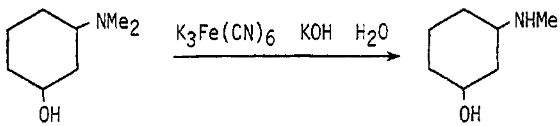


59%

Tetrahedron (1961) <u>14</u> 208
Tetr Lett (1971) 4661 4665

$PhNMe_2 \xrightarrow[\text{2 HCl} \quad H_2O]{\text{1 } O_3 \quad CH_2Cl_2} PhNHMe$ 41%

JCS C (1971) 1369



93%

JOC (1951) 16 1303

$C_{12}H_{25}\overset{+}{N}Me_3 \ \overset{-}{I} \xrightarrow[\text{DMF}]{\text{1,4-Diazabicyclo[2.2.2]octane}} C_{12}H_{25}NMe_2$ 68%

Synthesis (1972) 702

Dealkylation with LiI	JOC (1963) 28 2407
PrSLi	JOC (1973) 38 1961
OAc^-	Tetrahedron (1968) 24 5493
Ph_3P, $(NH_2)_2CO$ or NaN_3	Synth Comm (1973) 3 99

Section 98 Amines from Esters

No additional examples

Section 99 Amines from Epoxides

$PhCH\overset{O}{-}CH_2 \xrightarrow{HN_3 \quad SnCl_4 \quad C_6H_6} PhNH_2$ 17%

JACS (1952) 74 1168

Section 100 Amines from Halides

$$BuBr \xrightarrow[2\ Et_2NCCl_3]{1\ Mg\quad Et_2O} Bu_3CNEt_2$$ 37%

Synthesis (1972) 611

$$RX \xrightarrow{Me_2C{=}NOH\quad EtMgBr\quad toluene} RNH_2$$

62% (R=Ph)
48% (R=$PhCH_2CH_2$)

Tetr Lett (1972) 1007

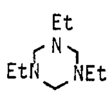
$$RBr \xrightarrow[2\ EtOCH{=}NSO_2Ph]{1\ Mg} R_2CHNHSO_2Ph \dashrightarrow R_2CHNH_2$$

<92% (R=Ph)
<74% (R=Pr)

Ber (1969) 102 1641

$$BuI \xrightarrow{Me_2NNO\quad (i\text{-}Pr)_2NLi} BuCH_2N(Me)NO \dashrightarrow BuCH_2NHMe$$

Angew (1972) 84 350
(Internat Ed 11 301)



$$PhCH_2Cl \xrightarrow{MeOH\quad H_2O} PhCH_2N(Me)Et$$ 65%

Synthesis (1971) 89

$$C_{12}H_{25}I \dashrightarrow^{EtNMe_2} C_{12}H_{25}\overset{+}{N}Me_2(Et)\ I^- \xrightarrow{PrSLi\quad HMPA} C_{12}H_{25}N(Me)Et$$

JOC (1973) 38 1961

$$CH_2{=}CHCH_2I \xrightarrow[\text{2 Na-Hg}]{\text{1 }(PhCH_2)_2NMe} CH_2{=}CHCH_2N(Me)CH_2Ph \xrightarrow[\text{2 Na-Hg}]{\text{1 PrI}} CH_2{=}CHCH_2N(Me)Pr$$

Arch Pharm (1911) 249 111

$$RBr \xrightarrow[\text{2 NaOH}]{\text{1 }(NH_2)_2C{=}NH \quad EtOH \quad H_2O} RNH_2$$

Bull Soc Chim Fr (1970) 1938

$$BuBr \xrightarrow{TsN(COOEt)Na \quad DMF} TsN(COOEt)Bu \xrightarrow{NaOH} TsNHBu \dashrightarrow BuNH_2 \qquad <60\%$$

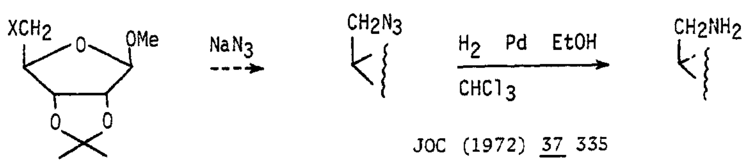
JOC (1971) 36 4102

$$RBr \xrightarrow[\text{2 HCl} \quad Et_2O \quad H_2O]{\text{1 }(PhS)_2NLi \quad THF} RNH_2$$

Bull Chem Soc Jap (1971) 44 2797

$$C_7H_{15}Br \xrightarrow[\text{base}]{PhCH_2NHSO_2CF_3} C_7H_{15}N(CH_2Ph)SO_2CF_3 \xrightarrow[\text{2 HCl} \quad H_2O \quad THF]{\text{1 NaH} \quad DMF} C_7H_{15}NH_2 \qquad 80\%$$

Tetr Lett (1973) 3839



JOC (1972) 37 335

Section 101 Amines from Hydrides

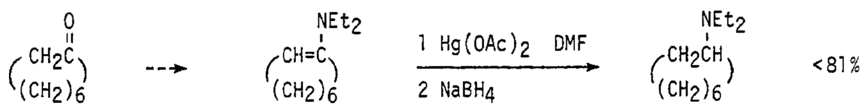
$$ArH \xrightarrow{Me_2NCl \quad H_2SO_4 \quad Na_2SO_4} ArNMe_2$$

Synthesis (1973) 1

Section 102 Amines from Ketones

$$R_2CO \xrightarrow[MeOH \quad pH\ 6\text{-}8]{Me_2NH \quad NaBH_3CN} R_2CHNMe_2$$

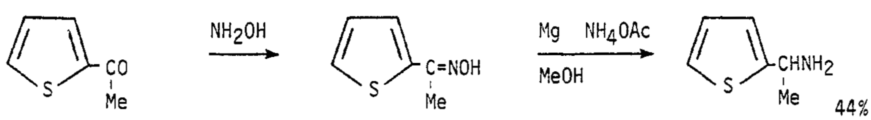
JACS (1971) 93 2897



Chem Comm (1971) 1433

$$R_2CO \dashrightarrow R_2C{=}NOH \xrightarrow{Na \quad R'OH} R_2CHNH_2$$

Chem Ind (1972) 683



Chem Ind (1969) 260

Related methods: Amines from Aldehydes (Section 94)

Section 103 Amines from Nitriles

$$PhCN \xrightarrow{EtMgBr \quad toluene} PhC(NH_2)Et_2 \qquad 60\%$$

Tetr Lett (1973) 1057

$$C_{12}H_{25}CN \xrightarrow{H_2 \quad Ni \quad Ac_2O \quad NaOAc} C_{12}H_{25}CH_2NHAc \dashrightarrow C_{12}H_{25}CH_2NH_2 \qquad \sim 100\%$$

JOC (1960) 25 1658

$$PrCN \xrightarrow{H_2 \quad PtO_2 \quad EtOH \quad CHCl_3} PrCH_2NH_2 \qquad 96\%$$

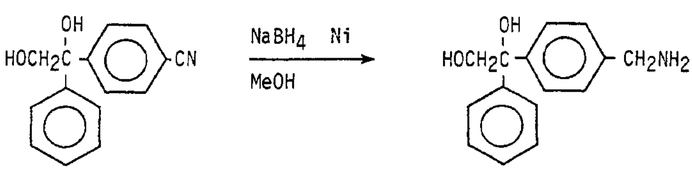
JOC (1972) 37 335

$$PrCN \xrightarrow{N_2H_4 \cdot H_2O \quad Ni \quad EtOH} PrCH_2NH_2 \qquad 75\%$$

JOC (1971) 36 3539

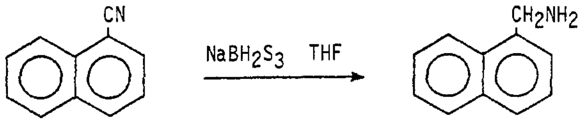
$$PhCH{=}CHCN \xrightarrow{AlH_3 \quad THF} PhCH{=}CHCH_2NH_2 \qquad 78\%$$

JACS (1968) 90 2927



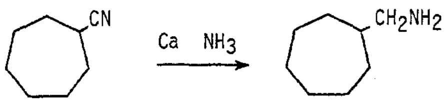
34%

Annalen (1972) 756 14



40%

Can J Chem (1971) 49 2990



63%

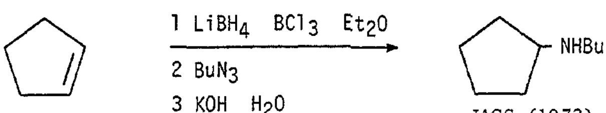
JOC (1972) 37 508

Section 104 Amines from Olefins

$(CH{=}CH)(CH_2)_{10}$ $\xrightarrow[\text{N-methylpyrrolidine } H_2O \text{ 140 atmos } 170°]{Me_2NH \quad CO \quad Rh_2O_3 \quad Fe(CO)_5}$ $(CH_2CH(CH_2NMe_2))(CH_2)_{10}$

90%

Helv (1971) 54 1440



64%

JACS (1972) 94 2114
(1971) 93 4329
(1973) 95 2394 2396

$EtCH{=}CH_2 \xrightarrow{B_2H_6} (EtCH_2CH_2)_3B \xrightarrow{Me_2NCl} EtCH_2CH_2NMe_2$

J Organometallic Chem (1970) 23 C11

$PhCH{=}CH_2 \xrightarrow{PrNH_2\quad Na} PhCH_2CH_2NHPr$ 18%

Ber (1950) 83 1
JOC (1972) 37 4243

$C_{14}H_{29}CH{=}CH_2 \xrightarrow[\substack{2\ H_2\quad Ni \\ 3\ Me_2NH}]{1\ O_3\quad MeOH} C_{14}H_{29}CH_2NMe_2$ 65%

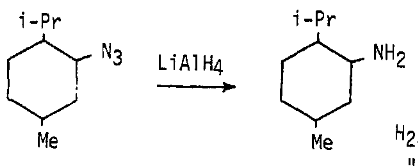
Tetr Lett (1971) 3591

$Ph_2C{=}CHEt \xrightarrow{NaN_3\quad H_2SO_4} PhNH_2$ 57%

JACS (1950) 72 5777

Also via: Amides (Section 89)

Section 105 Amines from Miscellaneous Compounds



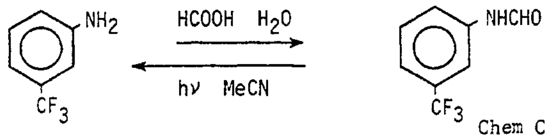
34%

JOC (1962) 27 2925
H_2/Pd Ber (1972) 105 1524
" " JOC (1972) 37 335

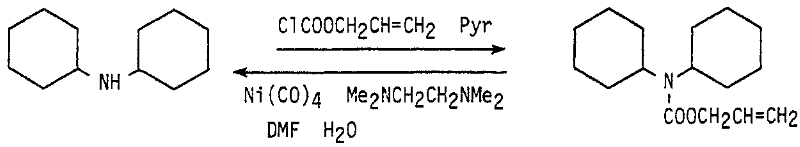
$ArNO_2 \longrightarrow ArNH_2$

Sn, HCl	JACS (1969) 91 3544
H_2/Pd	JOC (1972) 37 335
$NaBH_4$, $CoCl_2$	Tetr Lett (1969) 4555
$NaBH_2S_3$	Can J Chem (1971) 49 2990
CO, $RhCl_3$	Tetr Lett (1971) 3385
$Fe_3(CO)_{12}$	JOC (1972) 37 930
$Fe(CO)_5$	Can J Chem (1970) 48 1543

Section 105A Protection of Amines



Chem Comm (1972) 758

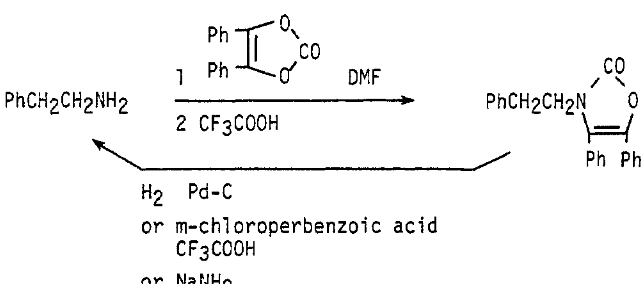


JOC (1973) 38 3223

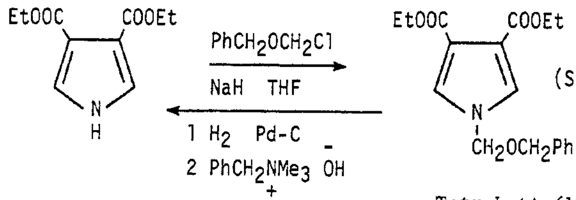
$RNH_2 \underset{Zn\ \ MeCN\ \ HCl\ \ H_2O}{\overset{ClCOOCH_2CCl_3}{\rightleftharpoons}} RNHCOOCH_2CCl_3$

JOC (1971) 36 1259

Selective removal of haloethoxycarbonyl groups by electrolysis
JACS (1972) 94 5139

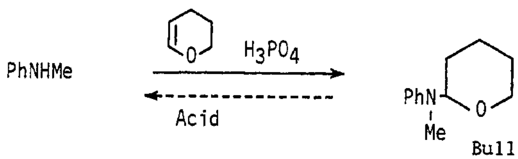


JACS (1972) 94 6561



(Stable to HCl, Ac_2O, KOH and $CdMe_2$)

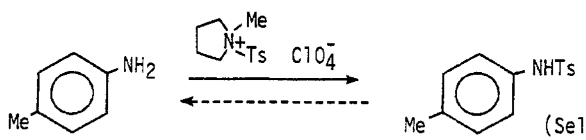
Tetr Lett (1971) 3165



Bull Soc Chim Fr (1954) 575

$$RNH_2 \underset{HOAc\quad H_2O}{\overset{Ph_3CCl\quad Pyr}{\rightleftarrows}} RNHCPh_3$$

J Med Chem (1973) 16 959



(Selective for NH in presence of OH)

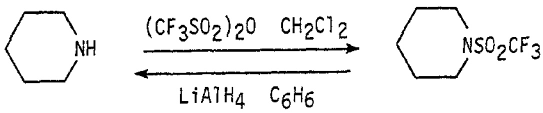
Chem Comm (1972) 1148

$$PhCH_2\underset{Me}{C}HNH_2 \underset{NaAlH_2(OCH_2CH_2OMe)_2\ \text{toluene}}{\overset{TsCl\quad Pyr\quad Et_2O}{\rightleftarrows}} PhCH_2\underset{Me}{C}HNHTs$$

JOC (1972) 37 2208

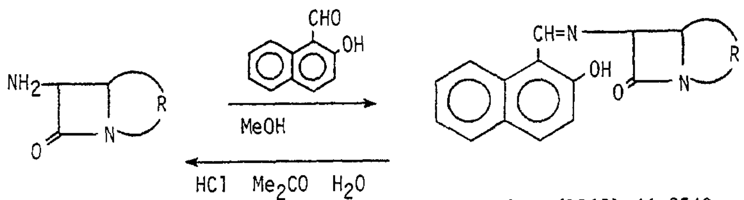
Cleavage of sulfonamides with hν Tetr Lett (1971) 4555 4559
Chem Pharm Bull (1970) 18 182

H_2SO_4, HOAc Chem Comm (1973) 664



(Stable to Zn/acid)

Tetr Lett (1973) 3839



Can J Chem (1968) 46 2549
JCS C (1971) 3864

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 8 PREPARATION OF ESTERS

Section 106 Esters from Acetylenes

$$PhC{\equiv}CEt \xrightarrow{Tl(NO_3)_3 \quad MeOH} PhCH(Et)COOMe \qquad 82\%$$

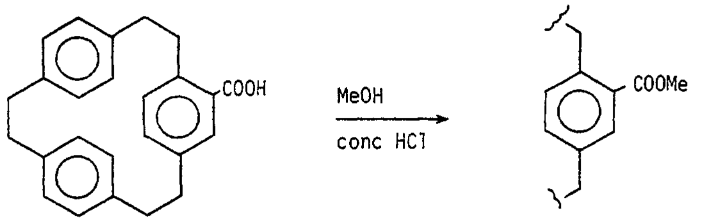
JACS (1973) 95 1296

Also via: Carboxylic Acids (Section 16)

Section 107 Esters from Carboxylic Acids and Acid Halides

$$RCOCl \xrightarrow[2\ PhCOOAg \quad Et_3N \quad EtOH]{1\ CH_2N_2 \quad Et_3N \quad Et_2O} RCH_2COOEt \qquad 85\text{-}92\%$$

Org Synth (1970) 50 77

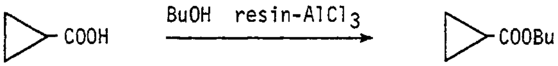


44%

Tetrahedron (1971) 27 4845

$$RCOOH \xrightarrow{R'OH \quad BF_3\cdot Et_2O} RCOOR'$$

Synthesis (1971) 316



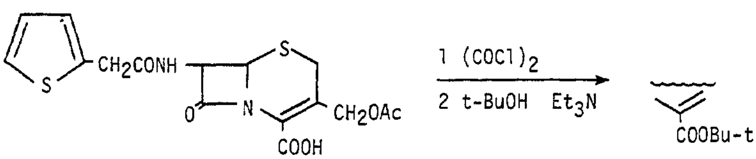
56%

Tetr Lett (1973) 1823

$$C_8H_{17}\underset{C_7H_{15}}{\overset{Bu}{C}}COOH \xrightarrow[ZnO]{MeC\equiv CH} C_8H_{17}\underset{C_7H_{15}}{\overset{Bu}{C}}COO\overset{Me}{C}{=}CH_2 \xrightarrow[TsOH]{t\text{-}BuOH} C_8H_{17}\underset{C_7H_{15}}{\overset{Bu}{C}}COOBu\text{-}t$$

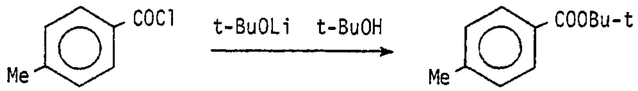
67%

JOC (1972) 37 3551



79%

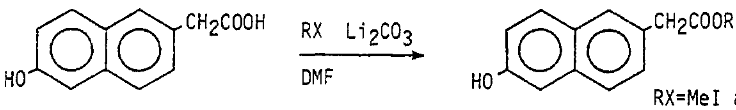
J Med Chem (1971) 14 420



79-82%

Org Synth (1971) 51 96

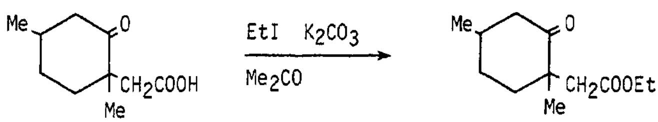
Further examples of the reaction RCOOH + ROH → RCOOR are included in section 108 (Esters from Alcohols and Phenols) and section 30A (Protection of Carboxylic Acids)



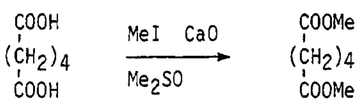
100%

RX=MeI at 25°
RX=$C_6H_{13}Br$ at 90°

J. Riegl, I. T. Harrison (Syntex Research) unpublished

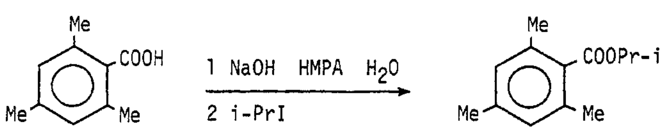


Tetr Lett (1972) 1853
JOC (1969) 34 3717



91%

Synthesis (1972) 262

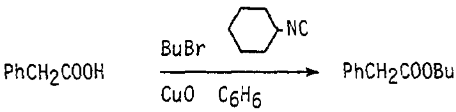


100%

Tetr Lett (1973) 689
(1972) 4063

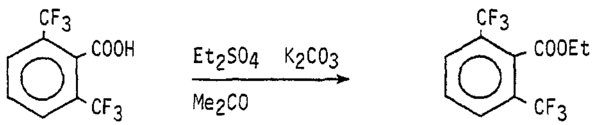
$$RCOOK \xrightarrow{PhCH_2Br \quad DMF} RCOOCH_2Ph$$

JOC (1962) 27 1381



86%

Synth Comm (1972) 2 1
JOC (1973) 38 1753



~90%

Chem Ind (1972) 691
Tetr Lett (1972) 757

$$PhCH{=}CHCOOH \xrightarrow[150°]{Et_2SO_4\text{-}HCONMe_2} PhCH{=}CHCOOEt$$

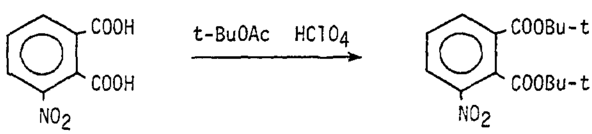
94%

Ber (1971) 104 3711

$$Me_2C(SH)CH(NH_2)COOH \xrightarrow{Me_2SO_3 \quad HCl \quad MeOH} Me_2C(SH)CH(NH_2)COOMe$$

83%

J Med Chem (1971) 14 868

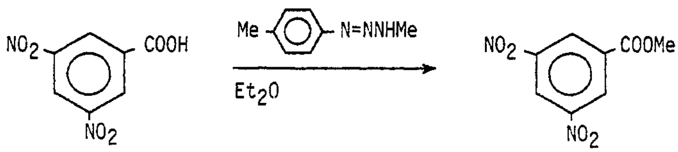


22%

Annalen (1961) 646 119 134

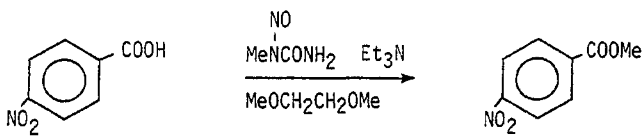
$$BuCOF \xrightarrow{Et_3SiH} BuCOOCH_2Bu$$

JOC (1971) 36 2547



70-90%

Org Synth (1968) 48 102



100%

Tetr Lett (1973) 1397

$$Et_3CCOOH \xrightarrow{Et_3\overset{+}{O}\ \overset{-}{BF_4}\quad (i\text{-}Pr)_2NEt} Et_3CCOOEt$$

90%

Tetr Lett (1971) 4741

$$C_{13}H_{27}COOH \xrightarrow[2\ \text{Toluene (reflux)}]{1\ Ph\overset{+}{N}Me_3\ \overset{-}{O}H\quad MeOH} C_{13}H_{27}COOMe$$

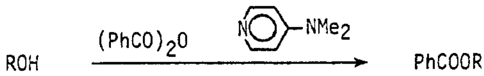
>90%

Synthesis (1973) 494

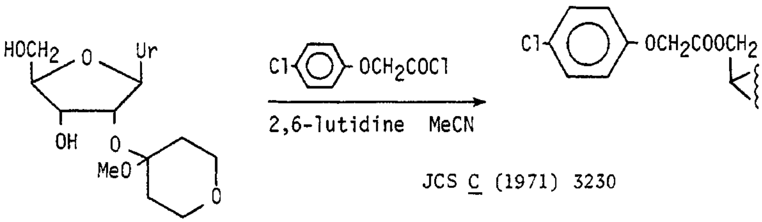
$$RCOOH \xrightarrow{Pb(OAc)_4} ROAc$$

Org React (1972) 19 279

Section 108 Esters from Alcohols and Phenols

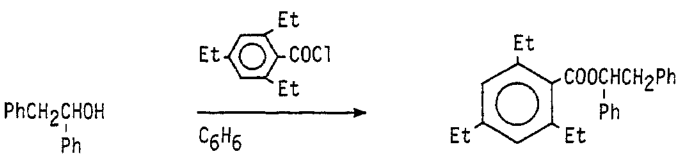


Synthesis (1972) 619

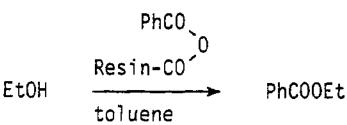


78%

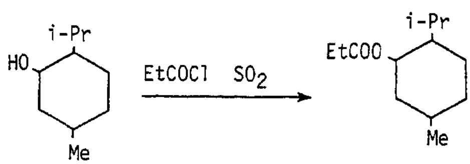
JCS C (1971) 3230



JACS (1953) 75 6011

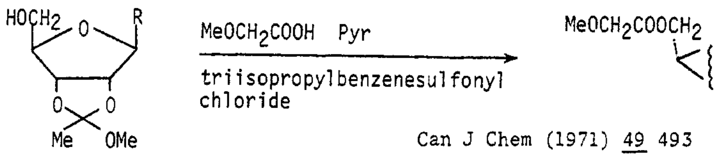


Tetr Lett (1973) 1627



92%

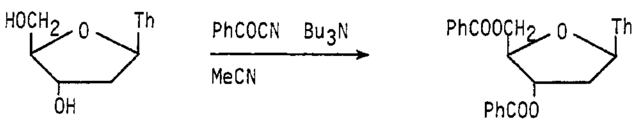
Synthesis (1971) 639



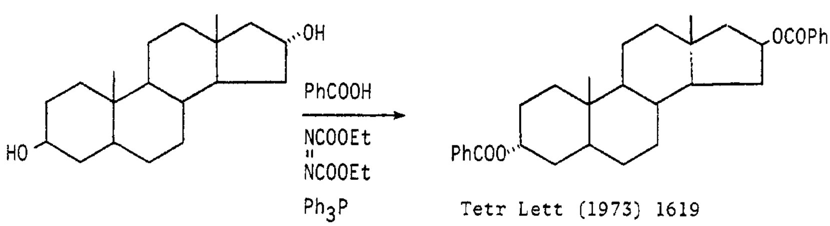
Can J Chem (1971) 49 493

ROH $\xrightarrow{\text{MeCOCl Mg}}$ ROAc 92%

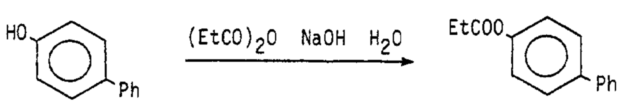
Tetrahedron (1971) 27 753



Tetr Lett (1971) 185

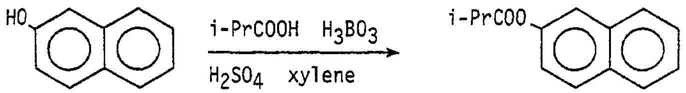


Tetr Lett (1973) 1619



73%

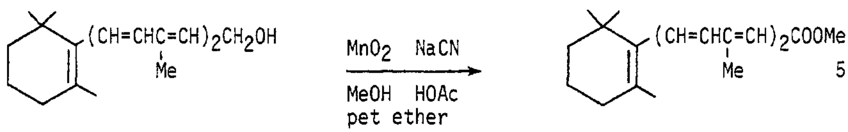
JACS (1942) 64 2271 3163



58%

Tetr Lett (1971) 3453

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)



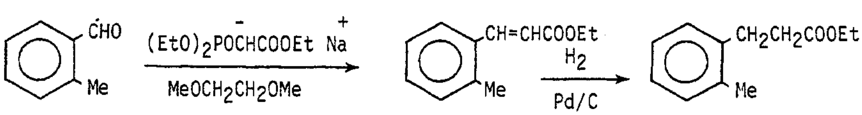
52%

Chem Ind (1971) 1016

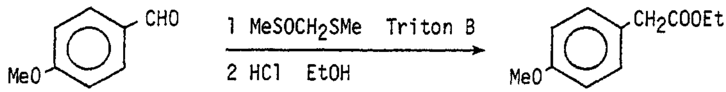
$$C_5H_{11}CH_2OH \xrightarrow[CoBr_2]{O_2 \quad Co(OAc)_2 \quad HOAc} C_5H_{11}COOCH_2C_5H_{11}$$

Can J Chem (1965) 43 1306

Section 109 Esters from Aldehydes

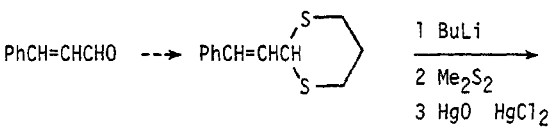


JOC (1971) 36 1040



93%

Tetr Lett (1972) 1383



<84%

JOC (1972) 37 2757

$C_6H_{13}CHO \dashrightarrow C_6H_{13}CH(OMe)_2 \xrightarrow[CH_2Cl_2]{O_3} C_6H_{13}COOMe$ <90%

Can J Chem (1971) 49 2465

$PhCHO \dashrightarrow PhCH(OEt)_2 \xrightarrow{NBS} PhCOOEt$

JACS (1951) 73 973

$BuCH(Et)CHO \xrightarrow[250°]{H_3BO_3 \quad heptane} BuCH(Et)COOCH_2CH(Et)Bu$ 47%

JOC (1973) 38 1433

Related methods: Esters from Ketones (Section 117)

Also via: Olefinic esters (Section 362)

Section 110 Esters from Alkyls, Methylenes and Aryls

No examples of the reaction RR $\rightarrow$ RCOOR' or R'COOR (R,R'=alkyl, aryl etc.) occur in the literature. For the reaction RH $\rightarrow$ RCOOR' or R'COOR see section 116 (Esters from Hydrides)

Section 111 Esters from Amides

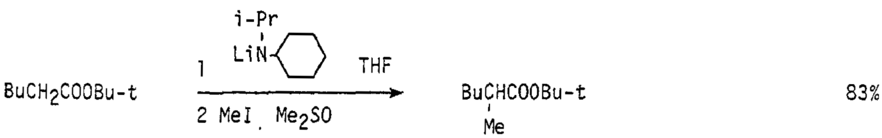
No additional examples

Section 112 Esters from Amines

$$C_6H_{13}NH_2 \dashrightarrow C_6H_{13}NTs_2 \xrightarrow[\text{HMPA}]{\text{KI} \quad \text{NaOAc}} C_6H_{13}OAc \qquad <95\%$$

Synth Comm (1972) 2 297

Section 113 Esters from Esters



JACS (1971) 93 2318
Tetr Lett (1973) 2425

$$\begin{matrix} EtCOOCH_2 \\ \quad C(SEt)_2 \\ EtCOOCH_2 \end{matrix} \xrightarrow{C_{17}H_{35}COOMe \quad MeONa} \begin{matrix} C_{17}H_{35}COOCH_2 \\ \quad C(SEt)_2 \\ C_{17}H_{35}COOCH_2 \end{matrix}$$

Can J Chem (1955) 33 717

$PrCOOPr \underset{}{\overset{EtOH \quad Bu_3SnOEt}{\rightleftarrows}} PrCOOEt$

Bull Soc Chim Fr (1969) 262

KCN Synthesis (1973) 790

$PrCOOEt \xrightarrow{BuOH \quad CO_2} PrCOOBu$ 27%

Bull Chem Soc Jap (1971) 44 852

$C_{11}H_{23}COOMe \xrightarrow[2\ Ac_2O]{1\ (i\text{-}Bu)_2AlH \quad octane} C_{11}H_{23}CH_2OAc$

Synthesis (1971) 309

$Pr_2C(COOEt)_2 \xrightarrow[178\text{-}183°]{NaCl \quad Me_2SO \quad H_2O} Pr_2CHCOOEt$

Tetr Lett (1973) 957

Section 114 Esters from Ethers

$i\text{-}PrCH_2OR \xrightarrow[H_2O]{Trichloroisocyanuric\ acid} i\text{-}PrCOOR$

Tetrahedron (1971) 27 2671

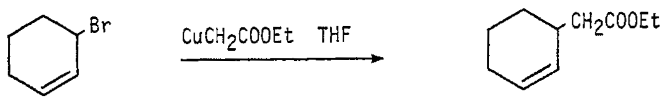
$R_2O \xrightarrow{TsOAc \quad MeCN} ROAc$

JOC (1971) 36 532 540

Section 115 Esters from Halides

BuBr $\xrightarrow[2\ H_2SO_4\quad HgO\quad EtOH]{1\ NaC\equiv COEt\quad NH_3}$ $BuCH_2COOEt$

JCS (1954) 1860
Advances in Org Chem (1960) 2 117

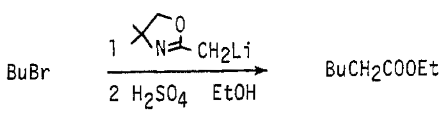


69%

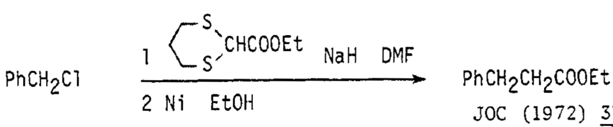
Tetr Lett (1972) 1163

ArBr $\xrightarrow[2\ CdCl_2]{1\ Mg}$ Ar_2Cd $\xrightarrow{BrCH_2COOEt}$ $ArCH_2COOEt$

JOC (1973) 38 3189



JACS (1970) 92 6644 6646

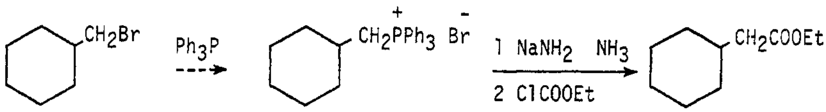


48%

JOC (1972) 37 505

RI $\xrightarrow[EtONa]{CH_2(COOEt)_2}$ $R_2C(COOEt)_2$ $\xrightarrow[H_2O\quad 178\text{-}183°]{NaCl\quad Me_2SO}$ $R_2CHCOOEt$

Tetr Lett (1973) 957



<65%

Annalen (1964) 674 11

$C_8H_{17}Cl \xrightarrow[\text{2 } I_2 \text{ N-methylpyrrolidone EtOH}]{\text{1 } Na_2Fe(CO)_4} C_8H_{17}COOEt$ 89%

JACS (1973) 95 249

$t\text{-}BuCl \xrightarrow[SO_2 \quad CH_2Cl_2]{CO \quad SbCl_5 \quad EtOH} t\text{-}BuCOOEt$ 66%

Synthesis (1971) 639
Bull Chem Soc Jap (1971) 44 2001

$RBr \xrightarrow{CuOAc \quad Pyr} ROAc$ (R is 1ry, 2ry or 3ry, alkyl, allylic or vinylic)

Tetr Lett (1972) 491

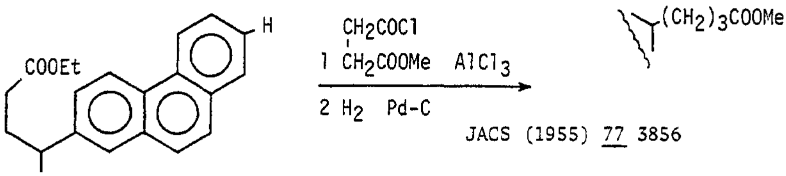
Related methods: Carboxylic Acids from Halides (Section 25)

Also via:

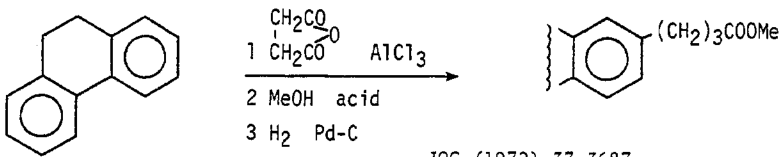
	Section
Acetylenic esters	306
Olefinic esters	362

Section 116 Esters from Hydrides

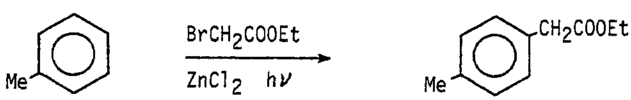
This section contains examples of the reaction RH ⟶ RCOOR' or R'COOR (R=alkyl, allyl, aryl etc.) and ArH ⟶ Ar-X-COOR (X=alkyl chain)



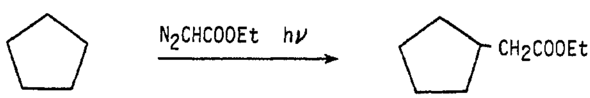
JACS (1955) 77 3856



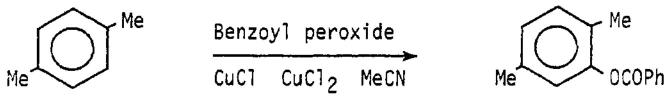
JOC (1972) 37 3687



Tetrahedron (1972) 28 211



JACS (1956) 78 4947



24%

Synthesis (1972) 1

$PhH \xrightarrow[LiOAc \quad HOAc]{Pd(OAc)_2 \quad K_2Cr_2O_7} PhOAc$

JOC (1971) <u>36</u> 1886
Synthesis (<u>1973</u>) 567

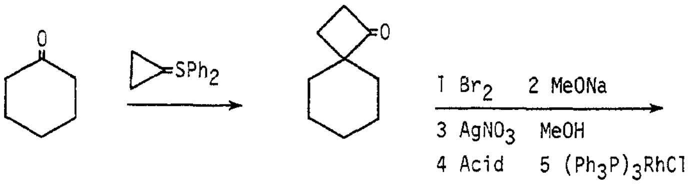
$R_2C{=}CHCHR_2 \longrightarrow R_2C{=}CHCR_2(OAc)$

$Hg(OAc)_2$	Synthesis (1971) 527
$PhCOO_2Bu$-t or $MeCOO_2Bu$-t, CuX	Synthesis (1972) 1
MnO_2, HOAc	JCS <u>C</u> (1971) 2355
$Co(OAc)_2$, O_2	Can J Chem (1965) <u>43</u> 1306
HOAc, electrolysis	JACS (1972) <u>94</u> 7892

Section 117 Esters from Ketones

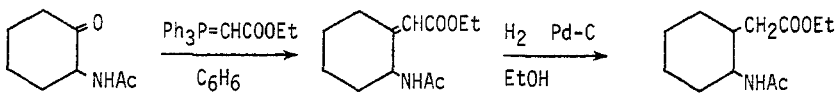
$Cl(CH_2)_3COMe \xrightarrow[2\ Ac_2O]{1\ C_5H_{11}MgBr \quad Et_2O} Cl(CH_2)_3C(OAc)(Me)C_5H_{11}$ >75%

JOC (1948) <u>13</u> 239



76%

JACS (1973) 95 2038



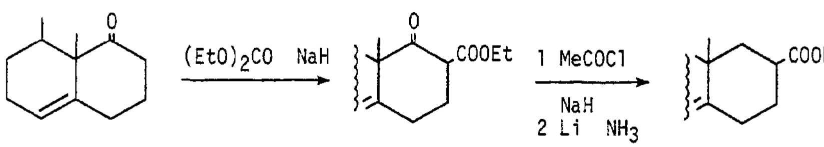
56%

JACS (1962) 84 4951

$$PhCOMe \xrightarrow{Tl(NO_3)_3 \quad HClO_4 \quad MeOH} PhCH_2COOMe$$

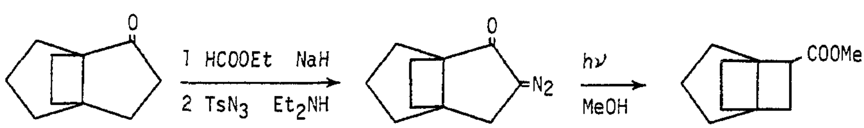
84%

JACS (1971) 93 4919



<34%

Tetr Lett (1968) 5405



JACS (1971) 93 2786

$$PhCOCH_3 \xrightarrow[2\ Me_2SO_4\quad NaOH\quad H_2O]{1\ i\text{-}PrCH_2CH_2ONO\quad HCl\quad Et_2O} PhCOOMe \qquad >90\%$$

Compt Rend (1942) 214 113

Also via:

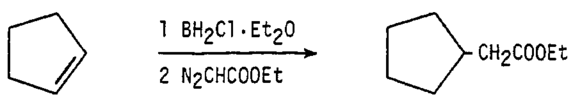
	Section
Carboxylic acids	27
Ketoesters	360
Olefinic esters	362

Section 118 Esters from Nitriles

$$RCN \xrightarrow{HCl\quad MeOH\quad Et_2O} RCOOMe \qquad 84\%$$

Ber (1972) 105 1778

Section 119 Esters from Olefins



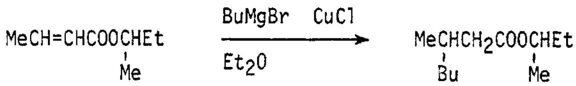
78%

JACS (1972) 94 3662

Also via:

	Section
Carboxylic acids	29
Olefinic esters	362

Section 120 Esters from Miscellaneous Compounds



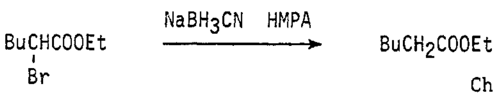
85%

Acta Chem Scand (1961) 15 271
Org React (1972) 19 1

$$PhCH{=}CHCOOMe \xrightarrow{NaBH_4\ \ NiCl_2\ \ MeOH} PhCH_2CH_2COOMe$$

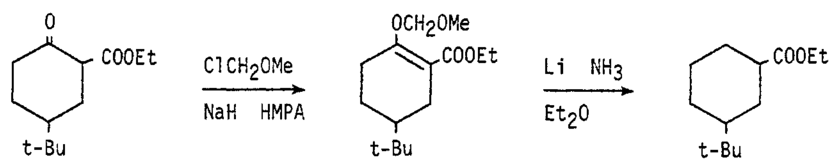
100%

Chem Pharm Bull (1971) 19 817



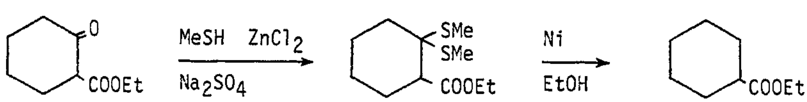
90%

Chem Comm (1971) 1097



32%

JOC (1970) 35 2601 2597
(1971) 36 1151



JACS (1950) 72 4296

$$C_6H_{13}COCH_2OH \xrightarrow{Tl(NO_3)_3 \quad MeOH} C_6H_{13}COOMe \qquad 76\%$$

JACS (1973) 95 1296

Section 120A Protection of Esters

$$C_{16}H_{33}CH_2COOMe \underset{HgO \quad BF_3 \quad THF \quad H_2O}{\overset{(Me_2Al)_2\text{-}SCH_2CH_2S \quad CH_2Cl_2}{\rightleftarrows}} C_{16}H_{33}CH{=}C\langle{}^{S}_{S}\rangle$$

(Stable to HOAc, KOH and $LiAlH_4$)

JACS (1973) 95 5829

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 9 PREPARATION OF ETHERS AND EPOXIDES

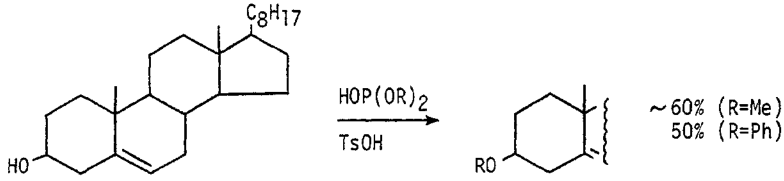
Section 121 Ethers and Epoxides from Acetylenes

No examples

Section 122 Ethers and Epoxides from Carboxylic Acids

No additional examples

Section 123 Ethers and Epoxides from Alcohols and Phenols



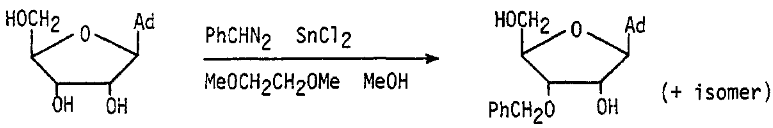
JOC (1972) 37 912

$$t\text{-BuOH} \xrightarrow[\text{2 } (i\text{-Pr})_3\text{CCOOMe} \quad \text{Me}_2\text{SO}]{\text{1 K}} t\text{-BuOMe}$$ ~50%

Tetr Lett (1964) 2969

$$C_7H_{15}OH \xrightarrow{\text{MeI} \quad \text{NaH} \quad \text{THF}} C_7H_{15}OMe$$ 40%

Tetr Lett (1973) 21

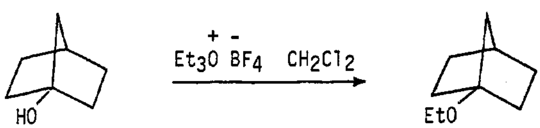


38%

JOC (1972) 37 3398

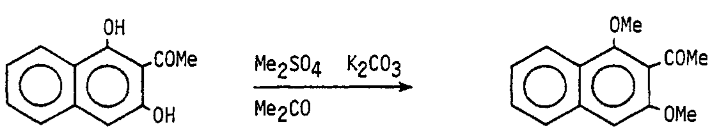
$$\text{ROH} \xrightarrow{CH_2N_2 \quad HBF_4 \quad CH_2Cl_2} \text{ROMe}$$

Org Synth (1961) 41 9

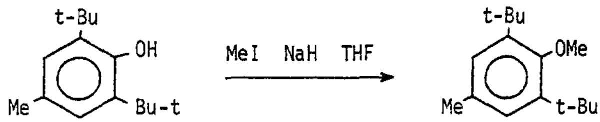


95%

Tetr Lett (1971) 1999

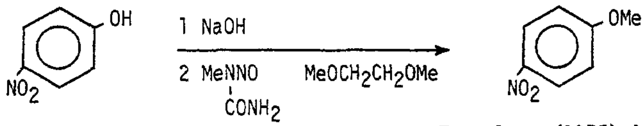


Chem Pharm Bull (1964) 12 312



86%

Tetr Lett (1973) 21

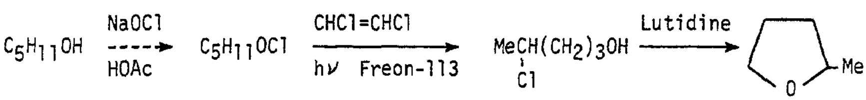


Tetr Lett (1973) 1397

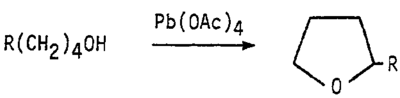
$$\mathrm{ArOH} \xrightarrow[\Delta]{\mathrm{Ph\overset{+}{N}Me_3\ \overset{-}{O}H}} \mathrm{ArOMe}$$ (Gas chrom scale)

J Pharm Sci (1969) 58 370

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



JOC (1972) 37 3514



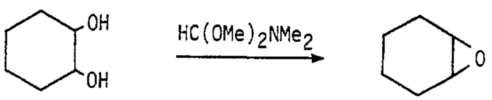
Synthesis (1971) 501

HO OH / MeCHCHMe $\xrightarrow{PhCHO}$ PhCH(O O) / MeCHCHMe $\xrightarrow[2\ NaOH\quad HOCH_2CH_2OH]{1\ NBS\quad CCl_4}$ MeCH(O)CHMe 80%

JOC (1973) 38 1691

HO OH / MeCHCHMe $\xrightarrow[\text{ion exch resin}\ C_6H_6]{MeCOCOOH}$ MeCCOOH(O O) / MeCHCHMe $\xrightarrow[2\ Base]{1\ PCl_5\quad CH_2Cl_2}$ MeCH(O)CHMe

JOC (1973) 38 1173



Chimia (1969) 23 267

Section 124 Ethers and Epoxides from Aldehydes

PhCHO $\xrightarrow{Ph_2PONa\quad 180°}$ PhCH(O)CHPh 88%

JCS Perkin I (1972) 1113

$C_7H_{15}CHO$ $\xrightarrow[THF]{MeCHBr_2\quad BuLi\ (or\ Li)}$ C_7H_{15}CH(O)CHMe 80%

Tetrahedron (1972) 28 3009
(1971) 27 6109

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 RH → ROR' (R,R'=alkyl) see section 131 (Ethers from Hydrides)

Section 126 Ethers and Epoxides from Amides

No additional examples

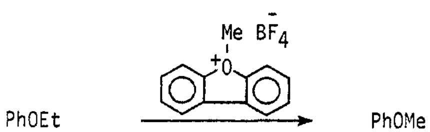
Section 127 Ethers and Epoxides from Amines

No additional examples

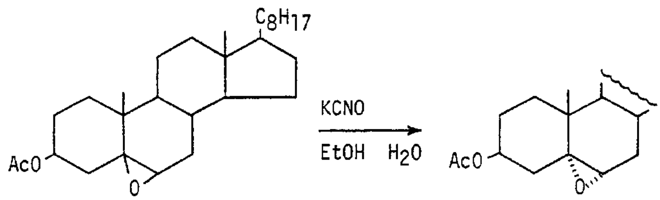
Section 128 Ethers and Epoxides from Esters

No additional examples

Section 129 Ethers and Epoxides from Ethers and Epoxides



Chem Comm (1972) 315



48%

Synthesis (1971) 32

Section 130 Ethers from Halides

$$PhBr \xrightarrow[2\ CdCl_2 \quad 3\ ClCH_2OMe]{1\ Mg \quad Et_2O} PhCH_2OMe$$

JOC (1973) 38 3189

$$PhBr \xrightarrow[2\ (BuO)_2P(O)OOBu\text{-}t]{1\ Mg \quad Et_2O} PhOBu\text{-}t$$

95%

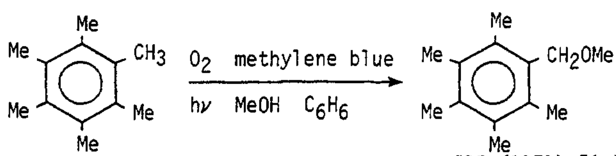
JOC (1972) 37 2267

Section 131 Ethers from Hydrides

This section lists examples of the reaction RH ⟶ ROR

$$R_2C{=}CHCH_2R \xrightarrow[MeOH]{Electrolysis \quad Et_4\overset{+}{N}\ \overset{-}{O}Ts} R_2C{=}CH\underset{OMe}{C}HR$$

JACS (1972) 94 7892



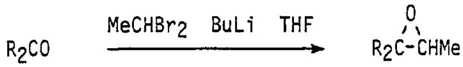
31%

JOC (1971) 36 1765

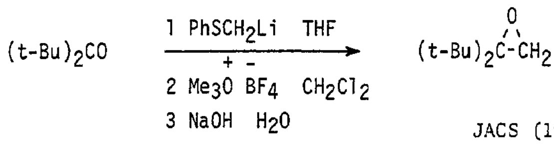
Section 132 Epoxides from Ketones

$$R_2CO \xrightarrow[2\ BuLi]{1\ LiCHCl_2 \quad Et_2O} R_2C\overset{O}{-}CHBu$$

Ber (1973) 106 2620



Tetrahedron (1972) 28 3009
(1971) 27 6109

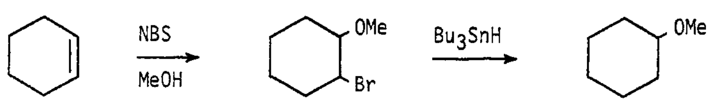


JACS (1973) 95 3429

Section 133 Ethers and Epoxides from Nitriles

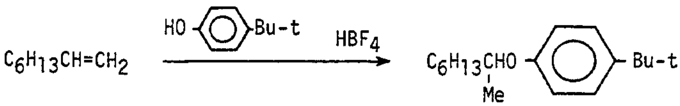
No examples

Section 134 Ethers and Epoxides from Olefins

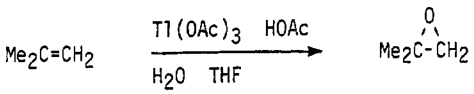


42%

Synthesis (1972) 483

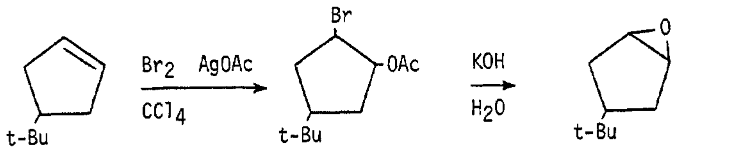


JCS C (1971) 1174

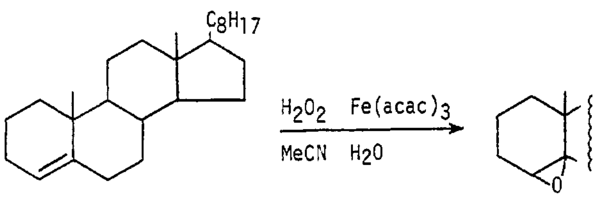


<82%

JOC (1971) 36 1154



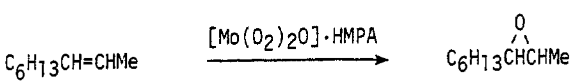
Tetrahedron (1972) 28 3475



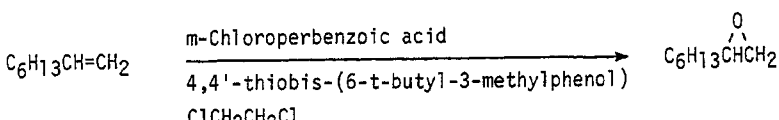
74%

( )

Tetr Lett (1973) 4359

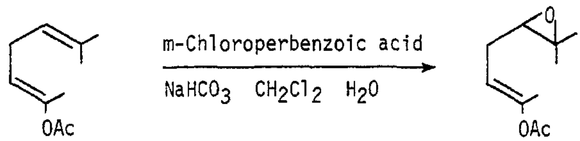


Tetrahedron (1970) 26 37



(Applicable to unreactive olefins)

Chem Comm (1972) 64



86%

(Method for acid sensitive compounds)

JOC (1973) 38 2267

$$R_2C{=}CR_2 \xrightarrow{\text{Peracid}} R_2\overset{\overset{O}{\wedge}}{C-C}R_2$$

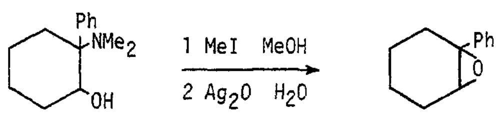
p-Methoxycarbonylperbenzoic acid JOC (1972) 37 4210

disuccinoyl peroxide Synthesis (1973) 156

o-Sulfoperbenzoic acid Tetr Lett (1971) 691

Preparation of $RCOO_2H$ from $RCOCl + (EtO)_2P(O)OAg$ JOC (1971) 36 2162

Section 135 Epoxides from Miscellaneous Compounds



JOC (1968) 33 4045

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Chapter 10 PREPARATION OF HALIDES AND SULFONATES

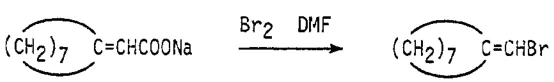
Section 136 Halides and Sulfonates from Acetylenes

No additional examples

Section 137 Halides from Carboxylic Acids

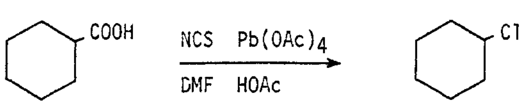
$$RCOOH \xrightarrow{Br_2\ \ HgO\ \ CCl_4} RBr$$

Org Synth (1971) 51 106
JOC (1972) 37 669 664



45%

JOC (1965) 30 2208
JCS C (1971) 2352



83%

Synthesis (1973) 493

$$RCOOH \xrightarrow{I_2 \quad Pb(OAc)_4} RI$$

Org React (1972) 19 279

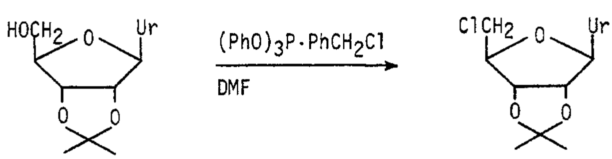
$$C_9H_{19}COOH \xrightarrow[2\ Br_2 \quad CCl_4]{1\ TlOEt \quad pet\ ether} C_9H_{19}Br \qquad 89\%$$

JOC (1969) 34 1172

Section 138 Halides and Sulfonates from Alcohols

$$ROH \xrightarrow{(PhO)_3P \cdot MeI} RI$$

Org Synth (1971) 51 44



70%

JOC (1972) 37 2289

$$ROH \xrightarrow{Ph_3P \quad CCl_4} RCl$$

JOC (1972) 37 1466

$BuOH \xrightarrow{Ph_3P \cdot Cl_2} BuCl$ 99%

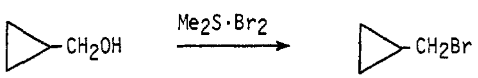
JACS (1964) 86 964

$ROH \xrightarrow{NBS \quad Ph_3P} RBr$

Chem Comm (1970) 602
Carbohydrate Res (1971) 18 342
Tetr Lett (1973) 3937

$Ph_2CHOH \xrightarrow[CH_2Cl_2]{(CH_2CO)_2N\text{-}\overset{+}{S}Me_2\ \overset{-}{Cl}} Ph_2CHCl$ >95%

(Specific for allylic and benzylic alcohols)
Tetr Lett (1972) 4339

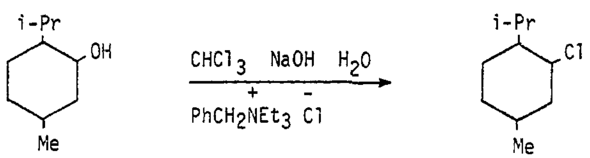


78%

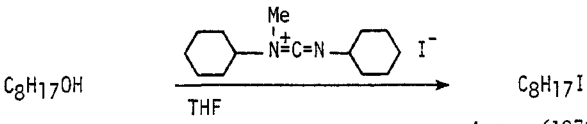
Chem Comm (1973) 212

$C_5H_{11}OH \xrightarrow{\text{Trichloroisocyanuric acid}} C_5H_{11}Cl$ 44%

JOC (1970) 35 3967
Chem Ind (1971) 1416

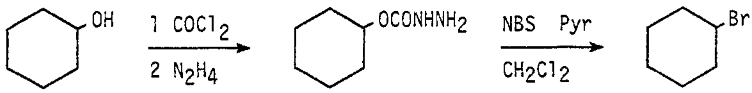


JACS (1971) 93 1820



89%

Angew (1972) 84 158
(Internat Ed 11 229)



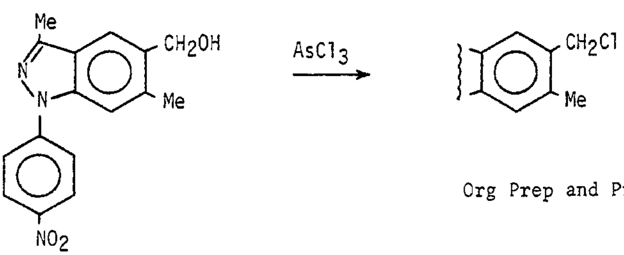
42%

(+38% dibromide)

Chem Comm (1971) 1112

$i\text{-PrOH} \xrightarrow{Br_2 \quad SO_2} i\text{-PrBr}$ 38%

Synthesis (1971) 639

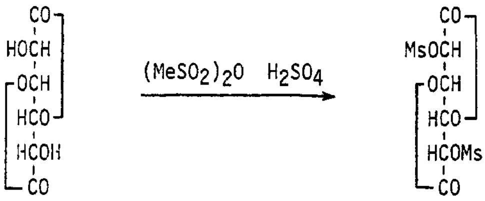


68%

Org Prep and Procedures (1970) 2 189

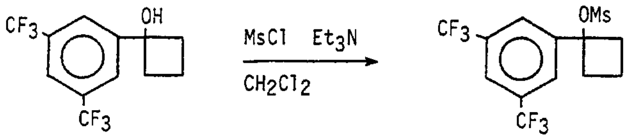
$Pr_2C{=}CHCH_2OH \xrightarrow{MsCl \quad LiCl \quad DMF} Pr_2C{=}CHCH_2Cl$ 93%

Tetrahedron (1971) 27 5979
JOC (1971) 36 3044



100%

JCS (1953) 1225
Chem Ind (1971) 702



92%

JOC (1970) 35 3195

Section 139 Halides and Sulfonates from Aldehydes

No additional examples

Section 140 Halides and Sulfonates from Alkyls

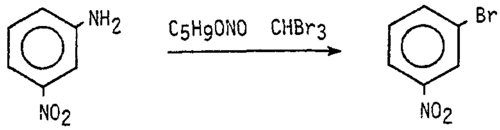
No additional examples

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



53%

JCS C (1966) 1249

$$RNMe_2 \xrightarrow[\text{2 KOH propylene glycol}]{\text{1 ClCOOEt } C_6H_6} RCl$$

J Med Chem (1971) 14 982

Section 143 Halides and Sulfonates from Esters

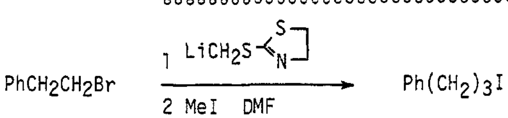
No additional examples

Section 144 Halides from Ethers

$$R_2O \xrightarrow{Ph_3P\cdot Br_2 \text{ PhCN}} RBr$$

JOC (1972) 37 626

Section 145 Halides from Halides and Sulfonates



<70%

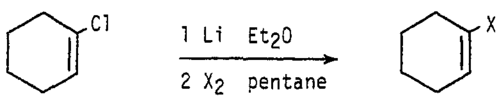
Tetr Lett (1972) 2743

$$Cl(CH_2)_6Cl \xrightarrow{NaI \quad Me_2CO} Cl(CH_2)_6I \qquad 50\%$$

JCS (1950) 2100

$$ROMs \xrightarrow{NaI \quad EtCOMe} RI$$

Tetrahedron (1971) 27 5987



57% (X=Br)
69% (X=I)

Tetrahedron (1972) 28 4883
Ber (1971) 104 2412

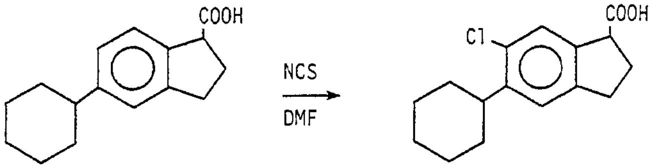
$$ArBr \xrightarrow{CuCl \quad picoline} ArCl$$

JACS (1958) 80 1716

Section 146 Halides from Hydrides

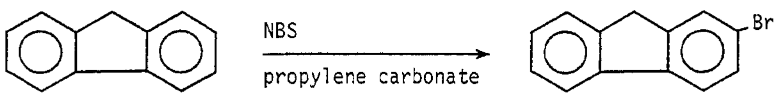
$$PhH \xrightarrow{MeCH(OH)CH_2Cl \quad BF_3 \quad P_2O_5} PhCH(Me)CH_2Cl \qquad 37\%$$

JACS (1948) 70 1772

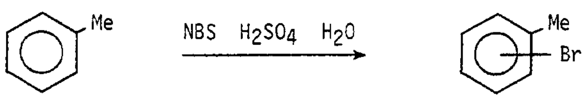


53%

J Med Chem (1972) 15 1297



JACS (1958) 80 4327



95%

JOC (1965) 30 304

Other Ar brominating agents: IBr JACS (1938) 60 256

Br_2-SO_2 Bull Soc Chim Fr (1971) 1785

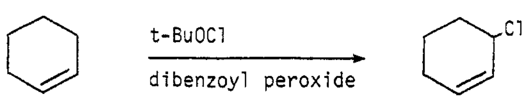
Br_2-Ag_2SO_4 Rec Trav Chim (1960) 79 1022

$Tl(OAc)_3$-Br_2 JOC (1972) 37 88

Ar chlorinating agents: $TiCl_4$-CF_3CO_2H Can J Chem (1972) 50 1233

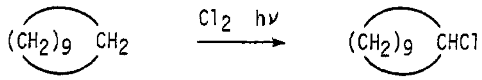
Ar iodinating agents: $Tl(OCOCF_3)_3$-KI JACS (1971) 93 4841

I_2-HIO_4 Org Synth (1971) 51 94

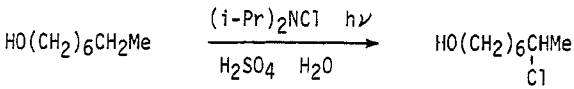


77%

Helv (1957) 40 130

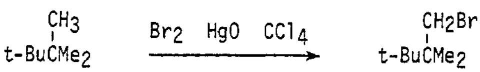


JOC (1967) 32 510



60-80%

JACS (1971) 93 438
Synthesis (1973) 1



32%

Can J Chem (1972) 50 3109

Section 147 Halides from Ketones

No additional examples

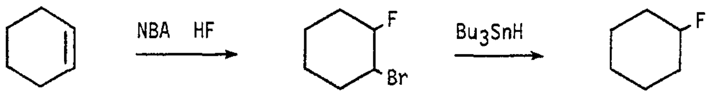
For the reaction C=O ⟶ $C(Hal)_2$ see section 368 (Halide-Halide)

Section 148 Halides and Sulfonates from Nitriles

No examples

Section 149 Halides from Olefins

For the conversion of olefins to dihalides see section 368 (Halide-Halide)
For allylic halogenation see section 146 (Halides from Hydrides)



Synthesis (1971) 255

$i\text{-PrCH=CHMe} \xrightarrow[\text{2 } Br_2 \quad CH_2Cl_2]{\text{1 9-BBN} \quad \text{THF}} i\text{-PrCH}_2\text{CH(Br)Me}$ 74%

J Organometallic Chem (1971) 26 C51

$BuCH{=}CH_2 \xrightarrow[\text{2 } CH_2{=}CHCH_2I \quad \text{air}]{\text{1 } B_2H_6 \quad \text{THF}} BuCH_2CH_2I$

JACS (1971) 93 1508

Section 150 Halides from Miscellaneous Compounds

$CH_2{=}CHCH_2Cl$, $MeCH{=}CHCl \xrightarrow[\text{Rh-}Al_2O_3]{H_2 \text{ (500 psi)}} MeCH_2CH_2Cl$ 42-58%

JOC (1964) 29 194

$C_7H_{15}SH \xrightarrow{\text{ClCOSCl} \quad Ph_3P} C_7H_{15}Cl$

Chem Comm (1972) 773

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Chapter 11 PREPARATION OF HYDRIDES

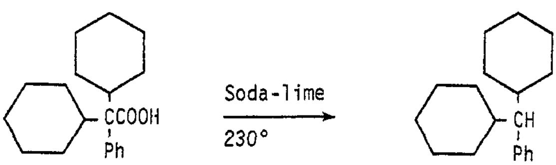
This chapter lists hydrogenolysis and related reactions by which functional groups are replaced by hydrogen, e.g. $RCH_2X \longrightarrow RCH_2\text{-}H$ or R-H

Section 151 Hydrides from Acetylenes

No examples of the reaction $RC \equiv CR \longrightarrow RH$ occur in the literature

Section 152 Hydrides from Carboxylic Acids

This section lists examples of the decarboxylation of acids, $RCOOH \longrightarrow RH$



JCS (1962) 1445
JACS (1950) 72 1849

Section 153 Hydrides from Alcohols and Phenols

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

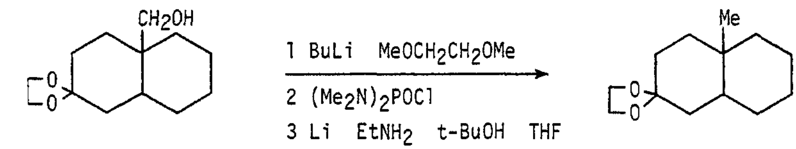
$Et_3COH \xrightarrow[CH_2Cl_2]{Ph_3SiH \quad CF_3COOH} Et_3CH$ 78%

(3ry only)

JOC (1971) 36 758

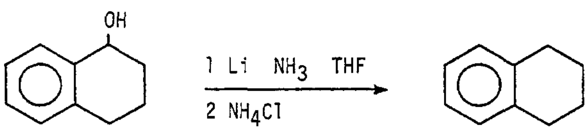
$C_{10}H_{21}OH \xrightarrow[HMPA]{(PhO)_3P\cdot MeI \quad NaBH_3CN} C_{10}H_{22}$ 99%

Chem Comm (1971) 1097

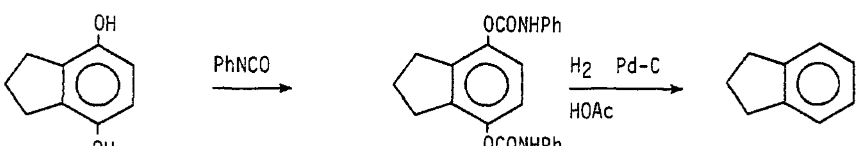


89%

JACS (1972) 94 5098

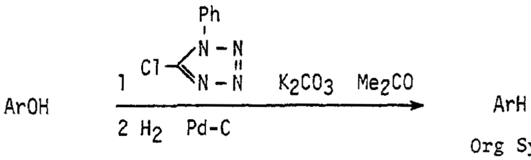


Tetr Lett (1971) 1853

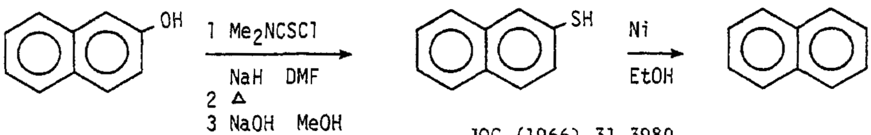


70%

Chem Ind (1973) 187



Org Synth (1971) 51 82



JOC (1966) 31 3980

Also via:

	Section
Halides and Sulfonates	160
Ethers	159

Section 154 Hydrides from Aldehydes

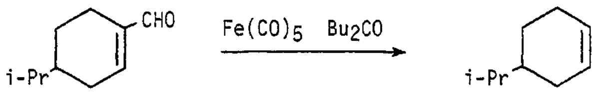
This section lists examples of the decarbonylation of aldehydes, RCHO → RH. For the conversion RCHO → RMe etc. see section 64 (Alkyls from Aldehydes)

$$\mathrm{RCHO} \xrightarrow{\text{Pd-C}\ \ 190°} \mathrm{RH}$$

JOC (1968) 33 923

$$C_6H_{13}CHO \xrightarrow{h\nu\ \ PhCH_2SH\ \ PhCOMe} C_6H_{14}$$

JACS (1963) 85 4010



36%

Tetr Lett (1973) 447

Section 155 Hydrides from Alkyls, Methylenes and Aryls

No additional examples

Section 156 Hydrides from Amides

This section lists examples of the conversion $RCONH_2 \longrightarrow RH$

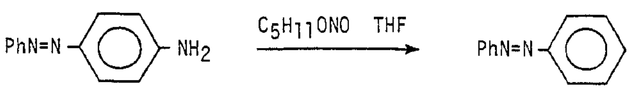
$$t\text{-}BuC{\equiv}CCONH_2 \xrightarrow{NaNH_2 \quad NH_3} t\text{-}BuC{\equiv}CH$$

JCS (1963) 4402

Also via: Carboxylic acids (Section 152)

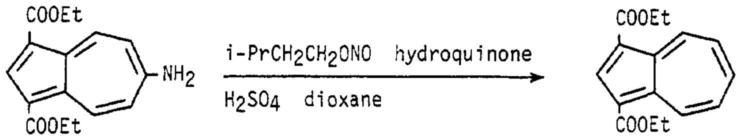
Section 157 Hydrides from Amines

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



66%

JCS Perkin I (1973) 541



Chem Comm (1973) 605

$$ArNH_2 \longrightarrow Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Y} ArH$$

$Y = RhCl(PPh)_3$ JOC (1971) 36 1725

Bu_3SnH Tetrahedron (1970) 26 4609

Section 158 Hydrides from Esters

This section lists examples of the reaction RCOOR' ⟶ R'H

$$PhCOOCHPh_2 \xrightarrow{Bu_2O_2 \quad Bu_3SnH} Ph_2CH_2$$

Tetr Lett (1968) 4351

Section 159 Hydrides from Ethers

$$PhOMe \xrightarrow{Ni \quad MeOH} PhH$$ 62%

Aust J Chem (1963) 16 20

$$\underset{(CH_2)_{10}OMe}{\overset{COOH}{|}} \xrightarrow{KOH \quad 360°} \underset{(CH_2)_8H}{\overset{COOH}{|}}$$

JCS C (1971) 1840

Section 160 Hydrides from Halides and Sulfonates

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

$$C_{12}H_{25}X \xrightarrow{NaBH_3CN \quad HMPA} C_{12}H_{26}$$

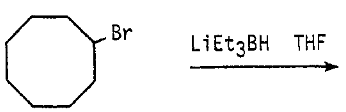
96% (X=I)
97% (X=Br)
78% (X=OTs)

Chem Comm (1971) 1097
JOC (1971) 36 1568
JACS (1973) 95 6131

$$C_8H_{17}X \xrightarrow{CuI\text{-}LiAlH(OMe)_3 \quad THF} C_8H_{18}$$

98% (X=Br)
95% (X=OMs)

JACS (1973) 95 6452



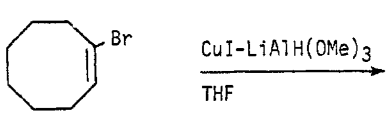
99%

JACS (1973) 95 1669

$$PhCH{=}CHCH_2Cl \xrightarrow[Me_2SO]{NaH \quad TsNHNH_2} PhCH{=}CHCH_2NHNHTs \xrightarrow{HOAc} PhCH_2CH{=}CH_2$$

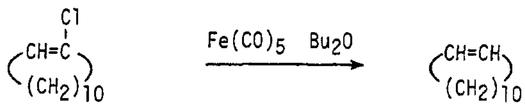
60%

Tetr Lett (1969) 871



99%

JACS (1973) 95 6452



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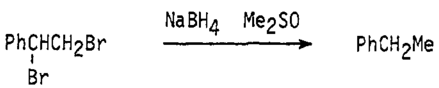
Tetr Lett (1973) 447



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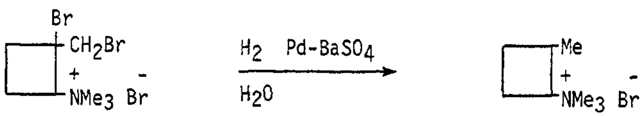
Tetr Lett (1969) 3495



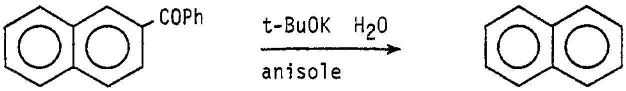
JACS (1948) 70 2517
(1947) 69 2555

Section 161 Hydrides from Hydrides

No additional examples

Section 162 Hydrides from Ketones

This section lists examples of the conversion $R_2CO \longrightarrow RH$. For the conversion $R_2CO \longrightarrow R_2CH_2$ or R_2CHR' see section 72 (Alkyls and Methylenes from Ketones)



95%

Ber (1971) 104 2637

Section 163 Hydrides from Nitriles

This section lists examples of the conversion RCN ⟶ RH

$$RCN \xrightarrow{Fe(acac)_3\text{-}Na \quad C_6H_6} RH$$

46% (R=Ph)
100% ($R=C_8H_{17}$)

JACS (1971) 93 7113

$$C_{12}H_{25}CN \xrightarrow{Li \quad EtNH_2} C_{12}H_{26}$$

35%

JACS (1969) 91 2059
Tetr Lett (1968) 1975

$$RCN \xrightarrow{Na \quad NH_3} RH$$

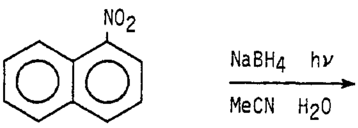
JOC (1972) 37 508

Section 164 Hydrides from Olefins

No additional examples

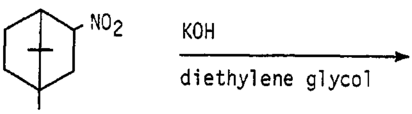
Section 165 Hydrides from Miscellaneous Compounds

This section lists examples of the replacement of miscellaneous functional groups by hydrogen (RX ⟶ RH)



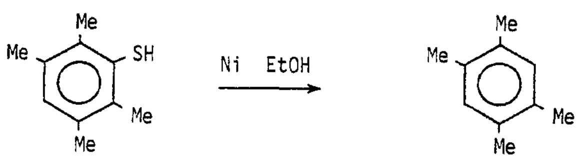
60%

Tetr Lett (1971) 2197



~60%

Tetr Lett (1971) 3203



70%

JOC (1966) 31 3980

Chapter 12 PREPARATION OF KETONES

Section 166 Ketones from Acetylenes

$$BuC{\equiv}CH \xrightarrow[\substack{2\ (C_8H_{17})_3B\quad hexane \\ 3\ Me_2SO_4\quad diglyme \\ 4\ NaOH\quad H_2O_2\quad H_2O}]{1\ RLi} \underset{\displaystyle Me}{BuCHCOC_8H_{17}}$$ 85%

Chem Comm (1973) 544

$$RC{\equiv}CR \xrightarrow[2\ H_2O_2\quad NaOH]{1\ BH} RCH_2COR$$

BH = BH_2Cl JOC (1973) 38 1617

BH = catechol borane JACS (1972) 94 4370

$$PhC{\equiv}CC_6H_{13} \xrightarrow[2\ H_2SO_4]{1\ NaNHNH_2\quad N_2H_4\quad Et_2O} PhCH_2COC_6H_{13}$$ 76%

Ber (1966) 99 1843

Also via:

	Section
Acetylenic ketones	309
Olefinic ketones	374

Section 167 Ketones from Acid Halides

$$RCOCl \xrightarrow{R'_2CuLi} RCOR'$$

Tetr Lett (1971) 829
Synthesis (1972) 701

$$PhCOF \xrightarrow{Bu_2CuLi \quad Et_2O} PhCOBu \qquad 87\%$$

JACS (1972) 94 5106

$$Br(CH_2)_{10}COCl \xrightarrow{(t\text{-}BuOCuCH(Me)Et)Li} Br(CH_2)_{10}COCH(Me)Et \qquad 83\%$$

Tetr Lett (1973) 1815

$$C_5H_{11}COCl \xrightarrow[2\ EtI]{1\ Na_2Fe(CO)_4 \quad HMPA \quad THF} C_5H_{11}COEt \qquad 87\%$$

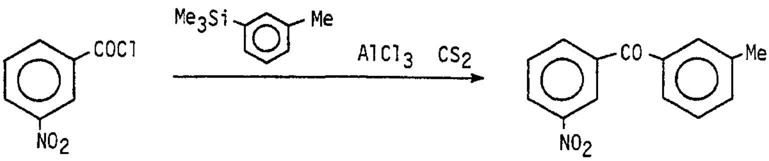
JACS (1972) 94 1788

$$PhCH{=}CHCOCl \xrightarrow{Li[PhCOFe(CO)_4]} PhCH{=}CHCOPh \qquad 22\%$$

Synthesis (1971) 55

$$PhCH{=}CHCOCl \xrightarrow[Et_2O \quad THF]{RhCl(CO)(PPh_3)_2 \quad PhLi} PhCH{=}CHCOPh \qquad 85\%$$

JACS (1973) 95 3040



50%

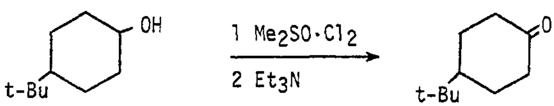
Organometallics in Chem Synth (1971) 1 151

Also via: Olefinic ketones (Section 374)

Section 168 Ketones from Alcohols and Phenols

$$Ph_2CHOH \xrightarrow[CCl_4 \quad H_2SO_4]{C_6H_{13}C{\equiv}CH} Ph_2CHCH_2COC_6H_{13}$$ 23%

JCS Perkin I (1972) 2100

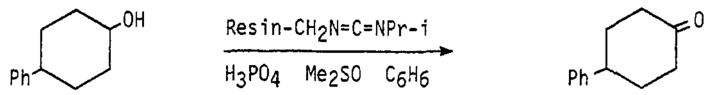


>97%

Tetr Lett (1973) 919

$$C_6H_{13}\underset{Me}{CH}OH \xrightarrow[Et_3N \quad toluene]{(CH_2CO)_2\overset{+}{N}SMe_2 \ \overset{-}{Cl}} C_6H_{13}\underset{Me}{CO}$$ 91%

JACS (1972) 94 7586



67%

Tetr Lett (1972) 3285

$$\underset{\displaystyle\text{Pr}}{\text{C}_5\text{H}_{11}\text{CHOH}} \xrightarrow[\text{(gas phase)}]{\text{Cu}_2\text{O}\quad 250\text{-}300°} \underset{\displaystyle\text{Pr}}{\text{C}_5\text{H}_{11}\text{CO}}$$

100%

Tetr Lett (1972) 257

$$\underset{\displaystyle\text{Me}}{\text{C}_6\text{H}_{13}\text{CHOH}} \xrightarrow{\text{CrO}_3\cdot\text{Pyr}\quad\text{HOAc}} \underset{\displaystyle\text{Me}}{\text{C}_6\text{H}_{13}\text{CO}}$$

68%

Acta Chem Scand (1971) 25 1125

CrO_3-3,5-dimethylpyrazole Tetr Lett (1973) 4499

$$\text{R}_2\text{CHOH} \xrightarrow{\text{RuO}_4} \text{R}_2\text{CO}$$

Tetr Lett (1970) 4003

$$\text{Ph}_2\text{CHOH} \xrightarrow{\text{PhICl}_2\quad\text{Pyr}\quad\text{CHCl}_3} \text{Ph}_2\text{CO}$$

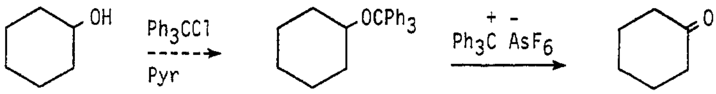
49%

Tetr Lett (1973) 3635

$$\underset{\displaystyle\text{Me}}{\text{PhCHOH}} \xrightarrow[\text{C}_6\text{H}_6]{\text{Ph}_2\text{C=NBr}\quad h\nu} \underset{\displaystyle\text{Me}}{\text{PhCO}}$$

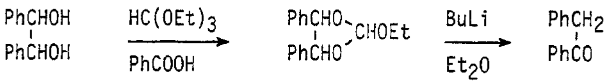
94%

JOC (1970) 35 4245



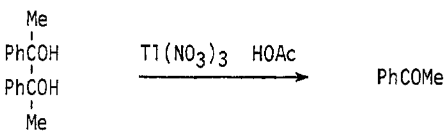
< 97%

JOC (1973) 38 625



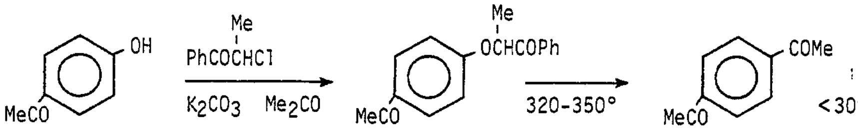
< 76%

Aust J Chem (1968) 21 2013



63%

JOC (1972) 37 4204

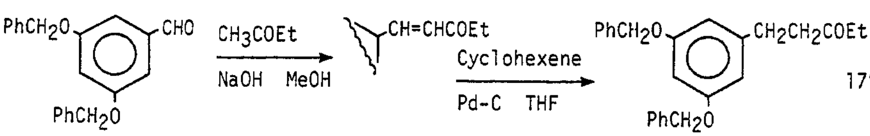


< 30%

JOC (1961) 26 4308

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

Section 169 Ketones from Aldehydes



17%

JOC (1972) 37 2204

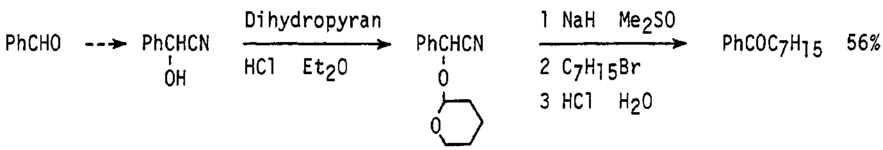
$$PhCHO \xrightarrow[\text{HOAc; 2 NaH MeI DMF}]{\text{1 PhSH } ZnCl_2} PhC(SPh)_2Me \xrightarrow[\text{HgO}]{HgCl_2} PhCOMe$$

JOC (1963) 28 961
(1971) 36 3553
J Med Chem (1973) 16 749

$$CH_2{=}CHCHO \xrightarrow[\text{2 } EtOCH{=}CH_2]{\text{1 HCN}} CH_2{=}CHCHCN(OCHMe(OEt)) \xrightarrow[\text{2 } C_6H_{13}Br\text{; 3 } H_2SO_4 \text{ MeOH; 4 NaOH } H_2O]{\text{1 } (i\text{-}Pr)_2NLi \text{ THF}} CH_2{=}CHCOC_6H_{13}$$

~75%

JACS (1971) 93 5286
Synthesis (1973) 777

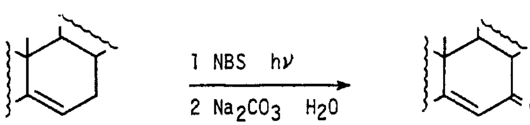


Synthesis (1973) 358

Related methods: Aldehydes from Aldehydes (Section 49)

Also via: Olefinic Ketones (Section 374)

Section 170 Ketones from Alkyls and Methylenes



Chem Comm (1972) 350

$$PhBu\text{-}t \xrightarrow[HOAc\quad PhCl]{O_2\quad Co(OAc)_2\quad HCl} PhCOMe \qquad 23\%$$

Chem Comm (1971) 1166

Section 171 Ketones from Amides

$$PhCONEt_2 \xrightarrow{EtBr\quad Li\quad THF} PhCOEt \qquad (79\%)$$

(One-step procedure)

Synthesis (1973) 160

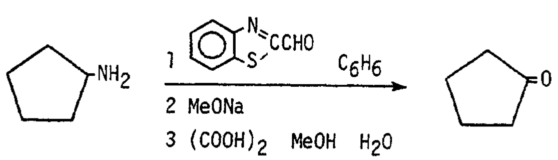
Section 172 Ketones from Amines

$$\overset{+}{Ph}NMe_3\ \overset{-}{I} \xrightarrow[2\ CrO_3\quad H_2SO_4]{1\ MeCOCH_2K\quad K\quad NH_3} PhCH_2COMe \qquad 56\%$$

JACS (1972) 94 683

$$\underset{Me}{EtCHNH_2} \xrightarrow[H_2O]{[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+\ PF_6^-} \underset{Me}{EtCO}$$

Chem Comm (1971) 1274

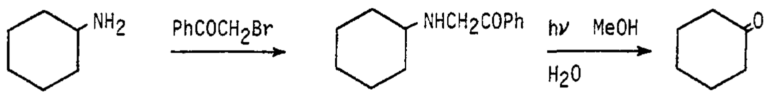


86%

JCS Perkin I (1972) 1652

$PhCH(Me)NH_2 \xrightarrow[2\ NaNO_2\ \ HOAc]{1\ TsCl} PhCH(Me)N(NO)Ts \xrightarrow{h\nu\ \ MeOH} PhCOMe$ < 25%

Rec Trav Chim (1971) 90 901



<71%

JOC (1972) 37 1254

Section 173 Ketones from Esters

$t\text{-}BuCOOMe \xrightarrow{PrMgCl\ \ HMPA} t\text{-}BuCOPr$ 98%

$t\text{-}BuCOOMe \xrightarrow[2\ MeI]{1\ EtCH_2MgCl\ \ HMPA} t\text{-}BuCOCH(Me)Et$ 81%

Tetrahedron (1973) 29 479

Section 174 Ketones from Ethers and Epoxides

$R_2CHOR \xrightarrow{t\text{-Butyl perbenzoate}} R_2C(OOCPh)OR \dashrightarrow R_2CO$

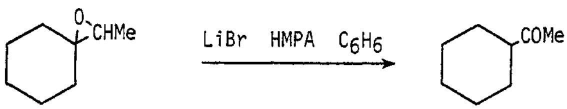
Synthesis (1972) 1

$(Me_2CH)_2O \xrightarrow{Ph_3\overset{+}{C}\ \overset{-}{BF_4}} Me_2CO$

JACS (1967) 89 3550

$$Me_2C\overset{O}{-}CHMe \xrightarrow[110°]{HF \quad MeCN} Me_2CHCOMe \qquad 67\%$$

Z Chem (1967) 7 229



JACS (1971) 93 1693
Ber (1973) 106 1365

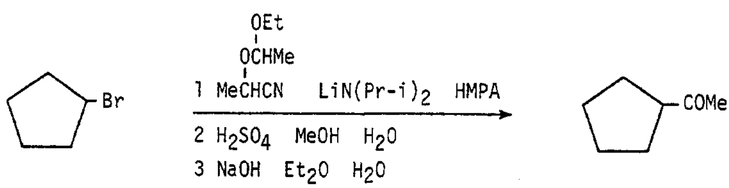
Also via: Olefinic Ketones (Section 374)

Section 175 Ketones from Halides

$$BuBr \xrightarrow[base]{MeCOCH_2COOEt} Bu\overset{COOEt}{\overset{|}{C}}HCOMe \xrightarrow[Me_2SO]{NaCl \quad H_2O} BuCH_2COMe$$

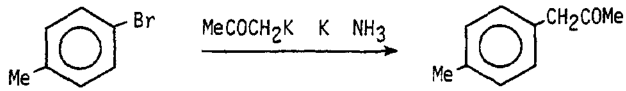
Tetr Lett (1973) 957

Cleavage of β-ketoesters with LiH-BuLi Tetr Lett (1971) 4585
B_2O_3 Tetr Lett (1970) 3903



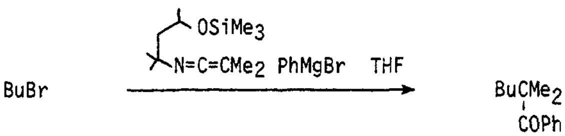
80%

JACS (1971) 93 5286



57%

JACS (1972) <u>94</u> 683



81%

JOC (1973) <u>38</u> 2129

$$\mathrm{BuBr} \xrightarrow[\text{2 } HClO_4]{\text{1 } EtS(SOEt)CHEt \quad BuLi \quad THF} \mathrm{BuCOEt}$$

Tetr Lett (1973) 3267

$$C_8H_{17}Br \xrightarrow[\substack{HMPA \quad THF \\ \text{2 } HgCl_2 \quad MeCN \quad H_2O}]{\text{1 } MeSCH{=}CHC_8H_{17} \quad EtCH(Me)Li} C_8H_{17}COC_9H_{19}$$

82%

JACS (1973) <u>95</u> 2694

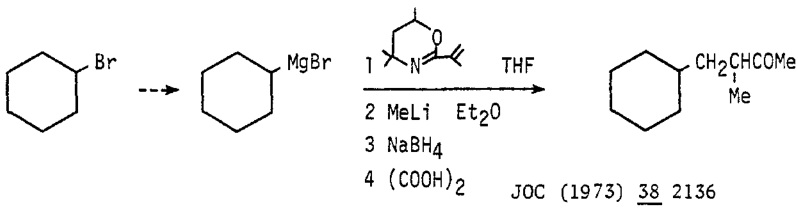
$$\mathrm{PrBr} \xrightarrow[\text{2 } Hg\text{-}Al \quad THF \quad H_2O]{\text{1 } MeSOCH_2COPh \quad NaH \quad DMF} PrCH_2COPh$$

44%

JOC (1966) <u>31</u> 2355
Tetr Lett (1974) 107

$C_5H_{11}Br \xrightarrow[\text{2 } H_2O \text{ EtOH}]{\text{1 } CH_3COCH{=}PPh_3 \text{ BuLi THF}} C_5H_{11}CH_2COMe$ 82%

JOC (1973) 38 4082



JOC (1973) 38 2136

$BuBr \dashrightarrow Bu_2CuLi \xrightarrow{CO \ \ Et_2O} Bu_2CO$ 70%

Tetr Lett (1972) 2803

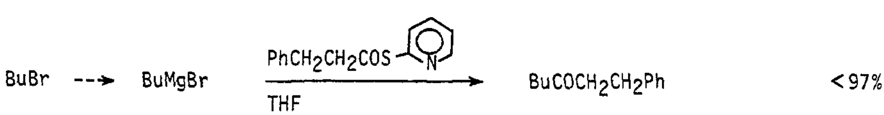
$i\text{-}PrCl \xrightarrow[\text{2 EtCOOMe HMPA}]{\text{1 Mg } Et_2O} i\text{-}PrCOEt$ 43%

Tetrahedron (1973) 29 479

$PhBr \xrightarrow{PhCONEt_2 \ \ Li \ \ THF} Ph_2CO$ 76%

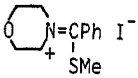
(One-step procedure)

Synthesis (1973) 160

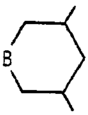


JACS (1973) 95 4763

$BuBr \xrightarrow[2]{1\ Mg} BuCOPh$ 55%



Chem Ind (1972) 380

t-BuCl $\dashrightarrow$ t-BuB  $\xrightarrow[2\ H_2O_2\quad NaOH\quad H_2O]{1\ CH_2{=}CHCOMe\quad THF}$ $t\text{-}BuCH_2CH_2COMe$ <90%

JACS (1971) 93 3777

$RHal \dashrightarrow R_2Hg \xrightarrow[h\nu\quad THF]{Co_2(CO)_8\quad CO} R_2CO$

Synthesis (1971) 55

$C_8H_{17}Br \xrightarrow[2\ EtI]{1\ Na_2Fe(CO)_4\quad N\text{-methylpyrrolidone}} C_8H_{17}COEt$ 80%

JACS (1972) 94 1788 2516

$RBr \xrightarrow{Li[R'COFe(CO)_4]\quad Et_2O\quad C_6H_6} RCOR'$

Synthesis (1971) 55

$PhCH_2Cl \xrightarrow{Fe_2(CO)_9\quad C_6H_6} (PhCH_2)_2CO$ 52%

J Organometallic Chem (1967) 9 361

$$PhCH_2I \xrightarrow{Fe(CO)_5 \quad BuLi \quad Et_2O} PhCH_2COBu \qquad 50\%$$

Tetr Lett (1969) 5189

$$MeCH_2Br \dashrightarrow MeCH{=}PPh_3 \xrightarrow[2\ HCl \quad H_2O]{1\ Ph\overset{OMe}{\overset{|}{C}}{=}W(CO)_5 \quad Et_2O} MeCH_2COPh$$

JACS (1972) 94 6543

$$\underset{\underset{Me}{|}}{PhCHBr} \xrightarrow[Me_2SO]{NaNO_2} \underset{\underset{Me}{|}}{PhCHNO_2} \xrightarrow[Me_2SO]{NaNO_2 \quad PrONO} \underset{\underset{Me}{|}}{PhCO} \qquad 39\%$$

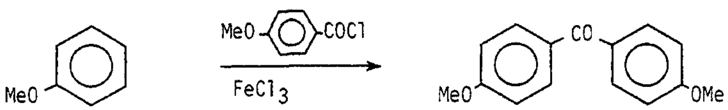
JOC (1973) 38 1418

Related methods: Ketones from Ketones (Section 177)

Also via: Olefinic ketones (Section 374)

Section 176 Ketones from Hydrides

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



88%

(Method for reactive compounds)

Synthesis (1972) 533

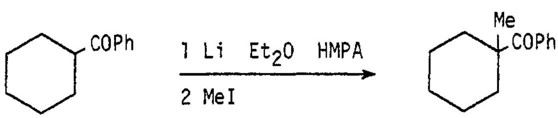
Section 177 Ketones from Ketones

$$PhCH_2COMe \xrightarrow[NaOH \quad H_2O]{BuBr \quad Et_3\overset{+}{N}CH_2Ph \ \overset{-}{Cl}} Ph\underset{\substack{|\\ Bu}}{C}HCOMe \qquad 90\%$$

Tetr Lett (1971) 1351

$$RCOCHR_2 \xrightarrow[2\ BuI]{1\ BuMgBr \quad HMPA} RCO\underset{\substack{|\\ Bu}}{C}R_2$$

Bull Soc Chim Fr (1969) 160



72%

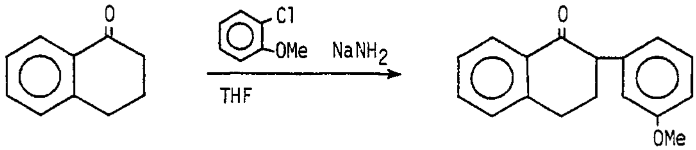
Bull Soc Chim Fr (1968) 595

$$PhCOCH_2Me \xrightarrow[2\ BuBr]{1\ (i\text{-}Pr)_2NLi \quad MeOCH_2CH_2OMe} PhCO\underset{\substack{|\\ Bu}}{C}HMe \qquad 75\%$$

JOC (1973) <u>38</u> 2756

$$PhCOCH_2Me \xrightarrow[KOH \quad EtOH]{HCHO \quad Fe(CO)_5} PhCOCHMe_2 \qquad 85\%$$

Tetr Lett (1973) 2491



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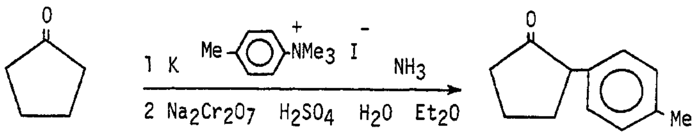
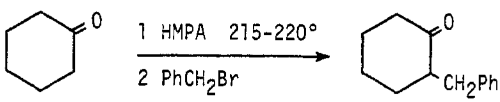
Chem Pharm Bull (1971) 19 1150



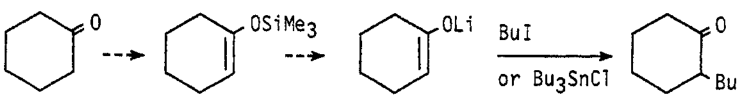
34%

JACS (1972) 94 683

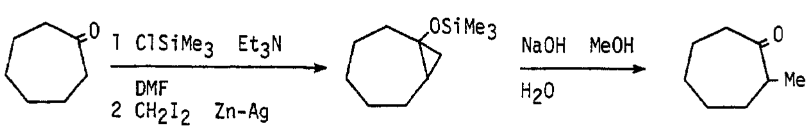


52%

Tetr Lett (1972) 929

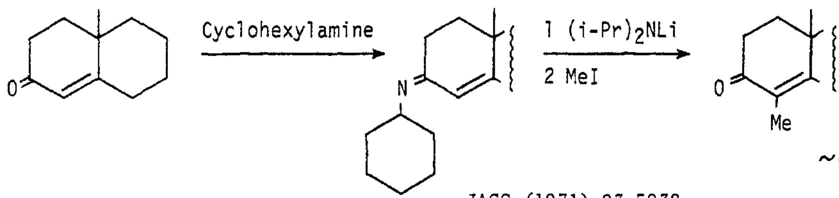


Tetr Lett (1969) 1117 505



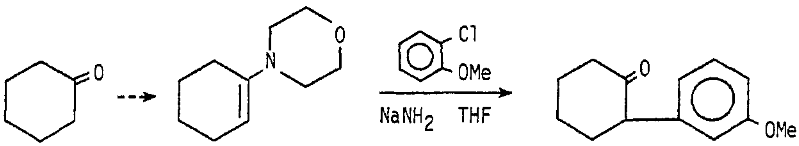
64%

Tetr Lett (1973) 2767



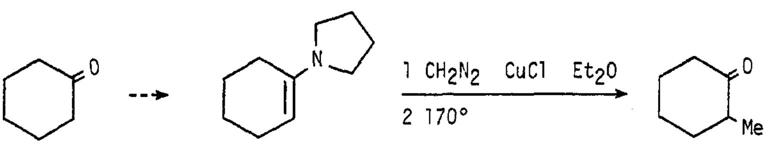
~80%

JACS (1971) 93 5938



40%

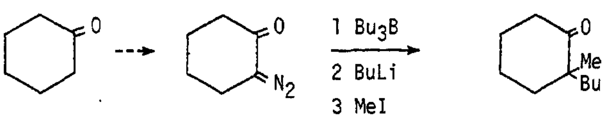
JCS C (1971) 1047



<70%

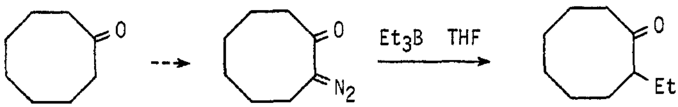
JOC (1973) 38 304

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

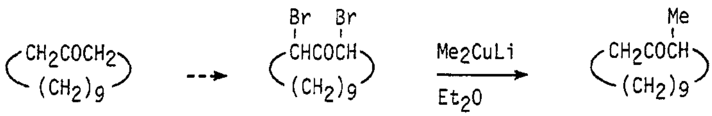


<61%

JOC (1971) 36 1790

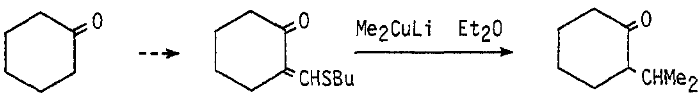


Can J Chem (1971) 49 2371

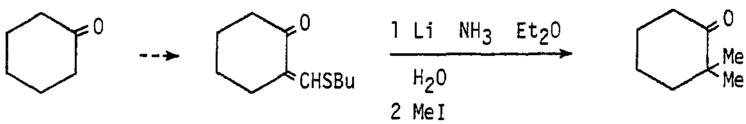


<97%

JACS (1973) 95 3076
Tetr Lett (1973) 4349



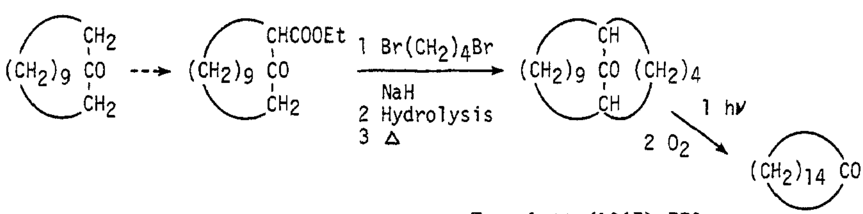
JACS (1971) 93 1027
JOC (1974) 39 275



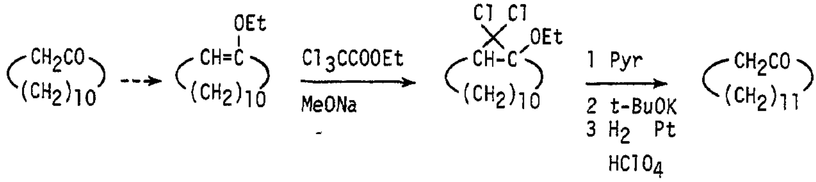
<83%

JACS (1971) 93 1027

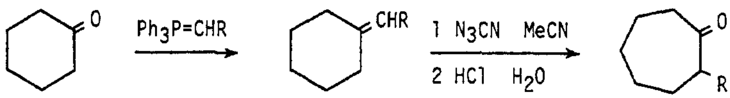
Ketones may also be alkylated and homologated via olefinic ketones (Section 374)



Tetr Lett (1967) 779

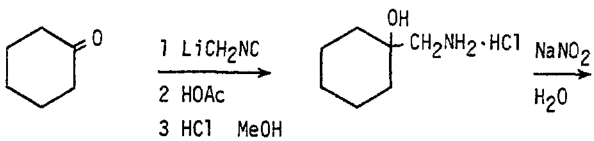


JOC (1967) 32 926



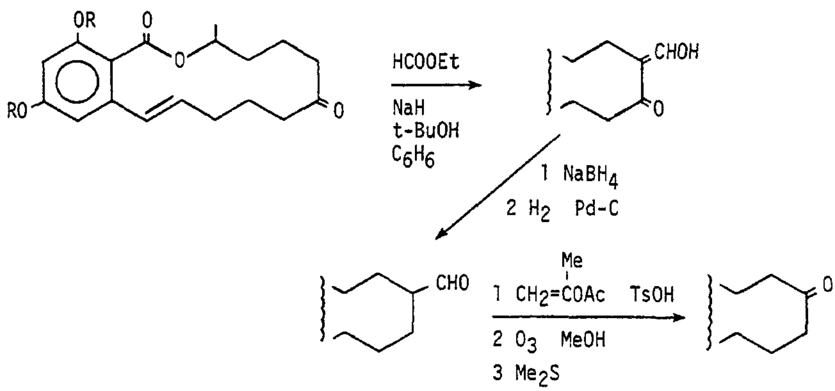
R = H or Me

JOC (1973) 38 2821 3862

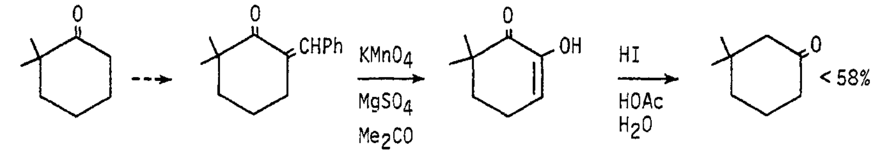


35%

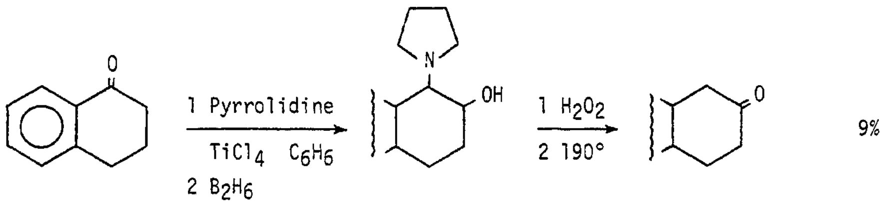
Angew (1971) 83 490
(Internat Ed 10 491)



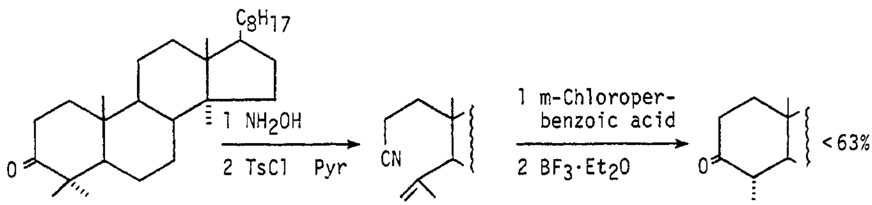
JOC (1972) 37 1639



JACS (1964) 86 3068



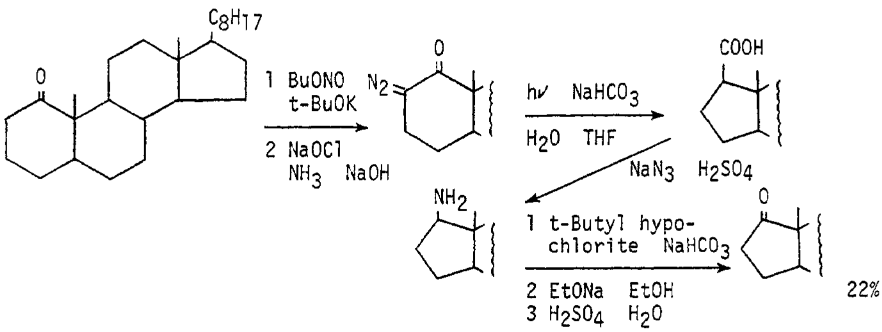
Bull Soc Chim Fr (1971) 1649



JCS Perkin I (1973) 2076

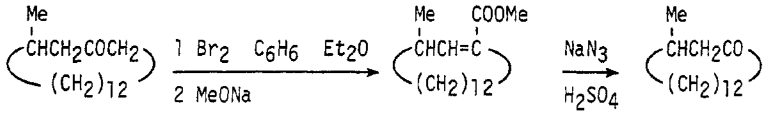
$$RCOCH_2R \xrightarrow{h\nu} RCOMe$$

Acc Chem Res (1971) 4 168

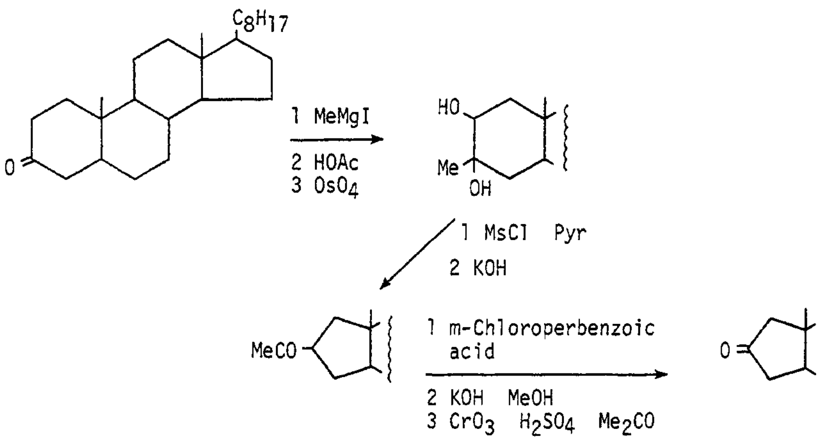


JOC (1965) 30 3775

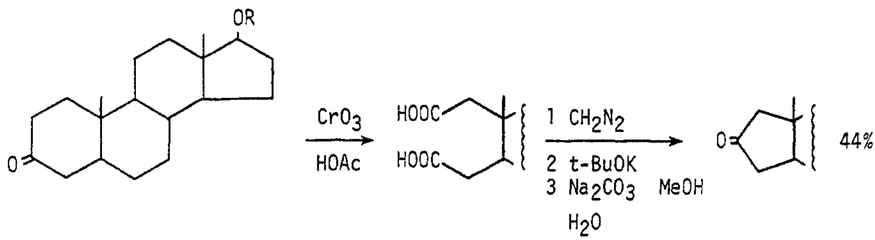
JACS (1971) 93 2786



JOC (1971) 36 3266



JOC (1971) 36 2400



JOC (1971) 36 81

Section 178 Ketones from Nitriles

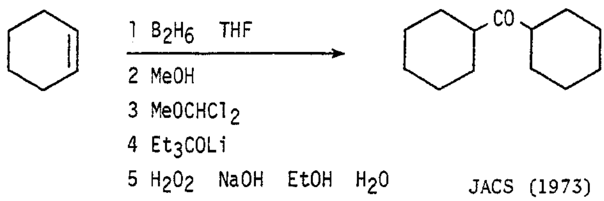
PhCN $\xrightarrow{(i\text{-}Bu)_2Be}$ PhCOBu-i

Chem Ind (1972) 689

$$\text{t-BuCN} \xrightarrow[\text{pet ether}]{\text{Na}} (\text{t-Bu})_2\text{C=NH} \xrightarrow[H_2O]{H_2SO_4} (\text{t-Bu})_2\text{CO}$$

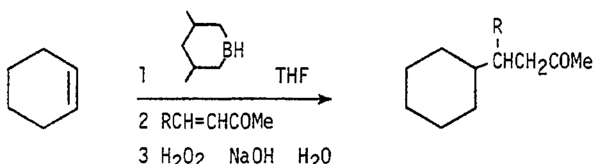
JACS (1971) 93 4527
Tetr Lett (1972) 2071

Section 179 Ketones from Olefins



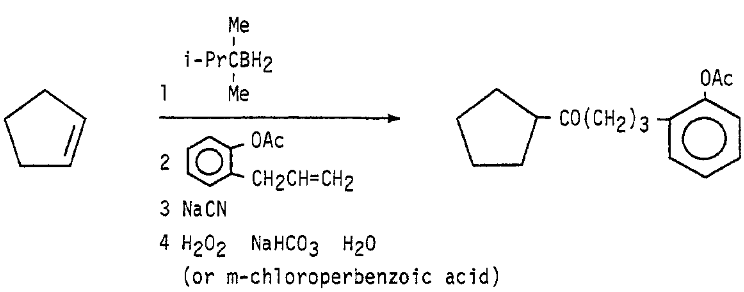
85%

JACS (1973) 95 6876



<81% (R=H)
<71% (R=Me)

JACS (1971) 93 3777

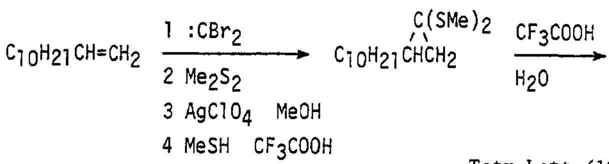


80%

Chem Comm (1971) 1048

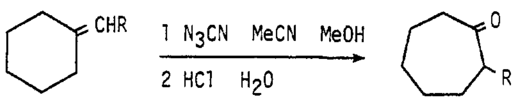
$$PhCH_2CH{=}CH_2 \xrightarrow{PhCSOMe\ \ h\nu} Ph(CH_2)_2COPh$$

Tetr Lett (1972) 4993



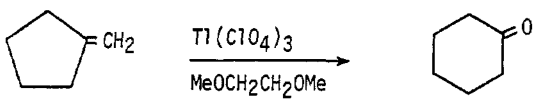
51%

Tetr Lett (1973) 3509

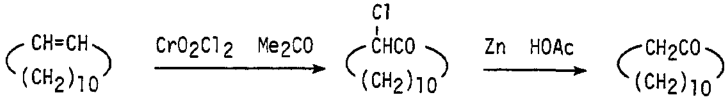


80% (R=H or Me)

JOC (1973) 38 2821

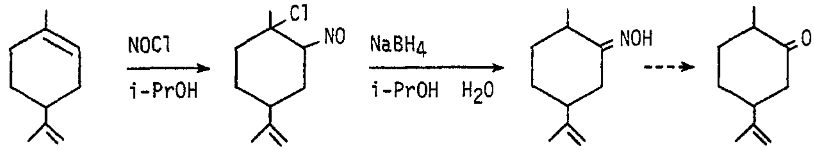


JOC (1973) 38 3455



75%

JOC (1973) 38 185



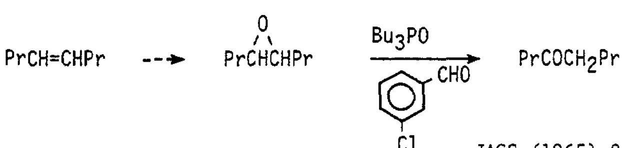
Aust J Chem (1971) <u>24</u> 1089

$C_5H_{11}CH{=}CH_2 \xrightarrow{O_2 \quad Rh(Ph_3P)_3Cl \quad C_6H_6} C_5H_{11}COMe$ 20-25%

Tetr Lett (1972) 5273

$BuCH{=}CH_2 \xrightarrow[2\ Li_2PdCl_4 \quad CuCl_2]{1\ Hg(OAc)_2 \quad MeOH} BuCOMe$ 100%

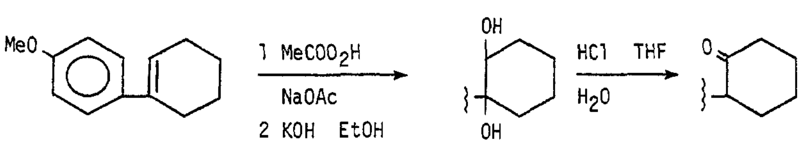
Chem Comm (1971) 818
Tetr Lett (1972) 3595
Synthesis (1971) 527



<85%

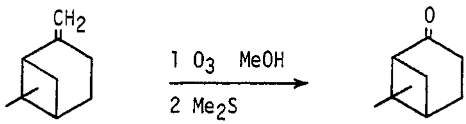
JACS (1965) <u>87</u> 1405

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



35%

Tetrahedron (1971) <u>27</u> 3013



70%

JCS Perkin I (1972) 50

Reduction of ozonides with EtCHO JACS (1971) <u>93</u> 3042

Section 180 Ketones from Miscellaneous Compounds

$$RCH{=}CHCOR \xrightarrow{R'_2CuLi} \underset{R'}{RCH}CH_2COR$$ (R'=alkyl or vinyl)

Org React (1972) <u>19</u> 1

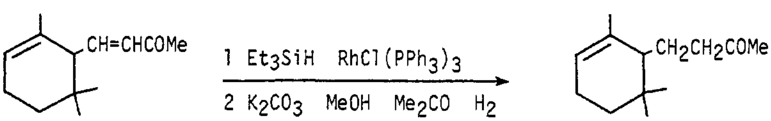
R'CuC≡CPr JACS (1972) <u>94</u> 7210

R'Li - t-BuOCu JACS (1972) <u>94</u> 658

$R'\underset{CN}{Cu}Li$ Chem Comm (1973) 88

$$PhCH{=}CHCOMe \xrightarrow{HCOOH\ \ RuCl_2(PPh_3)_3} PhCH_2CH_2COMe$$ 90%

Tetr Lett (1972) 1015



96%

Tetr Lett (1972) 5035

$Me_2C{=}CHCOMe \xrightarrow{H_2 \text{ nickel boride EtOH}} Me_2CHCH_2COMe$

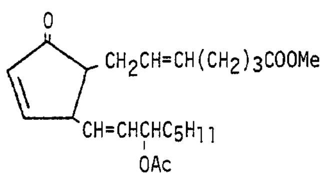
JOC (1971) <u>36</u> 2018

$RCH{=}CHCOR \xrightarrow{Bu_3SnH} RCH_2CH_2COR$

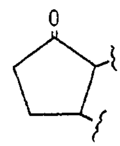
Organometallics in Chem Synth (1970) <u>1</u> 57
JCS <u>C</u> (1971) 1241

$PhCH{=}CHCOMe \xrightarrow[MeOH \;\; H_2O]{Fe(CO)_5 \;\; NaOH} PhCH_2CH_2COMe$ 90%

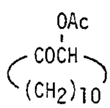
JOC (1972) <u>37</u> 1542



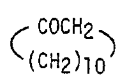
$\xrightarrow[2 \; CrO_3 \;\; H_2SO_4 \;\; Me_2CO]{1 \; NaBH_3CN}$



Tetr Lett (1973) 141



$\xrightarrow{Fe(CO)_5 \;\; Bu_2O}$

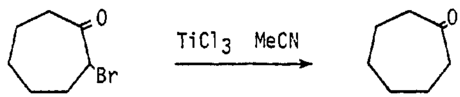


42%

Tetr Lett (1973) 447
$LiCuMe_2$ Tetr Lett (1973) 4349

$PhCOCH(Cl)Ph \xrightarrow{EtSNa \;\; EtOH} PhCOCH_2Ph$ 100%

Bull Chem Soc Jap (1971) <u>44</u> 828



86%

Synth Comm (1973) 3 237

$LiCuMe_2$ Tetr Lett (1973) 4349

$CONMe_2$
$(CH_2)_7$
CHCOOMe
CO
$(CH_2)_8$
$CONMe_2$

$\xrightarrow{\text{LiI collidine}}$

$CONMe_2$
$(CH_2)_7$
CH_2
CO
$(CH_2)_8$
$CONMe_2$

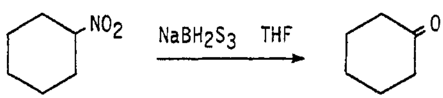
63%

JOC (1973) 38 1424

Org Synth (1965) 45 7

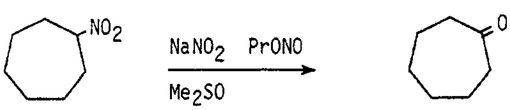
Decarboxylation with NaCl in Me_2SO Tetr Lett (1973) 957

NaCN in HMPA Tetr Lett (1973) 3565



(+ oxime) 75%

Can J Chem (1971) 49 2990



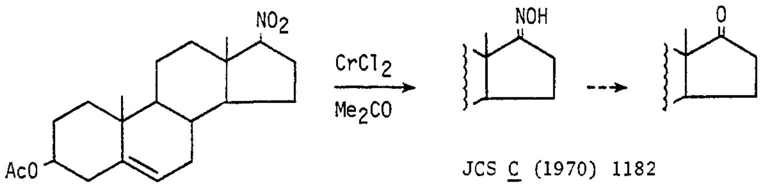
88%

JOC (1973) 38 1418

O_3 JOC (1974) 39 259

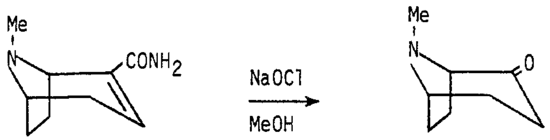
$$EtC{\equiv}C(CH_2)_2\underset{NO_2}{CH}(CH_2)_2COMe \xrightarrow[MeOCH_2CH_2OMe]{TiCl_3\ \ H_2O} EtC{\equiv}C(CH_2)_2CO(CH_2)_2COMe$$

JACS (1971) 93 5309



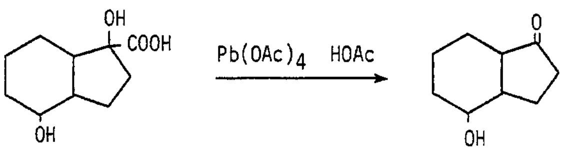
JCS C (1970) 1182

<73%



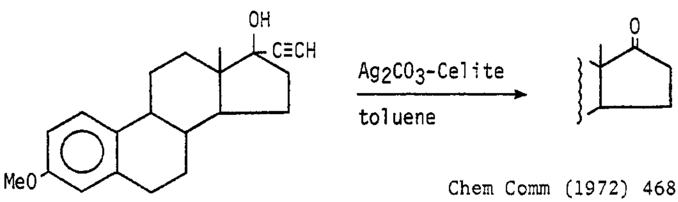
JACS (1960) 82 4642

40%



92%

JCS C (1971) 1292

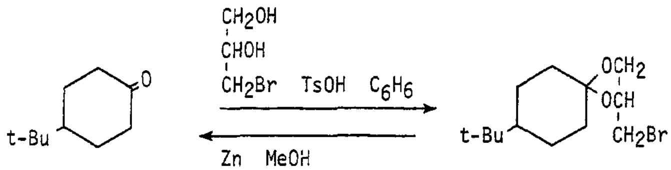


100%

Chem Comm (1972) 468

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

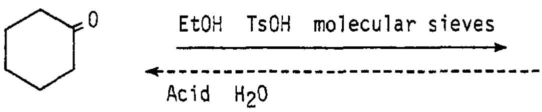
See also section 363 (Ether-Ether) for ketals and section 367 (Ether-Olefin) for enol ethers. Some of the methods in section 60A (Protection of Aldehydes) are also applicable to ketones



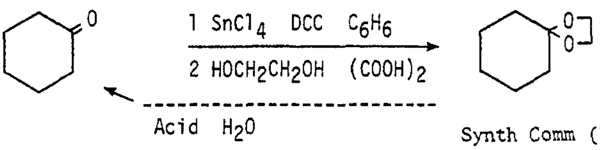
(Stable to MeLi, $NaBH_4$, NH_3, CrO_3 and peracids)

JOC (1973) 38 834

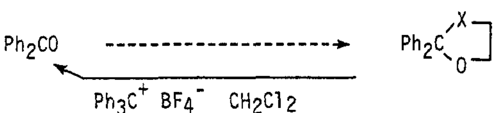
Trichloroethyl ketals JOC (1973) 38 554



Rec Trav Chim (1971) 90 1141

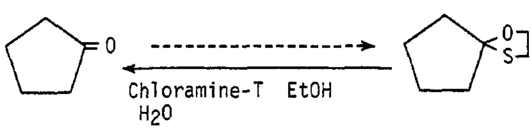


Synth Comm (1973) 3 125



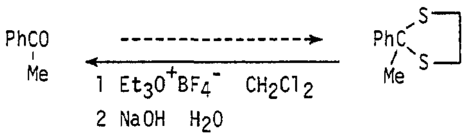
X=O or S

JCS Perkin I (1972) 542



Tetr Lett (1971) 3445 3449

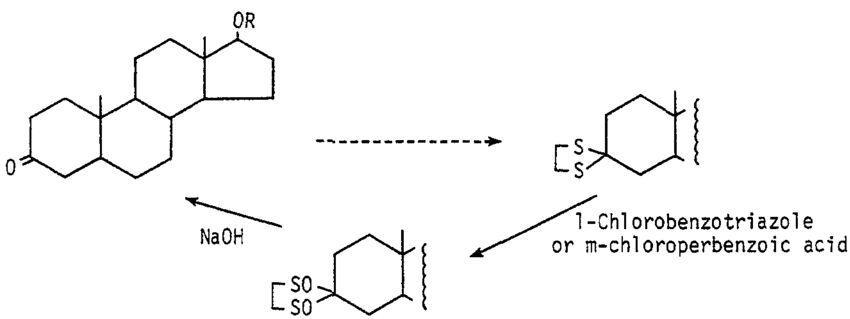
Nickel boride JCS Perkin I (1973) 654



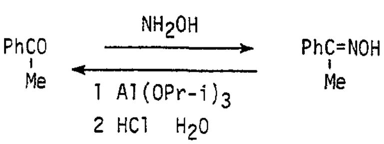
Tetr Lett (1972) 1085

The following reagents may also be used for the cleavage of thioketals:

$CuCl_2$-CuO	Bull Chem Soc Jap (1972) <u>45</u> 3724 JACS (1972) <u>94</u> 8641
$Ce(NH_4)_2(NO_3)_6$	Chem Comm (1972) 791
$MeOSO_2F$	Synthesis (1972) 561
MeI	Chem Comm (1972) 382
Ag_2O	Chem Comm (1972) 1323
$AgNO_3$	Tetrahedron (1968) <u>24</u> 4249
NCS, $AgNO_3$	JOC (1968) <u>33</u> 298
NBS	JOC (1971) <u>36</u> 3553
Chloramine-T	Tetr Lett (1971) 3445 3449
I_2, Me_2SO	Tetr Lett (1973) 3735
$Tl(OCOCF_3)_3$	Can J Chem (1972) <u>50</u> 3740
$Et_3O^+ BF_4^-$	Tetr Lett (1974) 11

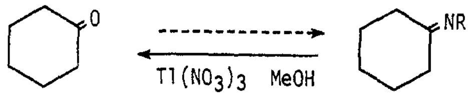


Chem Comm (1971) 750



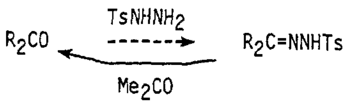
(Not applicable to hindered ketones)

Chem Ind (1972) 680

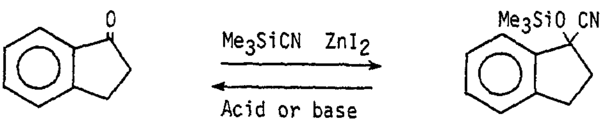


R=OH, $NHCONH_2$ or NHPh

JACS (1971) 93 4918



Chem Ind (1964) 153 footnote 3



Chem Comm (1973) 55
Tetr Lett (1973) 4929

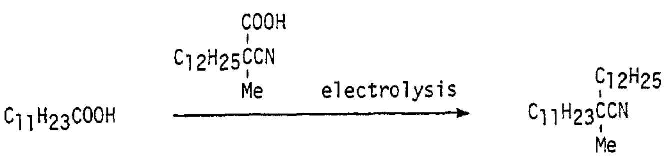
Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 13 PREPARATION OF NITRILES

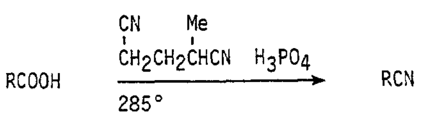
Section 181 Nitriles from Acetylenes

No additional examples

Section 182 Nitriles from Carboxylic Acids and Acid Halides



J Pharm Soc Jap (1944) 64 25



JOC (1971) 36 3050

$$RCOOH \xrightarrow[2\ DMF]{1\ ClSO_2NCO\quad CH_2Cl_2} RCN$$

Org Synth (1970) 50 18

$$C_5H_{11}COCl \xrightarrow[160°]{(PNCl_2)_3} C_5H_{11}CN$$

Tetr Lett (1973) 3825

Section 183 Nitriles from Alcohols

No additional examples

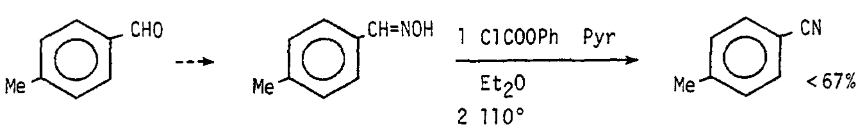
Section 184 Nitriles from Aldehydes

$$PhCHO \xrightarrow{\overset{NC}{|}{TsCHK}} \overset{NHCHO}{|}{PhCH{=}CTs} \xrightarrow[MeOH]{MeONa} PhCH_2CN \qquad <81\%$$

Angew (1973) <u>85</u> 402
(Internat Ed <u>12</u> 407)

$$RCHO \xrightarrow[NH_3 \quad i\text{-}PrOH]{MnO_2 \quad NaCN} RCN$$

Chem Comm (1971) 733



Can J Chem (1971) <u>49</u> 1321

The following reagents may also be used for dehydration of oximes to nitriles:

$TiCl_4$-Pyr	Tetr Lett (1971) 559
HCOONa, HCOOH	JCS (1965) 1564
Ph_3P, CCl_4, Et_3N	Ber (1971) 104 2025
$CHCl_3$, NaOH, $PhCH_2\overset{+}{N}Et_3\ Cl^-$	Tetr Lett (1973) 2121
1,1'-dicarbonyldiimidazole	Chem Comm (1973) 628
DCC (190°)	Synth Comm (1973) 3 101
CCl_3CN	JOC (1973) 38 2241
HgO	Tetr Lett (1971) 361

$$PhCHO \dashrightarrow PhCH{=}NN{=}CHPh \xrightarrow{h\nu \quad \text{cyclohexane}} PhCN \qquad 85\%$$

JACS (1963) 85 2679

Related methods: Nitriles from Ketones (Section 192)

Also via: Olefinic nitriles (Section 376)

Section 185 Nitriles from Alkyls, Methylenes and Aryls

No additional examples

Section 186 Nitriles from Amides

$$PhCH{=}CHCONH_2 \xrightarrow[NaOH \quad H_2O]{CHCl_3 \quad PhCH_2\overset{+}{N}Et_3\ Cl^-} PhCH{=}CHCN \qquad 52\%$$

Tetr Lett (1973) 2121

The following reagents may also be used for the conversion of amides into nitriles:

CCl_4, Ph_3P	Ber (1972) 105 244
$(PNCl_2)_3$	Can J Chem (1972) 50 3857
HMPA (220-240°)	Can J Chem (1971) 49 2897
$(HNSiMe_2)_3$	JOC (1970) 35 3253
$TiCl_4$, amine	Tetr Lett (1971) 1501

Section 187 Nitriles from Amines

$$\underset{\displaystyle\text{Et}}{\text{BuCHCH}_2\text{NH}_2} \xrightarrow[\text{H}_2\text{O}]{\text{Argentic picolinate}} \underset{\displaystyle\text{Et}}{\text{BuCHCN}} \qquad 35\%$$

Tetrahedron (1973) 29 751

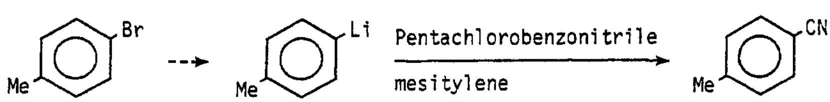
Section 188 Nitriles from Esters

No additional examples

Section 189 Nitriles from Ethers and Epoxides

No additional examples

Section 190 Nitriles from Halides



Tetr Lett (1972) 4169

Section 191 Nitriles from Hydrides

$$PhH \xrightarrow{Cl(CH_2)_3CN \quad AlCl_3} Ph(CH_2)_3CN$$

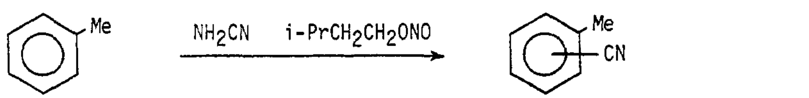
Tetr Lett (1972) 1929

$$ArH \dashrightarrow ArTlCl_2 \xrightarrow{CuCN \quad MeCN} ArCN$$

Tetrahedron (1972) 28 3025

$$ArH \xrightarrow{KCN \quad h\nu \quad t\text{-}BuOH \quad H_2O} ArCN$$

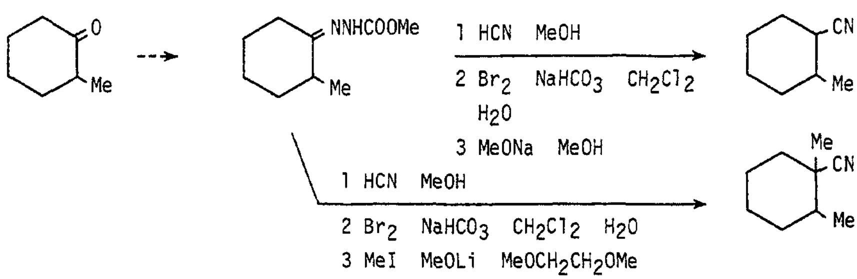
Tetrahedron (1972) 28 5081



12%

Acta Chem Scand (1972) 26 3870

Section 192 Nitriles from Ketones



JACS (1971) 93 4318

$Pr_2CO \xrightarrow[\text{2 KCN HOAc MeOH}]{\text{1 } NH_2NHTs} Pr_2C(CN)NHNHTs \xrightarrow[180°]{\text{Decalin}} Pr_2CHCN$

Chem Ind (1972) 213

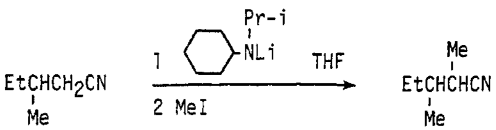
$Pr_2CO \xrightarrow[\text{t-BuOH } MeOCH_2CH_2OMe]{TsCH_2NC \text{ t-BuOK}} Pr_2CHCN$ 75%

Tetr Lett (1973) 1357
Angew (1973) 85 402
(Internat Ed 12 407)

Related methods: Nitriles from Aldehydes (Section 184)

Also via: Olefinic nitriles (Section 376)

Section 193 Nitriles from Nitriles



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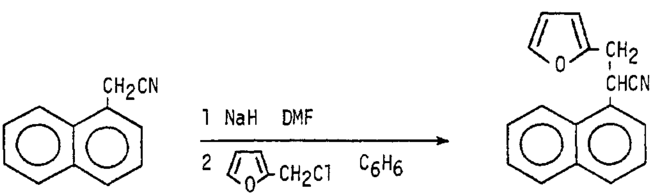
Ber (1973) 106 1376



86%

J Med Chem (1965) 8 598
(1973) 16 490
JOC (1958) 23 1346

$PhCH_2CN \xrightarrow[PhCOOMe \quad 210\text{-}220°]{C_7H_{15}ONa \quad C_7H_{15}OH} PhCH(C_7H_{15})CN$ 73%

JOC (1971) 36 2948
(1972) 37 526

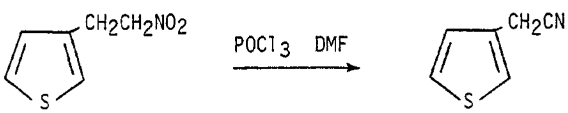
Section 194 Nitriles from Olefins

No additional examples

Section 195 Nitriles from Miscellaneous Compounds

$PhCH{=}CHCN \xrightarrow{H_2 \quad \text{nickel boride}} PhCH_2CH_2CN$

JOC (1972) 37 3552

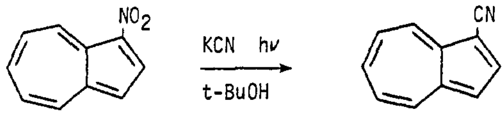


85%

Acta Chem Scand (1970) 24 3424

$PhCH_2NO_2 \xrightarrow{NaBH_2S_3 \quad THF} PhCN$ 80%

Can J Chem (1971) 49 2990



28%

Tetr Lett (1970) 4701

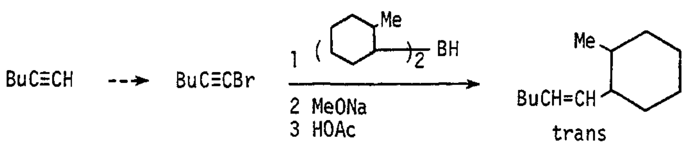
Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 14 PREPARATION OF OLEFINS

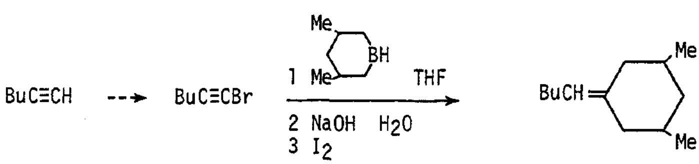
Section 196 Olefins from Acetylenes

Reviews: Stereoselective and Stereospecific Olefin Synthesis
Quart Rev (1971) 25 135

Catalytic Semihydrogenation of the Triple Bond
Synthesis (1973) 457



JACS (1971) 93 6309
(1972) 94 6560



Synthesis (1972) 557

$$\mathrm{EtC{\equiv}CEt} \xrightarrow[\text{2 HOAc THF}]{\text{1 BH}_2\text{Cl Et}_2\text{O}} \mathrm{EtCH{=}CHEt}$$ 81%

cis

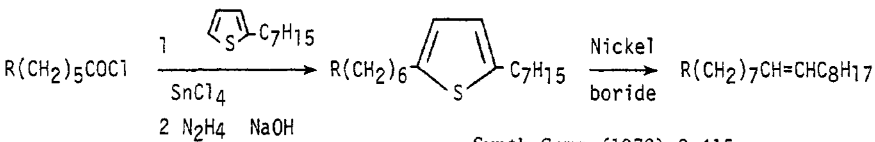
JOC (1973) 38 1617

Catecholborane JACS (1972) 94 4370

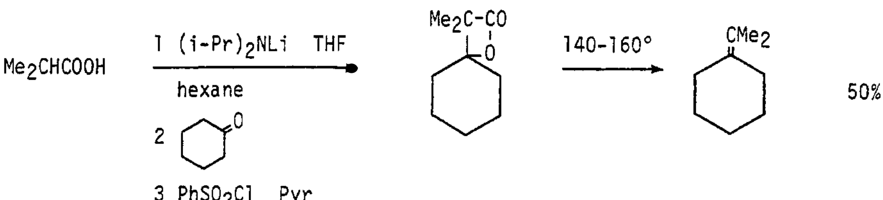
$$RC{\equiv}CR \xrightarrow[\text{or Li amine}]{\text{Na } NH_3} RCH{=}CHR$$

Synthesis (1972) 391

Section 197 Olefins from Carboxylic Acids and Acid Halides



Synth Comm (1972) 2 415



JACS (1972) 94 2000

$$EtCH_2CH_2COOH \xrightarrow[\text{KOH } H_2O]{\text{Electrolysis (carbon electrodes)}} EtCH{=}CH_2 \quad (+\text{ isomers})$$

JACS (1964) 86 4686

$$RCH_2CH_2COOH \xrightarrow{Pb(OAc)_4} RCH{=}CH_2$$

Org React (1972) 19 279

$$C_6H_{13}(CH_2)_3COCl \xrightarrow{PhH \quad AlCl_3} C_6H_{13}(CH_2)_3COPh \xrightarrow{h\nu} C_6H_{13}CH{=}CH_2 \qquad <75\%$$

JOC (1971) 36 1838

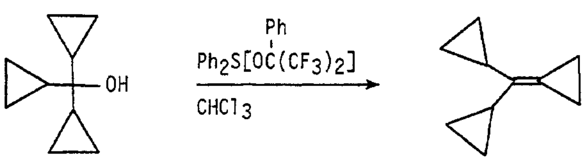
$$\begin{array}{l} RCHCOOH \\ | \\ RCHCOOH \end{array} \xrightarrow{Pb(OAc)_4} \begin{array}{l} RCH \\ \| \\ RCH \end{array}$$

Org React (1972) 19 279

Section 198 Olefins from Alcohols

$$\begin{array}{c} \quad OH \\ \quad | \\ R_2CHCR_2 \end{array} \xrightarrow{I_2 \quad xylene} R_2C{=}CR_2$$

Monatsh (1968) 99 642



32%

(2ry and 3ry only)

JACS (1971) 93 4327
(1972) 94 5003

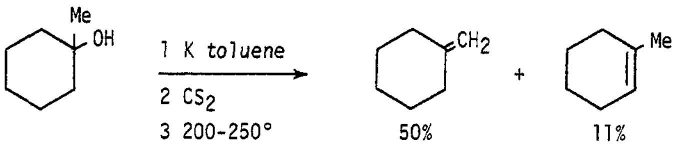
$$C_6H_{13}CH_2CH_2OH \xrightarrow{HMPA \quad 220\text{-}240°} C_6H_{13}CH{=}CH_2 \qquad 59\%$$

Tetr Lett (1971) 567
(1972) 165
JOC (1971) 36 3826

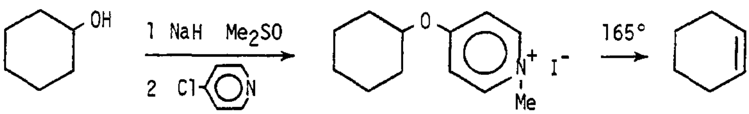
$BuCH(OH)CH_2Pr \xrightarrow{(PhO)_3P\cdot MeI \quad HMPA} BuCH{=}CHPr$ 88%

(2ry only)

JOC (1972) 37 4190

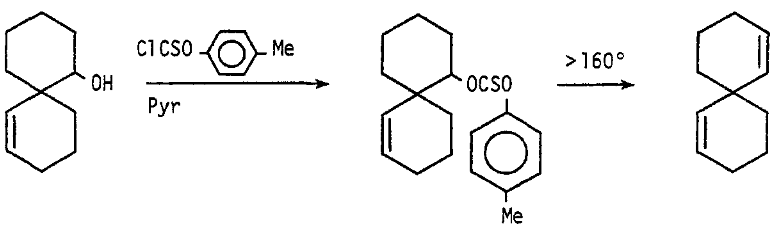


JCS C (1971) 582



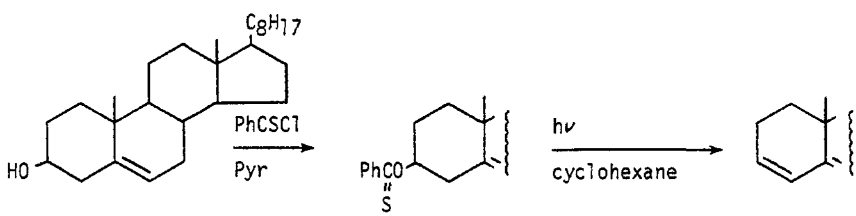
55%

Can J Chem (1972) 50 1181

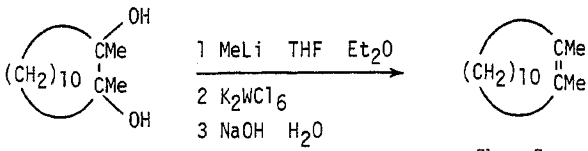


<60%

Chem Comm (1972) 1215

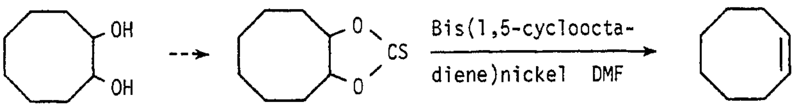


Chem Comm (1971) 1014



58%

Chem Comm (1972) 370



82%

Tetr Lett (1973) 2667

RCHOH–RCHOH $\xrightarrow[\text{diimidazole toluene}]{\text{N,N'-Thiocarbonyl}}$ (RCHO)(RCHO)CS $\xrightarrow{(RO)_3P}$ RCH=RCH

Ber (1973) 106 1076
JCS C (1971) 2960
Can J Chem (1970) 48 383

Section 199 Olefins from Aldehydes

Reviews: Stereoselective and Stereospecific Olefin Synthesis
Quart Rev (1971) 25 135

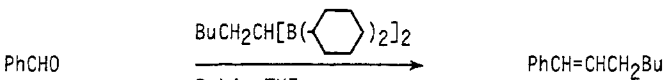
The Wittig Reaction   Org React (1965) 14 270

PhCHO $\xrightarrow[\text{2 MeONa}]{\text{1 } TsNHNH_2}$ $PhCHN_2$ $\xrightarrow[\text{MeCN pentane}]{Ce(NH_4)_2(NO_3)_6}$ PhCH=CHPh   <74%

JACS (1971) 93 2086

47%

JACS (1972) <u>94</u> 6538



45-50%

Tetr Lett (1966) 4315

$$\mathrm{PhCHO} \xrightarrow[\text{THF hexane; 2 } PhSO_2Cl \text{ Pyr}]{\text{1 } Me_2CHCOOH \ \ (i\text{-}Pr)_2NLi} \underset{\mathrm{O\,-\,CO}}{\mathrm{PhCH\text{-}CMe_2}} \xrightarrow{140\text{-}160°} \mathrm{PhCH{=}CMe_2} \qquad 29\%$$

JACS (1972) <u>94</u> 2000

$$\mathrm{PhCHO} \xrightarrow[C_6H_6]{\mathrm{Ph_2C(SH)COOH} \ \ \mathrm{TsOH}} \underset{\mathrm{O\,-\,CO}}{\mathrm{PhCHSCPh_2}} \xrightarrow[(Et_2N)_3P]{150\text{-}160°} \mathrm{PhCH{=}CPh_2} \qquad 89\%$$

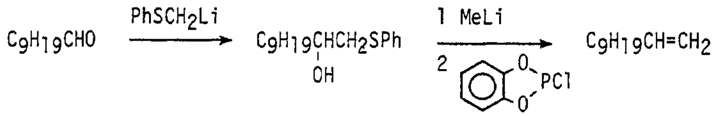
JCS Perkin I (1972) 305

$$\mathrm{PhCHO} \xrightarrow[\text{2 Al-Hg } H_2O \text{ THF}]{\text{1 } \mathrm{PhSO_2C(Ph)Li_2}} \mathrm{PhCH{=}CHPh} \qquad <90\%$$

Chem Comm (1973) 351

$$\mathrm{C_9H_{19}CHO} \xrightarrow[\text{2 Al-Hg HOAc}]{\text{1 } \mathrm{PhS(=NMe)O{-}CH(Me)Li} \ \ \mathrm{THF}} \mathrm{C_9H_{19}CH{=}CHMe} \qquad 60\%$$

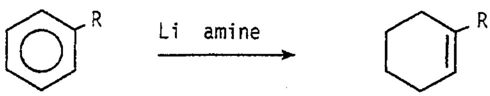
JACS (1973) <u>95</u> 6462



Tetr Lett (1972) 737

Related methods: Olefins from Ketones (Section 207)

Section 200 Olefins from Aryls

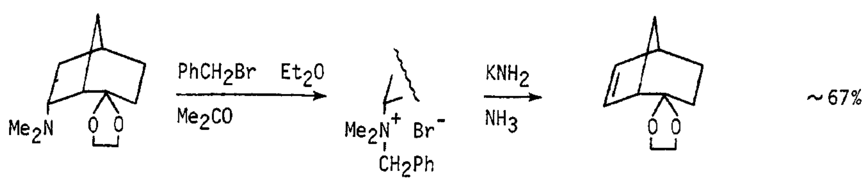


Synthesis (1972) 391

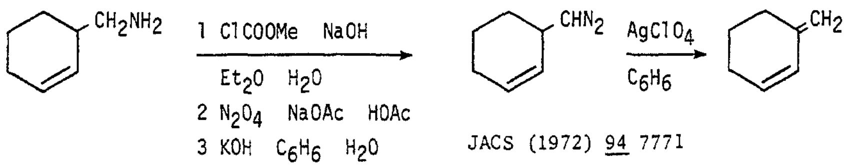
Section 201 Olefins from Amides

No additional examples

Section 202 Olefins from Amines



JOC (1972) 37 2896



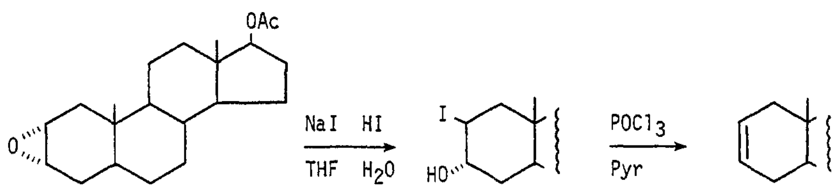
JACS (1972) 94 7771

Section 203 Olefins from Esters

$$C_9H_{19}COOMe \xrightarrow[\substack{2\ (PhCO)_2O \\ 3\ Li\quad NH_3}]{1\ PhSCH_2Li\quad THF} C_9H_{19}\underset{\displaystyle Me}{C}{=}CH_2 \qquad 46\%$$

JACS (1972) 94 4758

Section 204 Olefins from Epoxides



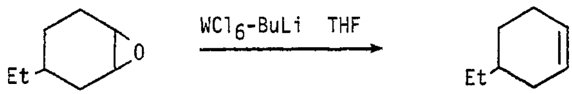
JCS Perkin I (1973) 91

$$\underset{\text{trans}}{\overset{\displaystyle O}{PrCH\!-\!CHPr}} \xrightarrow{Zn\text{-}Cu\quad EtOH} \underset{\text{trans}}{PrCH{=}CHPr}$$

JOC (1971) 36 1187

$C_5H_{11}\overset{O}{\widehat{CHCHMe}}$ (cis) $\xrightarrow[\text{2 MeI}]{\text{1 } Ph_2PLi \text{ THF}}$ $C_5H_{11}CH{=}CHMe$ (trans) 75%

JACS (1973) 95 822
Tetr Lett (1973) 1983



75%

JACS (1972) 94 6538

$Et\overset{O}{\widehat{CHCH_2}}$ $\xrightarrow[\text{THF}]{\text{1 Sodium (cyclopentadienyl)dicarbonylferrate}}$ $EtCH{=}CH_2$ ~91%

2 HBF_4
3 NaI Me_2CO

JACS (1972) 94 7170

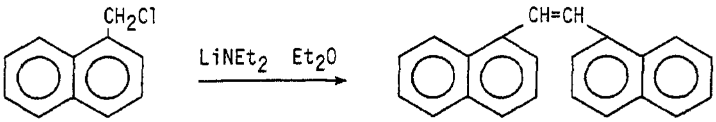
$C_6H_{13}\overset{O}{\widehat{CHCH_2}}$ $\xrightarrow[CH_2Cl_2]{Ph_3PSe \quad CF_3COOH}$ $C_6H_{13}CH{=}CH_2$ 71%

Chem Comm (1973) 253

Section 205 Olefins from Halides and Sulfonates

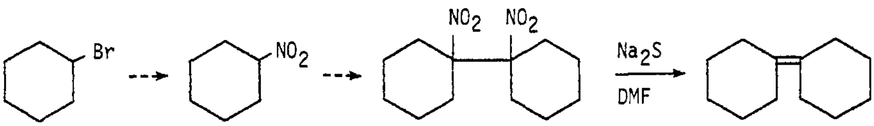
$PhCH_2Cl \xrightarrow{Ph_3P} PhCH_2\overset{+}{P}Ph_3\ \overset{-}{Cl} \xrightarrow[\text{toluene}]{\text{BuLi}} PhCH{=}PPh_3 \xrightarrow{S} PhCH{=}CHPh$

Ber (1970) 103 2995



65%

Organometallics in Chem Synth (1972) 1 375



JACS (1971) 93 4316

$PhCH_2Br \xrightarrow[]{EtCHO \quad Ph_3P \quad CH_2\text{-}CH_2 \text{ (epoxide, O)}} PhCH{=}CHEt$

Angew (1968) 80 535
(Internat Ed 7 536)

$BuBr \xrightarrow[\text{2 } NaBH_4 \quad \text{3 } MsCl \quad Na_2CO_3]{\text{1 } BuCOC(Me)HCOOEt \quad NaH} BuCHC(Me)Bu \text{ (O-CO)} \xrightarrow[\text{(reflux)}]{\text{Collidine}} BuCH{=}C(Me)Bu$

Tetr Lett (1968) 4569

$EtBr \xrightarrow[\text{2 } PhC\text{-}CHPh \text{ (N)}]{\text{1 } Mg} EtC(Ph)\text{-}CHPh \text{ (NH)} \xrightarrow{BuONO} EtC(Ph){=}CHPh$

Tetr Lett (1969) 4001

$C_5H_{11}Br \dashrightarrow C_5H_{11}MgBr \xrightarrow[\text{2 } NaOAc \quad HOAc]{\text{1 } Me_3SiCH_2COMe \quad Et_2O} C_5H_{11}C(Me){=}CH_2$ ~76%

Tetr Lett (1972) 1785

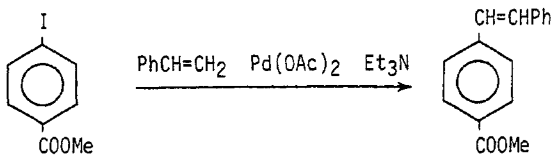
$C_6H_{13}Br \dashrightarrow C_6H_{13}MgBr \xrightarrow[\text{THF}]{\text{BrCH=CHMe} \quad \text{FeCl}_3} C_6H_{13}CH{=}CHMe$ ~67%

JACS (1971) 93 1487
Synthesis (1971) 303

$PhCH_2I \xrightarrow[\text{air} \quad \text{THF}]{\text{ICH}_2\text{CH=CH}_2 \quad \text{Et}_3\text{B}} PhCH_2CH_2CH{=}CH_2$ 72%

(Benzylic and allylic halides only)

JACS (1971) 93 1508



75%

JOC (1972) 37 2320

$C_8H_{17}Cl \dashrightarrow C_8H_{17}MgCl \xrightarrow[\text{Et}_2\text{O} \quad \text{C}_6\text{H}_6 \quad \text{THF}]{\text{CH}_2\text{=CHCl} \quad [\text{NiCl}_2(\text{dpe})]} C_8H_{17}CH{=}CH_2$ 95%

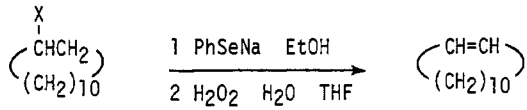
JACS (1972) 94 4374

$C_7H_{15}Br \xrightarrow{\text{MeCH=CHMgBr} \quad \text{THF}} C_7H_{15}CH{=}CHMe$ 71%

Bull Soc Chim Fr (1963) 1888

$RI \xrightarrow{(\text{R'CH=CH})_2\text{CuLi}} RCH{=}CHR'$

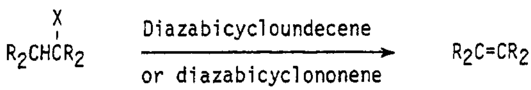
Helv (1971) 54 1939



<94%

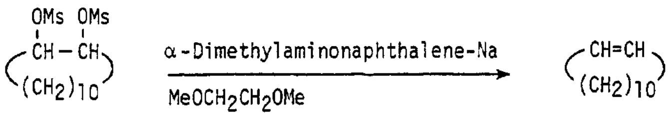
(X=halide or OTs)

Tetr Lett (1973) 1979



(X=halide or OTs)

Synthesis (1972) 591

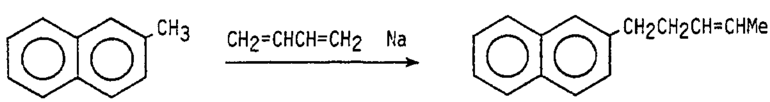


67%

Tetr Lett (1973) 2097
(1972) 3447

Section 206 Olefins from Hydrides

This section lists examples of the replacement of hydrogen by olefinic groups



19%

JOC (1965) 30 82

Section 207 Olefins from Ketones

Reviews: Stereoselective and Stereospecific Olefin Synthesis
Quart Rev (1971) 25 135

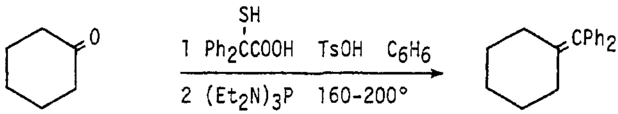
The Wittig Reaction — Org React (1965) 14 270

$$\underset{\mathrm{Me}}{\mathrm{EtCO}} \xrightarrow{\mathrm{WCl_6\text{-}BuLi \quad THF}} \mathrm{EtC(Me){=}C(Me)Et} \qquad 10\%$$

JACS (1972) 94 6538

$$\mathrm{R_2CO} \xrightarrow[\mathrm{H_2S}]{\mathrm{N_2H_4}} \mathrm{R_2C\text{-}NH\text{-}NH\text{-}CR_2}\ (\text{bridged by S}) \xrightarrow[\mathrm{Ph_3P}]{\mathrm{Pb(OAc)_4}} \mathrm{R_2C{=}CR_2}$$

JCS Perkin I (1972) 305

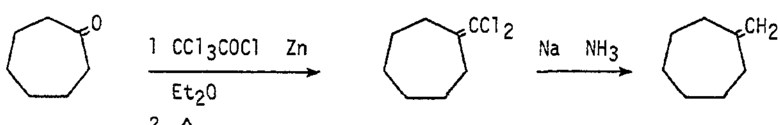


68%

JCS Perkin I (1972) 305

$$\mathrm{Ph_2CO} \xrightarrow[\text{2 } \mathrm{PhSO_2Cl}]{\text{1 } \mathrm{Me_2CHCOOH \quad LiN(Pr\text{-}i)_2}} \underset{\mathrm{O-CO}}{\mathrm{Ph_2C\text{-}CMe_2}} \xrightarrow{140\text{-}160°} \mathrm{Ph_2C{=}CMe_2} \qquad 47\%$$

JACS (1972) 94 2000
JOC (1971) 36 1149

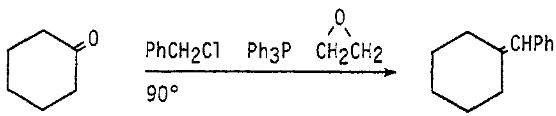


Synthesis (1972) 565

PhCO(Me) —Resin-Ph_3P=CHPr→ cis PhC(Me)=CHPr 100%

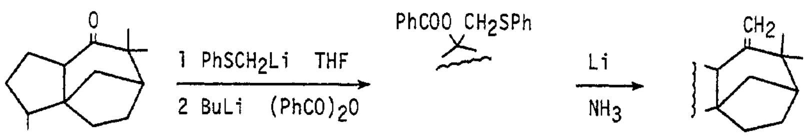
PhCO(Me) —1 Resin-Ph_3P=CHPr, 2 BuLi, 3 $LiClO_4$, 4 HCl Et_2O, 5 t-BuOK→ trans PhC(Me)=CHPr 59%

Annalen (1973) 227
Chem Comm (1972) 134



69%

Angew (1972) 84 1173
(Internat Ed 11 1041)



31%

JACS (1972) 94 4758

Ph_2CO —$PhSCH_2Li$→ $Ph_2C(OH)CH_2SPh$ —1 MeLi, 2 o-Phenylene phosphochloridite→ $Ph_2C=CH_2$

Tetr Lett (1972) 737

PhCO(Me) —t-$BuSOCH_2Et$, MeLi→ PhC(Me)(OH)-CHEt(SOBu-t) —NCS CH_2Cl_2→ PhC(Me)=CHEt 73%

JACS (1973) 95 3420
Tetr Lett (1972) 649

$$C_{15}H_{31}\underset{\substack{|\\ Me}}{C}O \xrightarrow[\text{2 Al-Hg HOAc}]{\text{1 Ph}\overset{\substack{NMe\\ \|}}{S}OCH_2Li\text{ THF}} C_{15}H_{31}\underset{\substack{|\\ Me}}{C}{=}CH_2$$ 90%

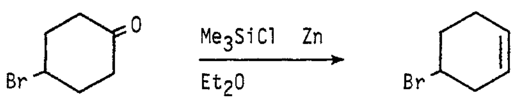
JACS (1973) 95 6462

$$Ph_2CO \xrightarrow{PhSO_2\overset{\substack{Ph\\ |}}{C}Li_2} Ph_2C{=}\overset{\substack{Ph\\ |}}{C}SO_2Ph \xrightarrow[\text{THF}]{\text{Al-Hg } H_2O} Ph_2C{=}CHPh$$ <85%

Chem Comm (1973) 351

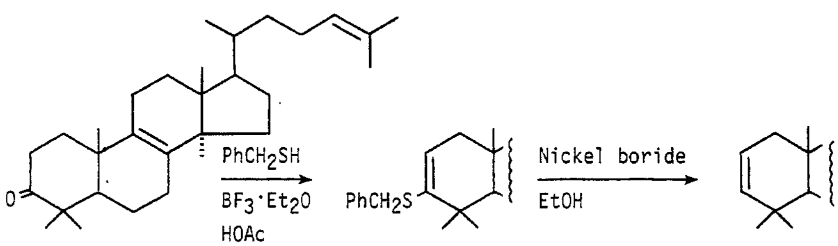
$$\left(\begin{matrix}COCH_2\\ (CH_2)_{10}\end{matrix}\right) \dashrightarrow \left(\begin{matrix}\overset{\substack{OAc\\ |}}{C}{=}CH\\ (CH_2)_{10}\end{matrix}\right) \xrightarrow[Bu_2O]{Fe(CO)_5} \left(\begin{matrix}CH{=}CH\\ (CH_2)_{10}\end{matrix}\right)$$ <40%

Tetr Lett (1973) 447



48%

Chem Comm (1973) 935



67%

JCS Perkin I (1973) 654

$BuCH_2CH_2CH_2COPh \xrightarrow{h\nu} BuCH{=}CH_2$ 74%

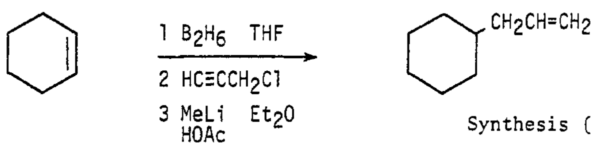
JOC (1971) <u>36</u> 1838

Related methods: Olefins from Aldehydes (Section 199)

Section 208 Olefins from Nitriles

No additional examples

Section 209 Olefins from Olefins

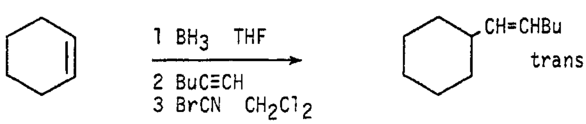


69%

Synthesis (1973) 672

$EtCH{=}CHEt$ (trans) $\xrightarrow[\text{2 BuC≡CBr; 3 MeONa MeOH; 4 i-PrCOOH}]{\text{1 i-PrC(Me)}_2\text{BH}_2}$ $EtCH(CH{=}CHBu)CH_2Et$ (trans) 78%

Synthesis (1972) 555
JACS (1971) <u>93</u> 6309
(1972) <u>94</u> 4013



69%

JACS (1972) <u>94</u> 6560

$$EtCH{=}CH_2 \xrightarrow[\text{2 MeC=CH (CH}_2\text{ bridged)} \quad \text{MeOH}]{1\ BH_3} Et(CH_2)_3\underset{\text{Me}}{C}{=}CH_2 \qquad 91\%$$

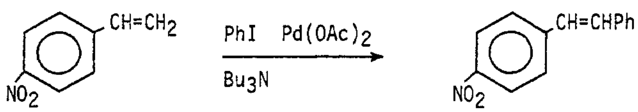
Tetr Lett (1972) 4627

$$BuCH{=}CH_2 \xrightarrow[Li_2PdCl_4 \quad MeOH]{MeCo(dmg)_2\cdot Pyr} BuCH{=}CHMe \qquad 32\%$$

Chem Comm (1971) 849

$$EtCH{=}\overset{CH_3}{C}Pr \xrightarrow[\substack{2\ MeSO_2\underset{Na}{C}HCOOMe \\ 3\ NaOH \\ 4\ 180°}]{1\ PdCl_2 \quad Na_2CO_3 \quad CH_2Cl_2} EtCH{=}\overset{CH_2CH_2SO_2Me}{C}Pr \xrightarrow[EtNH_2]{Li} EtCH{=}\overset{CH_2Me}{C}Pr$$

JACS (1973) 95 292

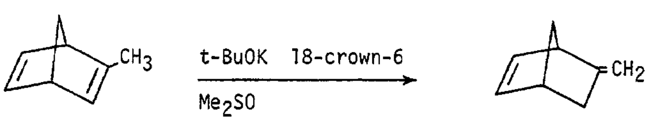


85%

JOC (1972) 37 2320

$$EtCH_2CH{=}CH_2 \underset{}{\overset{Ni\text{-}HCN \quad C_6H_6}{\rightleftarrows}} EtCH{=}CHMe$$

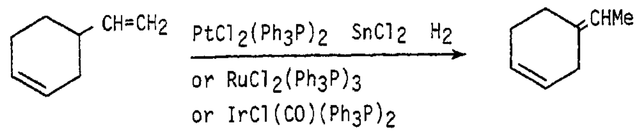
Chem Ind (1971) 1465



Tetr Lett (1972) 1797

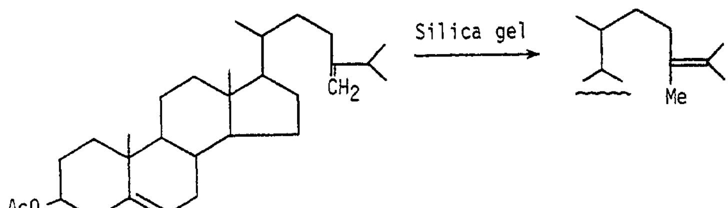
$$PhCH_2CH{=}CH_2 \xrightarrow[t\text{-}BuOOH]{RuCl_2(Ph_3P)_3} PhCH{=}CHMe$$

Chem Comm (1971) 562

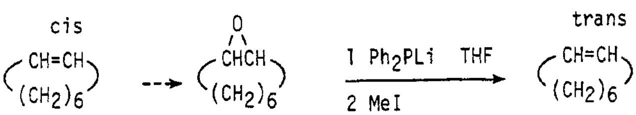


JOC (1971) 36 2497

$PtClH(PMe_2Ph)_2$-$MeSO_3F$ Chem Comm (1973) 766

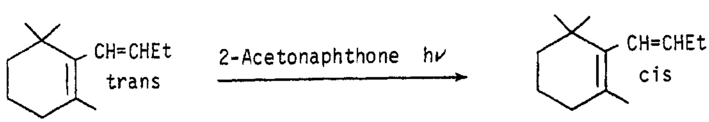


Tetr Lett (1971) 2513



<75%

JACS (1971) 93 4070
(1973) 95 822
Tetr Lett (1973) 1983



JOC (1973) 38 1247

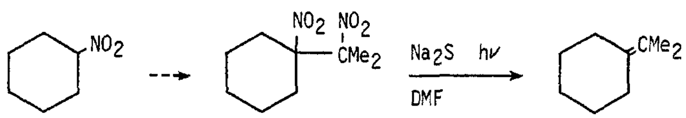
$$\underset{\text{cis}}{PrCH{=}CHPr} \quad \underset{}{\overset{SnBu_4 \quad h\nu}{\rightleftharpoons}} \quad \underset{\text{trans}}{PrCH{=}CHPr}$$

Ber (1973) 106 505

The following catalysts may also be used for cis-trans equilibration:

$CuCl_2$-$h\nu$	JOC (1972) 37 3561
Ph_2S-$h\nu$	JACS (1972) 94 2124
$HSCH_2COOH$	Chem Ind (1965) 507
$(i\text{-}Bu)_3Al$ γ-rays	Ber (1972) 105 88

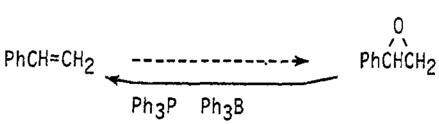
Section 210 Olefins from Miscellaneous Compounds



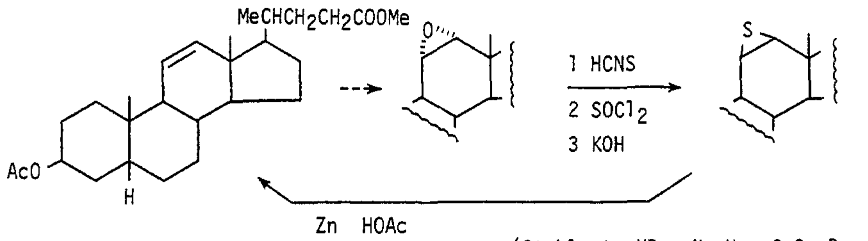
JACS (1971) 93 4316

Section 210A Protection of Olefins

The protection of isolated double bonds is considered in this section



Ber (1955) 88 1654



(Stable to HBr, Na-Hg, CrO_3-Pyr, $CrCl_2$ and H_2/Pt)

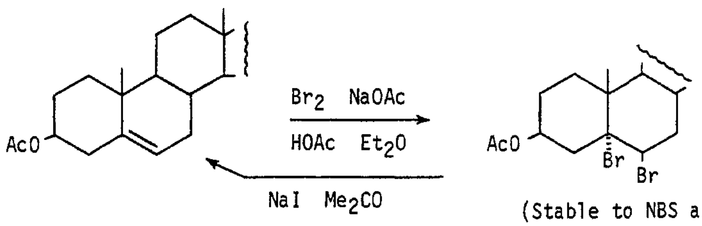
Chem Pharm Bull (1960) 8 621

$$C_8H_{17}CH{=}CH(CH_2)_7COOH \xrightarrow[2\ NaOH]{1\ H_2O_2\quad HCOOH} C_8H_{17}CH(OH)CH(OH)(CH_2)_7COOH$$

Reverse: 1 HBr H_2SO_4 HOAc; 2 Zn EtOH

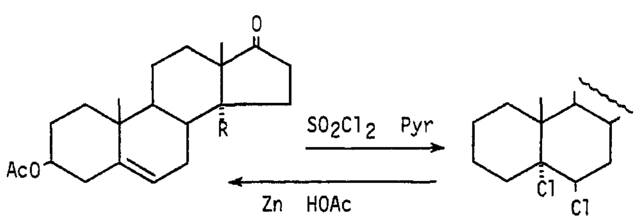
(Stable to Br_2)

Acta Chem Scand (1952) 6 1127
JCS (1951) 1079 1087



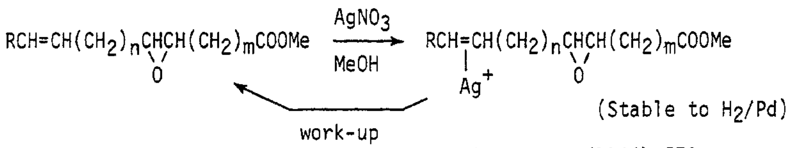
(Stable to NBS and H_2/Pd)

JOC (1965) 30 1658
J Biol Chem (1958) 230 447
Org Synth (1963) Coll Vol 4 195



(Stable to HBr, CrO_3, $SOCl_2$-Pyr and H_2/Pt)

Rec Trav Chim (1971) 90 549
JCS (1961) 4547



Tetr Lett (1966) 379

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

Compendium of Organic Synthetic Methods, Volume 2
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 15 PREPARATION OF DIFUNCTIONAL COMPOUNDS

Section 300 Acetylene — Acetylene

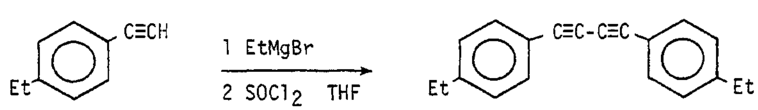
Diacetylenes

Review: The Coupling of Acetylenic Compounds

Advances in Org Chem (1963) 4 225

$$PhC\equiv CH \xrightarrow{Cu(OAc)_2 \quad Pyr \quad MeOH} PhC\equiv C\text{-}C\equiv CPh \qquad 70\text{-}80\%$$

Org Synth (1965) 45 39
JCS (1959) 889
(1960) 3614
JACS (1972) 94 658



61%

JOC (1972) 37 3749

$$BuC{\equiv}CH \xrightarrow[\substack{2\ CuCl_2 \\ 3\ I_2\ \ Et_2O}]{1\ EtMgBr\ \ Et_2O} BuC{\equiv}C\text{-}C{\equiv}CBu \qquad 71\%$$

JCS (1954) 1704

$$PhC{\equiv}CH \xrightarrow[THF\ \ H_2O]{Br_2\ \ NaOH} PhC{\equiv}CBr \xrightarrow[C_6H_6]{CuCl_2\ \ BuNH_2} PhC{\equiv}C\text{-}C{\equiv}CPh \qquad 84\%$$

Advances in Org Chem (1963) 4 318
JCS (1962) 3055

$$PhC{\equiv}CH \xrightarrow[\substack{NH_2OH\cdot HCl\ \ EtNH_2 \\ 2\ \text{Copper tetrammine sulfate} \\ Me_2CO}]{1\ BrC{\equiv}CCOOH\ \ CuCl_2} PhC{\equiv}C\text{-}C{\equiv}CH \qquad 41\%$$

Ber (1964) 97 2586

$$PhC{\equiv}CH \xrightarrow[\substack{EtNH_2\ \ DMF \\ 2\ NaOH\ \ MeOH\ \ H_2O}]{1\ BrC{\equiv}CSiEt_3\ \ CuCl_2\ \ NH_2OH\cdot HCl} PhC{\equiv}C\text{-}C{\equiv}CH \qquad \sim 50\%$$

Tetrahedron (1972) 28 4591 5221

$$C_5H_{11}C{\equiv}CH \xrightarrow[\substack{2\ CuCl_2 \\ 3\ BrCH_2C{\equiv}CC_5H_{11}}]{1\ EtMgBr\ \ Et_2O} C_5H_{11}C{\equiv}CCH_2C{\equiv}CC_5H_{11} \qquad 70\%$$

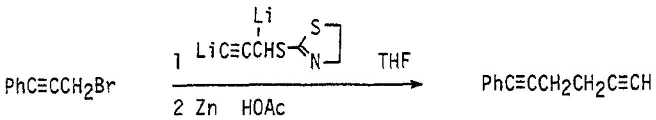
JACS (1951) 73 4601
Org Synth (1970) 50 97

$$BuBr \xrightarrow{ClCH_2C{\equiv}CCH_2Cl\ \ NaNH_2} BuC{\equiv}C\text{-}C{\equiv}CBu \qquad \sim 50\%$$

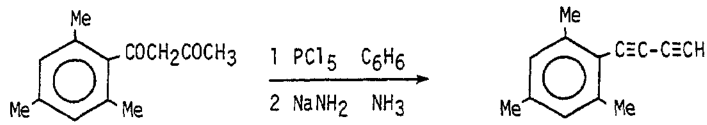
JCS (1951) 44

$C_5H_{11}Br \xrightarrow{ClCH_2C{\equiv}CCH_2Cl \quad NaNH_2} C_5H_{11}C{\equiv}C\text{-}C{\equiv}CH$

JCS (1955) 1007



Tetr Lett (1972) 2117



Tetrahedron (1972) 28 5221

$PhCOCH_2CH_2COPh \xrightarrow[\text{2 TsOH; 3 } Me_2SO_4\text{; 4 NaOH}]{\text{1 EtSH HCl dioxane}} PhC{\equiv}C\text{-}C{\equiv}CPh$

Z Chem (1969) 9 229

Section 301 Acetylene — Carboxylic Acid

Acetylenic acids

Review: Recent Developments in the Synthesis of Fatty Acids

Chem Rev (1957) 57 191

$C_{11}H_{23}C{\equiv}CH \xrightarrow[\text{2 } Br(CH_2)_4COOH \text{ THF}]{\text{1 } LiNH_2 \ NH_3} C_{11}H_{23}C{\equiv}C(CH_2)_4COOH$ 49%

JCS (1965) 894

$C_{12}H_{25}C\equiv CH \xrightarrow[\text{2 } CO_2]{\text{1 EtMgBr } Et_2O} C_{12}H_{25}C\equiv CCOOH$ 76%

Annalen (1965) 685 154

$LiAlH_4$, CO_2 Izv (1964) 2066
(Chem Abs 62 7629)

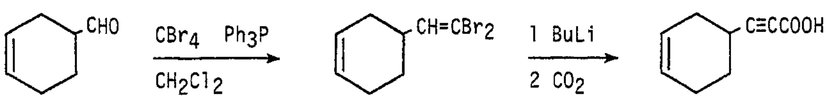
$PhCOCl \dashrightarrow PhCOCH(COOBu\text{-}t)_2 \xrightarrow{\text{1 t-BuOK}} PhC\equiv CCOOH$

2 β-Naphthalene sulfonic anhydride
3 Acid
4 $NaHCO_3$

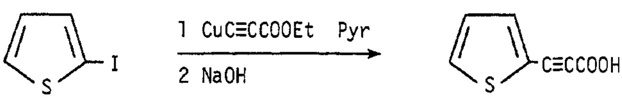
JCS C (1971) 2013

$PhCHO \xrightarrow[C_6H_6]{Ph_3P=C(Br)COOMe} PhCH=C(Br)COOMe \xrightarrow{\text{KOH MeOH}} PhC\equiv CCOOH$

Org React (1965) 14 270



Tetr Lett (1972) 3769



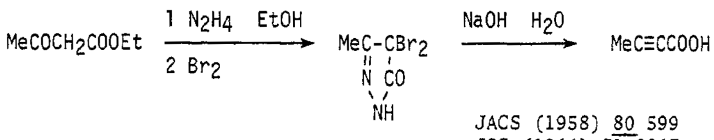
JCS C (1969) 2173

$PhCH=CHBr \xrightarrow[\text{2 } CO_2]{\text{1 BuLi } Et_2O} PhC\equiv CCOOH$ 42%

JACS (1940) 62 2327

$$HC{\equiv}CCH_2CH_2OH \xrightarrow[Me_2CO \quad H_2O]{CrO_3 \quad H_2SO_4} HC{\equiv}CCH_2COOH \qquad 28\%$$

JCS (1949) 604



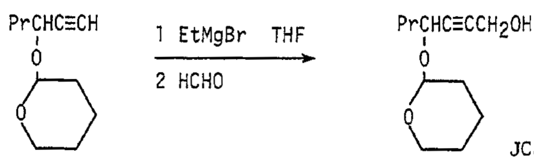
29%

JACS (1958) 80 599
JOC (1966) 31 2867

		Section
Also via:	Acetylenic esters	306
	Acetylenic amides	304

Section 302 Acetylene — Alcohol

Acetylenic alcohols, hydroxyacetylenes

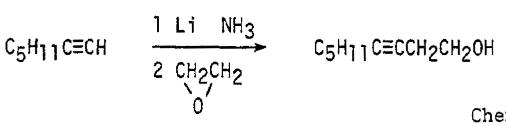


80%

JCS Perkin I (1973) 720
JCS (1950) 2100

$$BuCH_2C{\equiv}CH \xrightarrow{SeO_2 \quad EtOH} BuCH(OH)C{\equiv}CH \qquad 27\%$$

Compt Rend (1933) 196 706



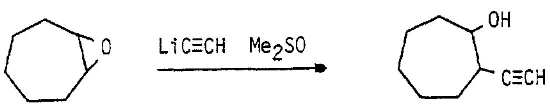
Chem Comm (1967) 1055

$$C_6H_{13}CHO \xrightarrow[\text{Mg} \quad Et_2O \text{ or Zn} \quad THF]{BrCH_2C{\equiv}CH} C_6H_{13}CH(OH)CH_2C{\equiv}CH$$

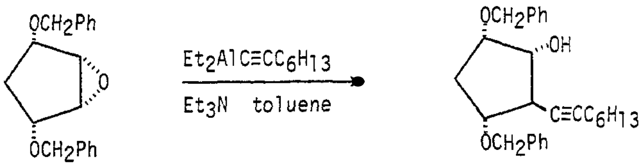
JCS (1955) 1740 1007

$$i\text{-}PrCHO \xrightarrow{HC{\equiv}CMgBr \quad THF} i\text{-}PrCH(OH)C{\equiv}CH \qquad 86\%$$

Bull Soc Chim Fr (1964) 3218



Chem Comm (1969) 674



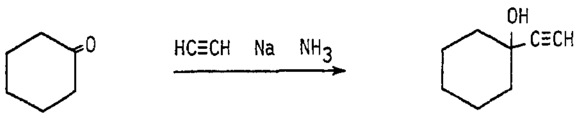
Chem Comm (1968) 634
Tetr Lett (1970) 2695

$$C_{11}H_{23}Br \xrightarrow[NH_3 \quad THF]{HC{\equiv}CCH_2OH \quad LiNH_2} C_{11}H_{23}C{\equiv}CCH_2OH \qquad 87\%$$

JCS (1963) 5889
(1965) 4373
JCS C (1969) 2173

$$HOOC(CH_2)_7Br \xrightarrow[LiNH_2\ \ THF]{HC{\equiv}C(CH_2)_8OH} HOOC(CH_2)_7C{\equiv}C(CH_2)_8OH$$

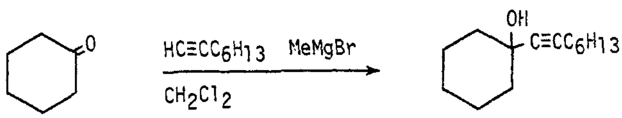
JCS C (1967) 1556
(1965) 894



65-75%

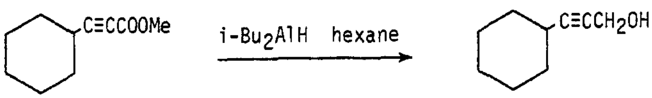
Org Synth (1955) Coll Vol 3 416

$LiC{\equiv}CH \cdot NH_2CH_2CH_2NH_2$ JOC (1964) 29 1872



~74%

Ber (1962) 95 2557
JCS (1957) 573



>80%

Tetr Lett (1973) 1495

Section 303 Acetylene — Aldehyde

Acetylenic aldehydes

$$HC{\equiv}C(CH_2)_7C{\equiv}CH \xrightarrow[2\ HC(OEt)_3]{1\ EtMgBr\ \ Et_2O} (EtO)_2CHC{\equiv}C(CH_2)_7C{\equiv}CCH(OEt)_2 \xrightarrow{(COOH)_2\ \ H_2O} OHCC{\equiv}C(CH_2)_7C{\equiv}CCHO$$

<82%

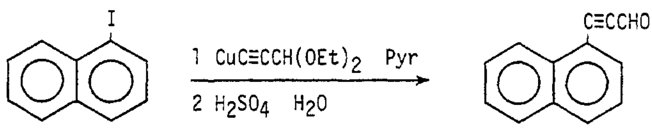
JCS (1951) 2693
Org Synth (1963) Coll Vol 4 801

$$\mathrm{BuC{\equiv}CH} \xrightarrow[\text{2 HCOOEt}\ \ \mathrm{Et_2O}\ \ \text{3 HOAc}]{\text{1 } \mathrm{NaNH_2}\ \ \mathrm{NH_3}} \mathrm{BuC{\equiv}CCHO}$$ 24%

JCS (1950) 3361

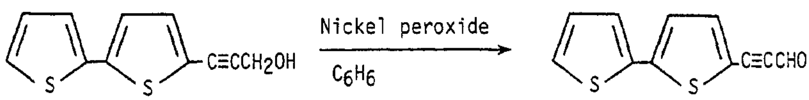
$$\mathrm{BuC{\equiv}CH} \xrightarrow[\text{2 } \mathrm{HCONMe_2}\ \ \text{3 } \mathrm{H_2SO_4}\ \ \mathrm{H_2O}]{\text{1 EtMgBr}\ \ \mathrm{Et_2O}} \mathrm{BuC{\equiv}CCHO}$$ 51%

JCS (1958) 1054



49%

JCS C (1969) 2173



72%

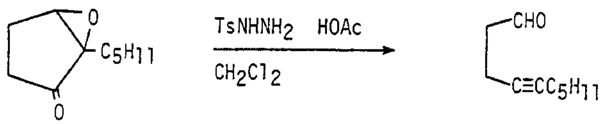
JCS C (1969) 2173

MnO_2 JCS (1958) 1054
Ber (1973) 106 2755

CrO_3-3,5-dimethylpyrazole Tetr Lett (1973) 4499

$$\mathrm{PhCH{=}CHCHO} \xrightarrow[\text{2 } \mathrm{K_2CO_3}\ \ \text{3 } \mathrm{HC(OEt)_3}\ \ \mathrm{NH_4Cl}\ \ \text{EtOH}\ \ \text{4 KOH}\ \ \text{EtOH}]{\text{1 } \mathrm{Br_2}\ \ \text{HOAc}} \mathrm{PhC{\equiv}CCH(OEt)_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{H_2SO_4}} \mathrm{PhC{\equiv}CCHO}$$

Org Synth (1955) Coll Vol 3 731



27%

Helv (1967) 50 2101
(1972) 55 1276

Section 304 Acetylene — Amide

Acetylenic amides

$$BuC\equiv CH \xrightarrow[2\ Me_2NCOCl]{1\ Na\quad NH_3} BuC\equiv CCONMe_2$$

60%

Compt Rend (1955) 240 989

Section 305 Acetylene — Amine

Acetylenic amines

Review: Synthesis and Reactions of the Alkynylamines
Angew (1967) 79 744
(Internat Ed 6 767)

$$MeC\equiv CH \xrightarrow[Zn(OAc)_2\quad 120°]{Et_2NH\quad Cd(OAc)_2} MeC\equiv CC(NEt_2)Me_2$$

JACS (1961) 83 216

$$PhC\equiv CH \xrightarrow[dioxane]{Et_2NH\quad HCHO} PhC\equiv CCH_2NEt_2$$

80%

Ber (1933) 66 418

$$PhC{\equiv}CH \xrightarrow[2\ ClNEt_2]{1\ EtMgBr\quad Et_2O} PhC{\equiv}CNEt_2$$ 2%

Annalen (1960) 638 33

$$PhC{\equiv}CH \xrightarrow[C_6H_6]{Me_2NH\quad O_2\quad Cu(OAc)_2} PhC{\equiv}CNMe_2$$ >40%

Tetr Lett (1968) 5357

$$BuBr \xrightarrow{LiC{\equiv}CN(Me)Ph\quad HMPA} BuC{\equiv}CN(Me)Ph$$ 75%

Bull Soc Chim Fr (1965) 2787

$$BuC{\equiv}COEt \xrightarrow[2\ 110\text{-}120^\circ]{1\ LiNEt_2\quad Et_2O} BuC{\equiv}CNEt_2$$ 65%

Rec Trav Chim (1964) 83 1211

$$PhC{\equiv}CCl \xrightarrow{LiNMe_2\quad Et_2O} PhC{\equiv}CNMe_2$$ 87%

Angew (1964) 76 537
(Internat Ed 3 506)

$$t\text{-}BuC{\equiv}CCl \xrightarrow{Me_3N\quad 135^\circ} t\text{-}BuC{\equiv}CNMe_2$$ 44%

Angew (1964) 76 537
(Internat Ed 3 506 582)
Ber (1970) 103 564

$$PhCH{=}CClF \xrightarrow{LiNEt_2\quad Et_2O} PhC{\equiv}CNEt_2$$ 86%

Angew (1963) 75 638
(Internat Ed 2 477)

Section 306 Acetylene — Ester

Acetylenic esters

$C_5H_{11}C\equiv CH \xrightarrow[\text{2 } BF_3 \text{ 3 } N_2CHCOOEt]{\text{1 BuLi THF}} C_5H_{11}C\equiv CCH_2COOEt$ 87%

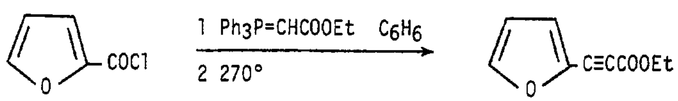
Can J Chem (1972) 50 1105

$MeC\equiv CH \dashrightarrow MeC\equiv CLi \xrightarrow{ClCOOEt} MeC\equiv CCOOEt$ 71%

JOC (1973) 38 3588
Annalen (1958) 614 37

$PhC\equiv CH \xrightarrow{C(OEt)_4 \ \ ZnCl_2} PhC\equiv CC(OEt)_3 \dashrightarrow PhC\equiv CCOOEt$ < 14%

JACS (1958) 80 4607

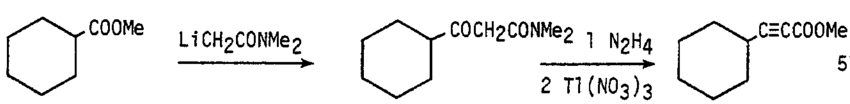


70%

J Med Chem (1973) 16 72
Ber (1961) 94 3005

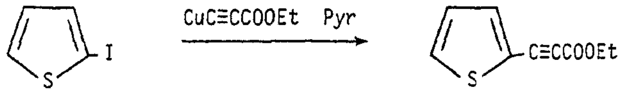
$C_6H_{13}CHO \xrightarrow{N_2CHCOOEt} C_6H_{13}CH(OH)C(=N_2)COOEt \xrightarrow[MeCN]{BF_3\cdot Et_2O} C_6H_{13}C\equiv CCOOEt$

Synth Comm (1972) 331



57%

Tetr Lett (1973) 1495



~61%

JCS C (1969) 2173

$$C_8H_{17}C{\equiv}C(CH_2)_7COOH \xrightarrow[\text{electrolysis}]{\overset{COOH}{|}\atop (CH_2)_4COOMe} C_8H_{17}C{\equiv}C(CH_2)_{11}COOMe$$

28%

JCS (1955) 2218

$$C_5H_{11}COCH_2COOMe \xrightarrow[2\ Tl(NO_3)_3]{1\ N_2H_4\quad MeOH} C_5H_{11}C{\equiv}CCOOMe$$

~90%

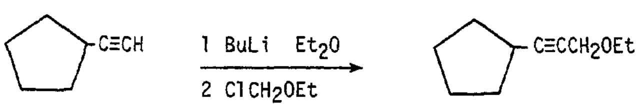
Angew (1971) 84 60
(Internat Ed 11 48)

Also via: Acetylenic acids (Section 301)

Section 307 Acetylene — Ether, Epoxide

Acetylenic ethers and acetylenic epoxides

Review: Ethynyl Ethers and Thioethers as Synthetic Intermediates
Advances in Org Chem (1960) 2 117



90%

Rec Trav Chim (1965) 84 31
Bull Soc Chim Fr (1969) 4514

$$EtCH_2CHO \xrightarrow[\substack{C_6H_6 \\ 2\ Br_2\quad C_6H_6}]{1\ PhCH_2OH\quad HCl\quad MgSO_4} \underset{\substack{| \quad | \\ Br\ \ Br}}{EtCH\text{-}CHOCH_2Ph} \xrightarrow[\substack{C_6H_6 \\ 2\ NaNH_2}]{1\ PhNEt_2} EtC{\equiv}COCH_2Ph \qquad 60\%$$

Rec Trav Chim (1964) 83 301

$$EtBr \xrightarrow{HC{\equiv}COBu\text{-}t\quad LiNH_2\quad NH_3} EtC{\equiv}COBu\text{-}t$$

Rec Trav Chim (1961) 80 810
JCS (1954) 1860
Org Prep and Procedures (1972) 4 89

$$BuC{\equiv}CH \xrightarrow[\substack{2\ BrCH_2COMe \\ 3\ KOH\quad Et_2O}]{1\ EtMgBr} BuC{\equiv}\underset{\substack{| \\ Me}}{C}\overset{O}{\frown}CH_2 \qquad 40\%$$

Zh Obshch Khim (1960) 30 1194
(Chem Abs 55 499)

Section 308 Acetylene — Halide

Acetylenic halides

$$BuC{\equiv}CH \xrightarrow[2\ I(CH_2)_4Cl]{1\ NaNH_2\quad NH_3} BuC{\equiv}C(CH_2)_4Cl \qquad 53\%$$

JACS (1948) 70 1699
JCS (1950) 2100
JOC (1951) 16 1405

$$C_5H_{11}C{\equiv}CH \xrightarrow[2\ Cl_2\quad Et_2O]{1\ KNH_2\quad NH_3} C_5H_{11}C{\equiv}CCl$$

JACS (1937) 59 1307
TsCl Annales de Chimie (1931) 16 309

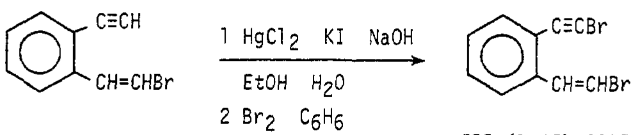
$PhC{\equiv}CH \xrightarrow[\text{THF} \quad \text{hexane}]{\text{BuMgCl} \quad SO_2Cl_2} PhC{\equiv}CCl$ 48%

JCS C (1968) 1265

$ClNEt_2$ or NBS Annalen (1960) 638 33
JACS (1961) 83 4663

$PhC{\equiv}CH \xrightarrow[\text{THF} \quad H_2O]{Br_2 \quad \text{NaOH}} PhC{\equiv}CBr$ 89%

JCS (1963) 2295
Org Synth (1965) 45 86



79%

JCS (1963) 2295

$C_5H_{11}C{\equiv}CH \xrightarrow[2\ Br_2]{1\ \text{EtMgBr} \quad Et_2O} C_5H_{11}C{\equiv}CBr$ 70%

JACS (1937) 59 1307

BrCN Annales de Chimie (1926) 5 5

$PrC{\equiv}CH \xrightarrow[2\ I_2]{1\ \text{MeMgBr} \quad Et_2O} PrC{\equiv}CI$

Annales de Chimie (1926) 5 5

$C_5H_{11}C{\equiv}CH \xrightarrow[\text{or } 1\ \text{Na} \quad NH_3 \quad 2\ I_2]{I_2 \quad NH_3} C_5H_{11}C{\equiv}CI$

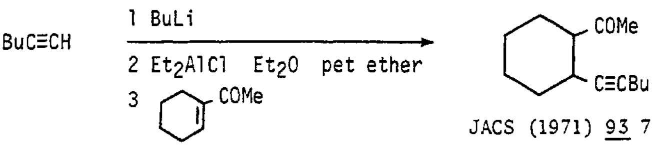
JACS (1933) 55 2150

$C_6H_{13}C{\equiv}CH \xrightarrow[CHCl_3 \quad Pyr]{(I\cdot Pyr_2)^+ \; NO_3^-} C_6H_{13}C{\equiv}CI$ 40%

Can J Chem (1971) 49 403

Section 309 Acetylene — Ketone

Acetylenic ketones

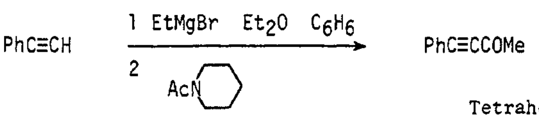


79%

JACS (1971) 93 7320

$t\text{-}BuC{\equiv}CH \xrightarrow[2\ EtCH(Me)\text{-}C(Cl){=}NOH]{1\ EtMgBr} t\text{-}BuC{\equiv}CCH(Me)C({=}NOH)Et \dashrightarrow t\text{-}BuC{\equiv}CCOCH(Me)Et$ <69%

Tetr Lett (1970) 2101



8%

Tetrahedron (1962) 18 1381

$PhC{\equiv}CH \xrightarrow{MeC(OEt)_3 \quad ZnCl_2} PhC{\equiv}CC(OEt)_2Me \dashrightarrow PhC{\equiv}CCOMe$ <34%

JACS (1958) 80 4607

$$C_6H_{13}C{\equiv}CH \xrightarrow[\text{MeOH} \quad H_2O \quad \text{2 MeCOCl}]{\text{1 } AgNO_3\text{-}NH_3} C_6H_{13}C{\equiv}CCOMe$$

JACS (1956) 78 1675

$$BuC{\equiv}CH \dashrightarrow BuC{\equiv}CSiMe_3 \xrightarrow[CS_2]{MeCOCl \quad AlCl_3} BuC{\equiv}CCOMe \qquad 75\%$$

Ber (1963) 96 3280

$$EtCOCl \xrightarrow{BuC{\equiv}CAg \quad CCl_4} BuC{\equiv}CCOEt \qquad \sim 53\%$$

JACS (1956) 78 1675
Tetr Lett (1970) 2659

$$PrCOOH \xrightarrow[\text{2 } PhC{\equiv}CLi]{\text{1 } ClCOOEt \quad Et_3N \text{ pet ether}} PhC{\equiv}CCOPr \qquad 57\%$$

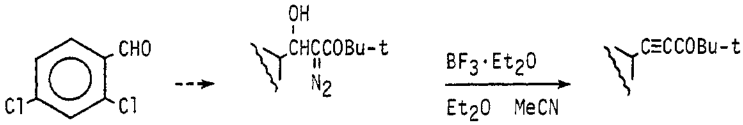
Ber (1964) 97 1649

$$MeCOCl \xrightarrow[CH_2Cl_2]{Na(Et_3BC{\equiv}CMe)} MeCOC{\equiv}CMe$$

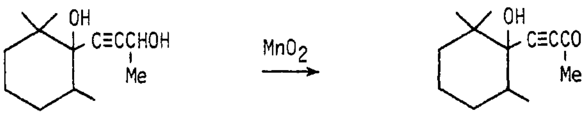
Angew (1967) 79 57
(Internat Ed 6 84)

$$(PhCO)_2O \xrightarrow[\text{2 } 250\text{-}280°]{\text{1 } Ph_3P{=}CHCOPh \quad CHCl_3} PhC{\equiv}CCOPh \qquad 60\%$$

JOC (1965) 30 1015



Synth Comm (1972) 2 331



Quart Rev (1959) 13 61
Chem Pharm Bull (1973) 21 2051

$$\underset{\text{Ph}}{\text{HC}\equiv\text{CCHOH}} \xrightarrow[\text{Me}_2\text{CO} \quad \text{H}_2\text{O}]{\text{CrO}_3 \quad \text{H}_2\text{SO}_4} \underset{\text{Ph}}{\text{HC}\equiv\text{CCO}}$$

80%

JCS (1946) 39

$$\underset{\text{Me}}{\text{PhC}\equiv\text{CCHOH}} \xrightarrow[\text{Et}_2\text{O} \quad \text{H}_2\text{O}]{\text{Na}_2\text{Cr}_2\text{O}_7\cdot 2\text{H}_2\text{O} \quad \text{H}_2\text{SO}_4} \underset{\text{Me}}{\text{PhC}\equiv\text{CCO}}$$

70%

Tetrahedron (1962) 18 1381

$$\text{PrC}\equiv\text{CCH}_2\text{Et} \xrightarrow{\text{CrO}_3\cdot\text{Pyr} \quad \text{CH}_2\text{Cl}_2} \text{PrC}\equiv\text{CCOEt}$$

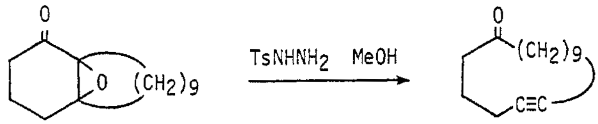
42%

Tetr Lett (1971) 4379

$$\text{MeC}\equiv\text{CCH}_2\text{Cl} \xrightarrow[\text{2 NaOH} \quad \text{H}_2\text{O}]{\text{1 Na}\overset{\text{COMe}}{\text{CH}}\text{COOEt}} \text{MeC}\equiv\text{CCH}_2\text{CH}_2\text{COMe}$$

37%

JCS (1951) 2445

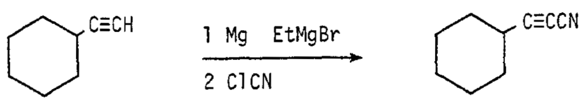


58%

Helv (1967) 50 2101 708
(1972) 55 1276

Section 310 Acetylene — Nitrile

Acetylenic nitriles



Annales de Chimie (1926) 5 5
Bull Soc Chim Fr (1915) 17 228

$$PhCOCl \xrightarrow[2\ 280°]{1\ Ph_3P{=}CHCN} PhC{\equiv}CCN$$

85%

Proc Chem Soc (1961) 302
JCS Perkin I (1973) 2241

Section 311 Acetylene — Olefin

Acetylenic olefins, enynes

$$C_5H_{11}C{\equiv}CH \xrightarrow{Cu_2O\ \ HOAc} C_5H_{11}C{\equiv}CCH{=}CHC_5H_{11}$$

60%

Chem Ind (1962) 1684
Proc Chem Soc (1958) 303

$$PrC\equiv CH \xrightarrow{Et_2Zn\quad Cr(OBu\text{-}t)_4} PrC\equiv C\underset{\substack{|\\ Pr}}{C}=CH_2$$

Bull Chem Soc Jap (1961) 34 892

$$C_5H_{11}C\equiv CH \dashrightarrow C_5H_{11}C\equiv CCu \xrightarrow[NaCN\quad DMF]{BrCH_2CH=CH_2} C_5H_{11}C\equiv CCH_2CH=CH_2 \qquad 96\%$$

Compt Rend (1970) 270 354

$$PhC\equiv CH \dashrightarrow PhC\equiv CCu \xrightarrow[DMF]{PhCH=CHBr} PhC\equiv CCH=CHPh \qquad \sim 75\%$$

Chem Comm (1967) 1259

$$EtCH_2C\equiv CNa \xrightarrow[HCl]{HCHO\quad EtOH} EtCH_2C\equiv CCH_2OEt \xrightarrow[NH_3]{NaNH_2} EtCH=CHC\equiv CH \qquad <42\%$$

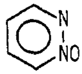
Rec Trav Chim (1963) 82 1115

$$BuC\equiv C\text{-}C\equiv CBu \xrightarrow[2\ HOAc]{1\ (i\text{-}Pr\overset{\substack{Me\\ |}}{C}H)_2BH\quad THF} BuCH=CHC\equiv CBu \qquad 76\%$$

JACS (1970) 92 4068

$$PhCHO \xrightarrow[NH_3\quad MeCN]{Ph_3\overset{+}{P}CH_2C\equiv CH\ \overset{-}{Br}} PhCH=CHC\equiv CH \qquad 59\%$$

Annalen (1965) 682 62
Tetr Lett (1973) 1495



$PhBr \xrightarrow{Mg} PhMgBr \xrightarrow{THF} PhCH{=}CHC{\equiv}CH$ 35%

Chem Comm (1969) 710

$C_6H_{13}Br \xrightarrow[NaNH_2\ \ NH_3]{MeCH_2C{\equiv}CSEt} MeCH{=}C{=}C(C_6H_{13})SEt \xrightarrow[NH_3]{KNH_2} C_6H_{13}CH{=}CHC{\equiv}CH$ ~68%

Rec Trav Chim (1964) 83 456

$MeC(Et){=}CHCH_2CH_2C(Et)O \xrightarrow[EtONa\ \ DMF]{Ph_3\overset{+}{P}CH_2CH_2CH_2C{\equiv}CH} MeC(Et){=}CHCH_2CH_2C(Et){=}CHCH_2CH_2C{\equiv}CH$ 36%

JCS Perkin I (1972) 361

$PrC(Me){=}CHCH_2Br \xrightarrow{HC{\equiv}CCH_2MgBr} PrC(Me){=}CHCH_2CH_2C{\equiv}CH$

JOC (1973) 38 2733

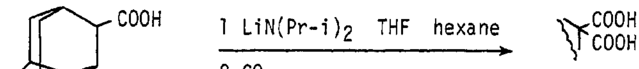
Section 312 Carboxylic Acid — Carboxylic Acid

Review: Synthesis of Alkylated Alkanedioic Acids

Chem Rev (1959) 59 89

$BuC{\equiv}CH \xrightarrow[2\ MeLi\ \ 3\ CO_2]{1\ (i\text{-}Bu)_2AlH\ \ THF} BuCH_2CH(COOH)_2$ 62%

Tetr Lett (1966) 6021



30%

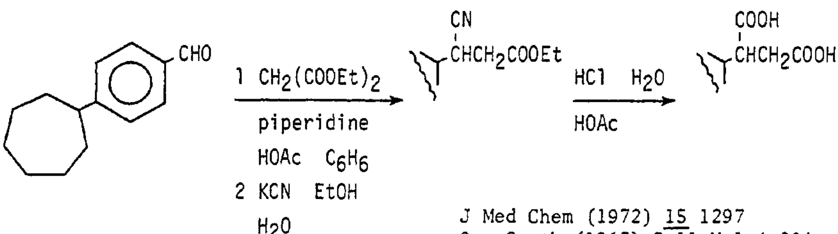
Tetr Lett (1971) 2339

$$C_{12}H_{25}CH_2COOH \xrightarrow{PBr_3} C_{12}H_{25}CH_2COBr \xrightarrow[2\ H_2O]{1\ CH_2(COBr)_2\ \ CCl_4} C_{12}H_{25}CH(COOH)_2 \qquad <42\%$$

Ber (1958) 91 297

$$C_7H_{15}Br \xrightarrow[BuONa\ \ BuOH]{CH_2(COOEt)_2} C_7H_{15}CH(COOEt)_2 \xrightarrow{KOH\ \ H_2O} C_7H_{15}CH(COOH)_2$$

Org Synth (1943) Coll Vol 2 474 416
(1932) Coll Vol 1 250
Org React (1957) 9 107



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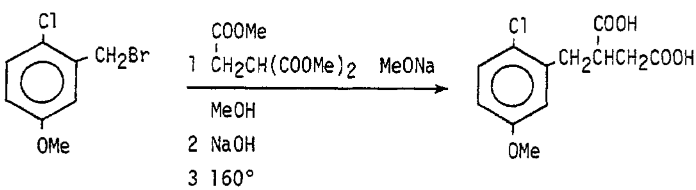
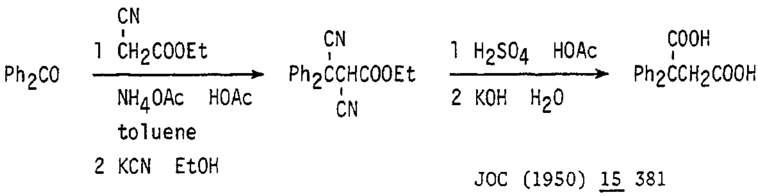
J Med Chem (1972) 15 1297
Org Synth (1963) Coll Vol 4 804



85%

JACS (1965) 87 933



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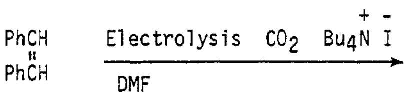
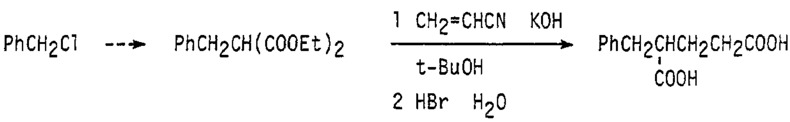
JOC (1950) 15 381

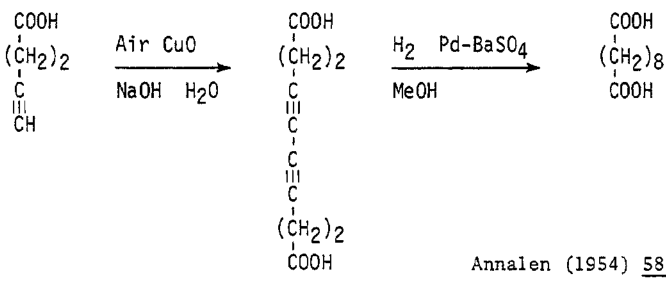


91%

Synthesis (1971) 285

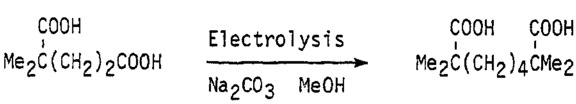


JCS (1950) 1683



~80%

Annalen (1954) 589 222



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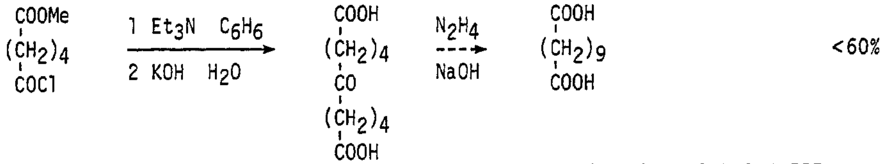
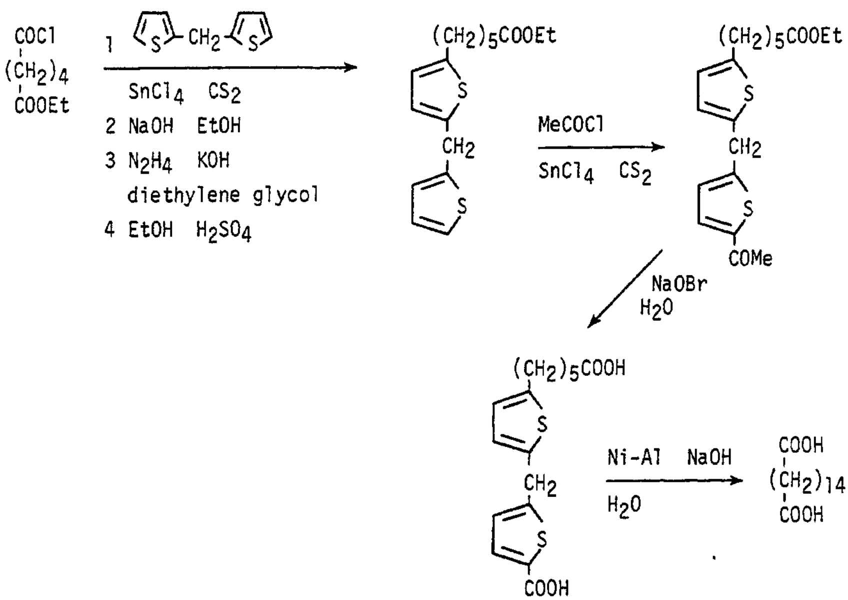
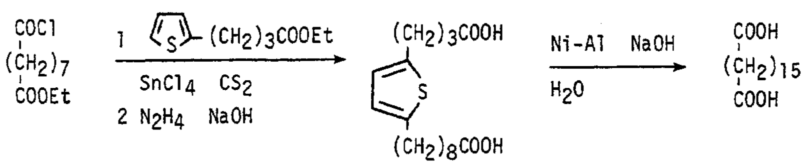
Bull Soc Chim Fr (1970) 183



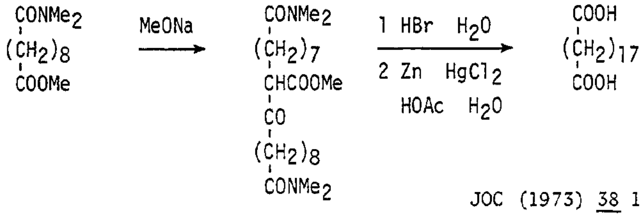
Org Synth (1963) Coll Vol 4 555



Bull Soc Chim Fr (1955) 1583

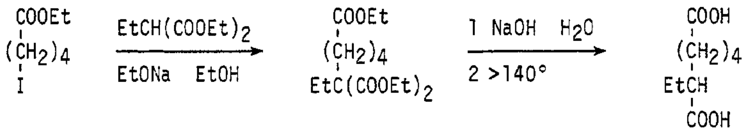


Bull Soc Chim Fr (1955) 1583

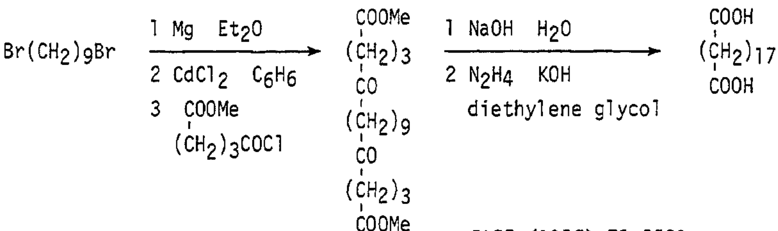


32%

JOC (1973) 38 1424



JACS (1928) 50 1967



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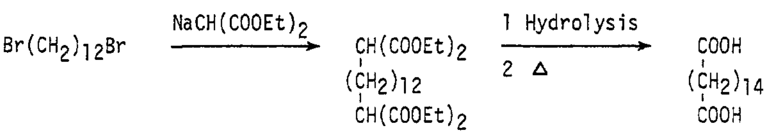
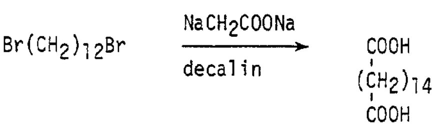
JACS (1953) 75 3339



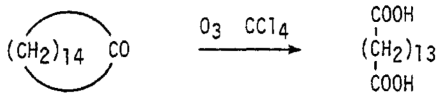
83%

JACS (1947) 69 2350



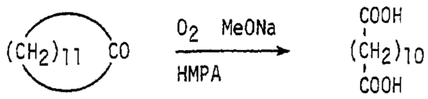
34%

Annalen (1966) 691 61



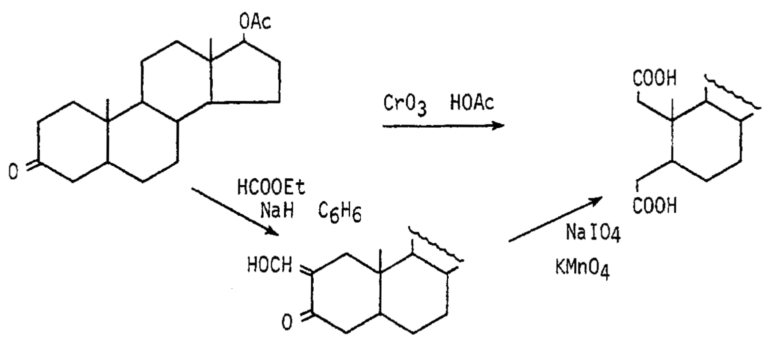
25%

Helv (1930) 13 142

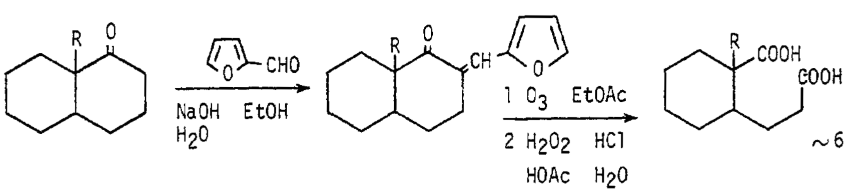


40%

JOC (1965) 30 3768

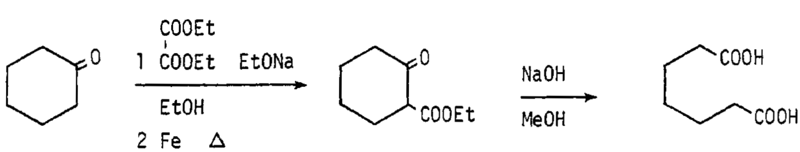


Tetrahedron (1964) 20 1271



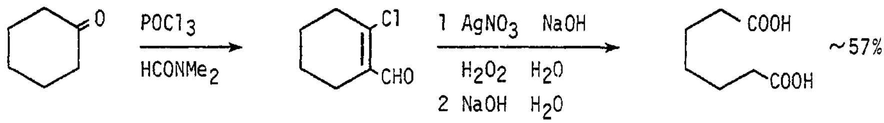
~67%

JACS (1956) 78 6331

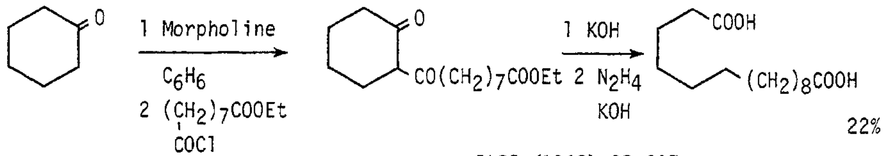


47-54%

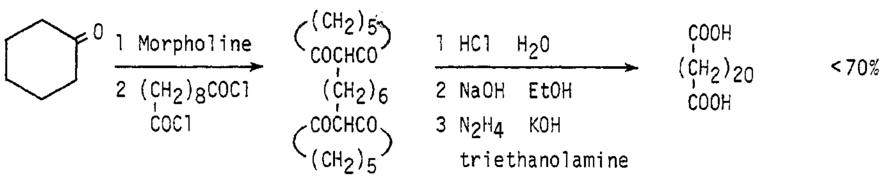
Org Synth (1943) Coll Vol 2 531



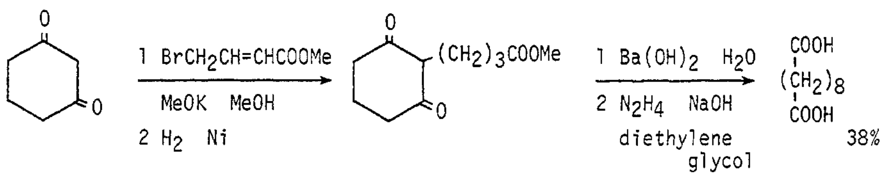
Ber (1960) 93 2743



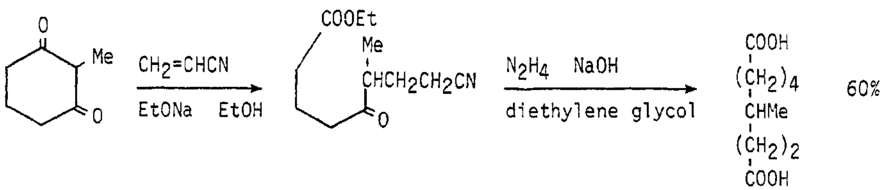
JACS (1963) 85 207



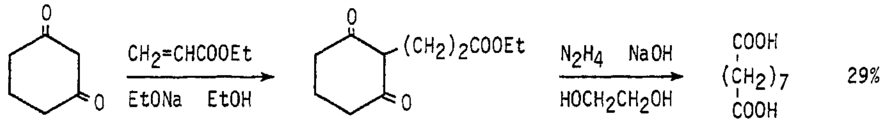
Org Synth (1963) 43 34
Ber (1967) 100 4017



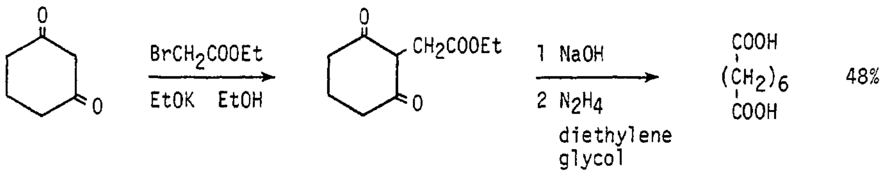
Ber (1953) 86 693



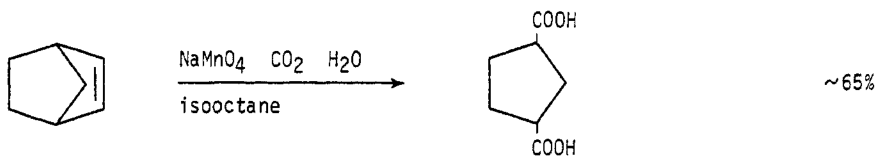
Ber (1954) 87 990
Newer Meth Prep Org Chem (1963) 2 51



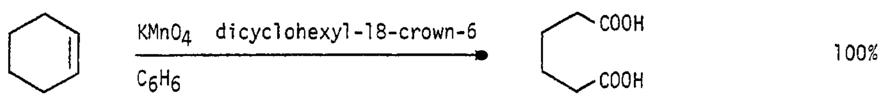
Newer Meth Prep Org Chem (1963) 2 51 96



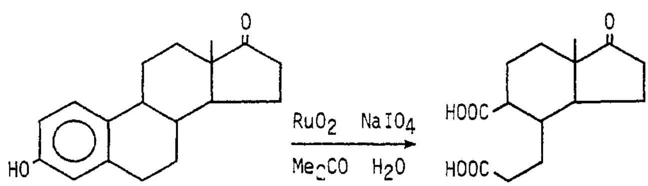
Ber (1952) 85 61 290
Newer Meth Prep Org Chem (1963) 2 51 95



JCS (1947) 818



JACS (1972) 94 4024



JOC (1969) 34 116

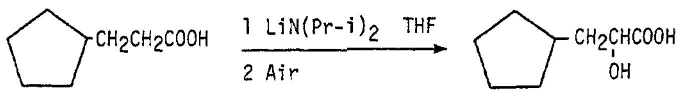
Also via: Section

Diesters	357
Dinitriles	375

Section 313 Carboxylic Acid — Alcohol

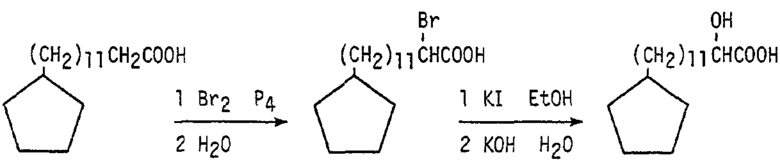
$$\mathrm{PhCOCl} \xrightarrow[\mathrm{Et_2O}]{\mathrm{CH_2N_2}} \mathrm{PhCOCHN_2} \xrightarrow{\mathrm{EtSCl}} \mathrm{PhCO\underset{Cl}{C}HSEt} \xrightarrow[\mathrm{H_2O}]{\mathrm{KOH}} \mathrm{Ph\underset{OH}{C}HCOOH}$$

Ber (1955) 88 1988



51%

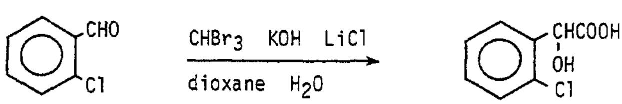
Synthesis (1971) 647



Ber (1942) 75 1181

$$\mathrm{PhCHO} \xrightarrow[\text{2 } \mathrm{HgCl_2} \ \ \mathrm{Me_2CO} \ \ \mathrm{H_2O}]{\text{1 } \mathrm{(PhS)_3CLi}} \mathrm{Ph\underset{OH}{C}HCOOH} \qquad 47\%$$

Angew (1967) 79 468
(Internat Ed 6 442)



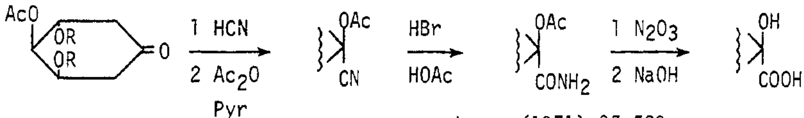
JOC (1968) 33 2565

$$PhCOOEt \xrightarrow[t\text{-}BuOK]{CH_3SOMe} PhCOCH_2SOMe \xrightarrow[2\ Cu(OAc)_2\ \ EtOH]{1\ HCl\ \ Me_2SO\ \ H_2O} \underset{\displaystyle OH}{PhCHCOOH}$$

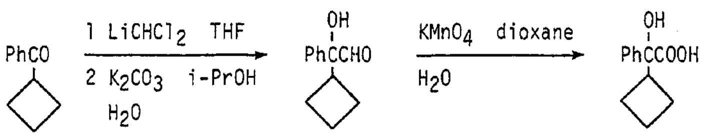
JACS (1966) 88 5498

$$\underset{\displaystyle Me}{PhCO} \xrightarrow[Et_2O\ \ H_2O]{NaCN\ \ HCl} \overset{\displaystyle OH}{\underset{\displaystyle Me}{PhCCN}} \xrightarrow[2\ NaOH\ \ H_2O]{1\ HCl\ \ H_2O} \overset{\displaystyle OH}{\underset{\displaystyle Me}{PhCCOOH}} \qquad 29\text{-}30\%$$

Org Synth (1963) Coll Vol 4 58
JOC (1949) 14 1013

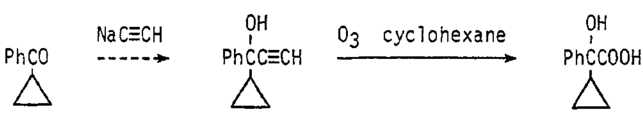


Angew (1971) 83 329
(Internat Ed 10 336)



<43%

JOC (1972) 37 1248

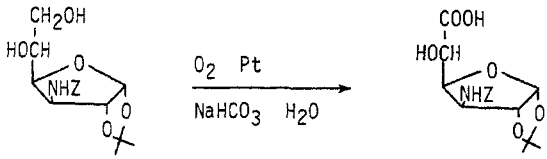


~40%

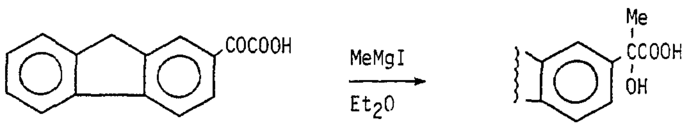
JOC (1964) 29 3419
Carbohydrate Res (1966) 2 315

$$PhCOCH_3 \xrightarrow{Cl_2\ \ HOAc} PhCOCHCl_2 \xrightarrow{NaOH\ \ H_2O} \underset{\displaystyle OH}{PhCHCOOH} \qquad 76\text{-}87\%$$

Org Synth (1955) Coll Vol 3 538

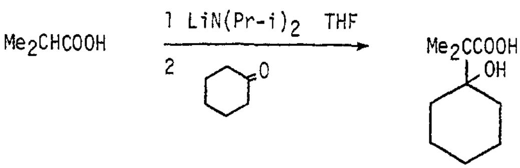


Ber (1972) 105 1524
(1956) 89 1648
Angew (1957) 69 600



88%

J Med Chem (1972) 15 1029



JACS (1972) 94 2000
(1951) 73 4221
JOC (1971) 36 1149 2403
Synthesis (1970) 615

$$Ph_2CHCHO \xrightarrow[THF]{Me_2CHCOOH \quad LiN(Pr\text{-}i)_2} Ph_2CHCH(OH)C(COOH)Me_2$$

50%

JOC (1971) 36 1149

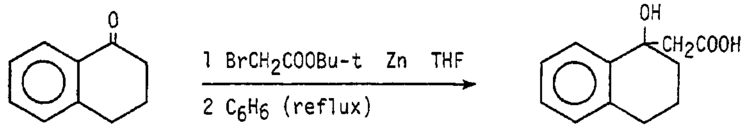
$$PhCHO \xrightarrow[2\ Acid]{1\ Me_2C{=}C(OH)OSiMe_3} PhCH(OH)C(COOH)Me_2$$

68%

Tetr Lett (1972) 79

$$PhCHO \xrightarrow[2\ H_2O_2\ \ MeOH\ \ H_2O]{1\ Bu_2BSBu\ \ CH_2{=}CO} \underset{\large OH}{PhCHCH_2COSBu} \dashrightarrow \underset{\large OH}{PhCHCH_2COOH}$$

Bull Chem Soc Jap (1971) 44 3215

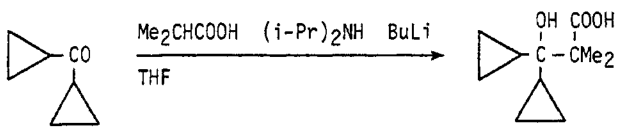


76%

Chem Comm (1969) 679
JCS C (1969) 2799

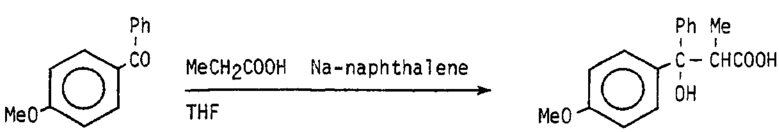
$$\underset{\large Et}{PhCO} \xrightarrow[2\ H_2O]{1\ BrCH_2COOSiMe_3\ \ Zn\ \ C_6H_6\ \ Et_2O} \underset{\large Et}{\overset{\large OH}{PhCCH_2COOH}} \qquad 80\%$$

Tetr Lett (1971) 3227



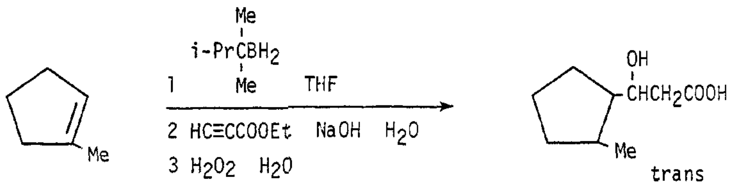
71%

JOC (1971) 36 1149 2403



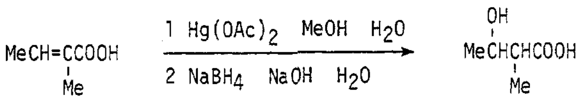
38%

Bull Soc Chim Fr (1970) 1848
Chem Ind (1969) 1811
(1972) 80
Israel J Chem (1971) 8 731



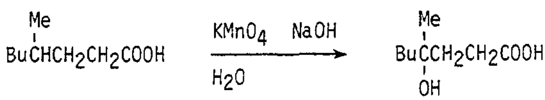
~71%

JACS (1973) 95 6837



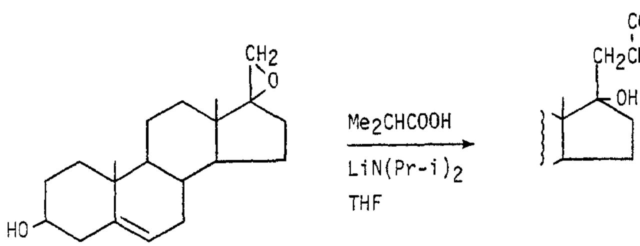
56%

JCS Perkin I (1973) 109



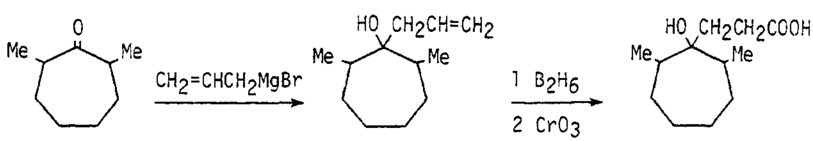
70%

JCS (1953) 2129 3580

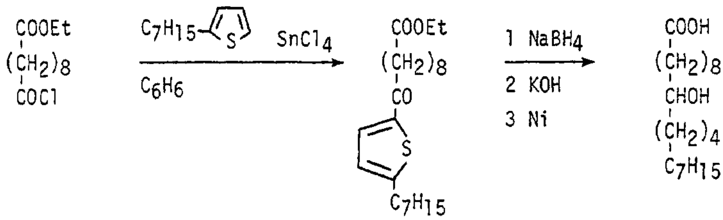


(→ lactone, 81%)

JACS (1967) 89 2500

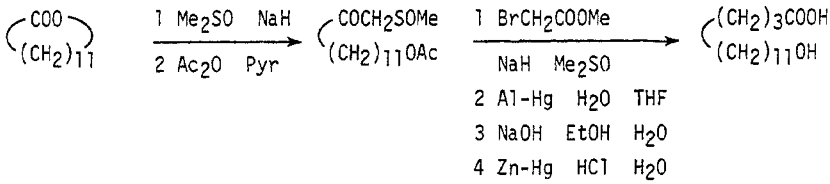


Chem Comm (1968) 122



29%

JOC (1961) 26 5217
JCS (1960) 1502



46%

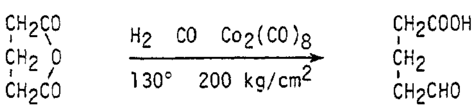
Can J Chem (1968) 46 3767
Tetr Lett (1966) 5669

Also via:

	Section
Hydroxyesters	327
Hydroxyamides	325
Carboxyesters	317

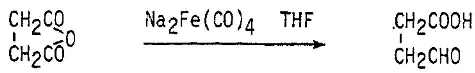
Section 314 Carboxylic Acid — Aldehyde

Carboxyaldehydes, aldehydic acids



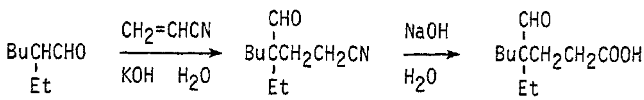
32%

Bull Chem Soc Jap (1971) 44 288

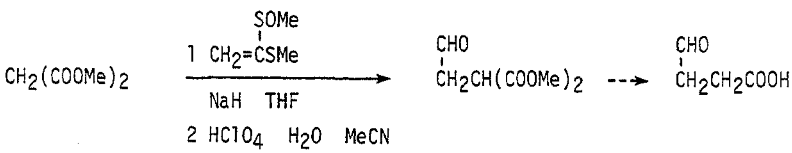


81%

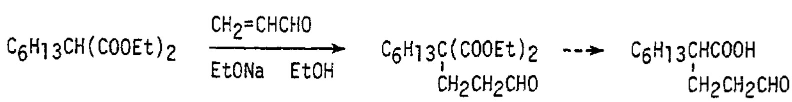
Tetr Lett (1973) 3535



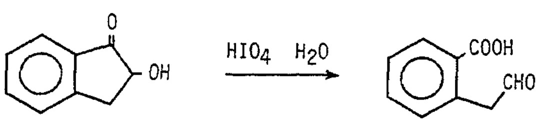
JACS (1944) 66 56



Tetr Lett (1973) 4711 4715



JACS (1948) 70 3470
Org React (1959) 10 179



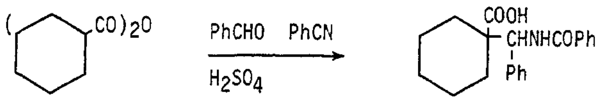
72%

Ber (1950) 83 390

Also via: Aldehydic esters (Section 336)

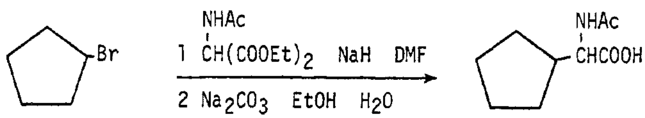
Section 315 Carboxylic Acid — Amide

Carboxyamides



19%

Synthesis (1973) 40



55%

JOC (1965) 30 1321
(1973) 38 457
Org React (1957) 9 107

Also via: Aminoacids (Section 316)

Section 316 Carboxylic Acid — Amine

α-Aminoacids, β-aminoacids and higher aminoacids

$$PhCH_2COOH \xrightarrow[\text{2 } NH_2OMe]{\text{1 } LiN(Pr\text{-}i)_2 \quad HMPA \quad THF} PhCH(NH_2)COOH$$

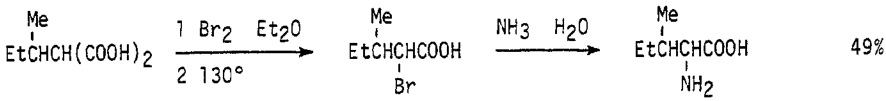
55%

Chem Comm (1972) 623

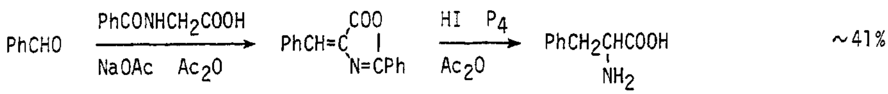
$$i\text{-}PrCH_2CH_2COOH \xrightarrow{Br_2 \quad PCl_3} i\text{-}PrCH_2CH(Br)COOH \xrightarrow[H_2O]{NH_3 \quad EtOH} i\text{-}PrCH_2CH(NH_2)COOH$$

~28%

Org Synth (1955) Coll Vol 3 523 848

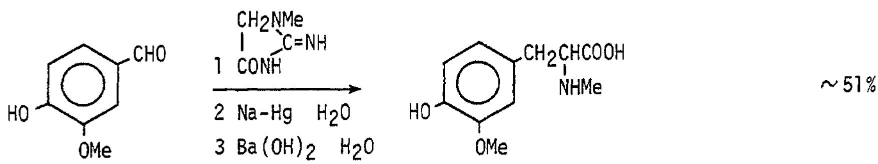


Org Synth (1955) Coll Vol 3 495 705

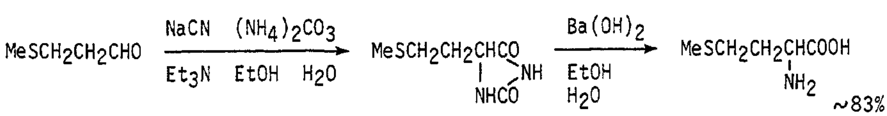


Org Synth (1943) Coll Vol 2 489
Org React (1942) 1 210

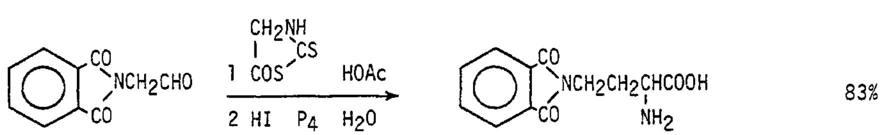
Catalytic reduction of azlactones JOC (1972) 37 2916



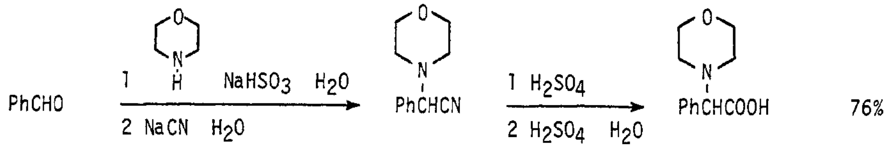
Org Synth (1955) Coll Vol 3 586
Org React (1942) 1 210



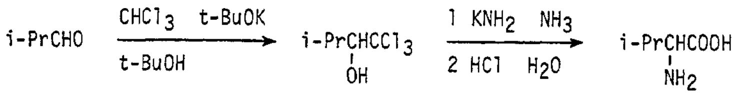
JCS (1952) 3403



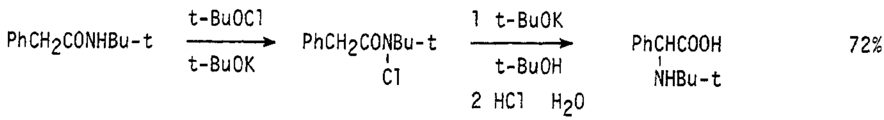
JOC (1952) 17 1459
Org React (1942) 1 210



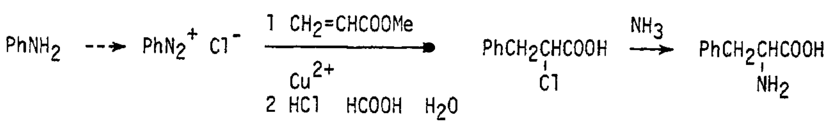
JOC (1961) 26 4741



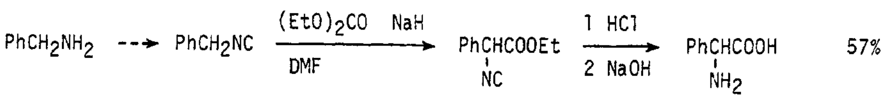
JOC (1964) 29 1148



JACS (1961) 83 4469



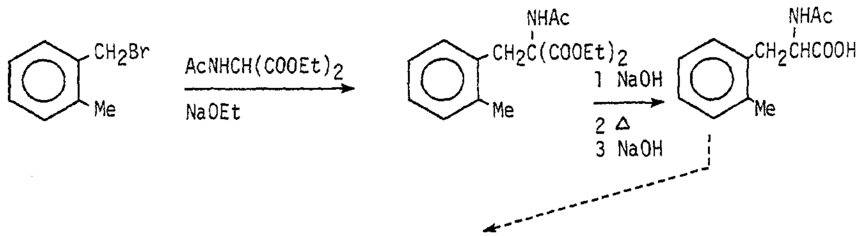
Proc Chem Soc (1962) 117

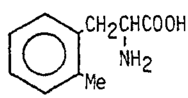


JOC (1973) 38 2094

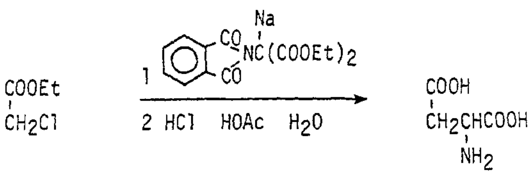
$$PhCH_2Cl \dashrightarrow PhCH_2CH(COOEt)_2 \xrightarrow[2\ NaN_3]{1\ Br_2} PhCH_2C(N_3)(COOEt)_2 \xrightarrow[2\ HBr]{1\ Ph_3P} PhCH_2CH(NH_2)COOH \quad 38\%$$

Annalen (1955) 591 117
Z Naturforsch (1960) 15b 811





JOC (1973) 38 457
(1959) 24 1397
Org React (1957) 9 107
JACS (1948) 70 3918
(1946) 68 450
J Biol Chem (1934) 106 595

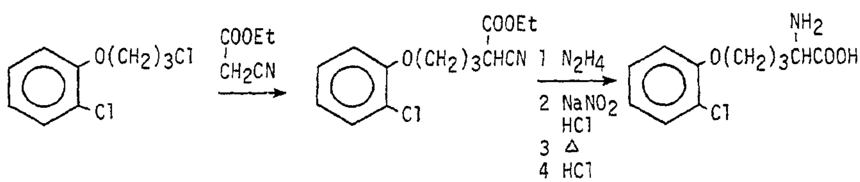


~41%

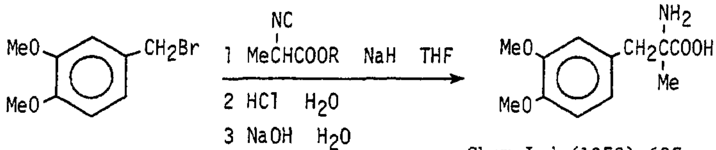
Org Synth (1963) Coll Vol 4 55

$$PrBr \dashrightarrow PrCH(COOEt)COOK \xrightarrow{1\ N_2H_4 \cdot H_2O;\ 2\ HNO_2;\ 3\ CCl_4\ (reflux);\ 4\ HCl\ \ H_2O} PrCH(NH_2)COOH$$

J Prakt Chem (1930) 125 211
JOC (1956) 21 1182



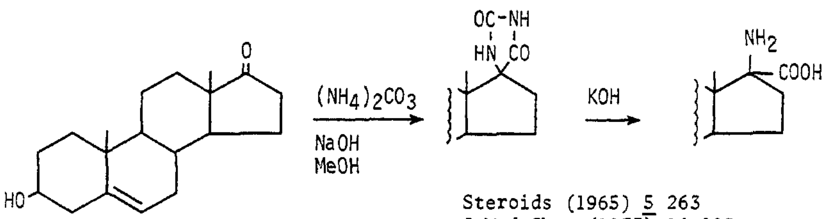
Can J Chem (1952) 30 592



Chem Ind (1972) 687

$$Et_2CO \xrightarrow[\text{2 } NH_3 \quad H_2O]{\text{1 NaCN} \quad NH_4Cl \quad H_2O} Et_2\underset{NH_2}{C}CN \xrightarrow{HCl \quad H_2O} Et_2\underset{NH_2}{C}COOH \qquad 39\text{-}43\%$$

Org Synth (1955) Coll Vol 3 66 84 88



Steroids (1965) 5 263
J Med Chem (1973) 16 823

$$BuCH_2COMe \xrightarrow[\text{2 } Et_2SO_4 \quad NaOH \quad H_2O]{\text{1 MeONO} \quad Et_2O} Bu\underset{NOEt}{C}COMe \xrightarrow[H_2O \quad \text{2 Zn} \quad HOAc]{\text{1 NaOCl} \quad \text{dioxane}} Bu\underset{NH_2}{C}HCOOH \qquad 45\%$$

JOC (1959) 24 1726

$$i\text{-}PrCN \xrightarrow[\text{2 MeOH} \quad \text{3 HCl} \quad H_2O]{\text{1 } Me_2\overset{OH}{C}CN \quad \text{diisopinocampheylborane}} i\text{-}Pr\underset{NH_2}{C}HCOOH$$

Tetr Lett (1972) 3145

$\text{i-PrCOCOOH} \dashrightarrow \text{i-PrC(=NNHPh)COOH} \xrightarrow[H_2O]{H_2\ \ Pd\text{-}C} \text{i-PrCH(NH}_2\text{)COOH}$ 87%

JOC (1973) 38 822

$PhCH_2COCOOH \xrightarrow{NH_2COOCH_2Ph} PhCH_2C(COOH)(NHCOOCH_2Ph)_2 \xrightarrow[EtOH]{H_2\ \ Pd} PhCH_2CH(NH_2)COOH$ 30%

JOC (1941) 6 878

$PhCOCOONa \xrightarrow[MeOH]{NH_4Br\ \ LiBH_3CN} PhCH(NH_2)COOH$ 49%

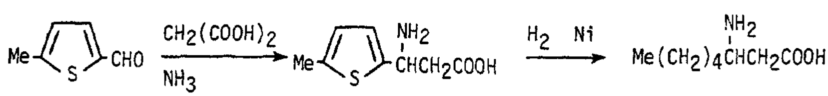
JACS (1971) 93 2897

$PhCH_2COCOOH \xrightarrow[NH_4Br\ \ MeOH]{NH_3\ \ PhCH(Me)NH_2\text{-}BH_3} PhCH_2CH(NH_2)COOH$ 66%

JOC (1972) 37 2347

$PhCHO \xrightarrow[EtOH]{CH_2(COOH)_2\ \ NH_4OAc} PhCH(NH_2)CH_2COOH$ 48%

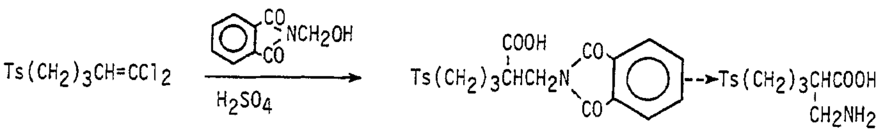
JACS (1936) 58 299
J Prakt Chem (1965) 30 18



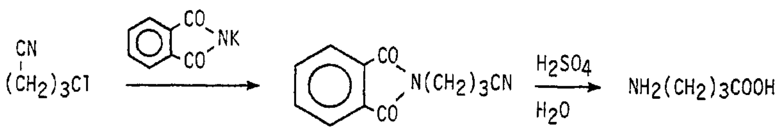
Tetrahedron (1962) 18 21
Zh Obshch Khim (1963) 33 2697
(Chem Abs 60 512)

$$PhCH{=}CHCOOH \xrightarrow{NH_2OH \quad EtOH} PhCH(NH_2)CH_2COOH \qquad 34\%$$

Org Synth (1955) Coll Vol 3 91

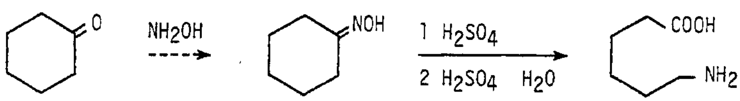


Ber (1973) 106 2513

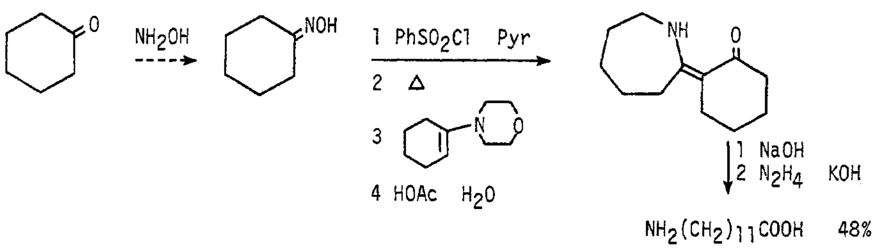


47-62%

Org Synth (1943) Coll Vol 2 25



Org Synth (1943) Coll Vol 2 76

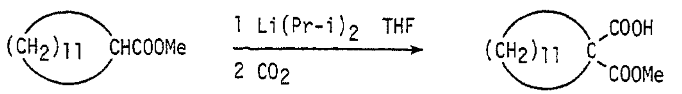


Ber (1967) 100 3039

		Section
Also via:	Aminoesters	351
	Amidoesters	344

Section 317 Carboxylic Acid — Ester

Carboxyesters



94%

Tetr Lett (1971) 3001

$$\begin{array}{c}\mathrm{Br}\\ |\\ \mathrm{Me_2CCOOEt}\end{array} \xrightarrow[\mathrm{THF}]{\mathrm{Zn}\quad \mathrm{CO_2}} \begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{Me_2CCOOEt}\end{array}$$

50%

Chem Ind (1966) 1457

$$\begin{array}{l}\mathrm{COOMe}\\ |\\ \mathrm{(CH_2)_9COOMe}\end{array} \xrightarrow{\mathrm{Ba(OH)_2}\quad \mathrm{MeOH}} \begin{array}{l}\mathrm{COOMe}\\ |\\ \mathrm{(CH_2)_9COOH}\end{array}$$

60-64%

Org Synth (1963) Coll Vol 4 635

$$\begin{array}{l}\mathrm{MeCHCOOEt}\\ \quad |\\ \mathrm{(CH_2)_4COOEt}\end{array} \xrightarrow{\mathrm{KOH}\quad \mathrm{EtOH}} \begin{array}{l}\mathrm{MeCHCOOEt}\\ \quad |\\ \mathrm{(CH_2)_4COOH}\end{array}$$

59%

JACS (1948) 70 3206 364

$$\begin{array}{l}\mathrm{COOEt}\\ |\\ \mathrm{(CH_2)_8COOEt}\end{array} \xrightarrow[\text{(vapor phase)}]{440^\circ} \begin{array}{l}\mathrm{COOEt}\\ |\\ \mathrm{(CH_2)_8COOH}\end{array}$$

69%

JOC (1964) 29 1252

$$\mathrm{PhCH_2COOH} \xrightarrow[\mathrm{Et_3N}]{\mathrm{PhCHO}\quad \mathrm{Ac_2O}} \begin{array}{l}\mathrm{PhCHOAc}\\ \quad |\\ \mathrm{PhCHCOOH}\end{array}$$

32%

Synthesis (1972) 263

$BuCH_2COOH \xrightarrow{Tl(OAc)_3}$ $BuCHCOOH$ with $BuCH_2COO$ on the CH

Tetr Lett (1970) 5285

Also via:

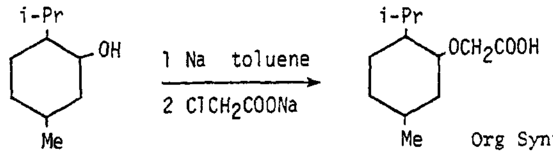
	Section
Diesters	357
Hydroxyacids	313

Section 318 Carboxylic Acid — Ether, Epoxide

Alkoxyacids and epoxyacids

$PhCHO \xrightarrow[MeOH]{CHCl_3 \quad KOH}$ $PhCHCOOH$ with OMe on the CH — 49%

JACS (1960) 82 4062
Chim Ther (1967) 2 9
(Chem Abs 67 99319)
Synthesis (1971) 131



78-84%

Org Synth (1955) Coll Vol 3 544
(1943) Coll Vol 2 260

$CH_2{=}CHCN \xrightarrow[2\ H_2SO_4 \quad H_2O]{1\ PrOH \quad MeONa}$ $PrOCH_2CH_2COOH$ — 50%

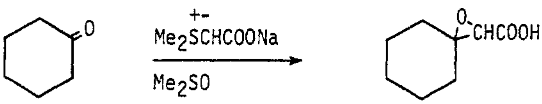
JACS (1949) 71 3480

$MeCH{=}C(Me)COOH \xrightarrow[2\ NaBH_4]{1\ Hg(OAc)_2 \quad MeOH}$ $MeCH(OMe)CH(Me)COOH$ — 72%

JCS Perkin I (1973) 109

$$\underset{\displaystyle OH}{PhCHCOOH} \xrightarrow{Me_2CO \quad H_2SO_4} \underset{\displaystyle \text{O O, CMe}_2}{PhCHCO} \xrightarrow[Et_2O]{t\text{-}BuMgCl} \underset{\displaystyle OCHMe_2}{PhCHCOOH} \qquad 44\%$$

JACS (1942) 64 1567



~60%

JOC (1970) 35 1600

$$MeCH{=}CHCOOH \xrightarrow[NaOH \quad H_2O]{H_2O_2 \quad Na_2WO_4} Me\overset{O}{CHCH}COOH \qquad 50\%$$

JOC (1959) 24 54
JCS (1962) 1116

Also via:

	Section
Alkoxyesters	358
Epoxyesters	358

Section 319 Carboxylic Acid — Halide

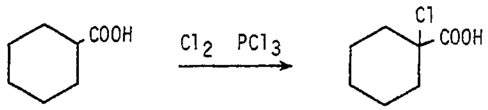
Haloacids, Halogenoacids

$$BuCH_2COOH \xrightarrow[\text{sulpholane}]{C_5H_{11}COCl \quad CuCl_2 \quad LiCl} \underset{\displaystyle Cl}{BuCHCOOH} \qquad <84\%$$

Chem Comm (1966) 544

$$i\text{-}PrCH_2CH_2COOH \xrightarrow{Br_2 \quad PCl_3} i\text{-}PrCH_2\underset{\displaystyle Br}{CH}COOH \qquad 63\text{-}66\%$$

Org Synth (1955) Coll Vol 3 523 848
(1943) Coll Vol 2 74



93%

JACS (1969) 91 7090

$$ClCH_2CH_2COCl \xrightarrow[HOAc]{NBS\quad HBr} ClCH_2\underset{Br}{C}HCOCl \dashrightarrow ClCH_2\underset{Br}{C}HCOOH$$

<70%

Tetr Lett (1970) 3431

$$C_{10}H_{21}CH_2COCl \xrightarrow{SOCl_2\quad h\nu} C_{10}H_{21}\underset{Cl}{C}HCOCl \dashrightarrow C_{10}H_{21}\underset{Cl}{C}HCOOH$$

~90%

JOC (1973) 38 3919

$$MeCH_2(CH_2)_3COOH \xrightarrow{(i\text{-}Pr)_2NCl\quad h\nu} Me\underset{Cl}{C}H(CH_2)_3COOH$$

JACS (1971) 93 438
Rec Trav Chim (1964) 83 891

$$i\text{-}PrCH(COOH)_2 \xrightarrow[2\ 125\text{-}130°]{1\ Br_2\quad Et_2O} i\text{-}Pr\underset{Br}{C}HCOOH$$

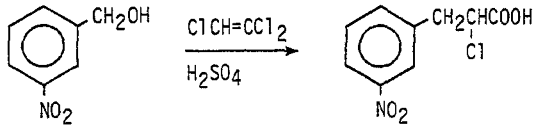
Org Synth (1943) Coll Vol 2 93

chloroacids JCS (1950) 2900

$$PhCHO \dashrightarrow Ph\underset{OH}{C}HCCl_3 \xrightarrow[H_2O]{KOH\quad oleic\ acid} Ph\underset{Cl}{C}HCOOH$$

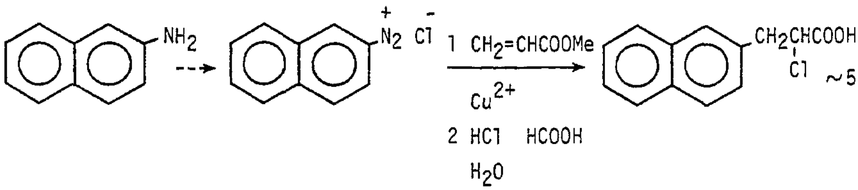
50%

Synthesis (1971) 131



82%

Ber (1970) 103 3850



~51%

Proc Chem Soc (1962) 117

Bromoacids Org Synth (1971) 51 1

$$C_5H_{11}\underset{\mathrm{F}}{\mathrm{CH}}CH_2Br \xrightarrow[\mathrm{DMF}]{\mathrm{NaOAc\ \ NaI}} C_5H_{11}\underset{\mathrm{F}}{\mathrm{CH}}CH_2OAc \xrightarrow[\mathrm{HOAc}]{HNO_3} C_5H_{11}\underset{\mathrm{F}}{\mathrm{CH}}COOH \qquad \sim 55\%$$

Org Synth (1966) 46 37

$$Me_2CO \xrightarrow[\overset{+}{\mathrm{Me_4N}}\ \overset{-}{\mathrm{Br}}]{CHCl_3\ \ \overset{\mathrm{O}}{CH_2\text{-}CH_2}} Me_2\underset{\mathrm{Cl}}{\mathrm{C}}COOCH_2CH_2Cl \dashrightarrow Me_2\underset{\mathrm{Cl}}{\mathrm{C}}COOH \qquad <24\%$$

Ber (1968) 101 1299

$$C_5H_{11}CH{=}CH_2 \xrightarrow[\text{2 HCl}\ \ H_2O]{\text{1 NOCl}\ \ \text{HCl}\ \ Et_2O} C_5H_{11}\underset{\mathrm{Cl}}{\mathrm{CH}}COOH$$

Zh Obshch Khim (1964) 34 1227
(Chem Abs 61 2967)

$$MeCH{=}\underset{\mathrm{Me}}{\mathrm{C}}COOH \xrightarrow[CHCl_3]{\mathrm{HI\ \ Ag}} Me\underset{\mathrm{I}}{\mathrm{CH}}\underset{\mathrm{Me}}{\mathrm{CH}}COOH$$

JACS (1929) 51 2528

Also via: Haloesters (Section 359)

Section 320 Carboxylic Acid — Ketone

$$PhCOCl \xrightarrow{CuCN} PhCOCN \xrightarrow{HCl \quad H_2O} PhCOCOOH \qquad \sim 45\%$$

Org Synth (1955) Coll Vol 3 114
Can J Chem (1971) 49 919

$$PhCHO \xrightarrow[NaOAc]{\overset{NHAc}{|}\atop CH_2COOH \quad Ac_2O} PhCH{=}\underset{N\,\,\,O\atop \diagdown CMe \diagup}{C{-}CO} \xrightarrow[2\ HCl \quad H_2O]{1\ H_2O \quad Me_2CO} PhCH_2COCOOH \qquad \sim 65\%$$

Org Synth (1943) Coll Vol 2 519 1
Org React (1942) 1 210

$$(PhCH_2)_2CHCHO \dashrightarrow (PhCH_2)_2\underset{OH}{CHCHCN} \xrightarrow[2\ CrO_3 \quad HOAc]{1\ H_2SO_4 \quad t\text{-}BuOH} (PhCH_2)_2CHCOCOOH \qquad 77\%$$

Synthesis (1971) 538

$$PrCHO \xrightarrow[Et_2NH \quad EtOH]{CH_3COCOOH} PrCH{=}CHCOCOOH \xrightarrow[H_2O]{KBH_4 \quad KHCO_3} PrCH_2CH_2COCOOH$$

Bull Soc Chim Fr (1966) 1435

$$C_5H_{11}CHO \dashrightarrow C_5H_{11}CH{=}C(COOEt)_2 \xrightarrow[2\ KOH \quad EtOH;\ 3\ 180\text{-}200°]{1\ H_2O_2 \quad Na_2WO_4 \quad H_2O} C_5H_{11}CH_2COCOOH$$

JOC (1964) 29 2080

$$PhCOOEt \xrightarrow[\text{2 HCl} \quad H_2O \quad Me_2SO]{\text{1 } Me_2SO \quad t\text{-BuOK}} PhCOCH(OH)SMe \xrightarrow[CHCl_3]{Cu(OAc)_2 \cdot H_2O} PhCOCOOH \qquad 64\text{-}73\%$$

JACS (1966) 88 5498

$$EtCH_2COOEt \xrightarrow[Et_2O]{(COOEt)_2 \quad EtONa} EtCH(COCOOEt)COOEt \xrightarrow[H_2O]{H_2SO_4} EtCH_2COCOOH$$

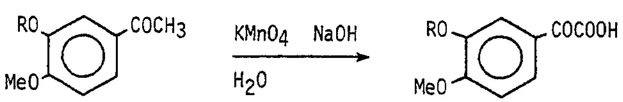
Annalen (1943) 555 41

$$EtCH(Me)Br \dashrightarrow EtCH(Me)Li \xrightarrow[\text{2 } CO_2 \quad \text{3 } (COOH)_2 \quad H_2O]{\text{1 } t\text{-}BuCH_2C(NC)Me_2 \quad Et_2O} EtCH(Me)COCOOH \qquad 80\%$$

JACS (1969) 91 7778
(1970) 92 6675

$$EtBr \dashrightarrow EtMgBr \xrightarrow{COOEt\text{-}CONEt_2} EtCOCONEt_2 \xrightarrow{NaOH} EtCOCOOH \qquad \sim 55\%$$

Compt Rend (1927) 184 825



Monatsh (1952) 83 883

$$Me_2CO \dashrightarrow Me_2C{=}C(CN)COOEt \xrightarrow[\substack{H_2O \quad EtOH \\ \text{2 KOH} \quad EtOH \\ \text{3 HCl} \quad H_2O}]{\text{1 } H_2O_2 \quad Na_2WO_4} Me_2CHCOCOOH$$

JOC (1963) 28 3088

PhCH(OMe)COOH $\xrightarrow{Br_2 \quad CHCl_3}$ PhCOCOOH 90%

Ber (1967) 100 3777

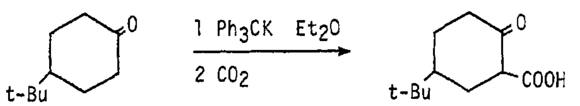
i-$PrCH_2CH(NH_2)COOH$ $\xrightarrow[2\ NaOH\quad H_2O]{1\ (CF_3CO)_2O}$ i-$PrCH_2COCOOH$

Annalen (1962) 658 128

$Me_2CHCOOH$ $\xrightarrow[2\ t\text{-}BuCOOMe]{1\ LiN(Pr\text{-}i)_2\quad THF}$ $Me_2C(COt\text{-}Bu)COOH$

3 Me_3SiCl
4 MeOH

JACS (1971) 93 6321



89%

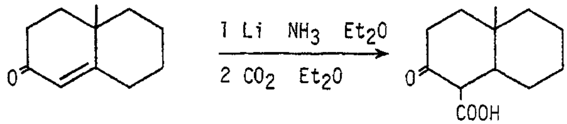
Coll Czech (1961) 26 847

$PhCOCH_3$ $\xrightarrow[DMF]{CO_2\quad PhOK}$ $PhCOCH_2COOH$ 60%

Chem Comm (1966) 618
JOC (1973) 38 4086

$PhCOCH_3$ $\xrightarrow{(MeOCOO)_2Mg\quad DMF}$ $PhCOCH_2COOH$ 68%

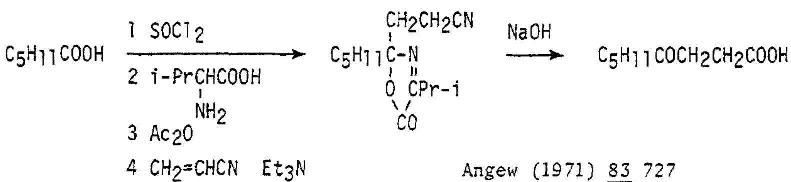
JACS (1959) 81 2598



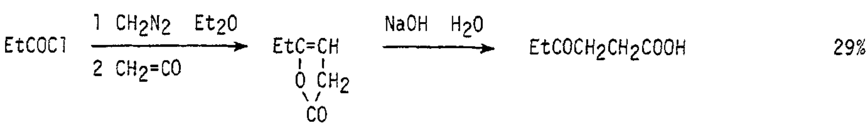
JACS (1965) 87 275
JOC (1968) 33 712

$$C_{10}H_{21}COCl \xrightarrow{NaC(COOCH_2Ph)_2 \atop CH_2COOCH_2Ph} C_{10}H_{21}COC(COOCH_2Ph)_2 \atop \quad\quad CH_2COOCH_2Ph \xrightarrow[2\ 170°]{1\ H_2\ Pd\text{-}C} C_{10}H_{21}COCH_2CH_2COOH \quad 66\%$$

JCS (1950) 325



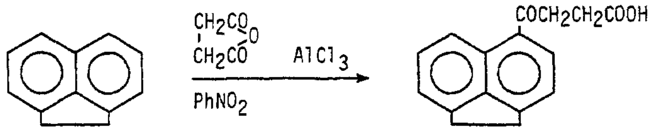
Angew (1971) 83 727
(Internat Ed 10 655)



Annalen (1964) 678 113

$$\begin{matrix} CH_2COCl \\ CH_2COCl \end{matrix} \xrightarrow[2\ H_2SO_4\quad H_2O]{1\ Et_3Al_2Cl_3} EtCOCH_2CH_2COOH \quad 90\%$$

Angew (1965) 77 810
(Internat Ed 4 785)



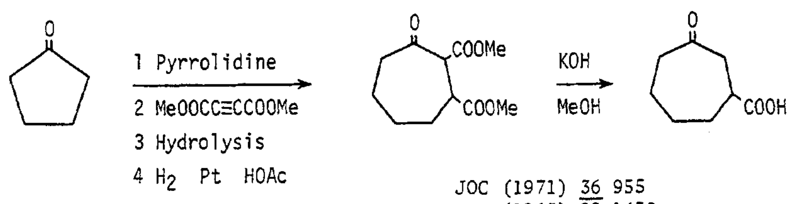
Org Synth (1955) Coll Vol 3 6
(1943) Coll Vol 2 81
(1932) Coll Vol 1 517

$$C_6H_{13}CHO \xrightarrow[\text{t-BuOK}]{CH_2COOEt \atop |\atop CH_2COOEt} C_6H_{13}CH{=}\underset{\textstyle CH_2COOEt}{\underset{|}{C}}COOEt \xrightarrow[\text{2 } Br_2 \quad CCl_4 \quad \text{3 NaOH} \quad H_2O]{\text{1 NaOH} \quad H_2O} C_6H_{13}COCH_2CH_2COOH \qquad <66\%$$

JOC (1966) 31 616
Org Synth (1963) Coll Vol 4 430

$$PhI \xrightarrow[HCl \quad H_2O \quad 30 \text{ atmos}]{HC{\equiv}CH \quad Ni(CO)_4 \quad CO} PhCOCH_2CH_2COOH$$

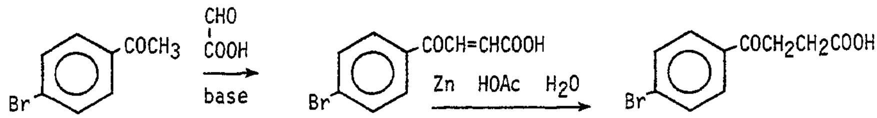
Tetr Lett (1964) 2777



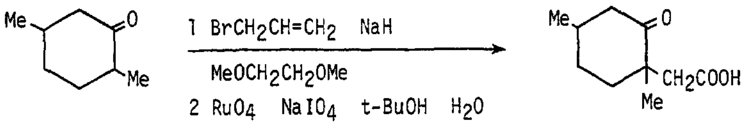
JOC (1971) 36 955
(1963) 28 1459

$$PhCOCH_3 \xrightarrow[\text{2 } BrCH_2COOH \quad Et_2O]{\text{1 } BrCH_2COOLi \quad LiNH_2 \quad NH_3} PhCOCH_2CH_2COOH \qquad 61\%$$

Chem Ind (1959) 255



JOC (1973) 38 4044
(1958) 23 1832



Tetr Lett (1972) 1853

$PhCOCH_2(Ph) \xrightarrow[Ac_2O]{HCHO \quad Me_2NH \cdot HCl} PhCOCH(Ph)CH_2NMe_2 \xrightarrow[2\ KCN \quad 3\ HCl \quad H_2O]{1\ MeI} PhCOCH(Ph)CH_2COOH$ 68%

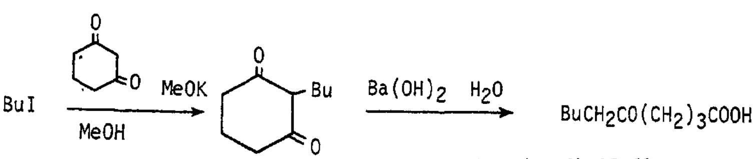
JOC (1973) 38 4044

$t\text{-}BuCOCH{=}CMe_2 \xrightarrow[2\ KOH]{1\ KCN \quad EtOH \quad H_2O} t\text{-}BuCOCH_2CMe_2(COOH)$ 8-12%

Annalen (1971) 751 168
JOC (1963) 28 1459

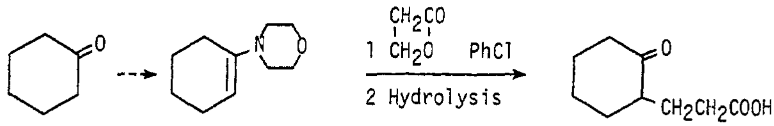
$PhCOCH_2CH_2\underset{O\text{———}CO}{CHCH_2CH_2} \xrightarrow[2\ CrO_3 \quad Pyr]{1\ NaOH \quad H_2O} PhCOCH_2CH_2COCH_2CH_2COOH$ >45%

JACS (1963) 85 2937



23%

Ber (1952) 85 61
JCS (1957) 2202
Newer Meth Prep Org Chem (1963) 2 51

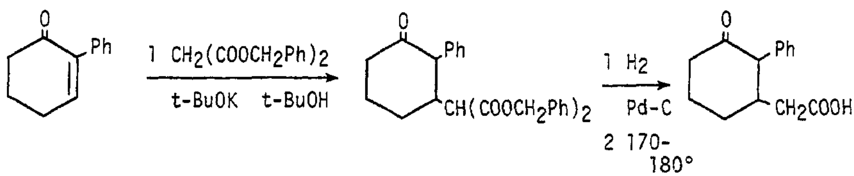


81%

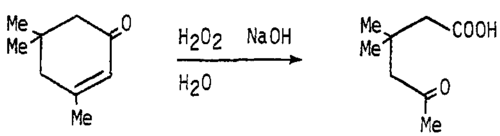
Acta Chem Scand (1964) 18 2201

$$PhCOCH_2Pr\text{-}i \xrightarrow[\text{MeOH dioxane; 2 KOH } H_2O]{1\ CH_2{=}CHCN\ \ KOH} PhCOCH(CH_2CH_2COOH)Pr\text{-}i$$

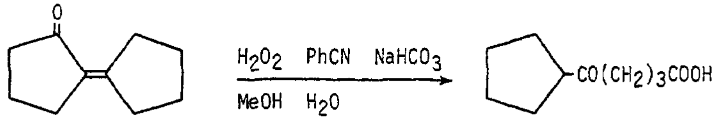
JCS (1948) 1741
Org React (1959) 10 179



Org React (1959) 10 179

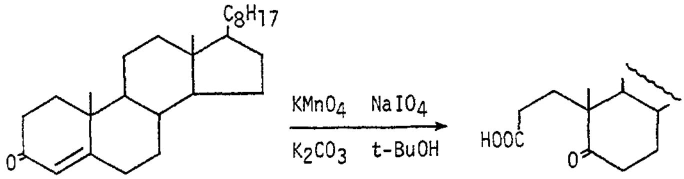


JOC (1970) 35 1275



30%

Bull Soc Chim Fr (1969) 2871

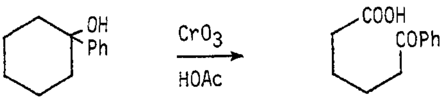


79-88%

Can J Chem (1961) 39 599

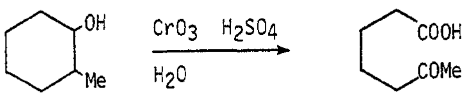
O_3 Can J Chem (1962) 40 2153

RuO_2, $NaIO_4$ JOC (1969) 34 112



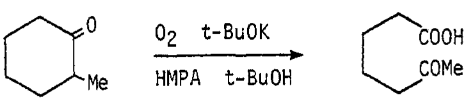
81%

JACS (1948) 70 3352

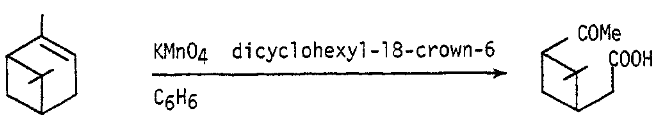


46-55%

Org Synth (1963) Coll Vol 4 19

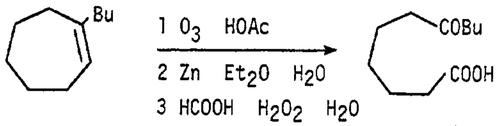


Bull Soc Chim Fr (1967) 3742



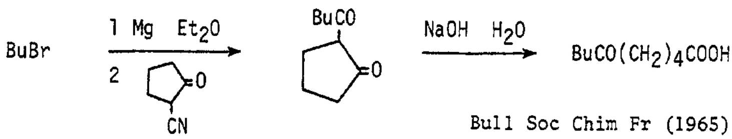
90%

JACS (1972) 94 4024

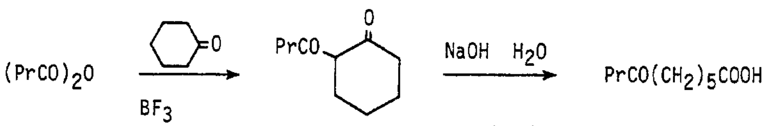


63%

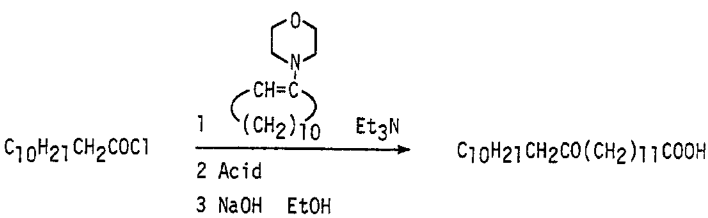
Can J Chem (1955) 33 1720



Bull Soc Chim Fr (1965) 3041

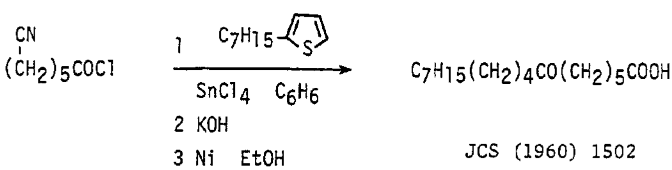


JACS (1953) 75 5030



71%

Ber (1967) 100 4010 4017



JCS (1960) 1502

Also via:

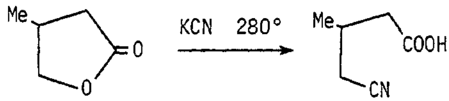
	Section
Ketoesters	360
Ketoamides	347

Section 321 Carboxylic Acid — Nitrile

Cyanoacids

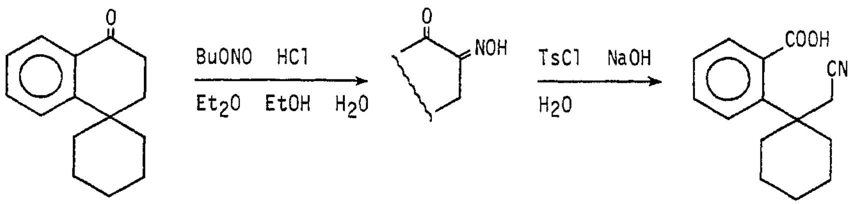
$$HOOC(CH_2)_7COOH \xrightarrow[160\text{-}360°]{(NH_2)_2CO} HOOC(CH_2)_7CN \qquad <49\%$$

JACS (1951) 73 343

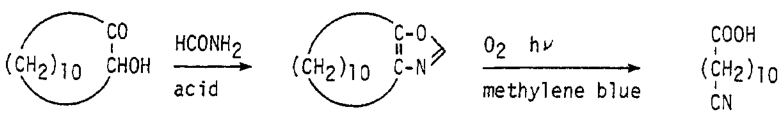


~94%

Bull Soc Chim Fr (1954) 88
Org Synth (1955) Coll Vol 3 174

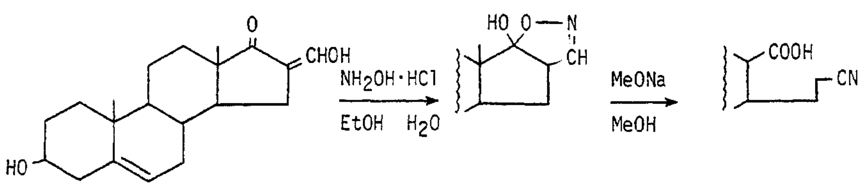


JOC (1941) 6 105
Tetr Lett (1968) 1127



~80%

JACS (1968) 90 2440



Ber (1961) 94 2897

Also via: Cyanoesters (Section 361)

Section 322 Carboxylic Acid — Olefin

Review: Recent Developments in the Synthesis of Fatty Acids

Chem Rev (1957) 57 191

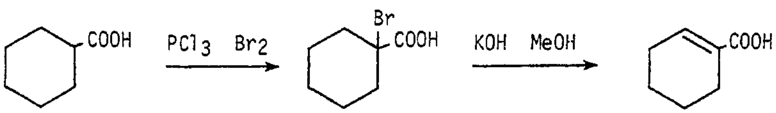
$$C_6H_{13}C{\equiv}CH \xrightarrow[\text{cyclohexane}]{Ni(CO)_4 \quad HOAc} C_6H_{13}C(COOH){=}CH_2$$

Chim Ind (Milan) (1964) 46 1063
Bull Chem Soc Jap (1968) 41 390
Annalen (1953) 582 1
JCS (1951) 48

$$BuC{\equiv}CH \xrightarrow[\substack{2\ MeLi \quad Et_2O \\ 3\ CO_2}]{1\ (i\text{-}Bu)_2AlH \quad heptane} BuCH{=}CHCOOH \qquad 78\%$$

trans

JACS (1967) 89 2754
J Organometallic Chem (1968) 11 P7



58%

J Med Chem (1970) 13 317

$$C_9H_{19}CH_2CH_2COONa \xrightarrow[2\ DDQ \quad C_6H_6]{1\ (i\text{-}Pr)_2NLi \quad HMPA \quad THF} C_9H_{19}CH{=}CHCOOH \qquad \sim 30\%$$

Chem Comm (1973) 94

$C_{16}H_{33}CH_2COOH \xrightarrow[2\ CH_2N_2]{1\ SOCl_2} C_{16}H_{33}CH_2COCHN_2 \xrightarrow[2\ KOH]{1\ Br_2\ \ CCl_4} C_{16}H_{33}CH{=}CHCOOH$ 35%

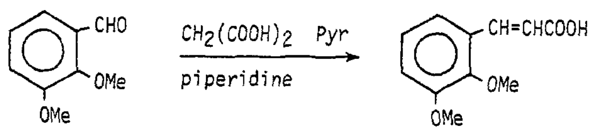
Chem Phys Lipids (1968) 2 213

$C_7H_{15}CH_2COOH \xrightarrow[2\ HCHO]{1\ (i\text{-}Pr)_2NLi\ \ HMPA\ \ THF} C_7H_{15}C({=}CH_2)COOH$ 90%

JOC (1972) 37 1256

$PhCHO \xrightarrow[EtCOONa]{(MeCH_2CO)_2O} PhCH{=}C(Me)COOH$ 60-70%

Org React (1942) 1 210

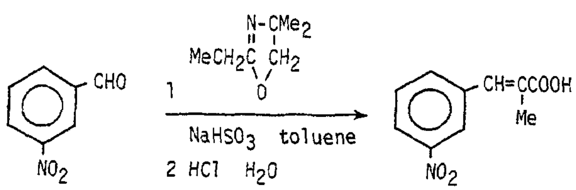


87-98%

Org Synth (1963) Coll Vol 4 327
(1955) Coll Vol 3 425
Org React (1942) 1 210

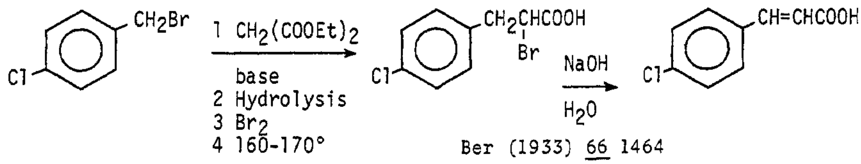
$t\text{-}BuCHO \xrightarrow[2\ Hydrolysis\ \ 3\ \Delta]{1\ CH_2(COOEt)_2\ \ ZnCl_2\ \ Ac_2O} t\text{-}BuCH{=}CHCOOH$

JOC (1965) 30 917
JACS (1938) 60 2901

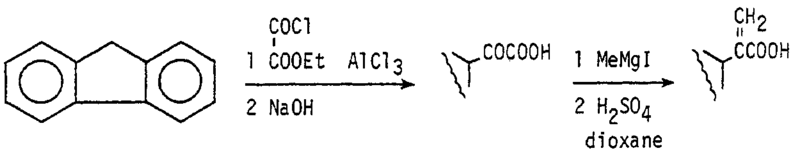


90%

JOC (1962) 27 4418



Ber (1933) 66 1464



76%

J Med Chem (1972) 15 1029

$i\text{-PrCH}_2\text{COCH}_3 \dashrightarrow i\text{-PrCH(Br)COCH}_2\text{Br} \xrightarrow{\text{KHCO}_3\ \ \text{H}_2\text{O}} i\text{-PrCH=CHCOOH}$

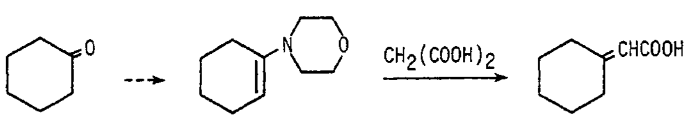
Acta Chem Scand (1965) 19 383
(1963) 17 2766
Chem Comm (1968) 306

$\text{PhC(Me)O} \xrightarrow[\text{BCl}_3]{\text{CH}_2\text{=CO}} \text{PhC(Me)=CHCOCl} \xrightarrow{\text{H}_2\text{O}\ \ \text{EtOH}} \text{PhC(Me)=CHCOOH}$ 47%

Ber (1970) 103 2003

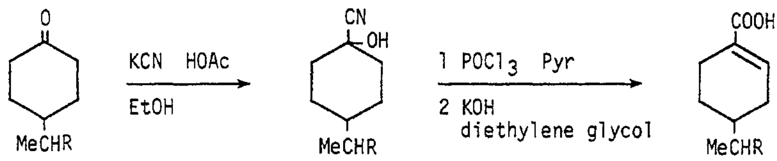
$\text{Pr}_2\text{CO} \xrightarrow[\text{CCl}_4\ \ \text{Pyr}\ \ \text{THF}]{\text{CH}_2(\text{COOEt})_2\ \ \text{TiCl}_4} \text{Pr}_2\text{C=C(COOEt)}_2 \dashrightarrow \text{Pr}_2\text{C=CHCOOH}$ <42%

Tetrahedron (1973) 29 635



<60%

JOC (1973) 38 399



Tetrahedron (1968) <u>24</u> 3127
JOC (1972) <u>37</u> 2201

$HOCH_2CH_2CH{=}CH_2 \xrightarrow[\text{dibenzoyl peroxide}]{CCl_4} HOCH_2CH_2CH(Cl)CH_2CCl_3 \xrightarrow[\text{2 Hydrolysis}]{\text{1 EtOK}} HOCH_2CH_2CH{=}CHCOOH$

Coll Czech (1966) <u>31</u> 3765

$PhC{\equiv}CCOOH \xrightarrow{N_2H_4 \quad O_2} PhCH{=}CHCOOH$

Tetr Lett (1961) 353

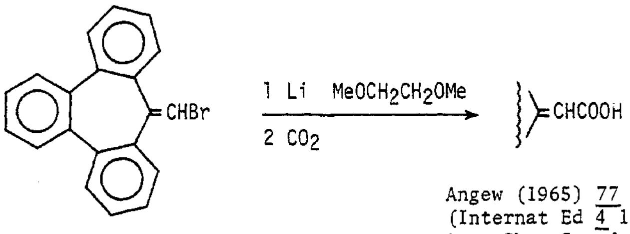
Catalytic and chemical reduction of acetylenic acids
Chem Rev (1957) <u>57</u> 191

$PhC{\equiv}CCOOH \xrightarrow{Me_2CuLi \quad Et_2O} PhC(Me){=}CHCOOH$ 93%

JACS (1969) <u>91</u> 6186

$MeCOCH(Ph)COOEt \xrightarrow{N_2H_4} MeC{-}CHPh$ (diaziridinone ring: N, CO, NH) $\xrightarrow[\text{2 NaOH} \quad H_2O]{\text{1 } Cl_2 \quad CH_2Cl_2} MeCH{=}C(Ph)COOH$ 31%

JACS (1958) <u>80</u> 601
JOC (1969) <u>34</u> 1717
(1966) <u>31</u> 2867



60%

Angew (1965) 77 173
(Internat Ed 4 156)
Acta Chem Scand (1959) 13 610

$Me_2C{=}CHCOMe \xrightarrow[H_2O]{KOCl \quad dioxane} Me_2C{=}CHCOOH$ 49-53%

Org Synth (1955) Coll Vol 3 302

$BuC{\equiv}CH \xrightarrow{HOAc \quad di\text{-}t\text{-}butyl\ peroxide} BuCH{=}CHCH_2COOH$ 24%

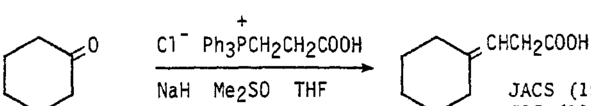
Can J Chem (1966) 44 2241

$C_6H_{13}C{\equiv}CH \xrightarrow[butyl\ peroxide]{HC(COOEt)_3 \quad di\text{-}t\text{-}} C_6H_{13}CH{=}CHC(COOEt)_3 \xrightarrow[EtOH \quad 2\ 160°]{1\ NaOH} C_6H_{13}CH{=}CHCH_2COOH$

Synthesis (1969) 76

$PhCHO \xrightarrow[2\ \Delta]{1\ \begin{matrix} CH_2COONa \\ CH_2COONa \end{matrix} \quad Ac_2O} PhCH{=}CHCH_2COOH$

Org React (1942) 1 210

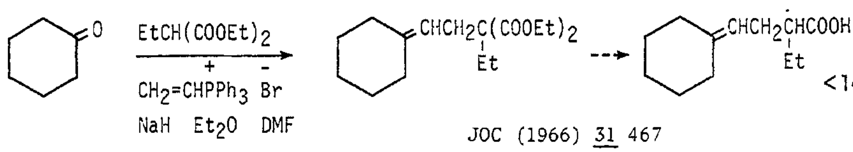


66%

JACS (1964) 86 1884
JOC (1962) 27 3404

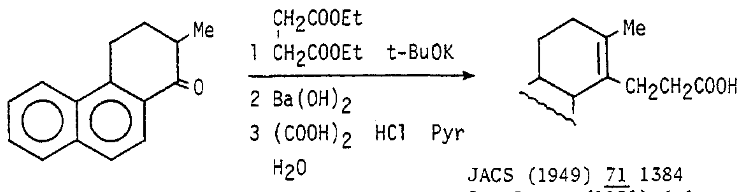
$C_7H_{15}CH_2CH{=}CHCOOH \xrightarrow{h\nu \quad hexane} C_7H_{15}CH{=}CHCH_2COOH$ 95%

JOC (1968) 33 1671



<14%

JOC (1966) 31 467



70%

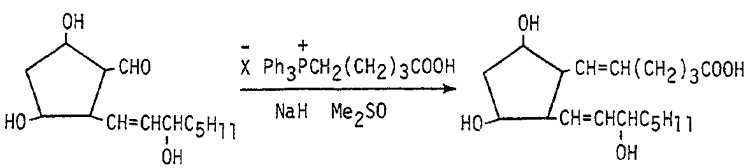
JACS (1949) 71 1384
Org React (1951) 6 1

$BuCH_2CH{=}CH_2 \xrightarrow[\text{2 Hydrolysis}]{\text{1 } CH_2(COOEt)_2 \quad Mn(OAc)_3 \quad Cu(OAc)_2 \quad HOAc} BuCH{=}CHCH_2CH_2COOH$

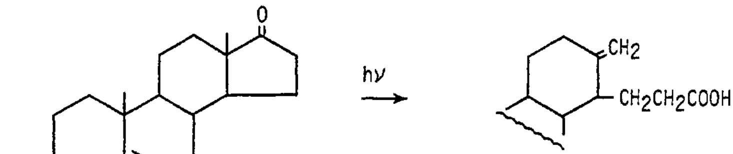
Chem Comm (1973) 694
Synthesis (1970) 99

$Me_2C(Br)COOCH_2CH{=}CH_2 \xrightarrow{Zn \quad toluene} Me_2C(COOH)CH_2CH{=}CH_2$ 100%

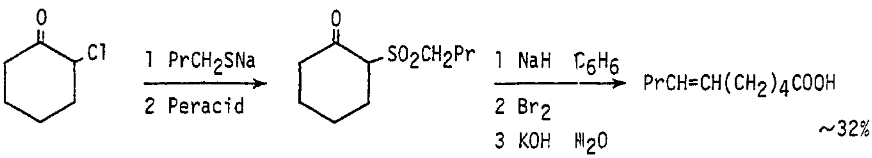
Chem Comm (1973) 117



Tetr Lett (1970) 311
JACS (1971) 93 1490



Tetr Lett (1963) 1659
Angew (1965) 77 229
(Internat Ed 4 216)



Bull Soc Chim Fr (1964) 723

		Section
Also via:	Olefinic esters	362
	Olefinic nitriles	376
	Olefinic amides	349
	Hydroxy acids	313
	Acetylenic acids	301

Section 323 Alcohol — Alcohol

$$C_{10}H_{21}COCl \xrightarrow[\text{2 HOAc}]{\text{1 } CH_2N_2 \quad Et_2O} C_{10}H_{21}COCH_2OAc \xrightarrow[\text{i-PrOH}]{Al(OPr\text{-}i)_3} C_{10}H_{21}CH(OH)CH_2OH \qquad 85\%$$

Org React (1954) 8 218 228

$$PhCOOH \xrightarrow[MeOCH_2CH_2OMe]{MeLi \quad TiCl_3} PhC(Me)(OH)-C(Me)(OH)Ph$$

Chem Comm (1970) 451

$$PhCHO \xrightarrow[HMPA]{Mg \quad Me_3SiCl} PhCH(OH){-}CH(OH)Ph \qquad > 90\%$$

Tetr Lett (1972) 75

$$PhCOOEt \xrightarrow[t\text{-}BuOK]{Me_2SO} PhCOCH_2SOMe \xrightarrow[2\ NaBH_4 \quad NaOH \quad EtOH \quad H_2O]{1\ HCl \quad Me_2SO \quad H_2O} PhCH(OH)CH_2OH \qquad 75\%$$

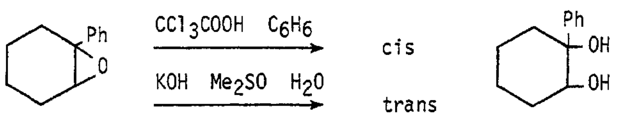
JACS (1966) 88 5498

$$\underset{Me}{\overset{COOMe}{CH=C}}(CH_2)_2CH=\underset{Me}{C}(CH_2)_2\overset{O}{CH{-}CMe_2} \xrightarrow[H_2O]{HClO_4 \quad THF} \underset{Me}{\overset{COOMe}{CH=C}}(CH_2)_2CH=\underset{Me}{C}(CH_2)_2\underset{OH}{CH}{-}\underset{OH}{CMe_2} \qquad 78\%$$

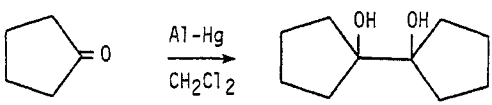
JACS (1972) 94 5379

HIO_4 JACS (1949) 71 3938

2,4,6-Trinitrobenzenesulfonic acid, Me_2SO Tetr Lett (1971) 411



Tetr Lett (1965) 3421
JACS (1973) 95 2361



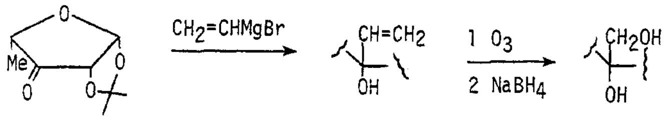
Tetr Lett (1970) 4271

Na Bull Soc Chim Fr (1967) 2011

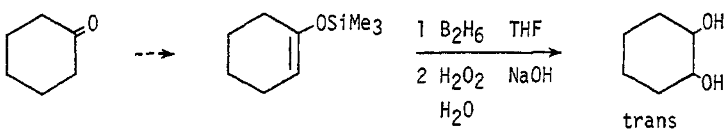
Mg, MgI_2 JACS (1942) 64 30

Bu_3SnH $h\nu$ JCS C (1971) 1241

Electrolysis Synthesis (1971) 285



JACS (1965) 87 654
Can J Chem (1967) 45 2921



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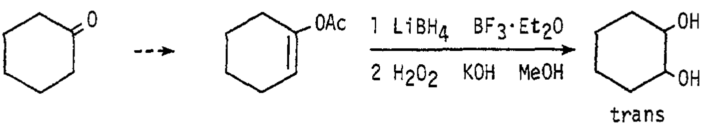
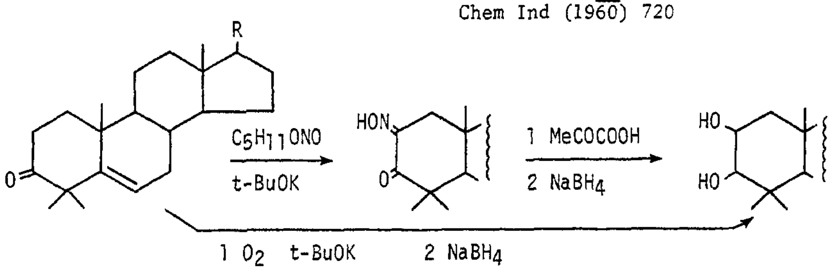
Tetr Lett (1972) 2845



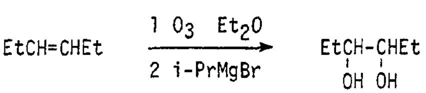
<61%

JACS (1969) 91 2632
Chem Ind (1960) 720



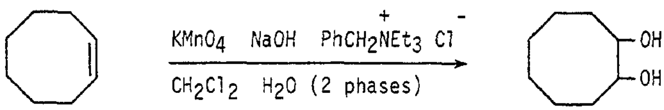
Annalen (1972) 758 89

Review: Hydroxylation Methods — Advances in Org Chem (1960) 1 103
Epoxidation and Hydroxylation of Ethylenic Compounds with Organic Peracids — Org React (1953) 7 378



46%

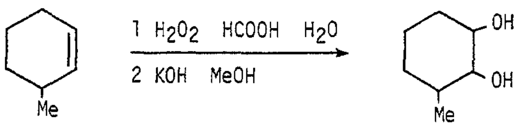
JOC (1963) 28 1159



50%

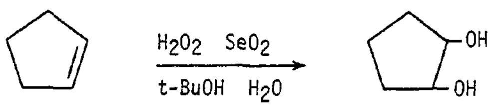
Tetr Lett (1972) 4907

$KMnO_4$, $MgSO_4$ (neutral conditions)	J Heterocyclic Chem (1972) 9 979
K_2MnO_4, NaOH	JCS (1956) 2452



Tetrahedron (1968) 24 5701
Org React (1953) 7 378

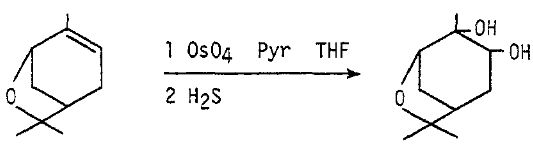
o-Sulfoperbenzoic acid	Tetr Lett (1971) 691
Disuccinoyl peroxide, detergent	Synthesis (1973) 156



trans 40%

Helv (1953) 36 268

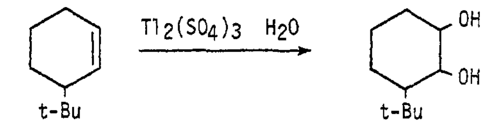
H_2O_2, H_2WO_4	JOC (1957) 22 1682
H_2O_2, V_2O_5	JACS (1937) 59 2342



cis 43%

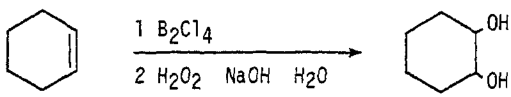
Tetrahedron (1971) 27 753
JOC (1960) 25 257

OsO_4 (catalytic quantity), $KClO_4$	JACS (1968) 90 5336
OsO_4 (" "), H_2O_2	JACS (1937) 59 2345



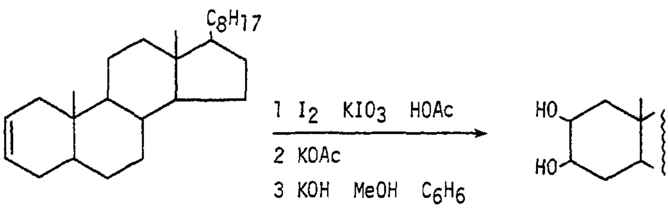
cis + trans <67%

Can J Chem (1971) 49 2586
Tetrahedron (1964) 20 1017



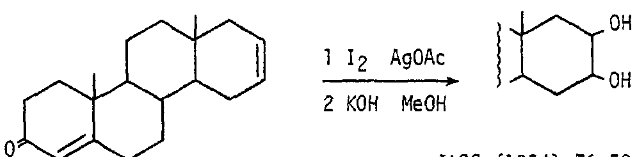
cis

JACS (1967) 89 4217



70%

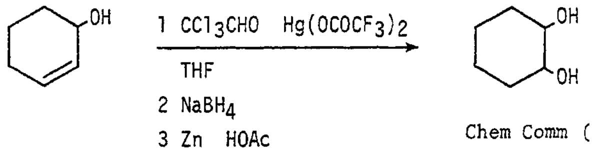
Tetr Lett (1973) 4485



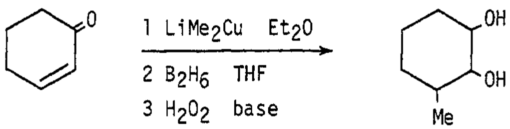
cis 67%

JACS (1954) 76 5014

I_2, silver benzoate	JCS C (1966) 1327 Org React (1957) 9 332 JOC (1942) 7 227
I_2, silver trifluoroacetate	Chem Comm (1966) 202
$I(OCOCF_3)_3$	Angew (1973) 85 175 (Internat Ed) 12 163



Chem Comm (1972) 1196



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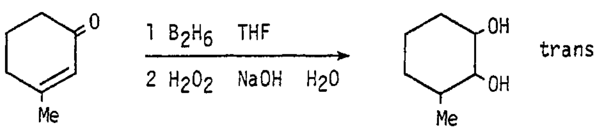
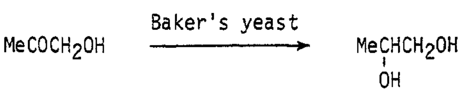
Tetr Lett (1972) 4031

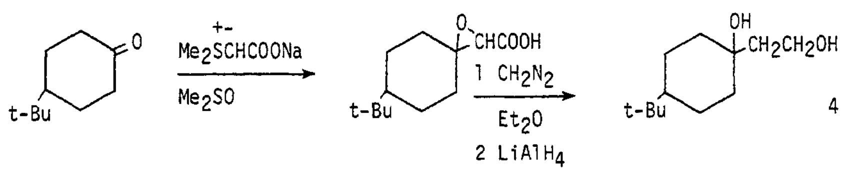


Tetrahedron (1968) 24 5701



49-58%

Org Synth (1943) Coll Vol 2 545



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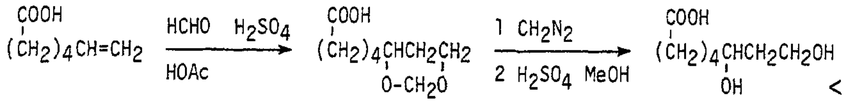
JOC (1970) 35 1600



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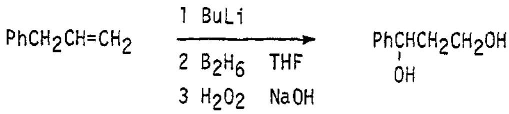
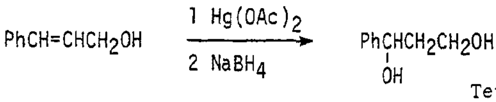
JCS (1956) 3074

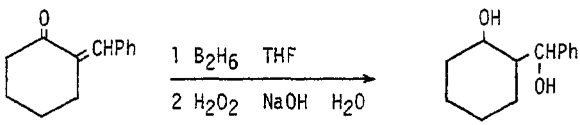


65%

JACS (1971) 93 6313

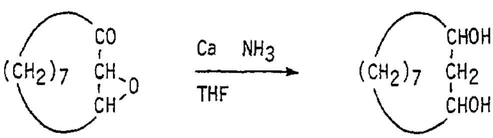


Tetr Lett (1968) 5105
Chem Comm (1968) 1073
(1967) 1283



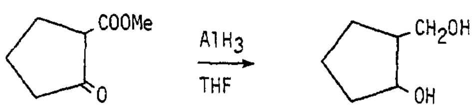
72%

JCS Perkin I (1973) 1707



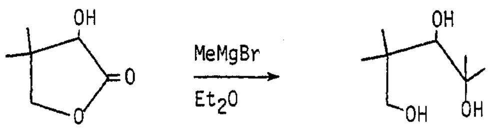
79%

JCS Perkin I (1972) 1509

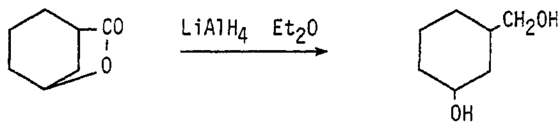


82%

JACS (1968) 90 2927

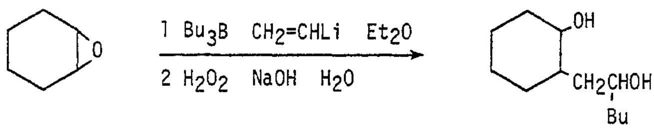


JACS (1940) 62 1779



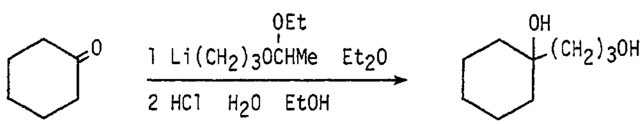
80%

JACS (1952) 74 5908 4336



77%

Tetr Lett (1973) 4527

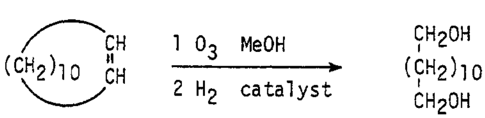


86%

JOC (1972) 37 1947

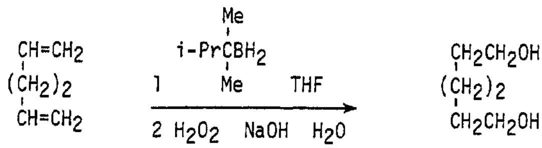
$$Me_2\overset{CH_3}{\overset{|}{C}}CH_2\underset{\underset{Me}{|}}{C}{=}CH_2 \xrightarrow[\text{2 160°; 3 } H_2O_2\ \ NaOH\ \ H_2O]{\text{1 } NaBH_4\ \ BF_3\ \ \text{diglyme}} Me_2\overset{CH_2OH}{\overset{|}{C}}CH_2\underset{\underset{Me}{|}}{C}HCH_2OH$$

JACS (1966) 88 1443



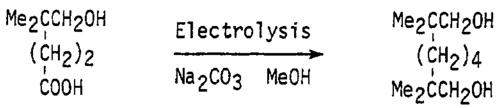
85%

Tetr Lett (1971) 3587
JACS (1957) 79 3165



~90%

JACS (1972) 94 3567
(1962) 84 190



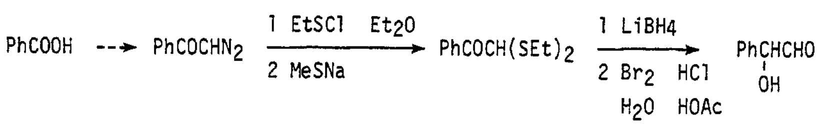
52%

Bull Soc Chim Fr (1970) 183

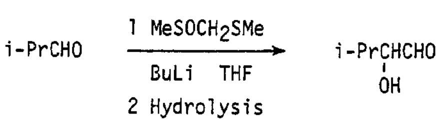
Also via:

	Section
Hydroxyesters	327
Diesters	357

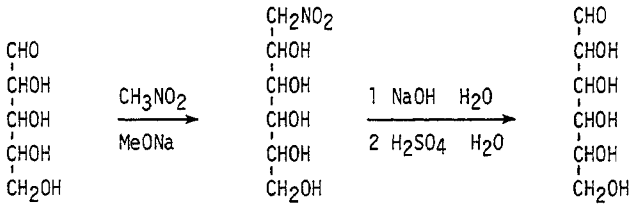
Section 324 Alcohol — Aldehyde



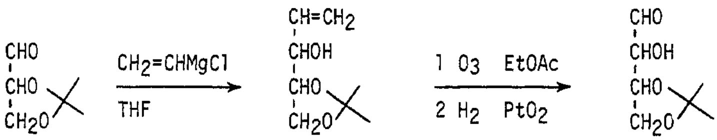
Ber (1958) 91 1043
(1957) 90 1230



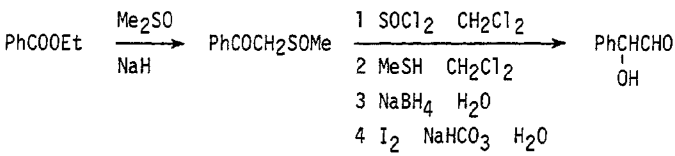
Tetr Lett (1973) 4707



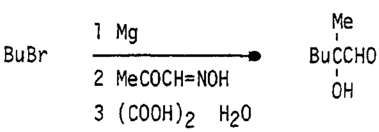
JOC (1964) 29 1790



Can J Chem (1967) 45 2921

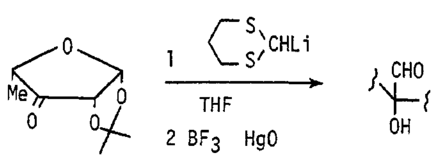


JOC (1969) 34 3618
JACS (1966) 88 5498



15%

Annales de Chimie (1939) 11 453



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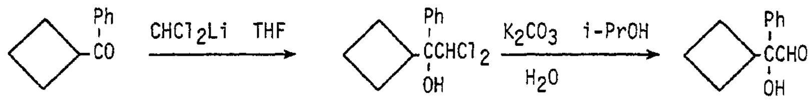
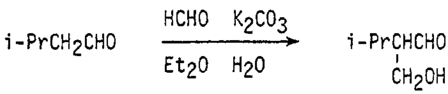
Ber (1972) 105 1978
Angew (1965) 77 1134
(Internat Ed 4 1075)
Annalen (1972) 758 89



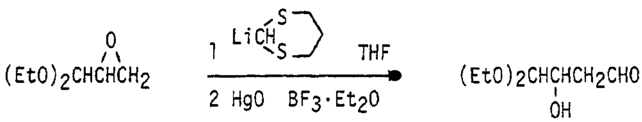
52%

JOC (1972) 37 1248
Ber (1973) 106 2620

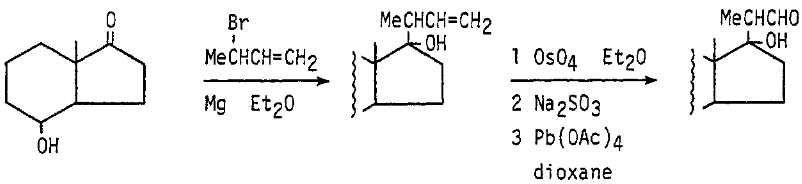


52%

JACS (1948) 70 1694
Org React (1968) 16 1

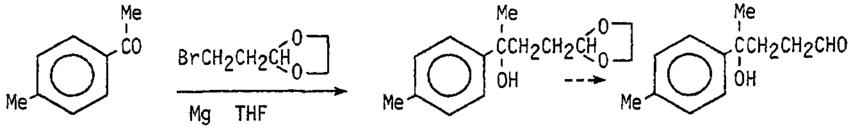


JOC (1971) 36 366

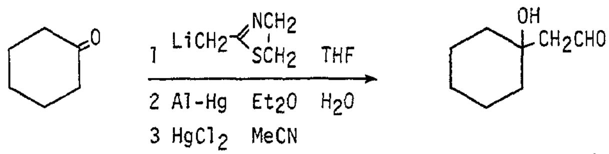


66%

Ber (1959) 92 1564

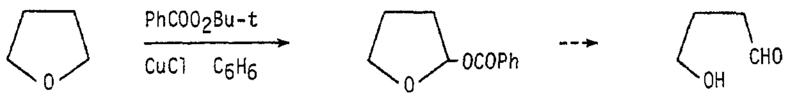


JOC (1969) 34 1122



51%

Tetr Lett (1972) 3929
JOC (1973) 38 36



Angew (1961) 73 65
Acta Chem Scand (1961) 15 249
Tetrahedron (1961) 13 241

64%

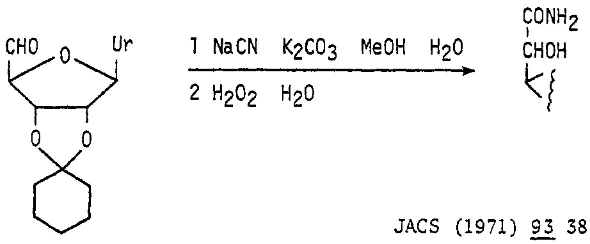
JACS (1953) 75 2413
$(i\text{-}Bu)_2AlH$ Helv (1963) 46 2799

Also via: Acetoxyaldehydes (Section 336)

Section 325 Alcohol — Amide

$$(PhCH_2)_2CHCHO \dashrightarrow (PhCH_2)_2CHCH(OH)CN \xrightarrow[t\text{-}BuOH]{H_2SO_4} (PhCH_2)_2CHCH(OH)CONHBu\text{-}t$$ 98%

Compt Rend C (1971) 272 1157
HCl, HCOOH Annalen (1971) 749 198

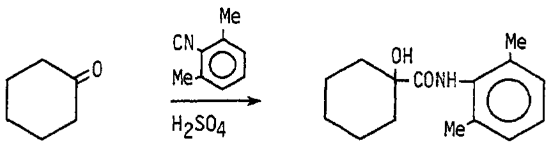


48%

JACS (1971) 93 3812

$Me_2CO \dashrightarrow Me_2C(OH)CN \xrightarrow{MnO_2 \quad CH_2Cl_2} Me_2C(OH)CONH_2$ <53%

Chem Comm (1966) 121



Ber (1965) 98 936
Tetrahedron (1968) 24 3795
Annalen (1968) 715 47

$PhC(Me)O \xrightarrow[THF]{(Et_2NCO)_2Hg \quad BuLi} PhC(OH)(Me)CONEt_2$ 66%

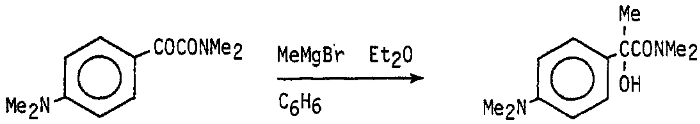
Angew (1967) 79 819
(Internat Ed 6 805)

$Ph_2CO \xrightarrow[THF]{Li[Me_2NCONi(CO)_3]} Ph_2C(OH)CONMe_2$ <30%

JOC (1971) 36 2721

$PhCH(OH)COOH \xrightarrow[2\ NH_3]{1\ Me_2CO \quad H_2SO_4} PhCH(OH)CONH_2$ 62%

Org Synth (1955) Coll Vol 3 536



79%

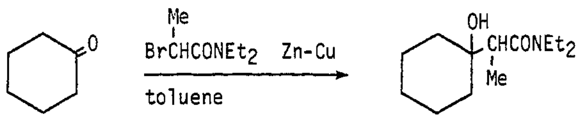
JOC (1959) 24 265

PhCHO ⟶ $PhCH(OH)C{\equiv}COEt$ $\xrightarrow{PhNH_2 \quad EtOH}$ $PhCH(OH)CH_2CONHPh$ <41%

Rec Trav Chim (1956) 75 1377

Ph_2CO $\xrightarrow{LiCH_2CONMe_2 \quad THF}$ $Ph_2C(OH)CH_2CONMe_2$ 90%

Ber (1968) 101 3113
JOC (1968) 33 4275

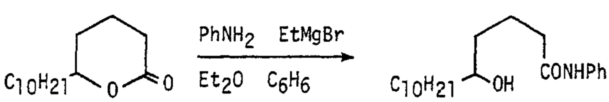


30%

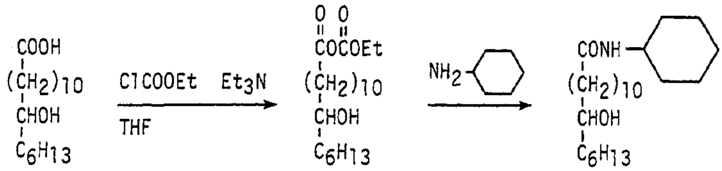
JACS (1948) 70 677
Organometallics in Chem Synth (1970) 1 57

$EtCH(O)CH_2$ (epoxide) $\xrightarrow[NaNH_2 \quad NH_3]{CH_3CONMe_2}$ $EtCH(OH)CH_2CH_2CONMe_2$ 44%

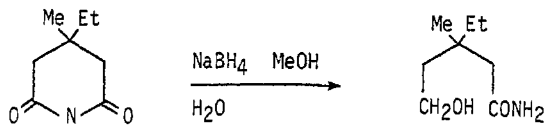
Ber (1972) 105 1621



Rec Trav Chim (1965) 84 1177
Can J Chem (1969) 47 3671
Pharm Acta Helv (1945) 20 79



J Am Oil Chem Soc (1963) 40 101
(Chem Abs 59 2641)



40%

JOC (1968) 33 206

Section 326 Alcohol — Amine

$PhCHO \xrightarrow[\text{hexane}]{Ph_2NCH_2SnBu_3 \quad BuLi} Ph_2NCH_2CH(OH)Ph$ 83%

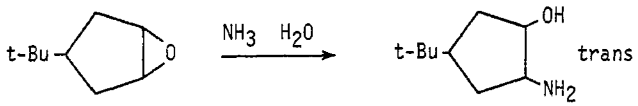
JACS (1971) 93 4027

$EtCH(Me)CHO \xrightarrow[2\ NaCN]{1\ NaHSO_3 \quad H_2O} EtCH(Me)CH(OH)CN \xrightarrow[Et_2O]{LiAlH_4} EtCH(Me)CH(OH)CH_2NH_2$ 46%

Ber (1973) 106 1365

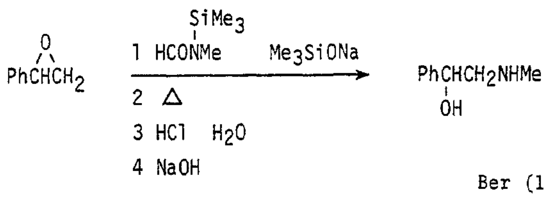
$PhCOCl \xrightarrow{CuCN} PhCOCN \xrightarrow[Et_2O]{LiAlH_4} PhCH(OH)CH_2NH_2$ 86%

JACS (1952) 74 5514

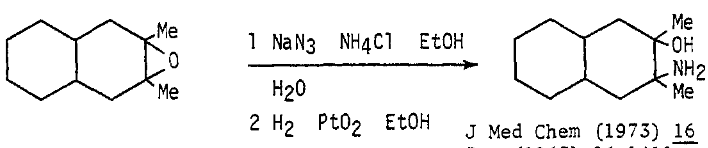


94%

Tetrahedron (1972) 28 3475
Helv (1961) 44 1164
Synth Comm (1973) 3 177
JACS (1965) 87 1353
Chem Ind (1973) 1111

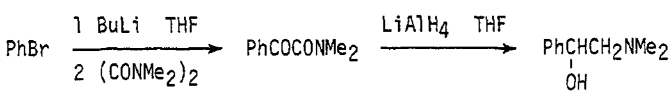


Ber (1969) 102 14



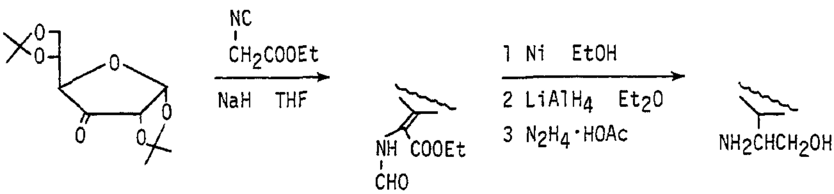
47%

J Med Chem (1973) 16 23
Ber (1963) 96 1411

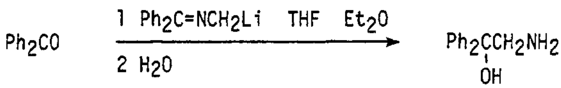


77%

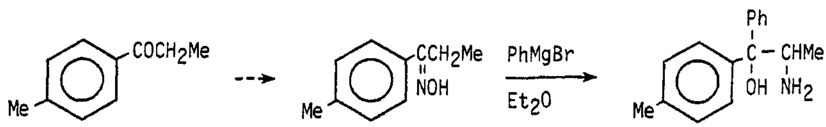
Synth Comm (1973) 3 325



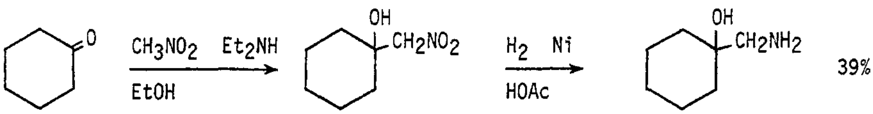
Tetr Lett (1972) 5353



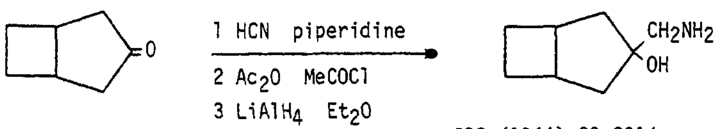
Angew (1970) 82 138
(Internat Ed 9 163)



JOC (1943) 8 99



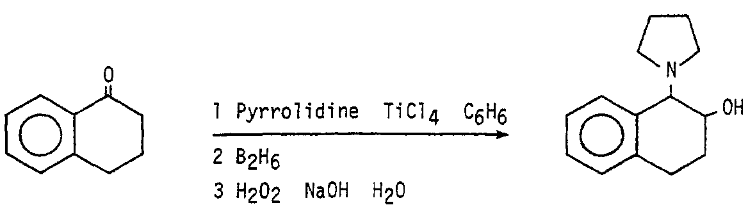
JACS (1951) 73 2359
(1952) 74 2924
Org Synth (1963) Coll Vol 4 221



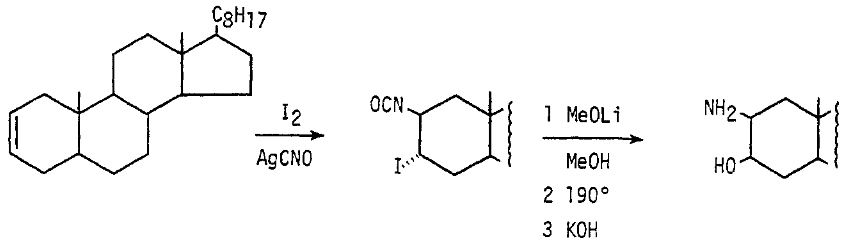
JOC (1964) 29 2914
Helv (1950) 33 1093
JACS (1952) 74 1861

Catalytic reduction of cyanohydrins Helv (1943) 26 288

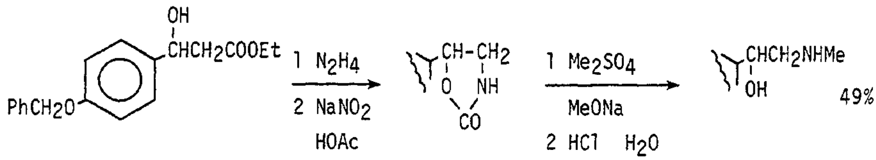
Reduction of cyanohydrin ethers Compt Rend (1953) 237 1006
236 387
Tetr Lett (1971) 923
Chem Comm (1973) 55



Bull Soc Chim Fr (1971) 1649 3978



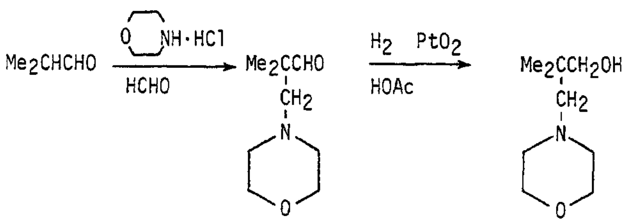
JOC (1967) 32 540



JOC (1951) 16 84

$PhCHO \dashrightarrow PhCH{=}C(COOMe)CN \xrightarrow{LiAlH_4\ \ Et_2O} PhCH_2CH(CH_2OH)CH_2NH_2$

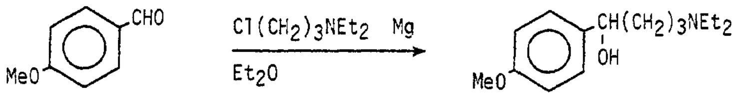
Ber (1950) 83 445



JACS (1951) 73 685

$MeCH\overset{O}{—}CHMe \xrightarrow[\text{pentane; 2 } HCl\ \ H_2O]{\text{1 } PhCH_2NC\ \ BuLi\ \ THF} MeCH(OH)CH(Me)CH(Ph)NH_2$ $<66\%$

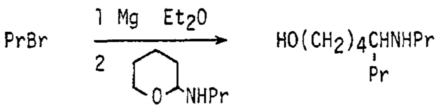
Angew (1973) 85 355
(Internat Ed 12 323)



JACS (1945) 67 1472

$$EtCH_2NO_2 \xrightarrow[EtOH]{CH_2{=}CHCHO \quad EtONa} EtCH(NO_2)(CH_2)_2CHO \xrightarrow[EtOH]{H_2 \quad PtO_2} EtCH(NH_2)(CH_2)_2CH_2OH \qquad 22\%$$

JACS (1952) 74 1064



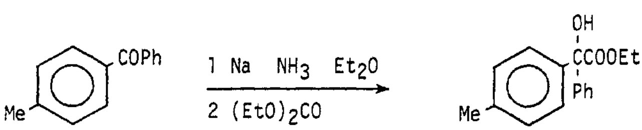
20%

Bull Soc Chim Fr (1963) 2468
(1954) 575

Section 327 Alcohol — Ester

$$C_9H_{19}COOEt \xrightarrow[\text{base; 2 } I_2 \text{ acid}]{\text{1 } Me_2SO} C_9H_{19}COCH(OMe)_2 \xrightarrow[H_2O]{SnCl_4 \quad \text{dioxane}} C_9H_{19}CH(OH)COOMe$$

JOC (1967) 32 3947

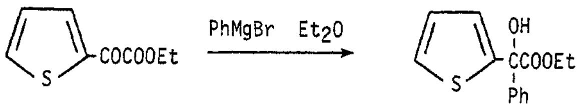


~70%

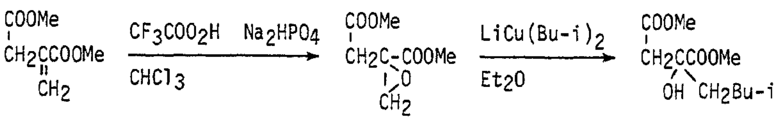
JOC (1965) 30 3804

74%

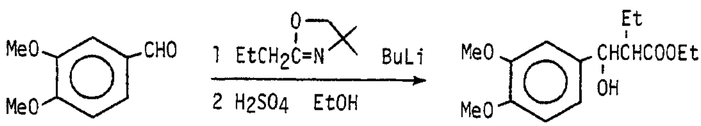
JCS (1957) 3262



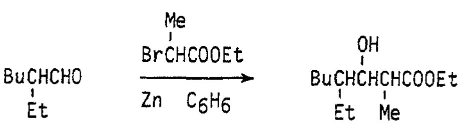
JACS (1951) 73 2216
Tetr Lett (1972) 3011



Tetr Lett (1973) 4561



JACS (1970) 92 6644



87%

Org Synth (1963) Coll Vol 4 444
(1955) Coll Vol 3 408
JOC (1970) 35 3966
Org React (1942) 1 1
JCS C (1969) 2799
Organometallics in Chem Synth (1970) 1 57

Continuous flow system JOC (1974) 39 269

$PhCHO \xrightarrow{LiCH_2COOEt \quad THF} PhCH(OH)CH_2COOEt$ 80%

JACS (1970) 92 3222
(1973) 95 3050
JOC (1972) 37 2468

$PhCH_2COOEt \xrightarrow[DMSO]{HCHO \quad EtONa} PhCH(CH_2OH)COOEt$ 55%

Ber (1966) 99 2407

$Me_2CHCOOEt \xrightarrow[2\ PhCHO]{1\ Ph_3CNa} Me_2C(COOEt)CH(OH)Ph$

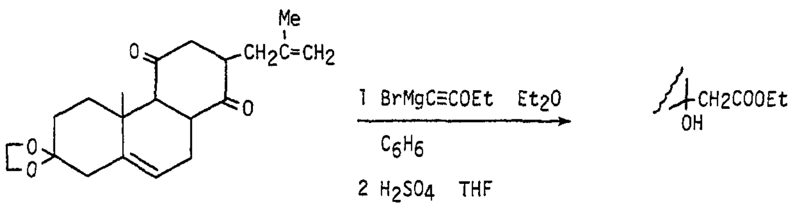
JACS (1939) 61 793

$MeCH(O)CH_2$ (epoxide) $\xrightarrow[MeOH]{CO \quad Co_2(CO)_8} MeCH(OH)CH_2COOMe$ 40%

JOC (1961) 26 2102
Bull Chem Soc Jap (1964) 37 672

$PrI \xrightarrow[THF]{HOCH_2CH_2COOMe \quad LiN(Pr\text{-}i)_2} PrCH(CH_2OH)COOMe$ 90%

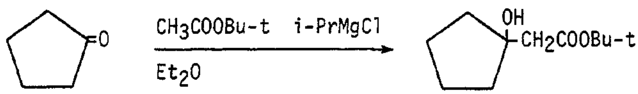
Tetr Lett (1973) 2429



JACS (1954) 76 1715
Advances in Org Chem (1960) 2 117

$$Ph_2CO \xrightarrow[\text{Mg}\quad Et_2O]{\text{BrCH(Me)COOBu-t}} Ph_2C(OH)CH(Me)COOBu\text{-}t \qquad 81\%$$

JOC (1966) 31 983



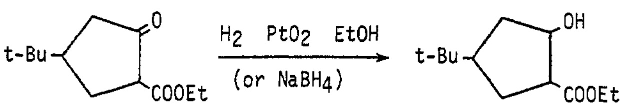
~75%

Bull Soc Chim Fr (1966) 3243 131 125

Et_2NMgBr, CH_3COOBu-t JACS (1952) 74 6254
Tetrahedron (1967) 23 4271

$$(i\text{-}Pr)_2CO \xrightarrow[Et_2O]{Ti(OPr\text{-}i)_4\quad CH_2{=}CO} (i\text{-}Pr)_2C(OH)CH_2COOPr\text{-}i \qquad 52\%$$

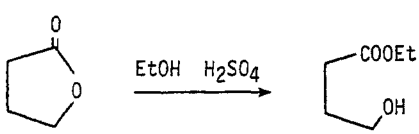
Synthesis (1972) 608



87-95%

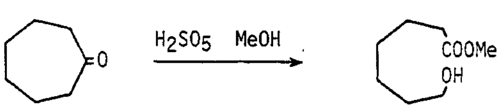
Tetrahedron (1972) 28 3475

KBH_4 JCS (1963) 2743



~53%

JOC (1966) 31 485



70%

Tetrahedron (1973) 29 1447

$C_7H_{15}CN \xrightarrow[\text{(reflux)}]{HOCH_2CH_2OH} C_7H_{15}COOCH_2CH_2OH$ 58%

JCS (1963) 2417
Tetr Lett (1972) 4643

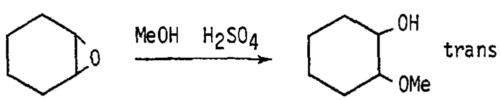
$BuCOOH \xrightarrow[H_2O]{\overset{O}{CH_2-CH_2}\ \ NaOH} BuCOOCH_2CH_2OH$ 58-63%

JACS (1944) 66 1420
JOC (1961) 26 4563

Also via: Hydroxyacids (Section 313)

Section 328 Alcohol — Ether, Epoxide

1,2-Hydroxyethers, 1,3-hydroxyethers, other hydroxyethers and hydroxy-epoxides



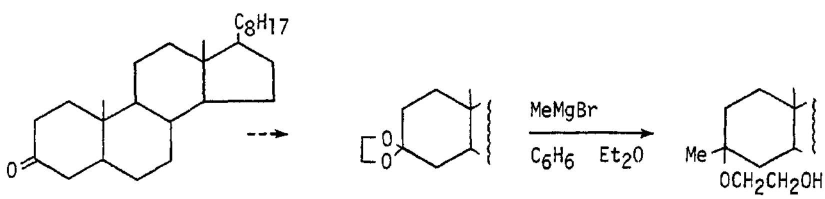
82%

JACS (1943) 65 2196

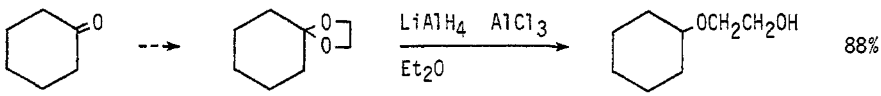
$Et_2CO \xrightarrow[CH_2(OMe)_2]{LiCH_2OMe} Et_2C(OH)CH_2OMe$ 75%

Tetr Lett (1964) 1503

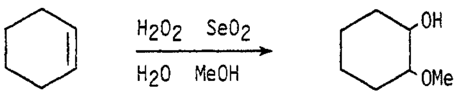
$EtOCH_2MgCl$ Compt Rend C (1966) 262 848
(1967) 264 399



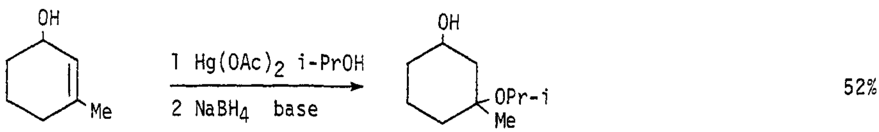
JOC (1967) 32 1417



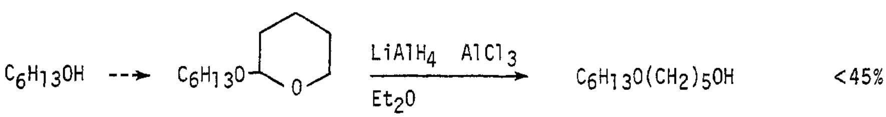
JACS (1962) 84 2371



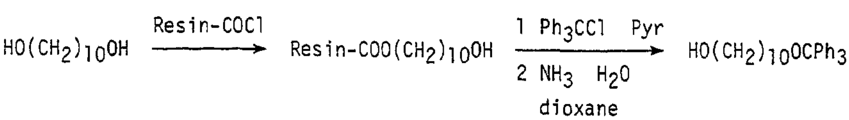
Bull Chem Soc Jap (1965) 38 958



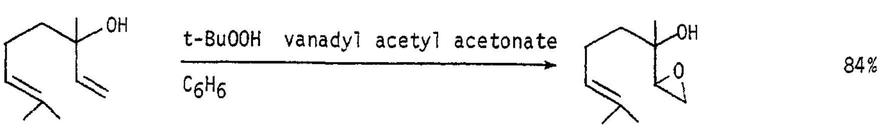
JOC (1970) 35 1041



Can J Chem (1967) 45 2547
JOC (1965) 30 2441



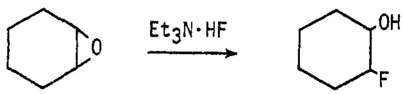
Can J Chem (1973) 51 2452
(1972) 50 2892



JACS (1973) 95 6136

Section 329 Alcohol — Halide

Fluorohydrins, chlorohydrins, bromohydrins and iodohydrins

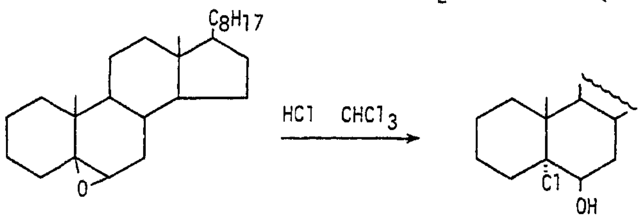


40%

Bull Soc Chim Fr (1969) 3647

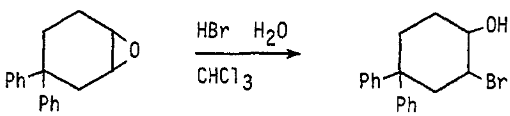
HF Can J Chem (1960) 38 1495

KHF_2 J Med Chem (1972) 15 1092



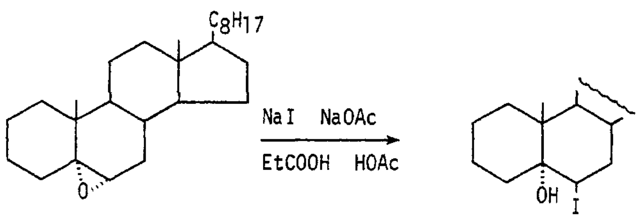
JCS (1958) 1657

JOC (1961) 26 2403



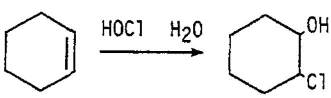
JOC (1968) 33 3385

JCS (1951) 2598



JCS C (1971) 1466

HI JCS (1951) 2598



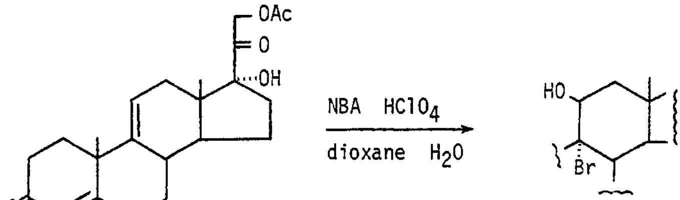
70-73%

Org Synth (1932) Coll Vol 1 158

$NH_2CONHCl$ Org Synth (1963) Coll Vol 4 157

CrO_2Cl_2 JACS (1956) 78 3749

(1950) 72 4353



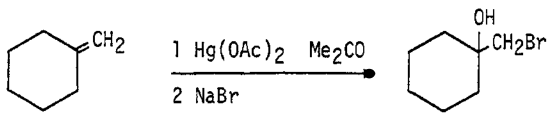
> 90%

JACS (1953) 75 2273
(1957) 79 1130

NBS, Me_2SO JACS (1968) 90 5498

KBr, H_2O_2, enzyme Tetr Lett (1968) 4057

BrN_3 Tetr Lett (1968) 3921



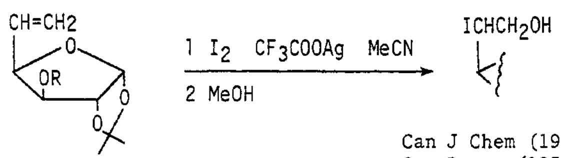
JOC (1968) 33 3953

$$PrCH{=}CH_2 \xrightarrow[2\ H_2O_2\quad Me_2CO\quad H_2O]{1\ I_2\quad H_2O} PrCH(OH)CH_2I$$

85%

Can J Chem (1964) 42 2710

KIO_3, H_2SO_4 JCS C (1970) 846

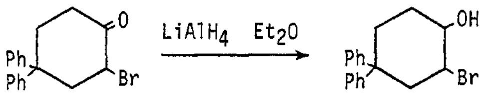


Can J Chem (1972) 50 507
Org React (1957) 9 332

$$PhCOCH_2Cl \xrightarrow{PhLi\quad Et_2O} Ph_2C(OH)CH_2Cl$$

78%

JACS (1951) 73 4030



trans 93%

JOC (1968) 33 3385

$NaBH_4$ JCS (1958) 1657
Bull Chem Soc Jap (1962) 35 2044

$LiBH_4$ Helv (1953) 36 1241

Fluorohydrins JCS Perkin I (1973) 1462

$$MeCH_2(CH_2)_3OH \xrightarrow[\text{2 } h\nu \text{ CHCl=CHCl}]{\text{1 NaOCl}} \underset{\substack{| \\ Cl}}{MeCH}(CH_2)_3OH$$ ~34%

JOC (1972) 37 3514

$(i\text{-}Pr)_2NCl$, $h\nu$ JACS (1971) 93 438

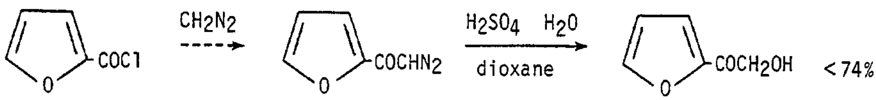
$$HO(CH_2)_6OH \xrightarrow[\text{toluene}]{HCl \quad H_2O} HO(CH_2)_6Cl$$ 45-50%

Org Synth (1955) Coll Vol 3 446

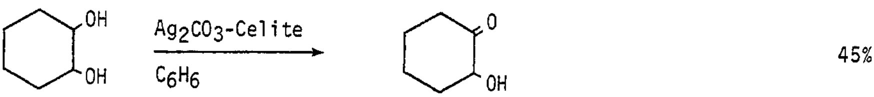
Section 330 Alcohol — Ketone

$$EtC\equiv CEt \xrightarrow[\text{glyme } H_2O]{Tl(NO_3)_3 \quad HClO_4} EtCO\underset{\substack{| \\ OH}}{CH}Et$$ 70-90%

JACS (1973) 95 1296

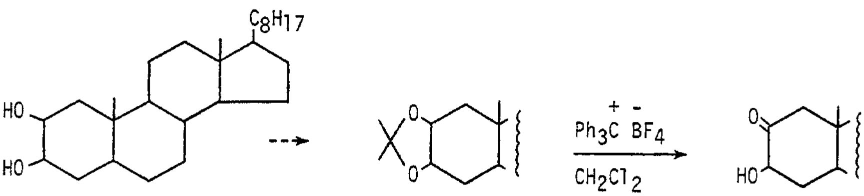


JACS (1948) 70 142
(1950) 72 5161

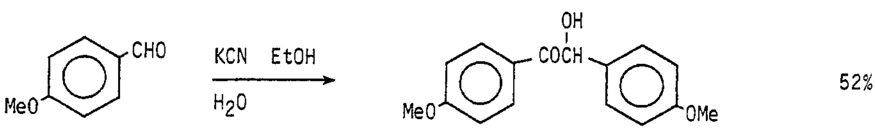


(Also applicable to 1,3 and 1,4-diols)

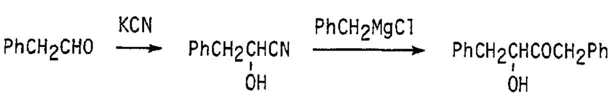
Chem Comm (1969) 1102
Tetrahedron (1973) 29 2867
NCS, Me_2S Tetr Lett (1974) 287



JCS Perkin I (1972) 542



Org React (1962) 4 269
Org Synth (1941) Coll Vol 1 94
$Bu_4\overset{+}{N}\ \overset{-}{CN}$ Tetr Lett (1971) 287



Helv (1945) 28 741
Bull Soc Chim Fr (1955) 784

$$PhCHO \xrightarrow[\substack{Me_2NCH_2CH_2NMe_2 \quad pentane \\ 2\ HCl}]{1\ CH_2{=}CHOEt \quad t\text{-}BuLi} PhCH(OH)COMe$$ 57%

Annalen (1972) 763 208

CH_2=CHSEt JACS (1973) 95 2694

$$CHO{-}HOCH{-}HCOH{-}HCOH{-}CH_2OH \xrightarrow[2\ H_2SO_4 \quad H_2O]{1\ HOCH_2CH_2NO_2 \quad base} CH_2OH{-}CO{-}HCOH{-}HOCH{-}HCOH{-}HCOH{-}CH_2OH$$ 23%

JACS (1950) 72 3325

$$PhCOOEt \xrightarrow[t\text{-}BuOK]{Me_2SO} PhCOCH_2SOMe \xrightarrow[\substack{2\ NaOSOCH_2OH \\ Cu(OAc)_2 \quad EtOH}]{1\ HCl \quad Me_2SO} PhCOCH_2OH$$ 60-65%

JACS (1966) 88 5498

$$C_{11}H_{23}COOMe \xrightarrow{Na \quad xylene} C_{11}H_{23}COCH(OH)C_{11}H_{23}$$ 80-90%

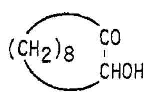
Org React (1962) 4 256

Org Synth (1963) Coll Vol 4 840

Review: The Acyloin Condensation as a Cyclization Method

Chem Rev (1964) 64 573

$$COOMe{-}(CH_2)_8{-}COOMe \xrightarrow[2\ HCl \quad H_2O \quad THF]{1\ Na \quad ClSiMe_3 \quad xylene}$$



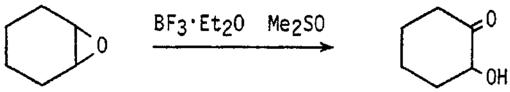
53%

Ber (1964) 97 1383

Can J Chem (1969) 47 3266

Synthesis (1971) 236

JACS (1953) 75 6231



76%

JOC (1961) 26 1681
Compt Rend (1965) 261 1990

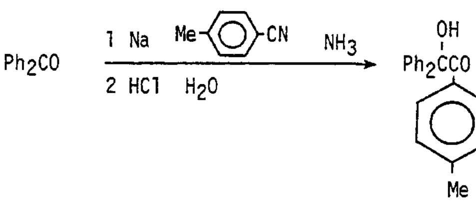
$$PhCH_2Br \xrightarrow{Li[BuCONi(CO)_3] \quad Et_2O} PhCH_2C(OH)(Bu)COBu$$

58%

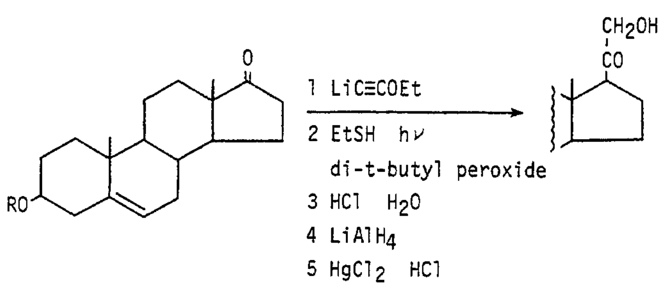
JOC (1970) 35 4183

$$BuBr \xrightarrow[\text{2 } MeCOC(Me)=NOH \quad \text{3 } (COOH)_2 \quad H_2O]{\text{1 Mg}} BuC(OH)(Me)COMe$$

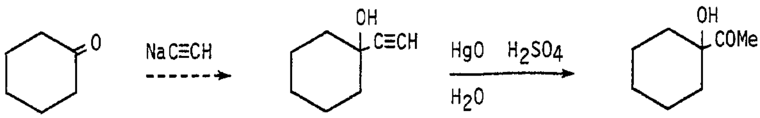
Annales de Chimie (1939) 11 453



JOC (1965) 30 3804

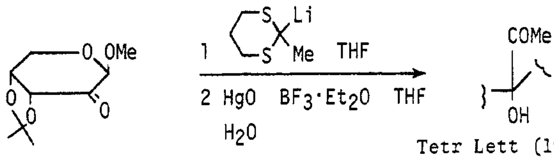


Rec Trav Chim (1960) 79 1293



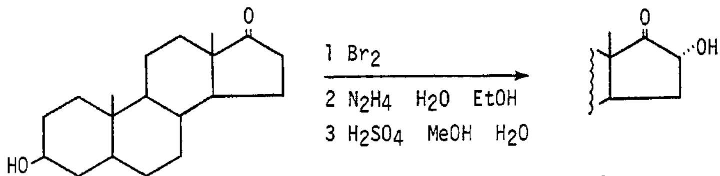
65-67%

Org Synth (1963) Coll Vol 4 13
Tetrahedron (1964) 20 1119

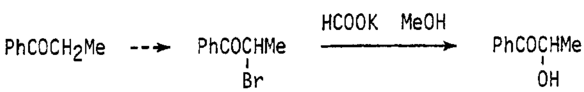


62%

Tetr Lett (1972) 3945
Annalen (1972) 758 89
JOC (1971) 36 2035

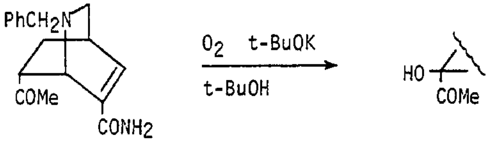


JOC (1967) 32 3723

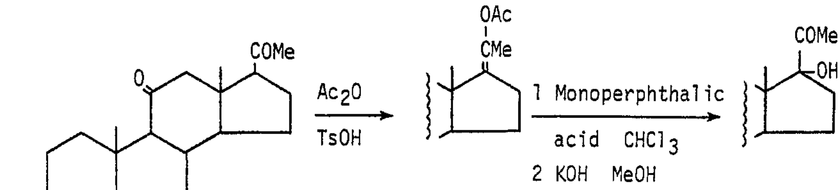


Annalen (1936) 526 143
Org Synth (1943) Coll Vol 2 5

NaOH JCS (1954) 3257



JACS (1968) 90 2448
JOC (1968) 33 3294

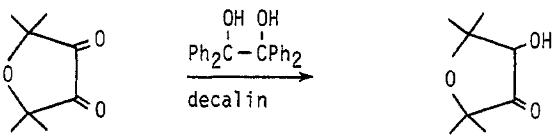


JCS (1954) 747
Helv (1959) 42 2043

t-BuCOCOBu-t $\xrightarrow{\text{Zn DMF } H_2O}$ t-BuCOCHBu-t (OH) 87%

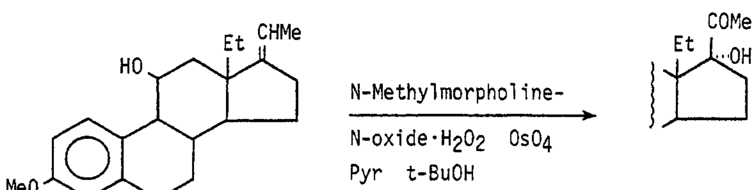
Annalen (1971) 745 164

$(EtO)_3P$ Can J Chem (1969) 47 3266



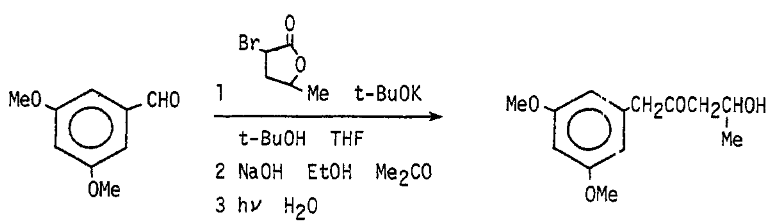
73%

Tetr Lett (1971) 3403



30%

JCS C (1968) 2647
JOC (1960) 25 1968



41%

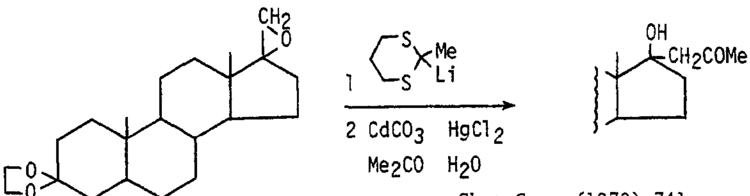
JACS (1971) 93 281

PhCHO $\xrightarrow{C_5H_{11}CH{=}C(Me)OBBu_2}$ PhCH(OH)CH(C_5H_{11})COMe 91%

JACS (1973) <u>95</u> 967

PhCHO $\xrightarrow[MeOCH_2CH_2OMe \quad Et_2O]{BuCH{=}C(Me)OLi \quad ZnCl_2}$ PhCH(OH)CH(Bu)COMe

JACS (1973) <u>95</u> 3310



Chem Comm (1970) 741

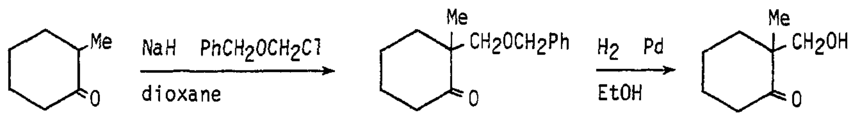
BuBr $\xrightarrow[2\ Me_2C(CN)CH_2Bu\text{-}t]{1\ Li}$ $Me_2C(CH_2Bu\text{-}t)$–BuC=NLi $\xrightarrow[2\ (COOH)_2 \quad H_2O]{1\ MeCH(O)CH_2}$ $BuCOCH_2CH(OH)Me$ 90%

JACS (1970) <u>92</u> 6675

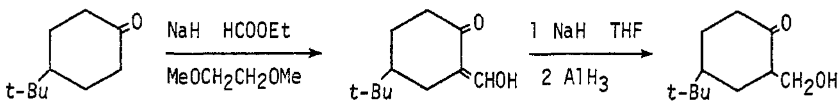
Review: The Aldol Condensation Org React (1968) <u>16</u> 1

$PhCOCH_2Me$ $\xrightarrow[C_6H_6 \quad Et_2O]{1\ PhNH_2\text{-}EtMgBr}$ 2 i-PrCHO → PhCOCH(Me)–i-PrCHOH 83%

Org React (1968) <u>16</u> 1



JCS (1963) 4634
(1964) 4521

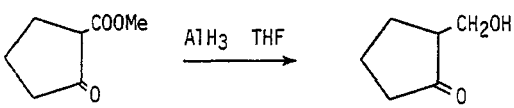


85%

JOC (1971) 36 3070

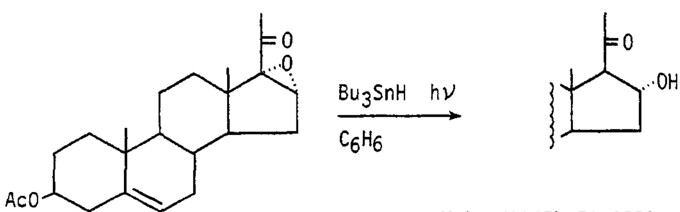
$$Ph_2CO \xrightarrow[\text{NaH BuLi THF; 2 Al-Hg}]{\text{1 PhSOCH}_2\text{COMe}} Ph_2C(OH)CH_2COMe \quad \sim 91\%$$

Tetr Lett (1974) 107



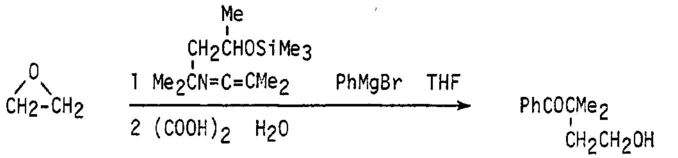
82%

JACS (1968) 90 2927



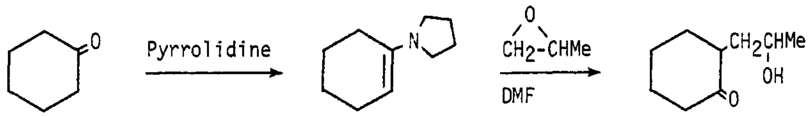
27%

Helv (1967) 50 2259
$Cr(OAc)_2$ Coll Czech (1961) 26 1207
Al-Hg JOC (1973) 38 3187



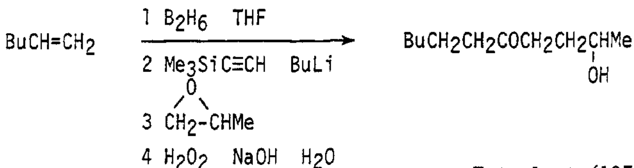
30%

JOC (1973) <u>38</u> 2129



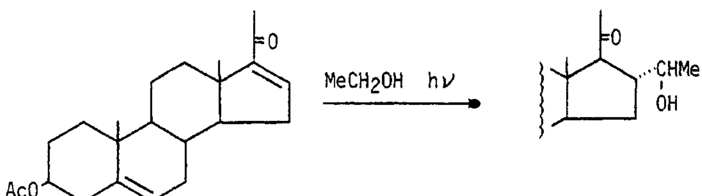
~60%

Tetrahedron (1969) <u>25</u> 3157



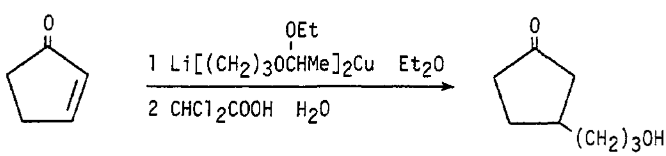
21%

Tetr Lett (1973) 2741

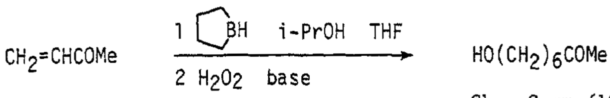


40%

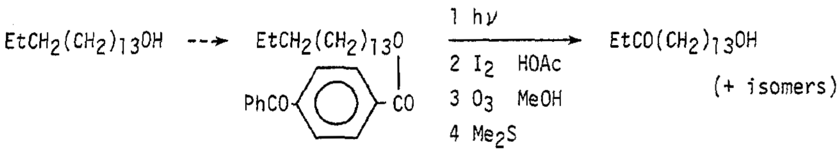
JCS (1967) 2032



JOC (1972) <u>37</u> 1947



Chem Comm (1969) 1009

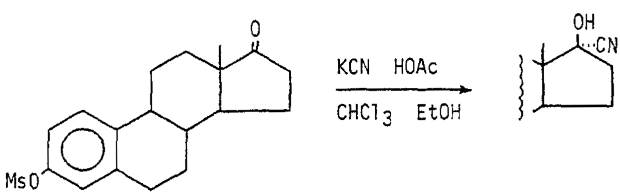


JACS (1969) 91 3083
(1973) 95 3251

Also via: Acyloxyketones (Section 360)

Section 331 Alcohol — Nitrile

α-Hydroxynitriles (cyanohydrins) and β-hydroxynitriles



JCS C (1968) 2283

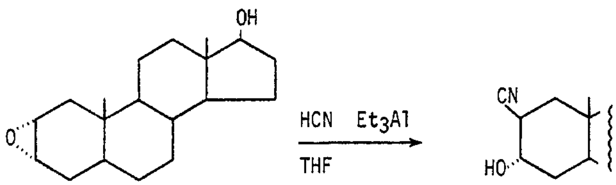
NaCN, $NaHSO_3$	Org Synth (1941) Coll Vol 1 336
HCN, Et_3N	JACS (1956) 78 4100
Et_2AlCN	Tetr Lett (1966) 1913
$Me_2C(OH)CN$	JACS (1953) 75 650

$$PrCHO \xrightarrow{Br\overset{Et}{C}HCN \quad Zn \quad THF} PrCH(OH)CH(Et)CN$$ 66%

Compt Rend C (1969) 269 861
Organometallics in Chem Synth (1970) 1 57

$$PhCHO \xrightarrow[THF]{CH_3CN \quad BuLi} PhCH(OH)CH_2CN$$ 83%

Ber (1968) 101 3113



56%

JCS C (1970) 2365

$$Ph_2CO \xrightarrow{CH_3CN \quad NaNH_2 \quad NH_3} Ph_2C(OH)CH_2CN$$ 93%

JOC (1968) 33 3402
Ber (1968) 101 3113

Also via:

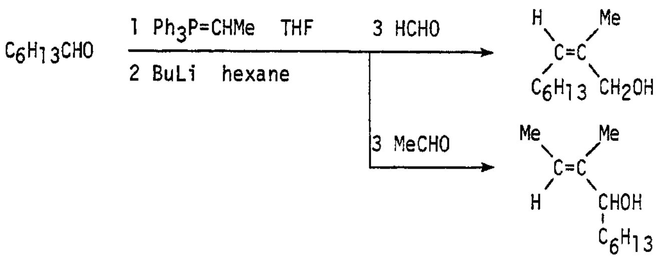
	Section
Cyanohydrin trimethylsilyl ethers	366
Cyanohydrin esters	361

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)

$BuC{\equiv}CH \xrightarrow[\text{2 MeLi } Et_2O \quad \text{3 RCHO}]{\text{1 } (i\text{-}Bu)_2AlH \text{ heptane}} BuCH{=}CHCH(R)OH$ (trans) 73% (R=H) 68% (R=Me)

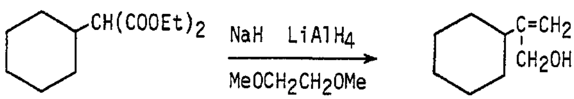
JACS (1967) 89 2754 5085
Tetr Lett (1971) 4571



73%

67%

JACS (1970) 92 226 6636
(1972) 94 4013
Tetr Lett (1970) 447

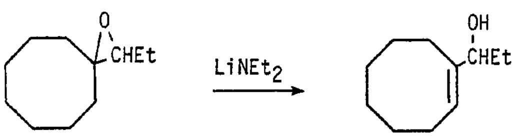


62%

JOC (1967) 32 113
Ber (1970) 103 3771

$EtCH_2CH(O)CHPr$ (epoxide) $\xrightarrow[\text{2 } H_2O_2 \quad H_2O]{\text{1 } Ph_2Se_2\text{-}NaBH_4 \quad EtOH}$ $EtCH{=}CHCH(OH)Pr$ 98%

JACS (1973) 95 2697
Tetr Lett (1973) 1979

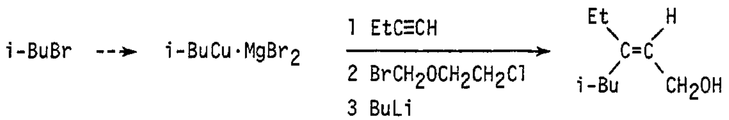


JOC (1971) 36 1365
(1969) 34 3583

$LiNPr_2$	JOC (1972) 37 2060
BuLi	JOC (1971) 36 3266
$(i\text{-}Bu)_2AlH$	Ber (1960) 93 2712
Li_3PO_4 (180°) or t-BuOK	Synthesis (1972) 194

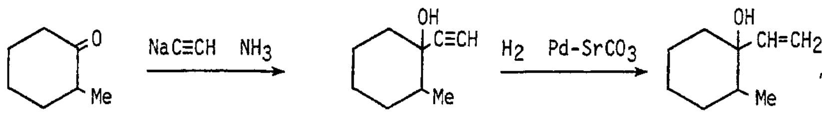
$$C_6H_{13}I \xrightarrow[2\ (MeO)_3P\quad MeOH]{1\ PhSOCH_2CH{=}CMe_2\quad (i\text{-}Pr)_2NLi\quad THF} C_6H_{13}CH{=}CHC(OH)Me_2$$

Tetr Lett (1973) 1385 1389
JOC (1973) 38 2245
Chem Comm (1972) 702



66%

Tetr Lett (1973) 2407



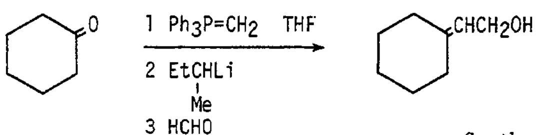
~ 75%

JCS (1952) 1610 642
Org Synth (1955) Coll Vol 3 416
JACS (1954) 76 4482

$$Me_2C{=}CH(CH_2)_2COMe \xrightarrow{CH_2{=}CHMgBr\quad THF} Me_2C{=}CH(CH_2)_2C(OH)(Me)CH{=}CH_2$$

83%

Advances in Org Chem (1960) 2 1



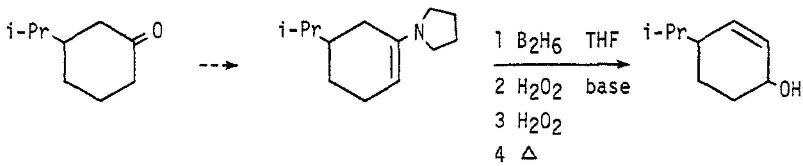
37%

Synthesis (1972) 575

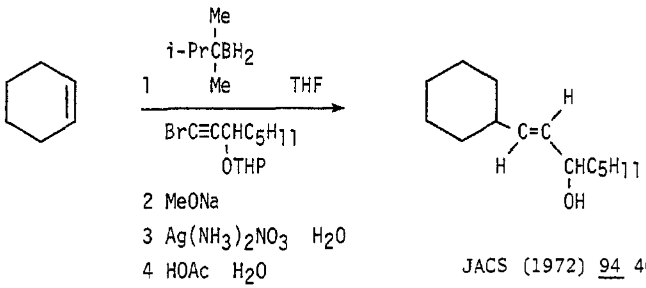
$$Me_2CO \xrightarrow[Et_2O]{BuCH{=}CHAl(Bu\text{-}i)_2} Me_2C(OH)CH{=}CHBu$$

42%

Tetr Lett (1971) 4571

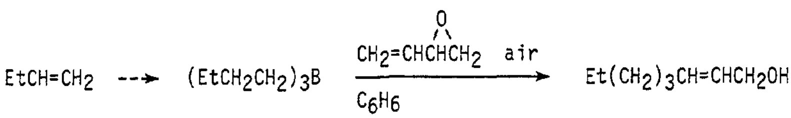


Bull Soc Chim Fr (1971) 3978



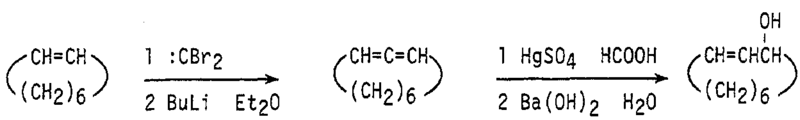
~65%

JACS (1972) 94 4013

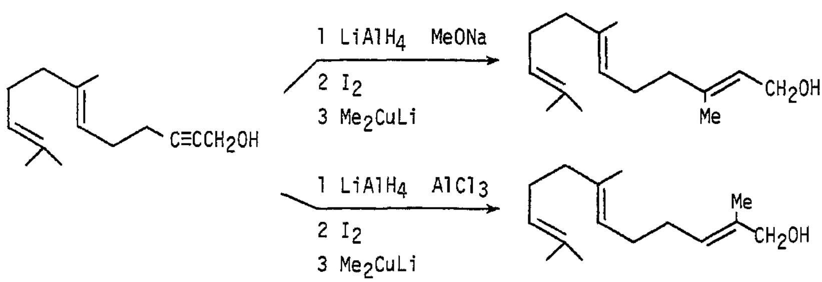


<73%

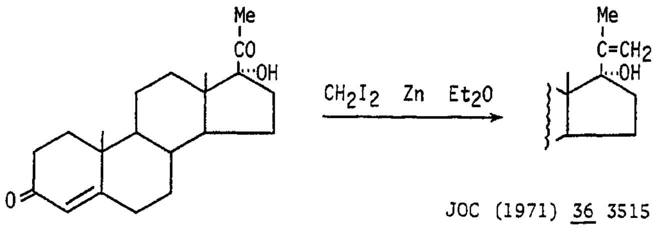
JACS (1971) 93 2792



Bull Soc Chim Fr (1964) 3273

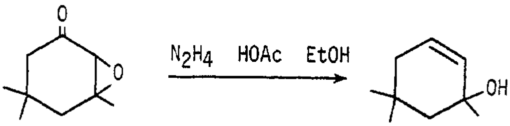


JACS (1967) 89 4245
(1968) 90 5618



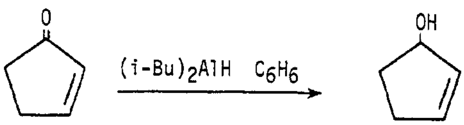
93%

JOC (1971) 36 3515



66%

JOC (1961) 26 3615
(1968) 33 3347

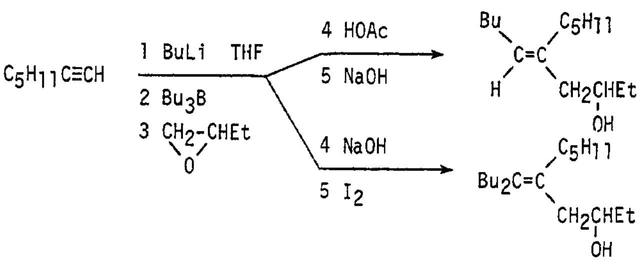


83%

Chem Comm (1970) 213

AlH_3 JOC (1969) 34 2206

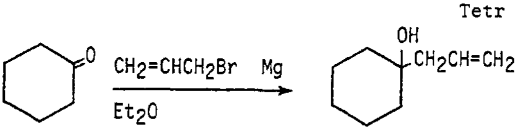
Et_2SiH, $(Ph_3P)_3RhCl$ Tetr Lett (1972) 5035



75%

34%

Tetr Lett (1973) 2741



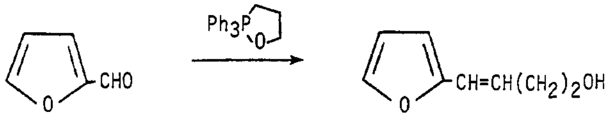
(One-step procedure)

95%

JOC (1973) 38 326
(1963) 28 3269

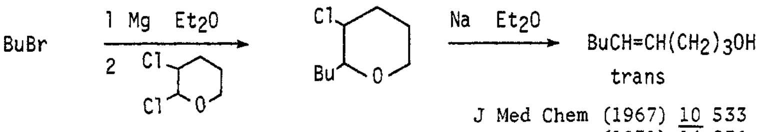
$(CH_2{=}CHCH_2)_2Cd$ Bull Soc Chim Fr (1969) 4038

π-Methallylnickel bromide JACS (1967) 89 2755



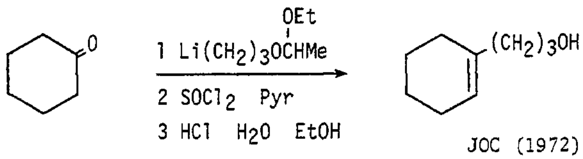
52%

JCS C (1968) 2448



71%

J Med Chem (1967) 10 533
(1971) 14 236



~73%

JOC (1972) 37 1947

$Pr_2C{=}CH(CH_2)_2CHO \xrightarrow[\text{THF}]{1\ Ph_3P{=}CH(CH_2)_4OLi} Pr_2C{=}CH(CH_2)_2CH{=}CH(CH_2)_4OH$ ~72%

Tetrahedron (1971) 27 5979

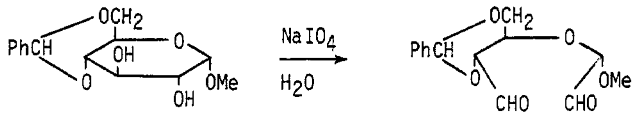
Also via: Acetylenic alcohols (Section 302)

Section 333 Aldehyde — Aldehyde

Dialdehydes

$PhCH_2CH_2CHO \dashrightarrow PhCH_2CH_2CH(OEt)_2 \xrightarrow[2\ NaOH\ \ H_2O]{1\ COCl_2\ \ HCONMe_2} PhCH_2CH(CHO)_2$

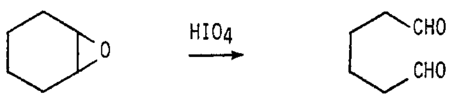
Coll Czech (1958) 23 452
Synthesis (1973) 604
Tetr Lett (1973) 3979



JCS (1959) 2441
Advances in Carbohydrate Chem (1961) 16 105

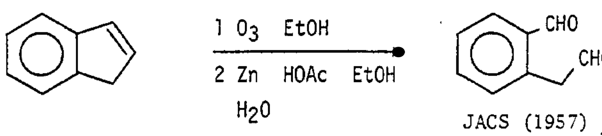
HIO_4 Ber (1956) 89 2224
Org React (1944) 2 341

$Pb(OAc)_4$ JACS (1949) 71 3310



82%

Tetr Lett (1973) 4599

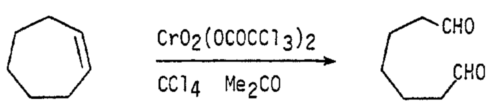


97%

JACS (1957) 79 3165

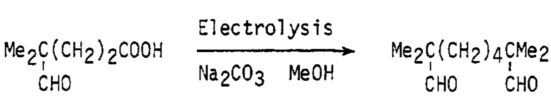
$NaIO_4$, OsO_4 JOC (1956) 21 478

RuO_4 JACS (1958) 80 6682



68%

Annalen (1962) 659 20



30%

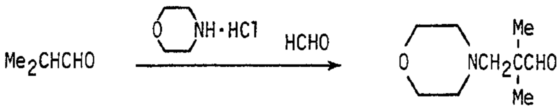
Bull Soc Chim Fr (1970) 183

Section 334 Aldehyde — Amide

No examples

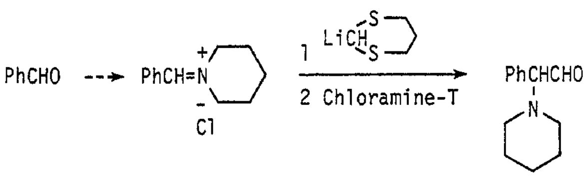
Section 335 Aldehyde — Amine

Aminoaldehydes



85%

JACS (1951) 73 685
(1948) 70 2592
Ber (1932) 65 378
Org React (1942) 1 303



<46%

Tetr Lett (1972) 2991

$$Me_2C{=}CH_2 \dashrightarrow \underset{Cl}{Me_2CCH_2NO} \xrightarrow[2\ NaNO_2\quad HCl\quad H_2O]{1\ EtNH_2\quad EtOH} \underset{EtNH}{Me_2CCHO}$$

Zh Obshch Khim (1960) 30 805
(Chem Abs 55 556)

$$\underset{Br}{Me_2CCHO} \xrightarrow{Me_2NH\quad H_2O} \underset{NMe_2}{Me_2CCHO}$$

32%

JACS (1948) 70 2592

Section 336 Aldehyde — Ester

Esters of hydroxyaldehydes and esters of carboxyaldehydes

$$C_5H_{11}CH_2CHO \xrightarrow[C_6H_6]{Pb(OAc)_4 \quad BF_3} C_5H_{11}\underset{\substack{|\\ OAc}}{C}HCHO$$

Bull Soc Chim Fr (1968) 4083
Synthesis (1973) 567

$Tl(OAc)_3$ JOC (1968) 33 3359

$$RCH_2CHO \dashrightarrow R\underset{\substack{|\\ I}}{C}HCHO \xrightarrow{AgOAc \quad DMF} R\underset{\substack{|\\ OAc}}{C}HCHO$$

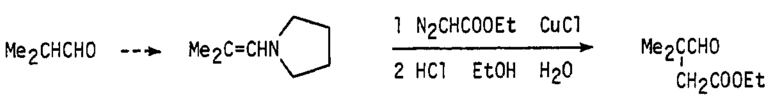
Bull Soc Chim Fr (1968) 4083

$$Me_2\underset{\substack{|\\ Cl}}{C}CHO \xrightarrow[Et_2O]{MeONa} Me_2\overset{O}{\overbrace{C-C}}HOMe \xrightarrow[2\ Et_3N]{1\ HOAc \quad Et_2O} Me_2\overset{\substack{OAc\\ |}}{C}CHO \qquad 10\%$$

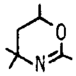
JACS (1957) 79 3448

$$Ph\underset{\substack{|\\ OAc}}{C}HCOCl \xrightarrow[diglyme]{LiAlH_4 \quad t\text{-}BuOH} Ph\underset{\substack{|\\ OAc}}{C}HCHO \qquad 55\%$$

Bull Soc Chim Fr (1968) 4083



Synth Comm (1973) 3 255

BuBr $\xrightarrow[\text{2 HCl } H_2O \quad \text{3 } NaBH_4 \text{ EtOH THF pH 5-6} \quad \text{4 } (COOH)_2]{1}$  CH_2COOEt t-BuOK THF → BuCHCHO (COOEt) 67%

JOC (1973) 38 36

Me-substituted: $CH_2{=}C(Me)COOMe \xrightarrow[Rh_2O_3 \;\; Bu_3P \;\; C_6H_6]{CO \;\; H_2 \; (600\ atmos)} MeC(Me)(CHO)COOMe$ 94%

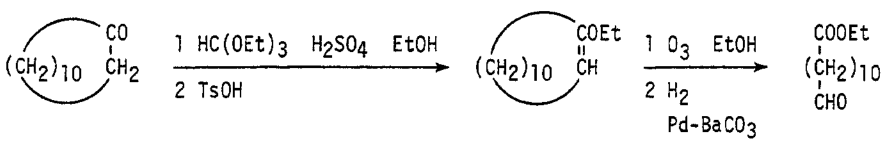
Brennst-Chem (1967) 48 46
(Chem Abs 66 85430)

$EtCH_2COOMe \xrightarrow[\text{2 } HClO_4 \;\; MeCN \;\; H_2O]{\text{1 } CH_2{=}C(SOMe)SMe \;\; LiN(Pr\text{-}i)_2 \;\; THF} EtCH(CH_2CHO)COOMe$ 90%

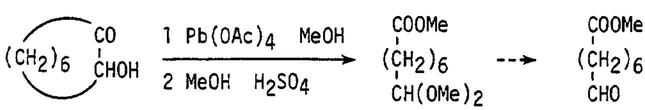
Tetr Lett (1973) 4711 4715

$MeCH{=}CHCOOMe \xrightarrow[\text{2 } HClO_4]{\text{1 } EtSCH_2SOEt \;\; BuLi \;\; THF} MeCH(CHO)CH_2COOMe$

Tetr Lett (1973) 3271



Annalen (1962) 656 97



~65%

JACS (1952) 74 5324

Also via: Carboxyaldehydes (Section 314)

Section 337 Aldehyde — Ether, Epoxide

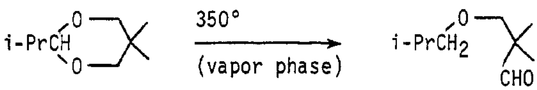
Aryloxyaldehydes, alkoxyaldehydes and epoxyaldehydes

$$PhOH \xrightarrow[\substack{2\ BrCH_2CH(OEt)_2 \\ 3\ H_2SO_4\quad H_2O}]{1\ EtONa} PhOCH_2CHO$$

JCS (1937) 1057

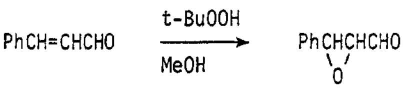
$$MeCH{=}CHCHO \xrightarrow{PrOH\quad NaOH} \underset{\displaystyle OPr}{MeCHCH_2CHO}$$ 45%

JCS (1952) 4083



50%

JACS (1960) 82 6419



73%

JOC (1960) 25 275

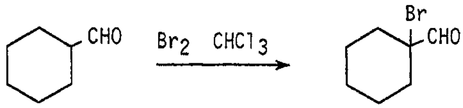
H_2O_2 JACS (1956) 78 3087

Section 338 Aldehyde — Halide

Haloaldehydes

$$t\text{-}BuC{\equiv}CH \xrightarrow[H_2SO_4\quad H_2O]{Et_2NCl\quad h\nu} \underset{\displaystyle Cl}{t\text{-}BuCHCHO}$$ 60%

JOC (1967) 32 3263

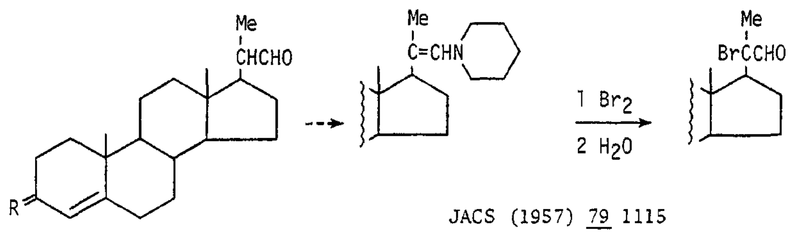


80%

	JCS (1949) 737
Br_2, $CaCO_3$	JACS (1957) 79 456 3448
IBr	Chem Comm (1968) 849
$CuBr_2$	JOC (1965) 30 587

$EtCH_2CHO \xrightarrow{CuCl_2 \quad DMF} EtCH(Cl)CHO$

	JOC (1965) 30 587
	(1967) 32 4008
SO_2Cl_2	JACS (1957) 79 3448
	(1954) 76 2695



JACS (1957) 79 1115

$C_5H_{11}CH_2CHO \xrightarrow[KOAc]{Ac_2O} C_5H_{11}CH{=}CHOAc \xrightarrow[2\ MeOH \quad 3\ HCl \quad H_2O]{1\ Br_2 \quad CCl_4} C_5H_{11}CH(Br)CHO$ ~35%

	Org Synth (1955) Coll Vol 3 127
Iodoaldehydes	JACS (1953) 75 3493

$EtCH_2CHO \dashrightarrow EtCH{=}CHOEt \xrightarrow[MeOH]{N\text{-Bromophthalimide}} EtCH(Br)CH(OMe)OEt \xrightarrow{Acid} EtCH(Br)CHO$

	Tetr Lett (1972) 4055
Br_2; $NaHCO_3$, H_2O	JACS (1955) 77 6365

$$Ph_2CO \xrightarrow[\text{2 LiCl}]{\text{1 LiCHCl}_2\ \text{THF}} Ph_2C(Cl)CHO$$ 74%

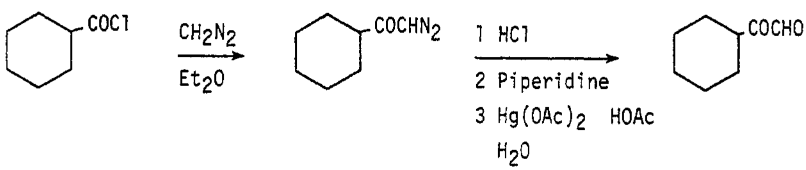
Tetr Lett (1969) 2181
(1972) 4661
Annalen (1966) <u>691</u> 33

$$MeCH{=}CHMe \xrightarrow[\text{2 CH}_2\text{=C(Br)CHO}]{\text{1 B}_2\text{H}_6\ \text{THF}} MeCH_2CH(Me)CH_2CH(Br)CHO$$ 81%

JACS (1968) <u>90</u> 4165

Section 339 Aldehyde — Ketone

Ketoaldehydes



Ber (1971) <u>104</u> 2475
Helv (1943) <u>26</u> 2050
Rec Trav Chim (1971) <u>90</u> 429

$$PhCH_2COCl \dashrightarrow PhCH_2COCHN_2 \xrightarrow[\text{2 EtSNa; 3 Br}_2\ \text{HCl}\ \text{HOAc}\ \text{H}_2\text{O}]{\text{1 EtSCl}\ \text{Et}_2\text{O}} PhCH_2COCHO$$

Ber (1957) <u>90</u> 1230

$$PhCH_2CH_2COCl \dashrightarrow PhCH_2CH_2COCHN_2 \xrightarrow[\text{2 NaNO}_2\ \text{HCl}\ \text{H}_2\text{O}\ \text{THF}]{\text{1 Ph}_3\text{P}} PhCH_2CH_2COCHO$$

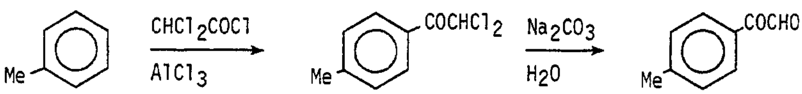
Ber (1963) <u>96</u> 2259
(1959) <u>92</u> 1345

$$\mathrm{PhCOOEt} \xrightarrow[\text{t-BuOH}]{\mathrm{Me_2SO}\quad \text{t-BuOK}} \mathrm{PhCOCH_2SOMe} \xrightarrow[\substack{2\ \mathrm{Cu(OAc)_2} \\ \mathrm{CHCl_3}}]{1\ \mathrm{HCl}\quad \mathrm{H_2O}} \mathrm{PhCOCHO}$$ 64-73%

Org Synth (1968) 48 109
JOC (1967) 32 2786
JACS (1966) 88 5498

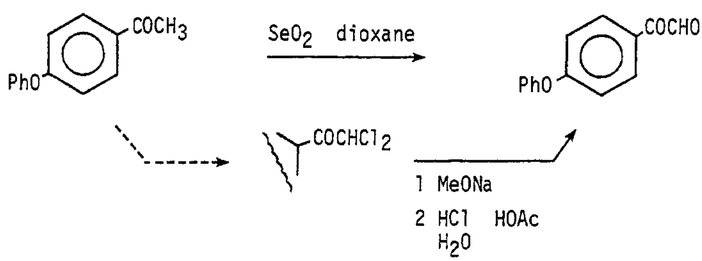
$$\mathrm{PrCOOEt} \xrightarrow[\text{BuLi}\quad \text{THF}]{\mathrm{MeSOCH_2SMe}} \mathrm{PrCO}\underset{\mathrm{SMe}}{\mathrm{CH}}\mathrm{SOMe} \xrightarrow{\text{Hydrolysis}} \mathrm{PrCOCHO}$$

Tetr Lett (1973) 4707



85%

Tetr Lett (1971) 199



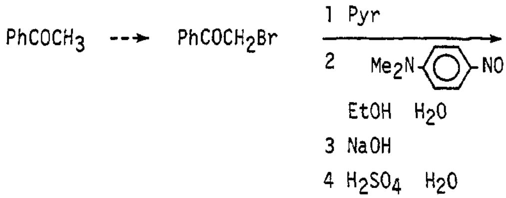
~71%

J Med Chem (1964) 7 255
Org Synth (1943) Coll Vol 2 509
Org React (1949) 5 331

$$\mathrm{PhCOCH_3} \dashrightarrow \mathrm{PhCOCH_2Br} \xrightarrow{\mathrm{Me_2SO}} \mathrm{PhCOCHO}$$ <71%

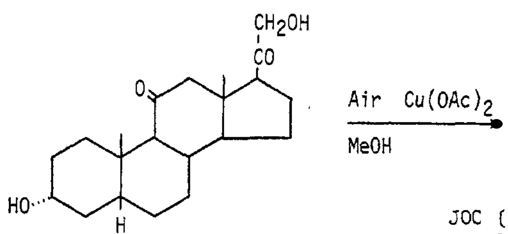
JACS (1957) 79 6562

α-picoline-1-oxide Yakugaku Zasshi (1964) 84 287
(Chem Abs 61 638)



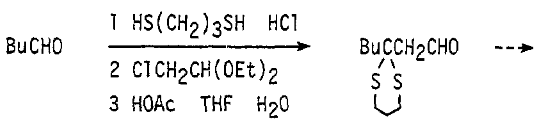
87%

Ber (1936) 69 2006



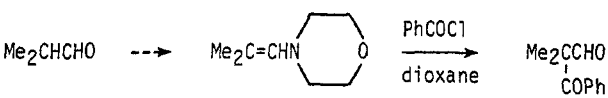
94%

JOC (1963) 28 2001
Annalen (1973) 2078



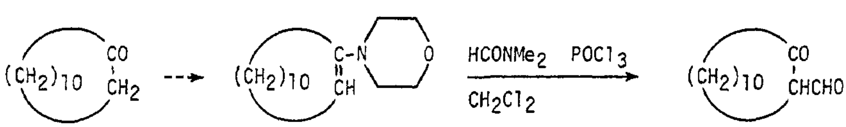
<47%

Tetr Lett (1972) 3735



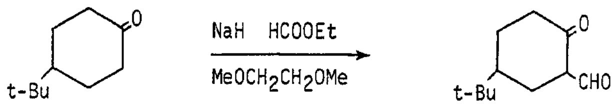
<86%

JOC (1967) 32 404



<59%

Angew (1965) 77 380
(Internat Ed 4 358)



90%

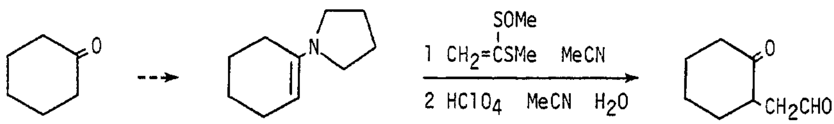
JOC (1971) 36 3070

HCOOEt, MeONa JCS Perkin I (1972) 1721

JOC (1965) 30 2502

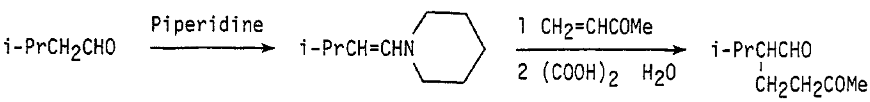
$C_{17}H_{35}COOCH{=}CH_2 \xrightarrow{AlCl_3 \quad hexane} C_{17}H_{35}COCH_2CHO$ 60%

Tetr Lett (1969) 5205



87%

Tetr Lett (1973) 4711



Chem Comm (1965) 340 60%

Section 340 Aldehyde — Nitrile

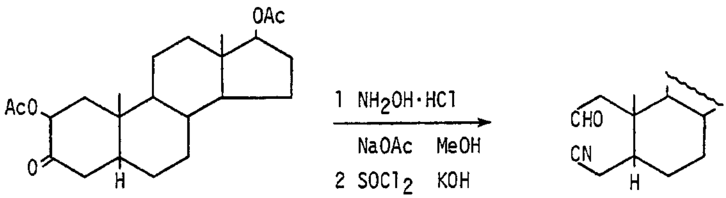
Cyanoaldehydes

$BuCH(Et)CHO \xrightarrow[KOH \quad H_2O]{CH_2{=}CHCN} BuC(Et)(CH_2CH_2CN)CHO$ 77%

JACS (1944) 66 56

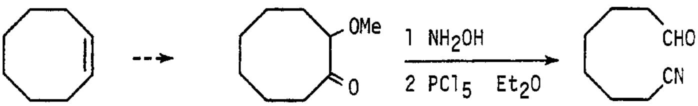
JCS (1958) 3986

Org React (1949) 5 79



49-56%

Tetr Lett (1972) 261



JACS (1966) 88 3168
JOC (1962) 27 29

Section 341 Aldehyde — Olefin

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

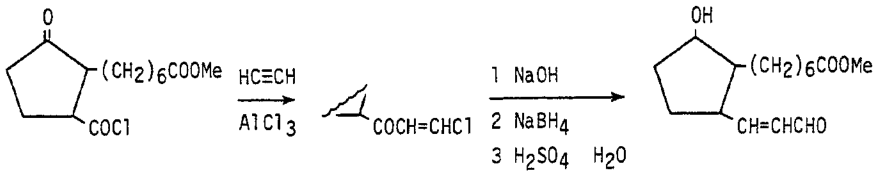
$$\begin{matrix} CH_2C{\equiv}CH \\ CH_2CH{=}CHPr \end{matrix} \xrightarrow[2\ CH(OEt)_3]{1\ EtMgBr\quad Et_2O} \begin{matrix} CH_2C{\equiv}CCH(OEt)_2 \\ CH_2CH{=}CHPr \end{matrix} \xrightarrow[2\ H_2SO_4\quad H_2O]{1\ H_2\quad Pd\quad EtOAc} \begin{matrix} CH_2CH{=}CHCHO \\ CH_2CH{=}CHPr \end{matrix}$$

JCS (1955) 4244 1007

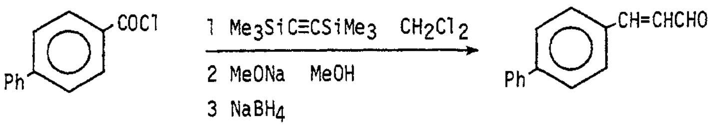
$$EtC{\equiv}CEt \xrightarrow[2\ LiAlH_4]{1\ ClSO_2CNO\quad CH_2Cl_2} \begin{matrix} Et & & Et \\ & C{=}C & \\ H & & CHO \end{matrix}$$

29%

Tetr Lett (1970) 27

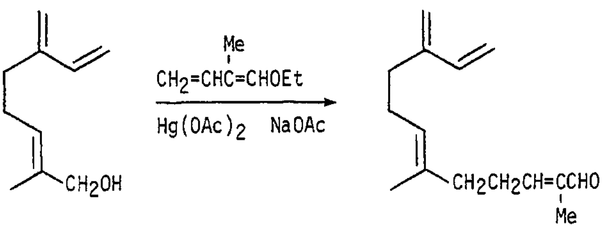


Tetr Lett (1966) 465



84%

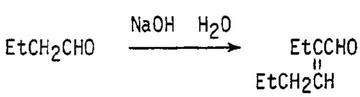
JOC (1973) 38 2254



<43%

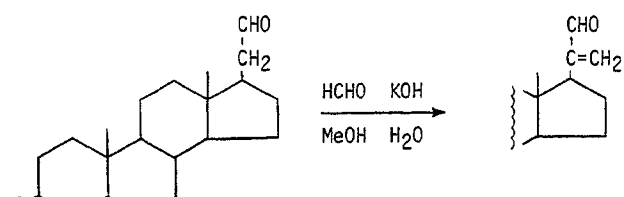
Chem Comm (1967) 947
JCS C (1970) 220
JCS Perkin I (1973) 2741

Review: The Aldol Condensation Org React (1968) 16 1



86%

Org React (1968) 16 1

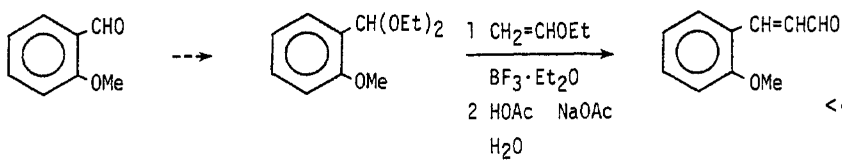


77%

Steroids (1969) 14 637

$$\mathrm{PhCHO} \xrightarrow[\substack{2\ H_2\ \ Pd\text{-}C\ \ Pyr\ \ EtOAc \\ 3\ m\text{-Chloroperbenzoic acid}}]{1\ ClMgC{\equiv}CSiMe_3\ \ Et_2O} \mathrm{PhCH(OH)CH\overset{O}{-}CHSiMe_3} \xrightarrow[MeOH]{H_2SO_4} \mathrm{PhCH{=}CHCHO} \quad 41\%$$

JACS (1971) 93 2080



<41%

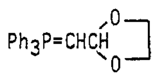
Ber (1961) 94 838
Bull Chem Soc Jap (1970) 43 1586
Helv (1956) 39 249

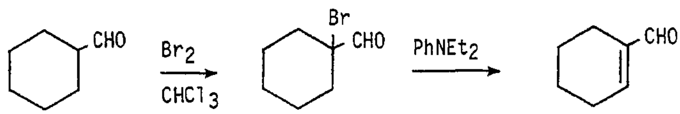
$$\mathrm{C_6H_{13}CHO} \xrightarrow{\mathrm{Ph_3P{=}C(Me)CHO}\ \ C_6H_6} \mathrm{C_6H_{13}CH{=}C(Me)CHO} \quad 72\%$$

Chem Ind (1960) 202

$Ph_3P{=}CHCHO$ JCS (1961) 1266

$(EtO)_2POCH_2CH(OEt)_2$, $NaNH_2$ Bull Chem Soc Jap (1962) 35 1498

 JCS Perkin I (1974) 37



60%

JCS (1949) 737
Bull Soc Chim Fr (1971) 4012
(1968) 283

$$\mathrm{C_8H_{17}CH_2CH_2CHO} \xrightarrow[KOAc]{Ac_2O} \mathrm{C_8H_{17}CH_2CH{=}CHOAc} \xrightarrow[\substack{2\ MeOH \\ 3\ KOH\ \ MeOH\ \ t\text{-}BuOH \\ 4\ Citric\ acid\ \ H_2O}]{1\ Br_2\ \ CCl_4} \mathrm{C_8H_{17}CH{=}CHCHO} \quad 9\%$$

JACS (1957) 79 889
Tetr Lett (1969) 3139

Via enamine JACS (1957) 79 1115

$$C_9H_{19}CH_2CH_2CHO \xrightarrow[\text{2 } H_2O_2 \quad H_2O \quad THF]{\text{1 } PhSeCl \quad HCl, \ EtOAc} C_9H_{19}CH{=}CHCHO$$

JACS (1973) 95 6137

$$C_5H_{11}Br \xrightarrow[\text{2 } HgCl_2 \quad MeCN \quad H_2O]{\text{1 } MeSCH_2\overset{OMe}{\overset{|}{C}}HCH_2SMe \quad (i\text{-}Pr)_2NLi} C_5H_{11}CH{=}CHCHO \qquad 52\%$$

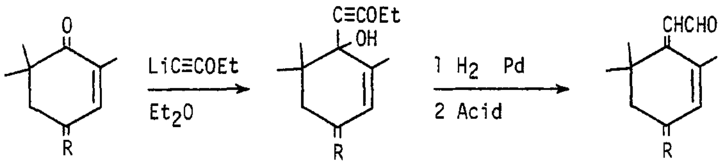
JACS (1971) 93 1724

$$C_8H_{17}Br \xrightarrow[\text{2 } \Delta \quad CaCO_3 \quad MeOCH_2CH_2OMe]{\text{1 } CH_2{=}CHCH_2SCH{=}CH_2 \quad Et\overset{Me}{\overset{|}{C}}HLi} C_8H_{17}CH{=}CHCHO \qquad 57\%$$

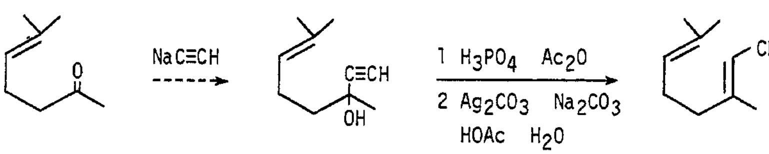
JACS (1973) 95 2693

$$PhBr \xrightarrow[\text{2 } Me_2NCH{=}CHCH{=}\overset{+}{N}Me_2 \ \overset{-}{ClO_4} \quad \text{3 } HCl \quad H_2O]{\text{1 } Mg \quad Et_2O} PhCH{=}CHCHO \qquad 53\%$$

Ber (1970) 103 222

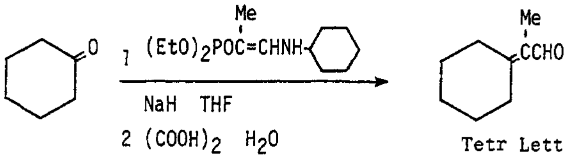


Helv (1967) 50 1606



~61%

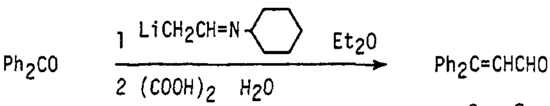
Helv (1959) 42 1945



86%

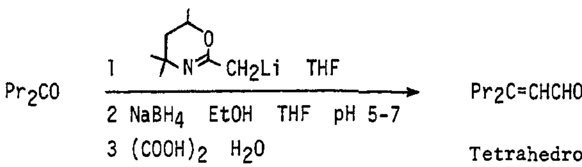
Tetr Lett (1968) 4359
JCS C (1969) 460

$(EtO)_2POCH_2CH{=}CHOEt$ Bull Soc Chim Fr (1970) 1369



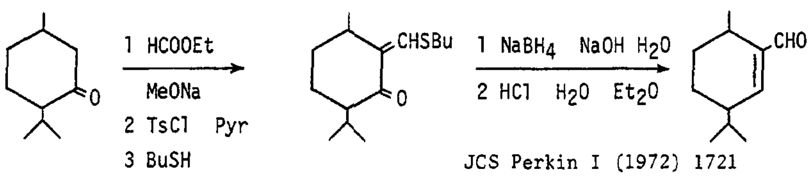
~ 70%

Org Synth (1970) 50 66
Angew (1968) 80 8
(Internat Ed 7 7)
JOC (1969) 34 1122

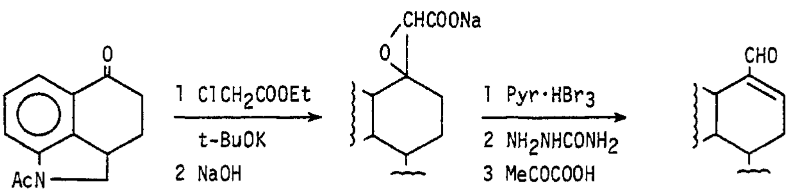


~65%

Tetrahedron (1971) 27 5979
JACS (1969) 91 764
JOC (1973) 38 36



JCS Perkin I (1972) 1721
Helv (1951) 34 728



30%

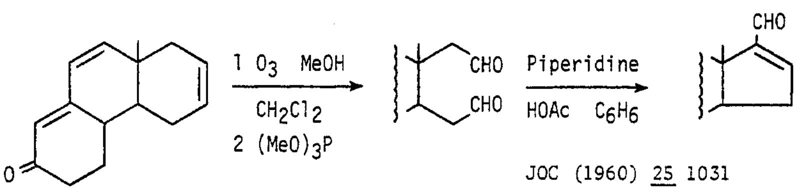
JACS (1956) 78 3087

$$C_5H_{11}CH_2COMe \xrightarrow[\text{2 Zn EtOH}]{\text{1 HCONMe}_2\text{ POCl}_3} C_5H_{11}C(CHO){=}CHMe$$

Chem Pharm Bull (1972) 20 309

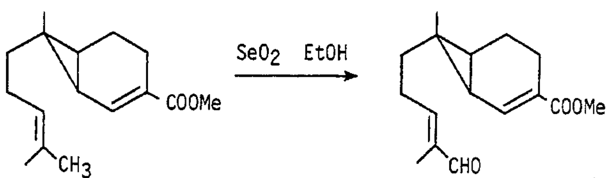
$$C_5H_{11}CH_2C(Me)O \xrightarrow[\text{2 }\Delta\text{; 3 LiClO}_4\text{ CaCO}_3\text{ HMPA}]{\text{1 LiCHCl}_2\text{ THF}} C_5H_{11}CH{=}C(Me)CHO \qquad 74\%$$

Tetr Lett (1973) 2465



54%

JOC (1960) 25 1031

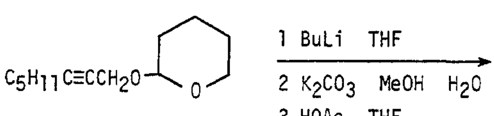


55%

JACS (1969) 91 4933

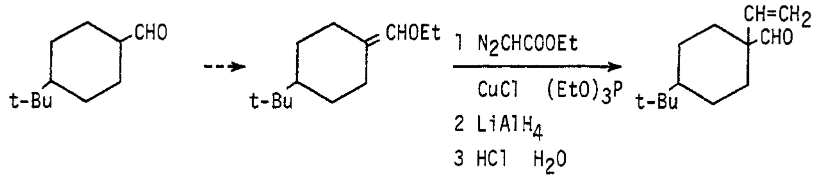
$$\overset{O}{CH_2{-}CHCHO} \xrightarrow[\text{THF; 2 HBF}_4\text{; 3 NaI Me}_2\text{CO}]{\text{1 Sodium (cyclopentadienyl)-dicarbonylferrate}} CH_2{=}CHCHO$$

JACS (1972) 94 7170

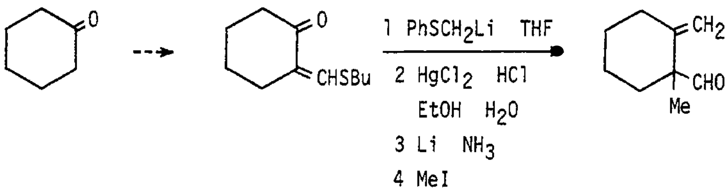


$C_5H_{11}CH{=}CHCHO$

Tetr Lett (1972) 1815
(1971) 591



Tetr Lett (1972) 5121



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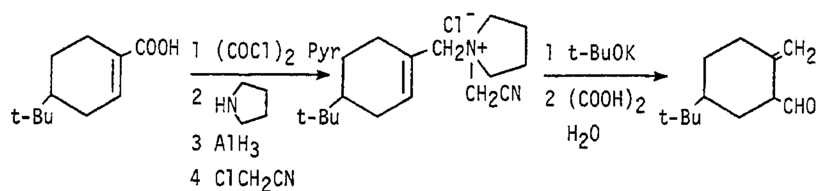
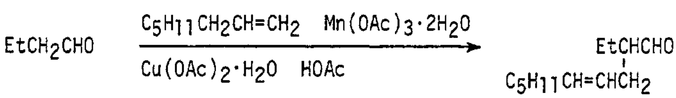
JACS (1972) 94 4758

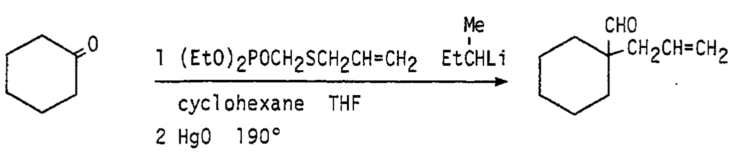


JOC (1973) 38 2915



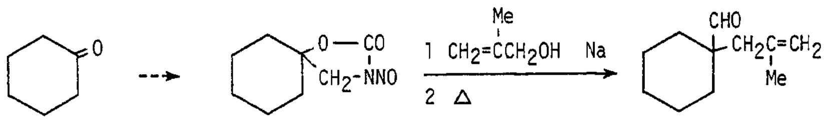
25%

Synthesis (1972) 376

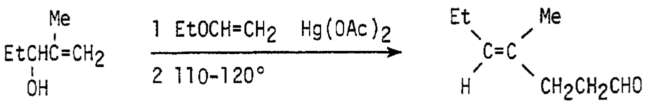


82%

JACS (1970) 92 5522



JOC (1969) 34 1220



35%

JACS (1973) 95 553
JCS Perkin I (1973) 1791

Also via: β-Hydroxyaldehydes (Section 324)

Section 342 Amide — Amide

Diamides

$$AcNH(CH_2)_5COOH \xrightarrow{\text{Electrolysis}} AcNH(CH_2)_{10}NHAc$$

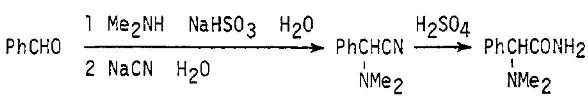
Z Naturforsch (1947) 2b 182

Also via:

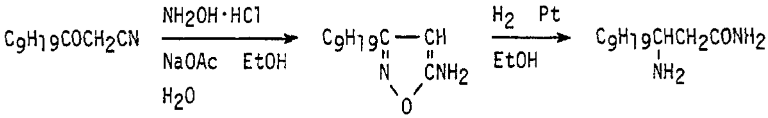
	Section
Diamines	350
Dicarboxylic acids	312

Section 343 Amide — Amine

Aminoamides



JOC (1961) 26 4741
Annalen (1971) 749 198
JCS (1949) 2323



83%

Can J Chem (1968) 46 3617

$$CH_2{=}CHCONHPh \xrightarrow[EtOH]{PhCH_2NH_2} PhCH_2NHCH_2CH_2CONHPh$$

93%

JOC (1960) 25 1822

$$NC(CH_2)_4CN \xrightarrow[(basic)\ \ H_2O]{Ion\ exch\ resin} H_2NOC(CH_2)_4CN \xrightarrow[NH_3]{H_2\ \ Ni} H_2NOC(CH_2)_4CH_2NH_2$$

50%

Ber (1959) 92 2616

Section 344 Amide — Ester

Acylaminoesters

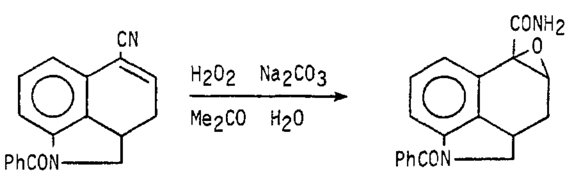
$$BuCH{=}CH_2 \xrightarrow[Me_2CO\ \ t\text{-}BuOH]{NHAc{-}CH_2COOEt\ \ h\nu} BuCH_2CH_2CH(NHAc)COOEt$$

10-12%

Chem Comm (1965) 471

Section 345 Amide — Epoxide

Epoxyamides



95%

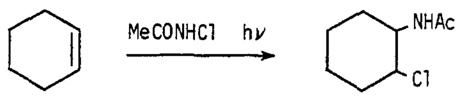
JACS (1956) 78 3087

Section 346 Amide — Halide

Haloamides

$PhCH(Br)COCl \xrightarrow{Et_2NH \quad CCl_4} PhCH(Br)CONEt_2$ 49%

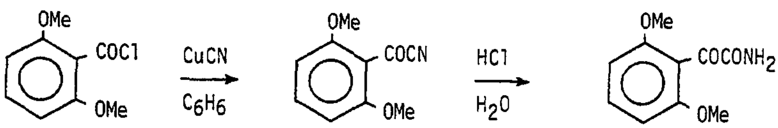
JACS (1949) 71 3479
(1955) 77 4840



Tetr Lett (1971) 4425

Section 347 Amide — Ketone

Amides of α, β, γ and δ-ketoacids, acylaminoketones



48%

Can J Chem (1971) 49 919

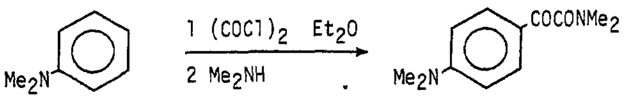
$PhCOCl \xrightarrow{BuNC} PhCOCONHBu$ Ber (1961) 94 1116 46%

$(PhCH_2)_2CHCHO \dashrightarrow (PhCH_2)_2CHCH(OH)CN \xrightarrow[2\ CrO_3 \quad HOAc]{1\ H_2SO_4 \quad t\text{-}BuOH} (PhCH_2)_2CHCOCONHBu\text{-}t$

Synthesis (1971) 538

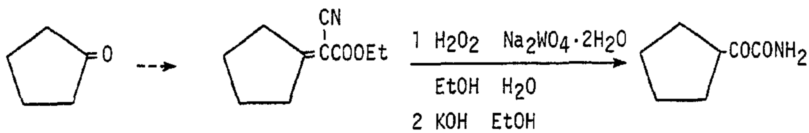
$$PhBr \xrightarrow[2\ (CONMe_2)_2]{1\ BuLi\quad THF} PhCOCONMe_2$$ 81%

Synth Comm (1973) 3 325
Compt Rend (1927) 184 825



68%

JOC (1959) 24 265



JOC (1963) 28 3088

$$BuCH_2CONMe_2 \xrightarrow{POCl_3\quad C_6H_6} \begin{matrix} BuCHCONMe_2 \\ | \\ BuCH_2CO \end{matrix}$$ 58%

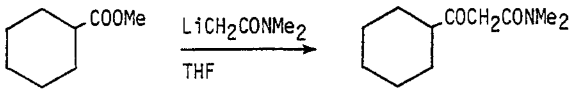
Ber (1959) 92 1456

$$PhNH_2 \xrightarrow[Et_2O]{MeCOCH_2COF} MeCOCH_2CONHPh$$ 74%

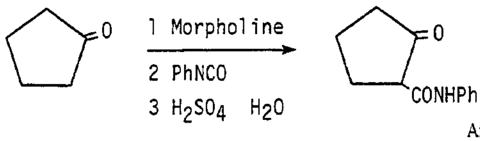
JOC (1961) 26 225

$$PhNH_2 \xrightarrow[C_6H_6]{Diketene} MeCOCH_2CONHPh$$ 74%

Org Synth (1955) Coll Vol 3 10
Ber (1959) 92 1456
JACS (1964) 86 5654



Tetr Lett (1973) 1495
JOC (1959) 24 1551

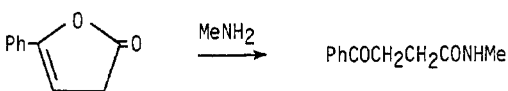


Annalen (1964) 673 132
Ber (1962) 95 926
JOC (1961) 26 3043

Via silyl enol ether Tetr Lett (1973) 4271

$$PhCOCH_2COOEt \xrightarrow[\text{xylene}]{PhNH_2} PhCOCH_2CONHPh$$ 74-76%

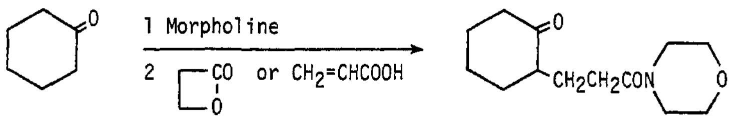
Org Synth (1955) Coll Vol 3 108
(1963) Coll Vol 4 80



JACS (1958) 80 4573

PhBr —(1 Mg Et_2O; 2 CH_2CO / CH_2CO > NH)→ $PhCOCH_2CH_2CONH_2$ 65%

Chem Pharm Bull (1971) 19 391



64%

Acta Chem Scand (1964) 18 2201
Tetr Lett (1965) 2869

$$\underset{\displaystyle NH_2}{MeCHCOOH} \xrightarrow{Ac_2O \quad Pyr} \underset{\displaystyle NHAc}{MeCHCOMe}$$

81-88%

Org Synth (1963) Coll Vol 4 5

Also via: Ketoacids (Section 320)

Section 348 Amide — Nitrile

Cyanoamides

$$\begin{matrix} CN \\ (CH_2)_4 \\ CN \end{matrix} \xrightarrow[H_2O]{H_2O_2 \quad KOH} \begin{matrix} CONH_2 \\ (CH_2)_4 \\ CN \end{matrix}$$

31%

JOC (1950) 15 800
Ber (1959) 92 2616

Also via: Cyanoacids (Section 321)

Section 349 Amide — Olefin

Olefinic amides

$$PhCHO \xrightarrow[\text{piperidine}]{\begin{matrix} COOH \\ CH_2CONH_2 \end{matrix}} PhCH{=}CHCONH_2$$

JACS (1948) 70 2596
(1949) 71 3562

$$PhCHO \xrightarrow[NaOAc]{MeCH_2CONHCOCH_3} \underset{46\%}{PhCH{=}CHCONH_2} + \underset{\text{Me } 37\%}{PhCH{=}CCONH_2}$$

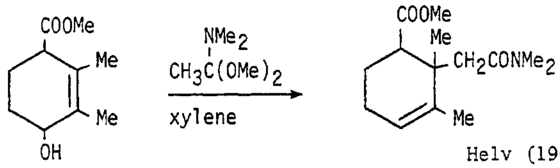
Rec Trav Chim (1951) 70 146

$$PhCOMe \xrightarrow[BF_3 \cdot Et_2O]{PhC{\equiv}CNMe_2} PhC(Me){=}C(Ph)CONMe_2 \qquad 84\%$$

Ber (1970) 103 564

$$EtCH{=}CHCH_2Br \xrightarrow[2\ MeCH{=}CHCONEt_2]{1\ Mg} CH_2{=}CHCH(Et)CH(Me)CH_2CONEt_2 \qquad 80\%$$

Tetr Lett (1971) 3251



Helv (1964) 47 2425
Ber (1971) 104 3689
JCS C (1971) 2950

Also via:

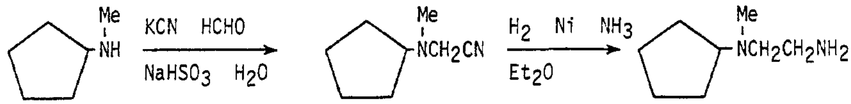
	Section
Acetylenic amides	304
Olefinic acids	322

Section 350 Amine — Amine

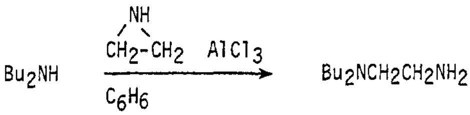
1,1-Diamines, 1,2-diamines, 1,3-diamines and higher diamines

$$Et_2NH \xrightarrow{HCHO} (Et_2N)_2CH_2$$

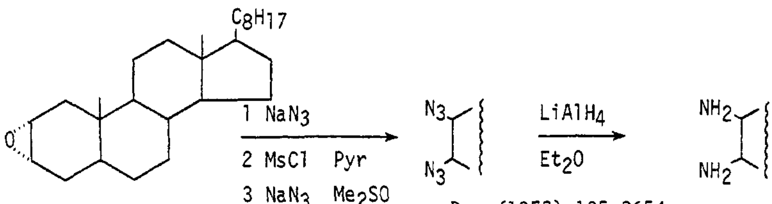
JACS (1932) 54 4172



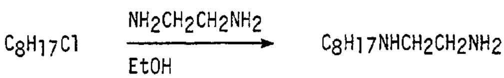
JACS (1946) 68 1905



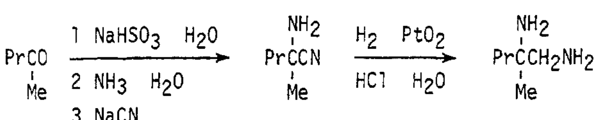
JACS (1946) 68 2006
(1948) 70 184



Ber (1972) 105 2654
(1966) 99 1502
JOC (1967) 32 511

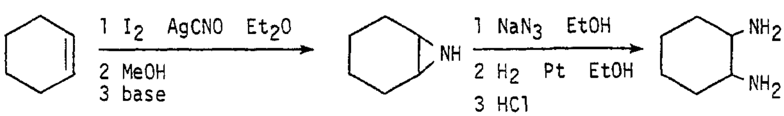


JACS (1945) 67 1581



28%

JACS (1960) 82 696
(1949) 71 2530



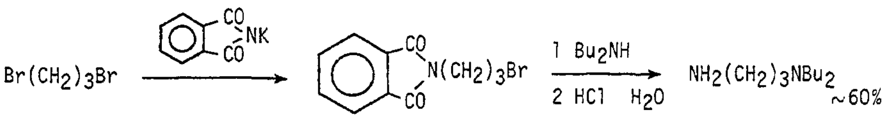
32%

trans

JOC (1967) 32 511
Tetrahedron (1973) 29 3137

$$BuNH_2 \xrightarrow{CH_2=CHCN} BuNH(CH_2)_2CN \xrightarrow[EtOH]{H_2 \quad Ni \quad NH_3} BuNH(CH_2)_2CH_2NH_2 \qquad <66\%$$

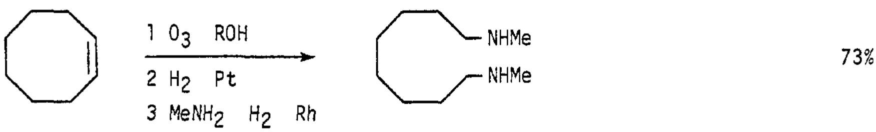
JACS (1946) 68 1217



Org Synth (1955) Coll Vol 3 256 254

$$C_9H_{19}COCH_2CN \xrightarrow[2\ H_2 \quad Pt \quad EtOH]{1\ NH_2OH\cdot HCl \quad NaOAc} C_9H_{19}CH(NH_2)CH_2CONH_2 \xrightarrow[THF]{B_2H_6} C_9H_{19}CH(NH_2)CH_2CH_2NH_2$$

Can J Chem (1968) 46 3617



Tetr Lett (1971) 3591 3587

Also via: Diamides (Section 342)

Section 351 Amine — Ester

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

$$MeCH(NH_2)COOH \xrightarrow[2\ PhCH_2OH \quad HCl \quad Et_2O]{1\ COCl_2 \quad THF} MeCH(NH_2)COOCH_2Ph \qquad 76\%$$

Coll Czech (1958) 23 1947

$PhCH_2CH(NH_2)COOH \xrightarrow{PhCH_2OH \quad PhSO_3H} PhCH_2CH(NH_2)COOCH_2Ph$ 75%

JACS (1952) 74 1092

TsOH Chem Ind (1955) 16

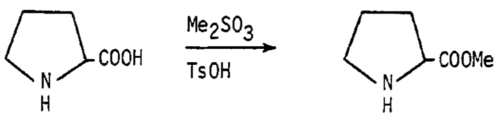
SO_2Cl_2 Annalen (1961) 640 139

$SOCl_2$ JOC (1965) 30 3575

Polyphosphoric acid JACS (1954) 76 5781

$i\text{-}PrCH_2CH(NH_2)COOH \xrightarrow{MeOH \quad SOCl_2} i\text{-}PrCH_2CH(NH_2)COOMe$ 83-86%

Helv (1953) 36 1109
JACS (1956) 78 381



91%

JCS (1963) 1927

$PhCH_2CH(NH_2)COOH \xrightarrow[dioxane]{Me_2C{=}CH_2 \quad H_2SO_4} PhCH_2CH(NH_2)COOBu\text{-}t$ ~70%

Chem Ind (1959) 1121

t-BuOAc $HClO_4$ Annalen (1961) 646 134

$HCl \cdot NH_2CH_2COCl \xrightarrow{PhCH_2OH} NH_2CH_2COOCH_2Ph$

Helv (1929) 12 332

$i\text{-}PrCH_2CH(NH_2)COOMe \xrightarrow{C_6H_{13}OH \quad MeONa} i\text{-}PrCH_2CH(NH_2)COOC_6H_{13}$ 93-96%

Helv (1953) 36 1109

$$PhCH_2Br \xrightarrow[Et_2O]{N(SiMe_3)_2CH_2COOEt \quad NaN(SiMe_3)_2} PhCH_2CH(N(SiMe_3)_2)COOEt \xrightarrow[H_2O]{HCl} PhCH_2CH(NH_2)COOEt$$

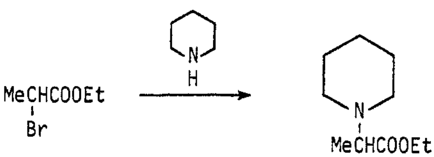
Angew (1968) 80 797
(Internat Ed 7 809)

$$MeCH_2CN \xrightarrow[HCl]{MeOH} MeCH_2C(OMe){=}NH \cdot HCl \xrightarrow[\text{2 t-BuOK} \quad \text{3 HCl} \quad H_2O]{\text{1 NaOCl} \quad H_2O} MeCH(NH_2)COOMe$$

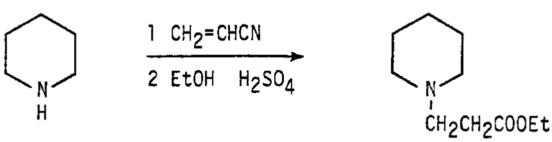
JACS (1960) 82 4422

$$Me_2C(Br)COCl \dashrightarrow Me_2C(Br)CONHPr \xrightarrow[Et_2O]{t\text{-}BuOK} Me_2C(NHPr)COOBu\text{-}t$$ 41%

JACS (1964) 86 1356



JACS (1934) 56 697



$<71\%$

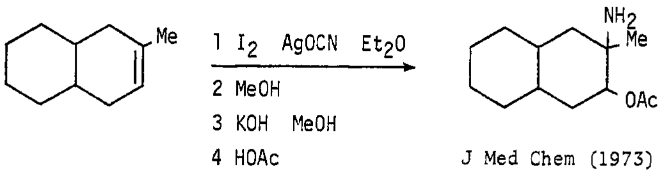
JACS (1945) 67 1071

$$PhNH_2 \xrightarrow[HOAc]{CH_2{=}CHCOOMe} PhNHCH_2CH_2COOMe$$ 69%

JACS (1949) 71 1901 2124 2532

$$Me_2C{=}CHCOOMe \xrightarrow[h\nu]{MeCH_2NEt_2} \underset{\displaystyle MeCHNEt_2}{Me_2\overset{}{C}CH_2COOMe}$$

Chem Comm (1968) 180



J Med Chem (1973) 16 23

Section 352 Amine — Ether

Aminoethers

$$C_7H_{15}OH \xrightarrow{Et_2NH \quad HCHO} C_7H_{15}OCH_2NEt_2$$

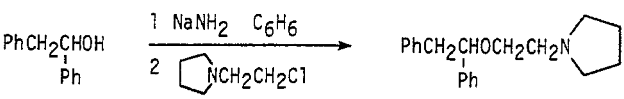
JACS (1932) 54 4172

$$PhCHO \xrightarrow[HgCl_2 \quad CaSO_4]{Et_2NH \quad BuOH} \underset{\displaystyle Et_2N}{PhCHOBu}$$ 47%

JACS (1955) 77 1098

$$PhCH_2OH \xrightarrow{\overset{NH}{CH_2{-}CH_2} \quad HBF_4} PhCH_2OCH_2CH_2NH_2$$ 51%

Ber (1964) 97 510



73%

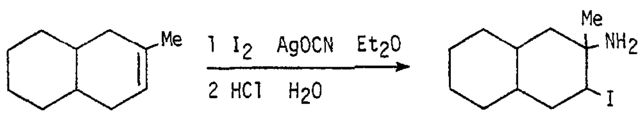
JACS (1948) 70 3098

Section 353 Amine — Halide

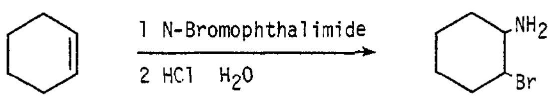
Aminohalides

$$Me_2C{=}CMe_2 \xrightarrow[\text{2 } SnCl_2 \quad HCl \quad H_2O]{\text{1 } NOCl \quad MeOH} Me_2C(NH_2){-}CMe_2Cl$$

JACS (1960) 82 6068



J Med Chem (1973) 16 23



Bull Soc Chim Fr (1966) 1910

$$Me_2NCH_2CH_2OH \xrightarrow{SOCl_2} Me_2NCH_2CH_2Cl$$ 67-80%

Org Synth (1963) Coll Vol 4 333

$$Et_2NH \xrightarrow{Br(CH_2)_3Cl} Et_2N(CH_2)_3Cl$$ 70%

JACS (1945) 67 1472

Also via: Haloamides (Section 346)

Section 354 Amine — Ketone

α, β, γ and δ-aminoketones

$PrCOCl \xrightarrow[\text{1,8-diazabicyclo[5.4.0]undecene; 2 HCl}]{\text{1 } NC\text{-}CH_2COOEt} PrCOCH_2NH_2$ 61%

JOC (1973) 38 3571
Synth Comm (1972) 2 237

$PhCOCl \xrightarrow{CuCN} PhCOCN \xrightarrow[\text{2 HCl } H_2O]{\text{1 } SnCl_2 \text{ HCl } Et_2O} PhCOCH_2NH_2$ 67%

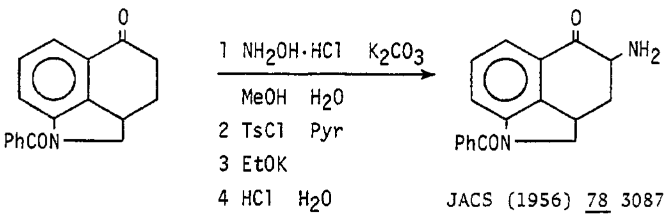
JOC (1972) 37 318

$PhCH(NH_2)CH_3 \xrightarrow[\text{2 MeONa MeOH; 3 HCl } H_2O]{\text{1 t-BuOCl } C_6H_6} PhCOCH_2NH_2$ 55-72%

Org Synth (1961) 41 82

$PhH \xrightarrow[AlCl_3 \ CS_2]{HCl\cdot NH_2CH_2COCl} PhCOCH_2NH_2$ 60%

J Prakt Chem (1957) 5 91

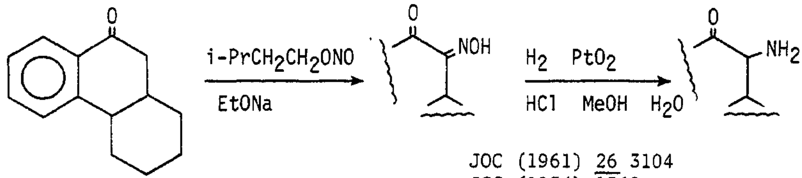


<43%

JACS (1956) 78 3087

$PhCH_2COMe \xrightarrow[\text{2 MeI EtOH; 3 Na}]{\text{1 } Me_2NNH_2} PhCH(NH_2)COMe$ 17%

JOC (1957) 22 358



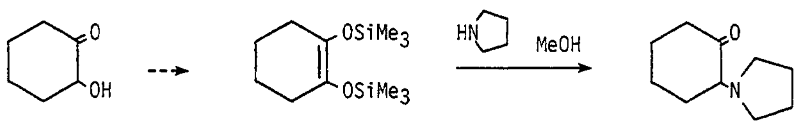
41%

JOC (1961) 26 3104
JCS (1934) 1568

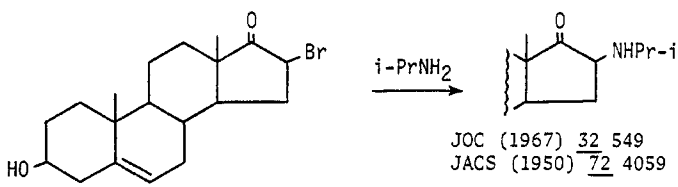
$$PhCN \xrightarrow[\substack{2\ NH_3 \\ 3\ t\text{-}BuOCl}]{1\ PhCH_2MgBr} \underset{\substack{\| \\ NCl}}{PhCCH_2Ph} \xrightarrow[2\ HCl]{1\ MeONa} \underset{\substack{| \\ NH_2}}{PhCOCHPh}$$

66%

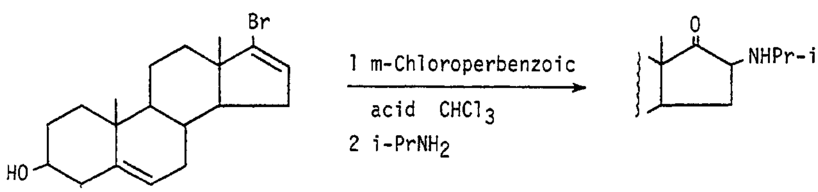
JACS (1960) 82 4422 459



Ber (1972) 105 975



JOC (1967) 32 549
JACS (1950) 72 4059



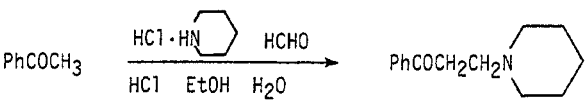
JOC (1967) 32 549

$$PrCOCl \xrightarrow{CH_2N_2} PrCOCHN_2 \xrightarrow[2\ Me_2\overset{+}{N}=CH_2\ \overset{-}{I}\quad Me_2SO]{1\ Et_3B\quad THF} PrCOCH(Et)CH_2NMe_2$$

JACS (1973) 95 602

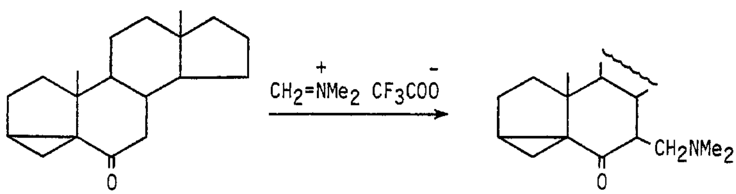
Reviews: The Mannich Reaction — Org React (1942) 1 303

Advances in the Chemistry of Mannich Bases — Synthesis (1973) 703



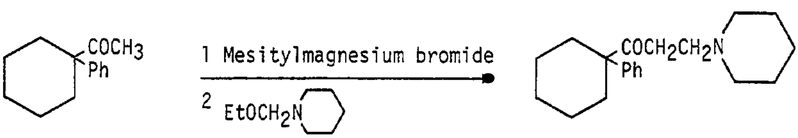
85%

Org React (1942) 1 303 329
Org Synth (1955) Coll Vol 3 305



94%

JACS (1968) 90 5622



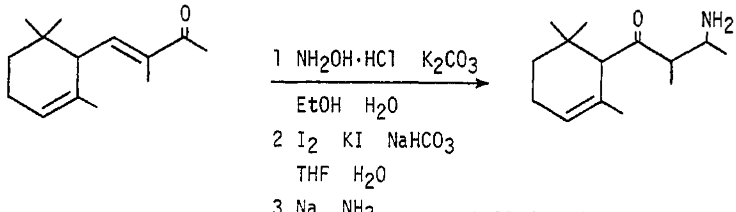
75%

Bull Soc Chim Fr (1962) 273

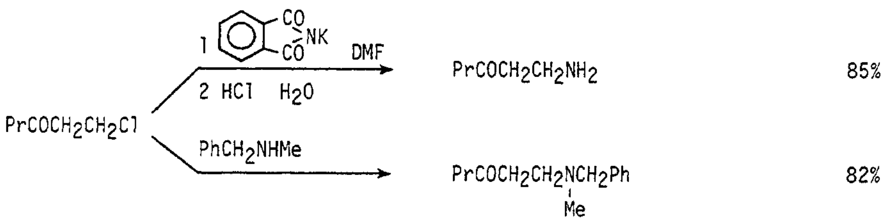
$$EtCOCH{=}CH_2 \xrightarrow{Et_2NH\quad Et_2O} EtCOCH_2CH_2NEt_2$$

>37%

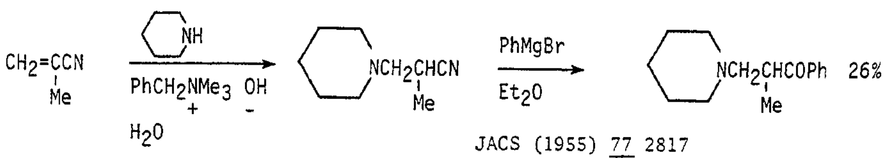
JACS (1950) 72 4059
Org Synth (1941) Coll Vol 1 196
JOC (1964) 29 2346



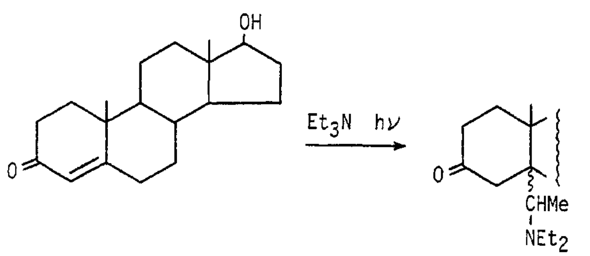
JACS (1972) 94 9128



JACS (1971) 93 2492



JACS (1955) 77 2817



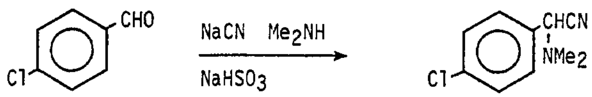
Chem Comm (1968) 180

$$Et_2N(CH_2)_3Cl \xrightarrow[\text{2 HCl } H_2O]{\text{1 } MeCOCH_2COOEt \text{ Na xylene}} Et_2N(CH_2)_3CH_2COMe$$

JACS (1947) 69 1258

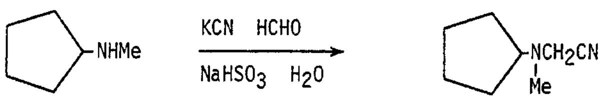
Section 355 Amine — Nitrile

Cyanoamines, aminonitriles



84%

JOC (1961) 26 4741
JACS (1960) 82 696



JACS (1946) 68 1905
Org Synth (1955) Coll Vol 3 275

$$PhBr \xrightarrow[2\ (CN)_2]{1\ Mg\quad Et_2O} Ph_2C(NH_2)CN$$

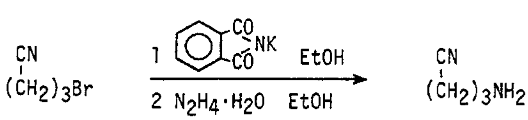
33%

JOC (1954) 19 285

$$PhNHEt \xrightarrow[AlCl_3]{CH_2=CHCN} PhN(Et)CH_2CH_2CN$$

70%

Annalen (1972) 760 151
Org React (1949) 5 79
Org Synth (1963) Coll Vol 4 146



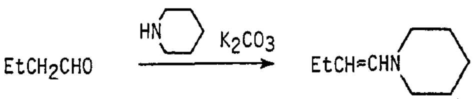
JCS (1947) 1369

Section 356 Amine — Olefin

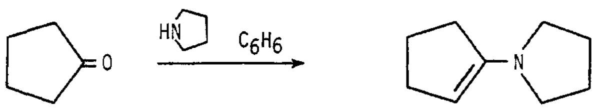
Olefinic amines, enamines

For allylic amination see section 101 vol 1 (Amines from Hydrides)

Reviews:	Enamines	Advances in Org Chem (1963) 4 1
	Enamines	Chem Ind (1970) 1188



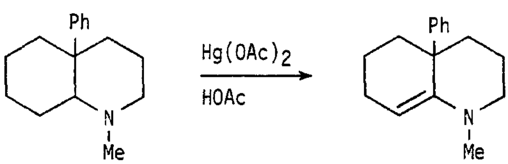
Ber (1936) 69 2106
JACS (1963) 85 207



80-90%

JACS (1963) 85 207

TsOH xylene	Org Synth (1968) 48 56
Molecular sieves	JOC (1971) 36 1570
	Rec Trav Chim (1972) 91 605
$TiCl_4$	JOC (1967) 32 213
Trisdialkylaminoboranes	JCS (1965) 5142



JOC (1961) 26 1104

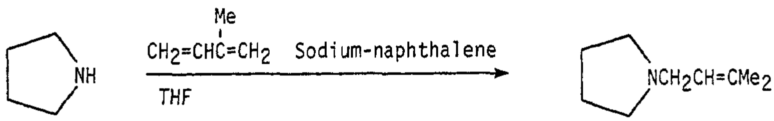
$$PrCH_2Br \xrightarrow[2\ HCONBu_2]{1\ Mg\quad Et_2O\quad THF} PrCH{=}CHNBu_2$$

80%

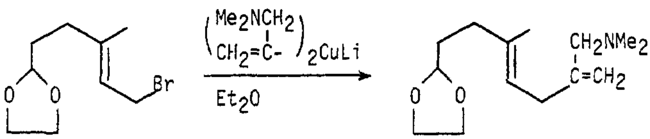
JOC (1973) 38 3074

$$EtCHO \xrightarrow[2\ CH_2=CH\overset{+}{P}Ph_3\ \overset{-}{Br}\quad DMF]{1\ NaH\quad Et_2NH} EtCH=CHCH_2NEt_2$$ 17%

JOC (1966) 31 467



Chem Ind (1973) 231



80-90%

JACS (1971) 93 7016

$$PhCH=C(Ph)CONMe_2 \xrightarrow{LiAlH_4\quad Et_2O} PhCH=C(Ph)CH_2NMe_2$$ 70%

Ber (1970) 103 564

Also via: Acetylenic amines (Section 305)

Section 357 Ester — Ester

$$PrCH_2COOEt \xrightarrow[EtONa]{CO(OEt)_2} PrCH(COOEt)_2 \qquad 45\%$$

JACS (1941) 63 2056

$(COOEt)_2$, EtONa — Org Synth (1963) Coll Vol 4 141
(1943) Coll Vol 2 288

ClCOOEt, Ph_3CNa — JACS (1941) 63 3156

$$BuBr \xrightarrow[EtOH]{CH_2(COOEt)_2\ \ EtONa} BuCH(COOEt)_2 \qquad 80\text{-}90\%$$

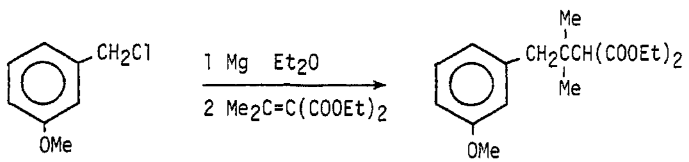
Org Synth (1932) Coll Vol 1 250
JOC (1971) 36 3944
Org React (1957) 9 107

$EtOMgCH(COOEt)_2$ — JACS (1950) 72 351

$CH_2(COOEt)_2$, NaH — JOC (1961) 26 644
Synth Comm (1973) 3 359

$CH_2(COOEt)_2$, basic ion exch resin — JOC (1963) 28 504

Aromatic halides — JACS (1959) 81 1627



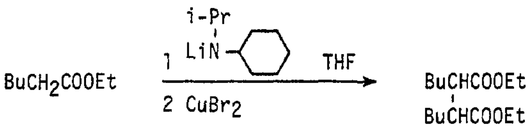
JOC (1971) 36 3260
Org Synth (1970) 50 38

$$C_5H_{11}CH{=}CH_2 \xrightarrow[Mn(OAc)_3\cdot 2H_2O]{CH_2(COOEt)_2} C_5H_{11}CH_2CH_2CH(COOEt)_2 \qquad 50\%$$

Chem Comm (1973) 693

$$\underset{Br}{MeCHCOOMe} \xrightarrow[CO\ \ MeOH]{NaCo(CO)_4\ \ dicyclohexylamine} MeCH(COOMe)_2 \qquad 18\%$$

JACS (1963) 85 2779



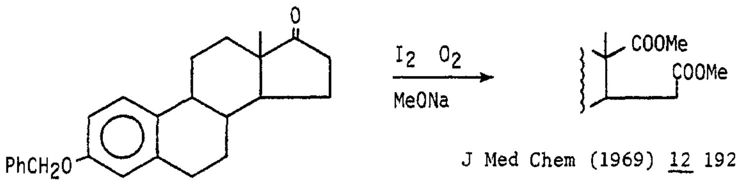
63%

JACS (1971) 93 4605

$$\mathrm{Me_2\underset{\displaystyle Br}{C}COOEt} \xrightarrow[\mathrm{THF}]{\mathrm{Zn\quad CuCl_2}} \begin{array}{l}\mathrm{Me_2CCOOEt}\\ \mathrm{Me_2CCOOEt}\end{array}$$

38%

Synthesis (1971) 306



43%

J Med Chem (1969) 12 192

$$\mathrm{Me_2C{=}CHCOOEt} \xrightarrow[\mathrm{DMF}]{\text{Electrolysis}\quad \mathrm{Et_4\overset{+}{N}\ Ts\overset{-}{O}}} \begin{array}{l}\mathrm{Me_2CCH_2COOEt}\\ \mathrm{Me_2CCH_2COOEt}\end{array}$$

Compt Rend (1967) 265 751
JOC (1964) 29 1670

$$\begin{array}{l}\mathrm{Br}\\ \mathrm{(CH_2)_{10}}\\ \mathrm{Br}\end{array} \xrightarrow[\mathrm{NH_3\quad Et_2O}]{\mathrm{CH_3COOBu\text{-}t\quad LiNH_2}} \begin{array}{l}\mathrm{CH_2COOBu\text{-}t}\\ \mathrm{(CH_2)_{10}}\\ \mathrm{CH_2COOBu\text{-}t}\end{array}$$

~98%

JACS (1959) 81 5817

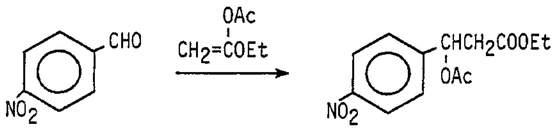
$$\begin{array}{l}\mathrm{COOMe}\\ \mathrm{(CH_2)_8COOH}\end{array} \xrightarrow[\mathrm{KOH\quad H_2O}]{\text{Electrolysis}} \begin{array}{l}\mathrm{COOMe}\\ \mathrm{(CH_2)_{16}COOMe}\end{array}$$

40-55%

Org Synth (1955) Coll Vol 3 401
JCS (1950) 3326
Advances in Org Chem (1960) 1 1

$$\mathrm{PrCOOH} \xrightarrow[\text{MeONa} \quad \text{MeOH}]{\mathrm{CH_2(COOH)-CH(OAc)COOEt} \quad \text{electrolysis}} \mathrm{PrCH_2CH(OAc)COOEt}$$

JCS (1954) 1460



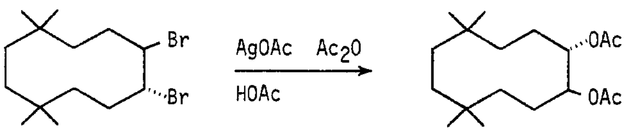
70%

Chem Comm (1969) 1216

$$\mathrm{BuCH(COOH)COOEt} \xrightarrow[2\ 200^\circ]{1\ \mathrm{Pb(OAc)_4} \quad \mathrm{C_6H_6}} \mathrm{BuCH(OAc)COOEt}$$

60%

Compt Rend (1960) <u>251</u> 2544



62%

Coll Czech (1969) <u>34</u> 340

$$\mathrm{PhCOCH_2Me} \xrightarrow[\text{Acid}]{\mathrm{CH_2{=}C(Me)OAc}} \mathrm{PhC(OAc){=}CHMe} \xrightarrow[2\ \mathrm{Ac_2O}]{1\ \mathrm{(i\text{-}Bu)_2AlH}} \mathrm{PhCH(OAc)CH(CHMe\text{-}OAc)Me}$$

Structure as printed: MeCHOAc over PhCHCHMe, with OAc under the first CH.

~65%

Annalen (1972) <u>763</u> 75
Synthesis (1972) 694

$$\mathrm{PhCH_2CH{=}CH_2} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{I_2} \quad \mathrm{PhCOOAg}} \mathrm{PhCH_2CH(OOCPh)CH_2OCOPh}$$

85%

Org React (1957) <u>9</u> 332
JOC (1972) <u>37</u> 789

$C_6H_{13}CH{=}CH_2 \xrightarrow[H_2SO_4]{SeO_2 \quad HOAc} C_6H_{13}CH(OAc)CH_2OAc$ 32%

Tetr Lett (1969) 4439
Bull Chem Soc Jap (1969) 42 2056

$AcO(CH_2)_5COOH \xrightarrow{\text{Electrolysis}} AcO(CH_2)_{10}OAc$ 83%

Chem Ing Tech (1970) 42 170
Synthesis (1971) 285

Also via:		Section
	Dicarboxylic acids	312
	Hydroxyesters	327
	Diols	323

Section 358 Ester — Ether, Epoxide

Alkoxyesters and epoxyesters (glycidic esters)

$CH_2{=}CHCOOPr \xrightarrow{PrOH \quad PrONa} PrOCH_2CH_2COOPr$ 59%

JACS (1946) 68 544
(1947) 69 2966

$BuCOONa \xrightarrow{ClCH_2OMe \quad H_2O} BuCOOCH_2OMe$

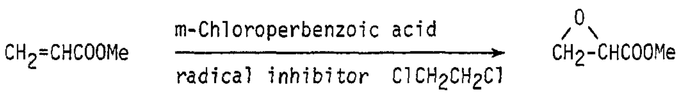
Suom Kemist (1969) 42 6
(Chem Abs 70 77263)
Synth Comm (1972) 2 361
JCS (1965) 2127

$PhC(Me){=}O \xrightarrow[C_6H_6]{ClCH_2COOEt \quad NaNH_2} PhC(Me)\overset{O}{-}CHCOOEt$ 62-64%

Org Synth (1955) Coll Vol 3 727
(1963) Coll Vol 4 649
Org React (1949) 5 413

continued

$ClCH_2COOBu$-t, t-BuOK	JACS (1953) 75 4995
	Rec Trav Chim (1970) 89 18
$BrCH_2COOEt$, $LiN(SiMe_3)_2$	Tetr Lett (1972) 3761
$Br_2CHCOOEt$, BuLi	Tetrahedron (1972) 28 3009



Chem Comm (1972) 64
JOC (1966) 31 2509
JACS (1959) 81 680

CF_3CO_2H Tetr Lett (1973) 4561

Also via:

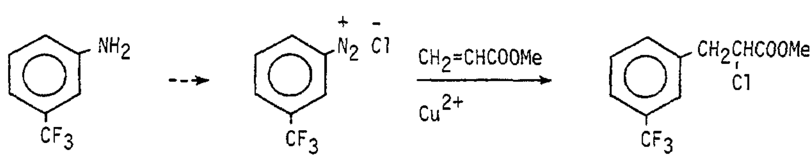
	Section
Alkoxyacids	318
Epoxyacids	318

Section 359 Ester — Halide

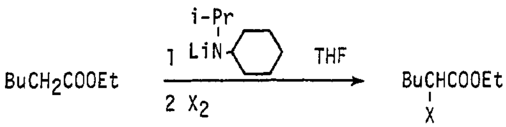
Esters of haloacids and esters of halohydrins

$$PhC{\equiv}CH \dashrightarrow PhC{\equiv}CBr \xrightarrow[MeOH]{Tl(NO_3)_3} \underset{\displaystyle Br}{PhCHCOOMe}$$

JACS (1973) 95 1296



Proc Chem Soc (1962) 117
Org React (1960) 11 189



95% (X=I)
92% (X=Br)

Tetr Lett (1971) 3995

$$\mathrm{C_{10}H_{21}CH(Me)COOMe} \xrightarrow[\mathrm{CCl_4}]{\mathrm{(CH_2CO)_2NX}\quad \text{benzoyl peroxide}} \mathrm{C_{10}H_{21}C(Me)(X)COOMe}$$

X=Cl or Br

JOC (1953) 18 842 649

Br_2 Ber (1960) 93 2222 2549

$$\mathrm{BuBr} \dashrightarrow \mathrm{BuCH(COOEt)_2} \xrightarrow[\mathrm{EtOH}]{\mathrm{KOH}} \mathrm{BuCH(COOH)COOEt} \xrightarrow[\mathrm{CCl_4}]{\mathrm{Br_2}} \mathrm{BuCH(Br)COOEt}$$

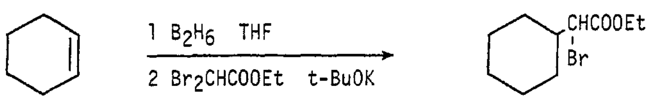
<67%

JACS (1949) 71 3107

$$\mathrm{BuI} \xrightarrow[\mathrm{NaH\quad THF}]{\mathrm{MeCOCH_2COOBu\text{-}t}} \mathrm{BuCH(COMe)COOBu\text{-}t} \xrightarrow[\substack{2\ \mathrm{Br_2}\quad \mathrm{CH_2Cl_2}\\ 3\ \mathrm{Ba(OH)_2}\quad \mathrm{EtOH}}]{1\ \mathrm{NaH}} \mathrm{BuCH(Br)COOBu\text{-}t}$$

87%

Tetr Lett (1972) 4067



47%

JACS (1968) 90 1911
Can J Chem (1972) 50 2387

$$\mathrm{RCH(OH)(CH_2)_NCOOEt} \xrightarrow{\mathrm{Ph_3P\quad CCl_4}} \mathrm{RCH(Cl)(CH_2)_NCOOEt}$$

N=0 or 5

Tetrahedron (1967) 23 359

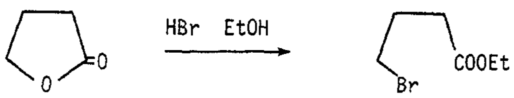
$(PhO)_3P{\cdot}MeI$ (iodoesters) JCS (1953) 2224

$CH_2{=}CHCOOMe \xrightarrow{HBr\quad Et_2O} BrCH_2CH_2COOMe$ 80-84%

Org Synth (1955) Coll Vol 3 576

$C_6H_{13}CH{=}CH_2 \xrightarrow[\text{diacetyl peroxide}]{BrCH_2COOEt} C_6H_{13}CH(Br)CH_2CH_2COOEt$

JACS (1948) 70 1055



77-84%

Org Synth (1965) 45 42
Synthesis (1973) 538

$EtCH_2COOMe \xrightarrow[2\ Br(CH_2)_3Br]{1\ LiN(Pr\text{-}i)_2\quad THF} EtCH(COOMe)(CH_2)_3Br$ 90%

Tetr Lett (1973) 2425

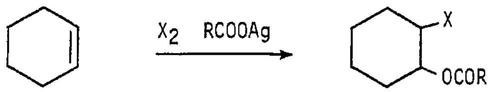
$MeCHOH{-}MeCHOH \xrightarrow{MeC(OMe)_3}$ (MeCHO)(MeCHO)C(OMe)(Me) $\xrightarrow{Me_3SiCl} MeCHCl{-}MeCHOAc$

JOC (1973) 38 4203 1173
JACS (1973) 95 278

$C_8H_{17}CH{=}CH_2 \xrightarrow{NCS\quad DMF} C_8H_{17}CH(OOCH)CH_2Cl$ 90%

Ber (1973) 106 606

1,2-Acyloxyhalides (acyl=HCO, MeCO, EtCO, etc., halide=Br, Cl) JACS (1959) 81 2195
Chem Pharm Bull (1972) 20 2707



X=Br or I
R=Me or Ph

Org React (1957) 9 332
Tetrahedron (1972) 28 3475

I_2, KIO_3, HOAc Tetr Lett (1973) 4485

Also via:

	Section
Haloacids	319
Halohydrins	329

Section 360 Ester — Ketone

$$\mathrm{BuC{\equiv}CH} \dashrightarrow \mathrm{BuC{\equiv}CBr} \xrightarrow{O_3 \quad MeOH} \mathrm{BuCOCOOMe} \qquad 40\%$$

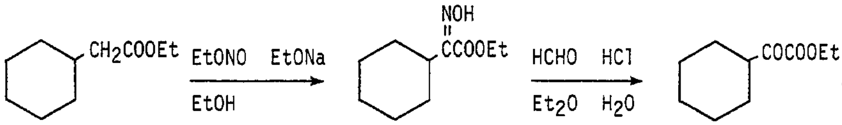
JOC (1973) 38 3653

$$\mathrm{PhCHO} \xrightarrow[\substack{Et_2O \quad EtOH \\ 2\ HCl \quad H_2O}]{1\ Me_2NCH_2COOEt \quad NaH} \mathrm{PhCH_2COCOOEt} \qquad 72\%$$

Annalen (1967) 703 37

$$\mathrm{PhCHO} \xrightarrow[HOAc]{PhSH \quad ZnCl_2} \mathrm{PhCH(SPh)_2} \xrightarrow[\substack{2\ ClCOOEt \\ 3\ Hydrolysis}]{1\ NaH \quad DMF} \mathrm{PhCOCOOEt}$$

JOC (1963) 28 961

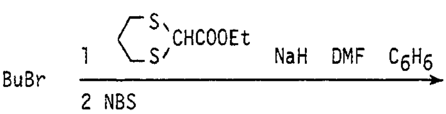


74%

Ber (1960) 93 1387

$PhCOOEt \xrightarrow[t\text{-}BuOK]{Me_2SO} PhCOCH_2SOMe \xrightarrow[EtOH]{H_2SO_4} PhCOCOOEt$ 55%

JACS (1966) 88 5498

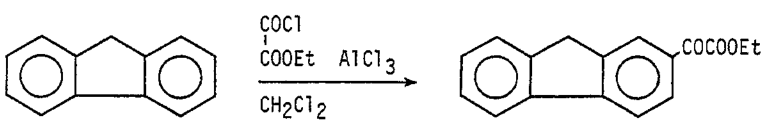


56%

JOC (1972) 37 505

$BuBr \dashrightarrow Bu_2Cd \xrightarrow{ClCOCOOEt \quad LiBr \quad THF} BuCOCOOEt$ 70%

JCS A (1966) 456
JACS (1954) 76 1914



99%

J Med Chem (1972) 15 1029

$PhCOCH_3 \dashrightarrow PhCOCH_2Br \xrightarrow{SeO_2 \quad EtOH} PhCOCOOEt$ <70%

JOC (1959) 24 1825

$BuC{\equiv}CCOOMe \xrightarrow[2\ H_2O_2 \quad H_2O \quad pH\ 8]{1\ (i\text{-}PrCH(Me))_2BH} BuCH_2COCOOMe$ 61%

Organometallics in Chem Synth (1971) 1 249

$PhCH(O)CHCOOEt \xrightarrow{BF_3 \quad C_6H_6} PhCH_2COCOOEt$ 80%

JACS (1958) 80 6386

$EtC{\equiv}CEt \xrightarrow[2\ MeOH]{1\ ClSO_2NCO \quad CH_2Cl_2} EtCOCH(Et)COOMe$ 58%

Tetr Lett (1970) 27

$PhCOCl \xrightarrow[2\ Ph_3P \quad i\text{-}Pr_2O;\ 3\ MeOH \quad H_2O;\ 4\ ZnCl_2 \quad Et_2O;\ 5\ Pyr]{1\ N_2CHCOOEt} PhCOCH_2COOEt$ 45%

Ber (1963) 96 1948

$EtCH_2COCl \xrightarrow[2\ HCl \quad H_2O]{1\ CH_2{=}C(OSi(Me_2)Bu\text{-}t)OEt \quad Et_3N \quad THF} EtCH_2COCH_2COOEt$ ~85%

Tetr Lett (1973) 1297

$EtCOCl \xrightarrow[2\ TsOH \quad C_6H_6]{1\ EtOMg\text{-}CH(COOBu\text{-}t)COOEt \quad Et_2O} EtCOCH_2COOEt$ 60%

JACS (1944) 66 1286
(1959) 81 2907
JCS C (1971) 2821

$PhCOCl \xrightarrow[2\ NH_3 \quad NH_4Cl \quad H_2O]{1\ MeCOCH_2COOEt \quad Na \quad C_6H_6} PhCOCH_2COOEt$ ~50%

Org Synth (1943) Coll Vol 2 266
(1963) Coll Vol 4 415

$t\text{-}BuOH \xrightarrow{Diketene} MeCOCH_2COOBu\text{-}t$ 75-80%

Org Synth (1962) 42 28

$MeCOCH_2COF$ JOC (1961) 26 225

Review: The Acetoacetic Ester Condensation

Org React (1942) 1 266

$CH_3COOEt \xrightarrow{Na} MeCOCH_2COOEt$ Org Synth (1932) Coll Vol 1 235

NaH Bull Soc Chim Fr (1954) 504

$NaN(SiMe_3)_2$ Angew (1963) 75 793 (Internat Ed 2 617)

Ba_3N_4 Z Naturforsch (1969) 24 937

$Me_2CHCOOEt \xrightarrow[2\ PhCOCl]{1\ Ph_3CNa\quad Et_2O} PhCOC(Me)_2COOEt$ 50-55%

Org Synth (1943) Coll Vol 2 268

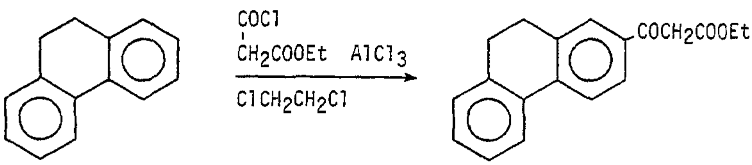
Lithium N-isopropylcyclohexylamide Tetr Lett (1971) 2953

$PhCH_2COCH_2COOEt \xrightarrow[2\ MeI]{1\ NaH\quad DMF\quad C_6H_6} PhCH_2COCH(Me)COOEt$ 77%

JOC (1956) 21 245

RX, K_2CO_3 Synthesis (1973) 316

γ-Alkylation of β-ketoesters JACS (1970) 92 6702

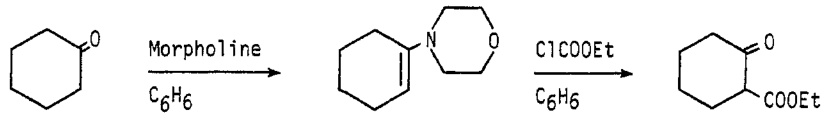


<73%

JOC (1972) 37 3687

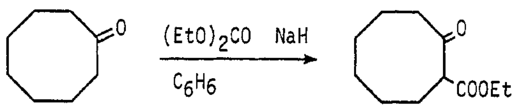
$EtCOEt \xrightarrow[CH_2Cl_2]{N_2CHCOOEt\quad Et_3\overset{+}{O}\ \overset{-}{B}F_4} EtCOCH(COOEt)Et$ 86%

JACS (1970) 92 5767



<62%

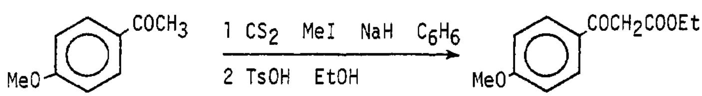
JACS (1963) 85 207



91-94%

Org Synth (1967) 47 20
JOC (1973) 38 3244
(1972) 37 2202

$(COOEt)_2$, EtONa; Δ	Org Synth (1943) Coll Vol 2 531
$(EtO)_2POCOOEt$, NaH	Tetr Lett (1966) 2201
Ph_3CNa; CO_2; CH_2N_2	Helv (1945) 28 1677
$(COBr)_2$; EtOH	Ber (1960) 93 551



72%

Tetr Lett (1973) 4207

$$EtCN \xrightarrow[C_6H_6]{Me_2C(Br)COOEt \quad Zn} EtCOC(Me)_2COOEt$$

80%

Bull Soc Chim Fr (1966) 1819
Org Synth (1963) Coll Vol 4 120

$$C_6H_{13}C\equiv CH \xrightarrow{1\ BuLi\ \ hexane} C_6H_{13}COCH(C_6H_{13})CH_2COOEt$$

2 $(C_6H_{13})_3B$ diglyme
3 $BrCH_2COOEt$
4 NaOAc H_2O_2 H_2O

78%

Tetr Lett (1973) 4491

$PhCHO \xrightarrow[NaCN \quad DMF]{MeCH{=}CHCOOEt} PhCOCH(Me)CH_2COOEt$ 33%

Angew (1973) 85 89
(Internat Ed 12 81)

$PhCOOEt \xrightarrow[t\text{-}BuOK]{Me_2SO} PhCOCH_2SOMe \xrightarrow[\text{2 } BrCH_2COOEt \quad \text{3 Zn HOAc}]{\text{1 NaH THF}} PhCOCH_2CH_2COOEt$ <52%

JOC (1969) 34 3624 3618

$EtCH_2COOEt \xrightarrow[\text{2 MeI} \quad \text{3 } HClO_4 \ MeCN \ H_2O]{\text{1 } CH_2{=}C(SOMe)SMe \quad LiN(Pr\text{-}i)_2 \quad THF} EtCH(CH_2COMe)COOEt$

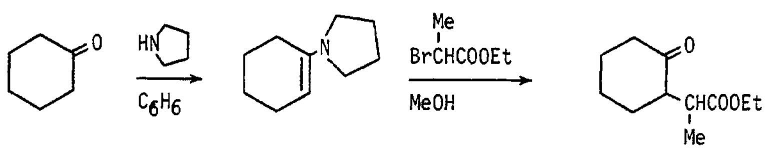
Tetr Lett (1973) 4715

$i\text{-}Pr(CH_2)_2Br \xrightarrow[\text{2 } CdCl_2 \quad \text{3 } ClCO(CH_2)_2COOMe \ C_6H_6]{\text{1 Mg } Et_2O} i\text{-}Pr(CH_2)_2CO(CH_2)_2COOMe$ 59%

JACS (1944) 66 46
Org Synth (1955) Coll Vol 3 601

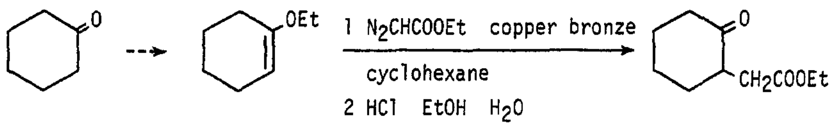
$PhI \xrightarrow[ROH \quad HCl]{HC{\equiv}CH \quad Ni(CO)_4} PhCOCH_2CH_2COOR$

Tetr Lett (1964) 2777



<44%

JACS (1963) 85 207
Coll Czech (1966) 31 602



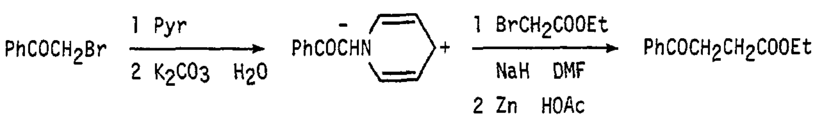
Synth Comm (1973) 3 255

$PhCH{=}CHCOOMe \xrightarrow[Et_2O]{BuLi \quad Ni(CO)_4} PhCH(COBu)CH_2COOMe$ 59%

JACS (1969) 91 4926

$C_5H_{11}C{\equiv}CCH_2COOEt \xrightarrow[EtOH]{HgSO_4 \quad H_2SO_4} C_5H_{11}COCH_2CH_2COOEt$ 85%

Can J Chem (1972) 50 1105

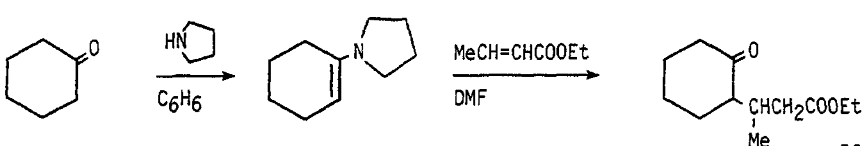


56%

Aust J Chem (1967) 20 2441

$PhCH_2COOEt \xrightarrow[LiNH_2]{CH_2{=}CHCOMe} PhCH(CH_2CH_2COMe)COOEt$ 29%

JOC (1964) 29 2346



<56%

JACS (1963) 85 207
Tetrahedron (1964) 20 1737

$$t\text{-BuCOCH}_3 \xrightarrow[\text{NaNH}_2]{\text{PhCH=CHCOOEt}} t\text{-BuCOCH}_2\underset{\text{Ph}}{\text{CH}}\text{CH}_2\text{COOEt} \qquad 64\%$$

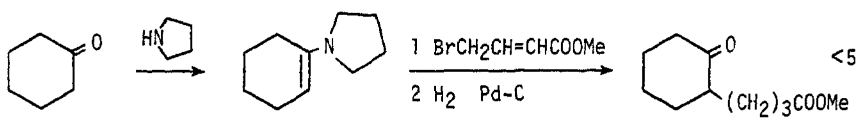
JOC (1949) <u>14</u> 261

$$\text{Me}_2\text{C=CH}_2 \xrightarrow[\substack{2\ \text{CH}_2\text{=CHCH}_2\text{COOEt} \\ 3\ \text{CO}}]{1\ i\text{-Pr}\overset{\text{Me}}{\underset{\text{Me}}{\text{C}}}\text{BH}_2} \text{Me}_2\text{CHCH}_2\text{CO(CH}_2)_3\text{COOEt} \qquad 84\%$$

JACS (1967) <u>89</u> 5285

$$\text{Br(CH}_2)_4\text{COOEt} \xrightarrow[2\ \text{EtI}]{1\ \text{Na}_2\text{Fe(CO)}_4} \text{EtCO(CH}_2)_4\text{COOEt} \qquad 74\%$$

JACS (1972) <u>94</u> 1788

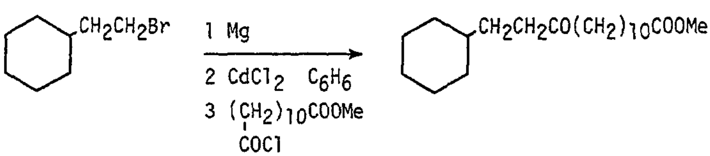


<52%

Tetr Lett (1965) 959

$$\text{C}_6\text{H}_{13}\text{CHO} \xrightarrow[\text{benzoyl peroxide}]{\text{CH}_2\text{=CH(CH}_2)_8\text{COOEt}} \text{C}_6\text{H}_{13}\text{CO(CH}_2)_{10}\text{COOEt}$$

Rec Trav Chim (1953) <u>72</u> 84



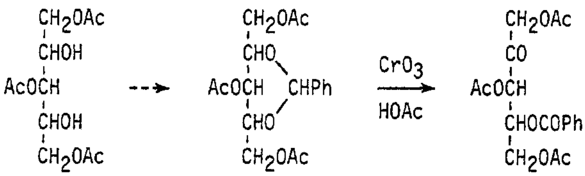
Nippon Kagaku Z (1968) <u>89</u> 516
(Chem Abs <u>69</u> 76716)
Org Synth (1955) Coll Vol 3 601

$$\underset{(CH_2)_4COOH}{\overset{COOMe}{|}} \xrightarrow[MeONa \quad MeOH]{MeCOCH_2CH_2COOH \quad electrolysis} \underset{(CH_2)_4CH_2CH_2COMe}{\overset{COOMe}{|}} \qquad 20\%$$

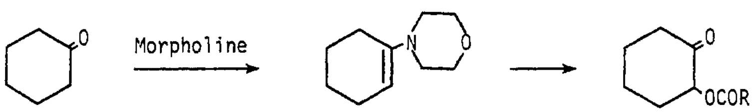
Nippon Kagaku Z (1956) 77 163
(Chem Abs 52 268)

$$C_{10}H_{21}COOH \xrightarrow[2\ CH_2N_2 \quad Et_2O]{1\ SOCl_2} C_{10}H_{21}COCHN_2 \xrightarrow{HOAc} C_{10}H_{21}COCH_2OAc \qquad >90\%$$

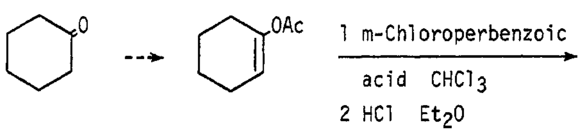
Org React (1954) 8 228



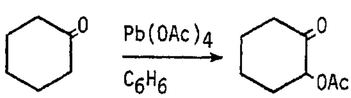
Aust J Chem (1971) 24 1219



$Tl(OAc)_3$ JOC (1968) 33 3359
Dibenzoyl peroxide JOC (1963) 28 581

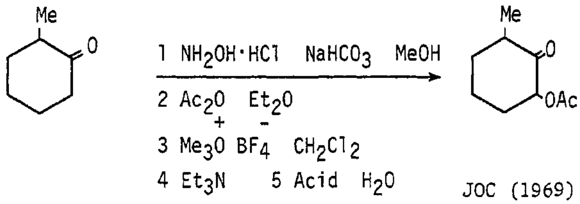


JOC (1967) 32 3934
(1962) 27 2131
Chem Pharm Bull (1972) 20 2156



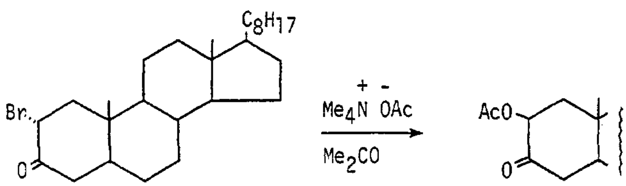
61%

JCS (1955) 4426
Synthesis (1973) 567
JCS (1961) 4472
Chem Comm (1970) 406



40-51%

JOC (1969) 34 1430



JOC (1961) 26 4563
JCS (1961) 2725
Tetrahedron (1963) 19 861

$$C_6H_{13}CH{=}CH_2 \xrightarrow[\text{HOAc}]{\text{Mn(OAc)}_3\ \ \text{Me}_2\text{CO}} C_6H_{13}\underset{\text{OAc}}{\underset{|}{C}}HCH_2CH_2COMe$$

24%

JACS (1971) 93 524

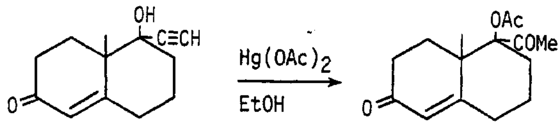
$$C_8H_{17}CH{=}CH_2 \xrightarrow{\text{KMnO}_4\ \ \text{Ac}_2\text{O}} C_8H_{17}COCH_2OAc$$

38%

JACS (1971) 93 3303

$$C_5H_{11}Br \xrightarrow[\text{EtONa}\ \ \text{EtOH}]{\text{MeCOCH}_2\text{COOBu-t}} C_5H_{11}\underset{\text{COOBu-t}}{\underset{|}{C}}HCOMe \xrightarrow[\text{2 Benzoyl peroxide}\quad \text{3 TsOH}]{\text{1 NaH}\ \ \text{C}_6\text{H}_6} C_5H_{11}\underset{\text{PhCOO}}{\underset{|}{C}}HCOMe$$

Acta Chem Scand (1960) 14 1445



Tetrahedron (1967) <u>23</u> 2453
Bull Soc Chim Fr (<u>1960</u>) 1079

Also via:

	Section
Ketoacids	320
Hydroxyketones	330

Section 361 Ester — Nitrile

α, β and higher cyanoesters. Esters of cyanohydrins

$$PrCHO \xrightarrow[HOAc]{\overset{CN}{|}\,CH_2COOEt \quad H_2 \quad Pd\text{-}C} PrCH_2\overset{CN}{\overset{|}{C}}HCOOEt \qquad 94\text{-}96\%$$

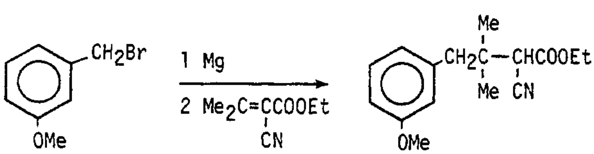
Org Synth (1955) Coll Vol 3 385

Review: The Alkylation of Esters and Nitriles

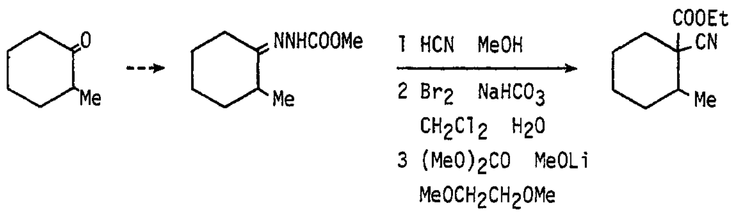
Org React (1957) <u>9</u> 107

$$i\text{-}PrBr \xrightarrow[EtOH]{Bu\overset{CN}{\overset{|}{C}}HCOOEt \quad EtONa} Bu\underset{i\text{-}Pr}{\overset{CN}{C}}COOEt \qquad 87\%$$

Org React (1957) <u>9</u> 161
Tetr Lett (1972) <u>1</u>279



JOC (1972) <u>37</u> 825



<25%

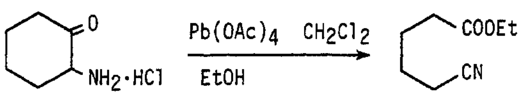
JACS (1971) 93 4318

$PhCH_2CN \xrightarrow[\text{toluene}]{CO(OEt)_2 \quad EtONa} PhCH(COOEt)CN$ 70-78%

Org Synth (1963) Coll Vol 4 461
JACS (1971) 93 4237

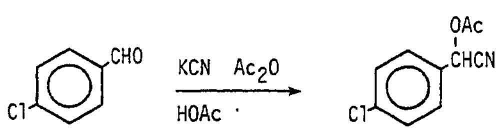
$PhCH{=}C(COOEt)_2 \xrightarrow{KCN \quad H_2O} PhCH(CN)CH_2COOEt$

Org Synth (1963) Coll Vol 4 804
(1955) Coll Vol 3 377
J Med Chem (1972) 15 1297

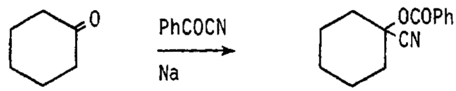


25%

JOC (1971) 36 3668



JOC (1959) 24 1650
(1949) 14 1013



80%

Compt Rend (1971) 272 1554

Also via:

	Section
Hydroxynitriles	331
Cyanoacids	321

Section 362 Ester — Olefin

For allylic acetoxylation see section 116 vol 1 and 2 (Esters from Hydrides)

$C_5H_{11}CH_2C{\equiv}CH \xrightarrow[\text{HOAc} \quad H_2O]{\text{NBS} \quad \text{NaOAc}} C_5H_{11}CH_2COCHBr_2 \xrightarrow[\text{MeOH}]{Et_3N} C_5H_{11}CH{=}CHCOOMe$ (cis) 46%

Proc Chem Soc (1964) 148

$C_9H_{19}CH_2CH(Me)COOH \xrightarrow[\text{2 MeOH}]{\text{1 } Br_2 \quad PBr_3} C_9H_{19}CH_2CBr(Me)COOMe \xrightarrow{\text{Quinoline}} C_9H_{19}CH{=}C(Me)COOMe$

Org Synth (1963) Coll Vol 4 608 616

$PhCHO \xrightarrow[\text{EtOH}]{CH_3COOEt \quad \text{EtONa}} PhCH{=}CHCOOEt$ 68-74%

Org Synth (1932) Coll Vol 1 252

BuCHO $\xrightarrow[\text{piperidine}]{\text{HOOC}CH_2COOEt\ \ \text{Pyr}}$ BuCH=CHCOOEt 78%

JACS (1948) 70 2601

PhCHO $\xrightarrow[\text{2 NaOH EtOH}]{\text{1 NCS}CH_2COOEt\ \ \text{KF}\ \ Et_2O}$ PhCH=CHCOOEt

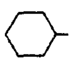
Bull Chem Soc Jap (1971) 44 1357

$OHC(CH_2)_3CHO$ $\xrightarrow{Ph_3P\text{=CHCOOMe}}$ $OHC(CH_2)_3$CH=CHCOOMe

Annalen (1962) 658 91
Org React (1965) 14 270

Ph_3P=C(Me)COOEt	JACS (1972) 94 4298
$(EtO)_2POCH_2COOEt$, NaH	JOC (1971) 36 1040
$BrCH_2COOEt$, $(Me_2N)_3P$, MeONa	Annalen (1965) 682 58
CH_2=CHCOOEt, Ph_3P	JACS (1968) 90 1647 Tetr Lett (1964) 1653

PrCH(Et)CH_2COOMe

1  -N(Pr-i)Li THF

2 Me_2S_2

3 $NaIO_4$ MeOH H_2O

4 120°

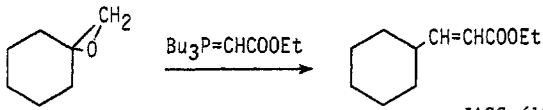
PrC(Et)=CHCOOMe 72%

JACS (1973) 95 6840

$C_9H_{19}CH_2CH_2COOEt$ $\xrightarrow[\text{2 PhSeCl}]{\text{1 } R_2NLi\ \ \text{THF}}$ C_9H_{19}CH=CHCOOEt

3 $MeCOO_2H$ EtOAc

JACS (1973) 95 6137



JACS (1967) <u>89</u> 5850
(1971) <u>93</u> 1693

$C_6H_{13}I \xrightarrow[\text{NaH THF}]{CH_2(COOMe)_2} C_6H_{13}CH(COOMe)_2 \xrightarrow[\text{Me}_2\text{NH·HCl}]{\text{1 HCHO Me}_2\text{NH}} C_6H_{13}C(=CH_2)COOMe$ <47%

2 MeI
3 75°

Synth Comm (1973) <u>3</u> 359

$PrCH_2Br \dashrightarrow PrCH{=}PPh_3 \xrightarrow[C_6H_6]{MeCH(I)COOEt} PrCH{=}C(Me)COOEt$ 55%

Ber (1970) <u>103</u> 685

$PhI \xrightarrow[\text{N-methylpyrrolidone}]{CH_2{=}CHCOOMe\ \ Pr_3N\ \ Pd(OAc)_2} PhCH{=}CHCOOMe$ 81%

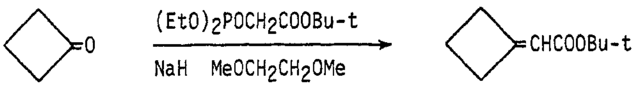
JOC (1972) <u>37</u> 2320

$CH_2Br\text{-}CH{=}CMe_2 \xrightarrow[\text{NaH BuLi THF}]{\text{1 MeCOCH}_2\text{COOMe}} (CH{=}CMe_2)CH_2CH_2C(OAc){=}CHCOOMe \xrightarrow[Et_2O]{Me_2CuLi} (CH{=}CMe_2)CH_2CH_2C(Me){=}CHCOOMe$

2 $CH_2{=}C(Me)OAc$ TsOH

Synth Comm (1973) <u>3</u> 321

Review: The Wittig Reaction Org React (1965) <u>14</u> 270



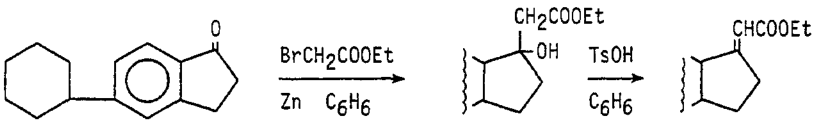
83%

JOC (1971) 36 1024
Org Synth (1965) 45 44

$Ph_3P=CHCOOMe$ 150° Proc Chem Soc (1961) 454

$Ph_3P=CHCOOEt$, PhCOOH Angew (1963) 75 858 (Internat Ed 2 619)

Review: The Reformatsky Reaction Org React (1942) 1 1



42%

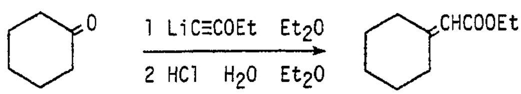
J Med Chem (1972) 15 1297

$BrCH_2COOBu$-t, Mg JOC (1966) 31 983

Dehydration of β-hydroxyesters with:

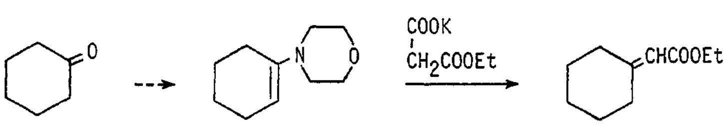
DCC, $CuCl_2$ JCS Perkin I (1973) 2738

AcCl, $PhNMe_2$; EtONa Tetr Lett (1969) 5017



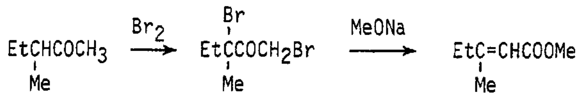
~50%

Advances in Org Chem (1960) 2 117 203 204
Rec Trav Chim (1956) 75 1377



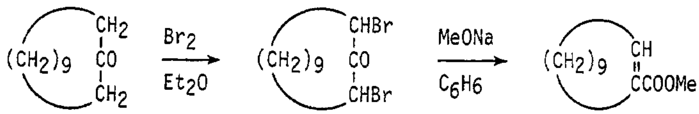
<29%

JOC (1973) 38 399



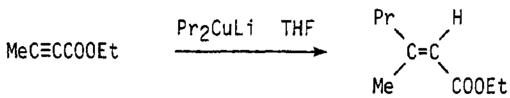
29%

JACS (1950) 72 974
JOC (1971) 36 3266
Org React (1960) 11 261



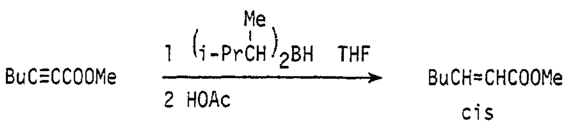
~90%

JOC (1968) 33 2157

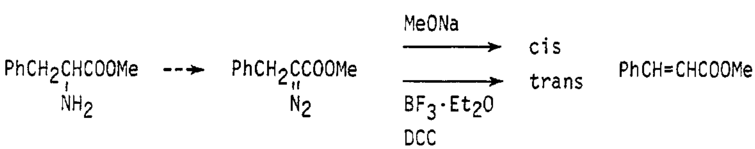


49%

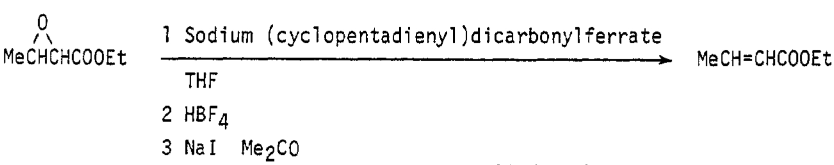
Tetr Lett (1973) 1277
Org React (1972) 19 1
JACS (1969) 91 1851 1853 6186



Organometallics in Chem Synth (1971) 1 249



Tetr Lett (1973) 4267



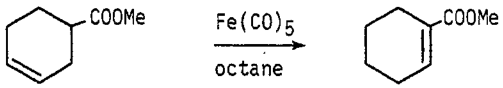
96%

JACS (1972) 94 7170

Ph_2PLi; MeI JACS (1973) 95 822

PhCOCOOMe $\xrightarrow[\text{THF}]{Ph_3P{=}CMe_2}$ PhC(=CMe$_2$)COOMe 72%

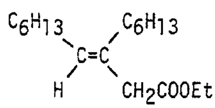
Can J Chem (1971) 49 2143



85%

JOC (1968) 33 1550

$C_6H_{13}C{\equiv}CH$ — 1 BuLi hexane; 2 $(C_6H_{13})_3B$ diglyme; 3 $BrCH_2COOEt$; 4 HOAc →



69%

Tetr Lett (1973) 4491

$EtCH{=}CH_2$ — 1 B_2H_6 THF; 2 $BrCH_2CH{=}CHCOOEt$ potassium 2,6-di-t-butylphenoxide → $EtCH_2CH_2CH{=}CHCH_2COOEt$ 72%

JACS (1970) 92 1761

MeCH=CHCOOEt — 1 $LiN(Pr\text{-}i)_2$ THF; 2 EtI → $CH_2{=}CHCH(Et)COOEt$ 96%

Tetr Lett (1973) 2433

MeCH=CHCOOEt $\xrightarrow{h\nu\ \ MeCN}$ $CH_2{=}CHCH_2COOEt$

Tetr Lett (1968) 4987
Chem Comm (1965) 137

$C_8H_{17}Br \xrightarrow[\text{2 MeI; 3 } CuCl_2 \text{ CuO EtOH}]{\text{1 } MeCSSCH_2C(Me)=CH_2 \text{ EtCH(Me)Li THF}} C_8H_{17}CH=C(Me)CH_2CH_2COOEt$

JACS (1973) 95 5803

$CH_2=C(Me)CH_2CH_2CH(OH)C(Me)=CH_2 \xrightarrow[EtCOOH]{MeC(OEt)_3} CH_2=C(Me)CH_2CH_2CH=C(Me)CH_2CH_2COOEt$ 92%

JACS (1970) 92 741
Synthesis (1971) 175

$C_8H_{17}CH=CH(CH_2)_7COOH \xrightarrow[MeOH]{HOOC(CH_2)_6COOMe \text{ electrolysis}} C_8H_{17}CH=CH(CH_2)_{13}COOMe$ ~37%

JCS (1954) 448

$ClCO(CH_2)_5COOEt$ → $C_7H_{15}CH_2CH=CHCH_2(CH_2)_6COOMe$

1 C_7H_{15}- $SnCl_4$
2 KOH H_2O
3 Wolff-Kishner
4 MeOH acid
5 Nickel boride

Synth Comm (1972) 2 415

$RCHO \xrightarrow{Ph_3P=CH(CH_2)_NCOOR'} RCH=CH(CH_2)_NCOOR'$

N=2 Acta Chem Scand (1966) 20 992
N=4 Bull Soc Chim Fr (1965) 2988
N=9 Ber (1972) 105 3591
N=10 Ivz (1960) 1900
(Chem Abs 55 14294)

$C_6H_{13}C{\equiv}CH \xrightarrow[\text{2 KOH } Et_2O \text{ } H_2O]{\text{1 } Hg(OAc)_2 \text{ } BF_3{\cdot}Et_2O \text{ } Ac_2O} C_6H_{13}C(OAc)=CH_2$ ~70%

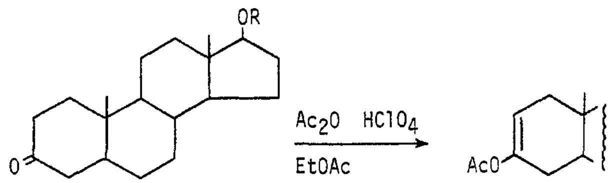
JOC (1973) 38 4254

$C_5H_{11}CH_2CHO \xrightarrow{Ac_2O \quad KOAc} C_5H_{11}CH{=}CHOAc$ 45-50%

Org Synth (1955) Coll Vol 3 127
JOC (1967) 32 489
JCS (1953) 3864

$EtCH(Me)COCHMe_2 \xrightarrow[2\ Ac_2O]{1\ i\text{-}PrMgCl \quad HMPA} EtCH(Me)C(OAc){=}CMe_2$

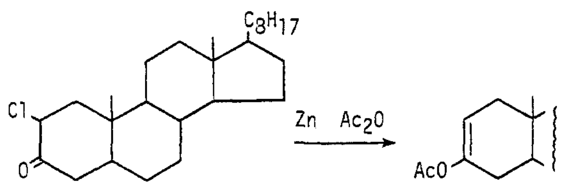
Tetrahedron (1973) 29 479



96%

JOC (1966) 31 324

Ac_2O, $HClO_4$, CCl_4	Org Synth (1972) 52 39
$(PhCO)_2O$, $HClO_4$ (enol benzoate)	JOC (1969) 34 1962
Ac_2O, BF_3	JOC (1969) 34 1425
$CH_2{=}C(Me)OAc$, acid	Tetrahedron (1971) 27 5987 JCS (1962) 1323



JCS (1953) 3869

Also via:

	Section
Acetylenic esters	306
β-Hydroxyesters	327
Olefinic acids	322

Section 363 Ether — Ether

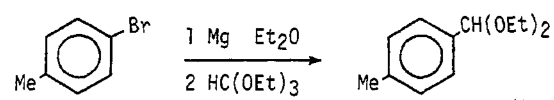
1,1-Diethers (acetals and ketals)

$$C_6H_{13}CHO \xrightarrow[HC(OMe)_3]{MeOH\ \ TsOH} C_6H_{13}CH(OMe)_2$$

JCS Perkin I (1973) 2738

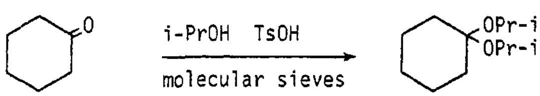
The following reagents may also be used for the preparation of acetals from aldehydes and alcohols:

NH_4Cl, $HC(OEt)_3$	Bull Soc Chim Fr (1965) 1007
NH_4NO_3, $HC(OEt)_3$	Org Synth (1963) Coll Vol 4 21
TsOH, molecular sieves	Synthesis (1972) 419
HCl	JCS (1953) 3864
$CaCl_2$	JOC (1966) 31 3406
$PhSO_2NHOH$	JOC (1970) 35 1962
Me_2SO_4, NaOH	Ber (1958) 91 410



>74%

JOC (1941) 6 489
Org Synth (1955) Coll Vol 3 701



82%

Synthesis (1972) 419

The following reagents may also be used for the preparation of ketals from ketones and alcohols:

Ion exch resin (acid)	JOC (1959) 24 1731
$BF_3 \cdot Et_2O$	JACS (1954) 76 1728
TsOH, $HC(OMe)_3$	JACS (1968) 90 2448 Annalen (1962) 656 97
TsOH, $Me_2C(OMe)_2$	JOC (1960) 25 521 525

continued

SeO_2 JACS (1954) 76 6113

$(Ph_3P)_3RhCl$ Ber (1968) 101 1154

Section 364 Ether — Halide

α-Haloethers, β-haloethers, γ-haloethers and higher haloethers

Review: The α-Haloalkyl Ethers Chem Rev (1955) 55 301

$$HO(CH_2)_{10}OH \xrightarrow[C_6H_6]{HCHO\quad HCl} Cl(CH_2)_{10}OCH_2Cl$$

JOC (1949) 14 754 696

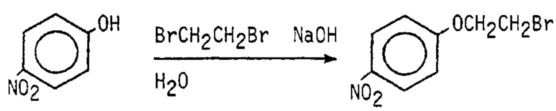
α-Bromoethers JACS (1949) 71 258

$$PhCH_2CHO \xrightarrow[Na_2SO_4]{EtOH\quad HCl} PhCH_2CH(Cl)OEt \qquad <94\%$$

JACS (1949) 71 4007

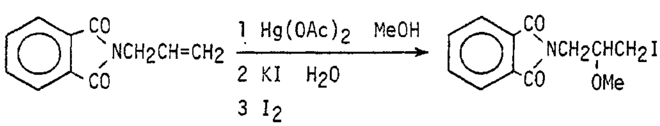
$$EtOCH_2Me \xrightarrow{PhICl_2\quad h\nu} EtOCH(Cl)Me \qquad 79\%$$

Annalen (1969) 728 12



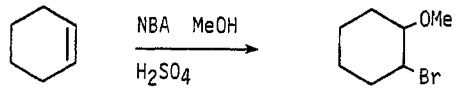
56%

Synthesis (1972) 693



75%

JOC (1952) 17 68
JACS (1955) 77 1738



JACS (1943) 65 2196

t-BuOBr Bull Soc Chim Fr (1961) 2360

BrN_3 Tetr Lett (1968) 3921

$Me_2C{=}CH_2 \xrightarrow[ZnCl_2]{ClCH_2OMe} Me_2C(Cl)CH_2CH_2OMe$ 60%

Ber (1936) 69 2706

$MeCH_2(CH_2)_4OMe \xrightarrow[H_2SO_4 \quad H_2O]{(i\text{-}Pr)_2NCl \quad h\nu} MeCH(Cl)(CH_2)_4OMe$

JACS (1971) 93 438

Section 365 Ether, Epoxide — Ketone

α-Alkoxyketones, β-alkoxyketones and epoxyketones

$EtC{\equiv}CEt \xrightarrow{Tl(OAc)_3 \quad MeOH} EtCOCH(OMe)Et$ 85%

JACS (1973) 95 1296

$PhCOCl \dashrightarrow PhCOCHN_2 \xrightarrow{i\text{-}PrOH \quad BF_3 \cdot Et_2O} PhCOCH_2OPr\text{-}i$ ~69%

JACS (1950) 72 5161

$MeCOCl \xrightarrow{Et_2O \quad h\nu} MeCH(OEt)COMe$

Angew (1965) 77 216
(Internat Ed 4 239)

$$PhBr \xrightarrow[2\ MeOCH_2CN]{1\ Mg\quad Et_2O} PhCOCH_2OMe$$

71-78%

Org Synth (1955) Coll Vol 3 562

$$BuC{\equiv}CCH(OEt)_2 \xrightarrow[2\ H_2O_2\quad NaOH\quad H_2O]{1\ (i\text{-}Pr\overset{Me}{C}H)_2BH\quad THF} BuCH_2COCH_2OEt$$

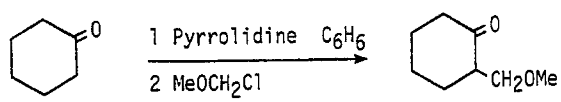
61%

JACS (1974) 96 316

$$PhBr \xrightarrow[\substack{2\ CdCl_2\quad C_6H_6 \\ 3\ EtOCH_2CH_2COCl}]{1\ Mg\quad Et_2O} PhCOCH_2CH_2OEt$$

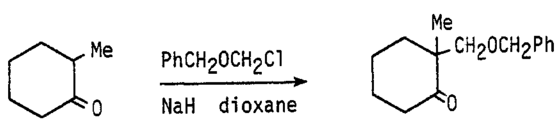
82%

JACS (1949) 71 3480



33%

JACS (1963) 85 207



JCS (1963) 4634
(1964) 4521

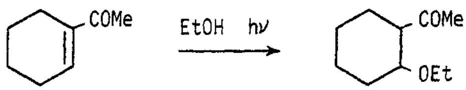
$$PhCOCH_3 \xrightarrow{CH_2{=}\overset{OEt}{C}Ph\ .\ BF_3{\cdot}Et_2O} PhCOCH_2\underset{Ph}{\overset{OEt}{C}}Me$$

37%

Synthesis (1972) 378

$Me_2C{=}CHCOMe \xrightarrow{\text{MeOH ion exch resin (acid)}} Me_2C(OMe)CH_2COMe$ 57%

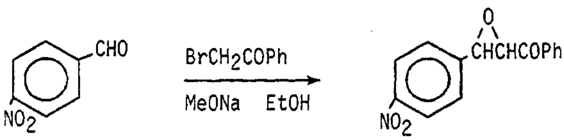
JOC (1958) 23 937



62%

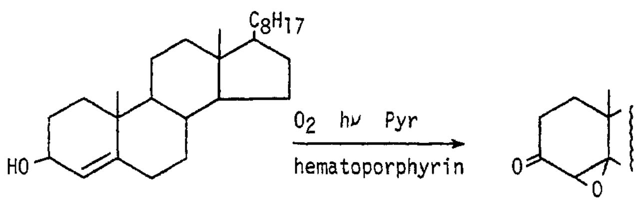
JACS (1967) 89 3949
Tetr Lett (1968) 2025
Bull Chem Soc Jap (1967) 40 945

Review: The α-Epoxyketones Annales de Chimie (1966) 11 159



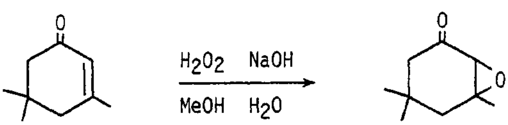
88%

JACS (1955) 77 590
JCS C (1970) 1154



75%

JACS (1963) 85 1894



70-72%

Org Synth (1963) Coll Vol 4 552
JCS Perkin I (1972) 2051

t-BuOOH, $PhCH_2\overset{+}{N}Me_3\ \overset{-}{O}H$ JACS (1958) 80 5845
(1968) 90 6495

continued

H_2O_2, DMF (neutral)	Chem Pharm Bull (1969) 17 1206
NaOCl, Pyr	JOC (1963) 28 250 Tetrahedron (1968) 24 6583
$PhCO_2H$	JACS (1950) 72 367

Section 366 Ether, Epoxide — Nitrile

α-Cyanoethers, β-cyanoethers and epoxynitriles

$$C_6H_{13}C(O)Me \xrightarrow[\text{18-crown-6}]{Me_2C(OSiMe_3)CN \quad KCN} C_6H_{13}C(OSiMe_3)(Me)CN$$ 95%

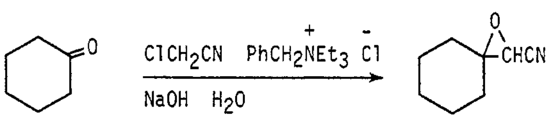
Tetr Lett (1973) 4929
Ber (1973) 106 587

$$BuOH \xrightarrow{CH_2{=}CHCN \quad PhCH_2\overset{+}{N}Me_3 \ \overset{-}{O}H} BuOCH_2CH_2CN$$ 86%

Org React (1949) 5 79 110
JCS (1945) 535

$$Me_2C\overset{O}{-}CH_2 \xrightarrow{Me_3SiCN \quad AlCl_3} Me_2C(CN)CH_2OSiMe_3$$ 93%

Tetr Lett (1973) 1449



79%

Tetr Lett (1972) 2395
J Indian Chem Soc (1963) 40 114

EtCH(Cl)CHO $\xrightarrow{\text{NaCN} \quad H_2O}$ EtCH(–O–)CHCN 30%

Bull Soc Chim Fr (1967) 1587

Section 367 Ether — Olefin

Vinyl ethers (enol ethers) and allyl ethers

$C_6H_{13}C\equiv CH$ $\xrightarrow[\text{2 } NaBH_4 \quad NaOH]{\text{1 } Hg(OAc)_2 \quad MeOH}$ $C_6H_{13}C(OMe)=CH_2$ 59%

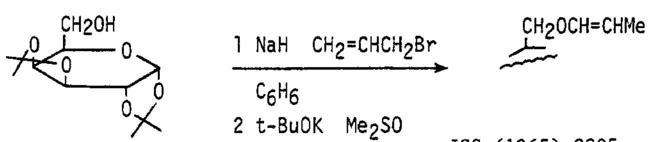
JOC (1973) 38 4254

$CH_2=C(Et)(Me)CHOH$ $\xrightarrow[Hg(OAc)_2]{EtOCH=CH_2}$ $CH_2=CC(Et)(Me)HOCH=CH_2$ 77%

JACS (1973) 95 553

JCS Perkin I (1973) 1791

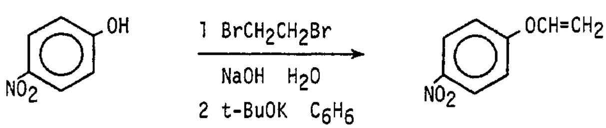
$CH_2=CHOAc$ JACS (1953) 75 2678



JCS (1965) 2205

JCS Perkin I (1972) 1535

JOC (1973) 38 3224



Synthesis (1972) 693

$Me_2CHCHO \xrightarrow[EtOH]{HC(OEt)_3\ \ NH_4Cl} Me_2CHCH(OEt)_2 \xrightarrow{H_3PO_4} Me_2C{=}CHOEt$ 55%

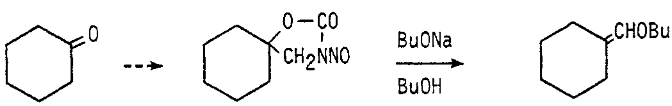
Bull Soc Chim Fr (1965) 1007

$PrCH_2CHO \xrightarrow[HCl]{EtOH} PrCH_2CH(Cl)OEt \xrightarrow{NaOAc} PrCH{=}CHOEt$ 37%

JOC (1958) 23 670
Ber (1956) 89 1468

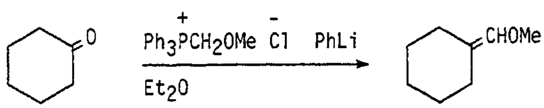
$C_{11}H_{23}CH_2Br \xrightarrow[2\ MeONa\ \ THF]{1\ Ph_3P} C_{11}H_{23}CH{=}PPh_3 \xrightarrow{HCOOEt} C_{11}H_{23}CH{=}CHOEt$ 6%

Zh Org Khim (1966) 2 2181
(Chem Abs 66 85406)



<85%

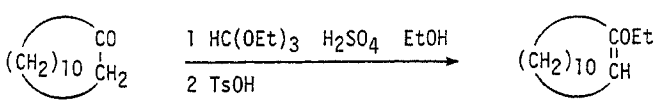
JOC (1969) 34 1220



71%

Org React (1965) 14 270 399

$(Me_2N)_2POCH_2OR$ Compt Rend (1971) 272 100



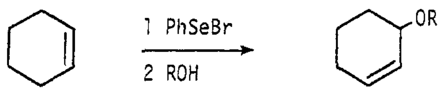
Annalen (1962) 656 97

$$PhCOCH_3 \xrightarrow[2\ Me_2SO_4]{1\ t\text{-}BuOK\ \ Me_2SO} \underset{\displaystyle OMe}{PhC}{=}CH_2 \qquad 68\%$$

Chem Comm (1966) 51

$$PhCHO \xrightarrow[EtOH]{CH_2{=}CHP^{+}Ph_3\ Br^{-}\ \ EtONa} PhCH{=}CHCH_2OEt \qquad 54\%$$

JOC (1966) 31 467



JOC (1974) 39 429

$$BuC{\equiv}CCH(OEt)_2 \xrightarrow[\substack{2\ HOAc \\ 3\ H_2O_2\ \ NaOH\ \ H_2O}]{1\ (i\text{-}PrCH(Me))_2BH\ \ THF} BuCH{=}CHCH_2OEt\ (cis) \qquad 65\%$$

JACS (1974) 96 316

Section 368 Halide — Halide

1,1-Dihalides and 1,2-dihalides

$$BuC{\equiv}CH \xrightarrow{HF\ \ Pyr\ \ THF} BuCF_2Me \qquad 70\%$$

Synthesis (1973) 779

$$C_6H_{13}CHO \xrightarrow{R_2NSF_3\ \ CCl_4} C_6H_{13}CHF_2 \qquad 75\%$$

Synthesis (1973) 787

MoF_6 Tetrahedron (1971) 27 3965

$PhCHO \xrightarrow{Ph_3P\cdot Cl_2} PhCHCl_2$ 59%

Annalen (1959) 626 26

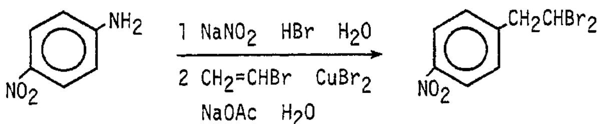
PCl_5 Org Synth (1943) Coll Vol 2 549

$MeOCHCl_2$ Ber (1959) 92 83

$NH_2OH;\ Cl_2$ JOC (1971) 36 2146

$i\text{-}PrCHO \xrightarrow[2\ I_2\quad Et_3N\quad Et_2O]{1\ N_2H_4} i\text{-}PrCHI_2$ 62%

Aust J Chem (1970) 23 989
JCS (1962) 470

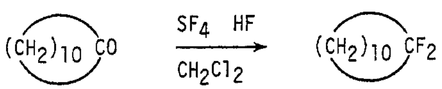


<77%

JACS (1954) 76 3005
Org React (1960) 11 189

$BuCHMe_2 \xrightarrow{PhHgCCl_2Br} BuC(CHCl_2)Me_2$ 20%

JOC (1970) 35 1989
Annalen (1969) 729 33



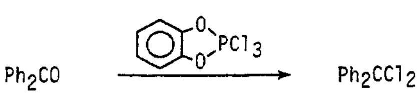
23%

JOC (1971) 36 818
(1961) 26 2436
JACS (1960) 82 543

R_2NSF_3 Synthesis (1973) 787

COF_2 JACS (1962) 84 4275

MoF_6 Tetrahedron (1971) 27 3965

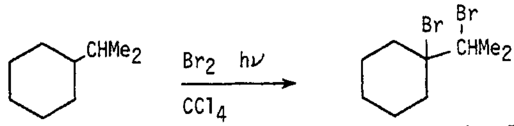


86%

Ber (1963) 96 1387

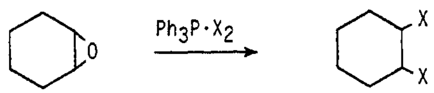
$i\text{-PrCOMe} \xrightarrow[\text{2 } I_2 \quad Et_3N \quad Et_2O]{\text{1 } N_2H_4} i\text{-PrCI}_2\text{Me}$ 50%

Aust J Chem (1970) 23 989



~50%

Rec Trav Chim (1964) 83 67



X=Cl or Br

Tetrahedron (1971) 27 2617
Tetr Lett (1972) 3869

$COCl_2$ Ber (1962) 95 2976

SO_2Cl_2 Can J Chem (1966) 44 2339

$Me_2\overset{+}{N}{=}CHCl\ \overset{-}{Cl}$ Chem Comm (1967) 1152

$MeCH_2C(Br)Me_2 \xrightarrow{\text{NBS} \quad CCl_4} MeCH(Br)\text{-}C(Br)Me_2$ 20%

JOC (1953) 18 649

$Me_2C{=}CMe_2 \xrightarrow[\text{2 AgF}]{\text{1 HF} \quad \text{NBS} \quad \text{Pyr} \quad Et_2O} Me_2C(F)\text{-}C(F)Me_2$

Synthesis (1973) 780

$Pb(OAc)_4$, HF JACS (1962) 84 1050

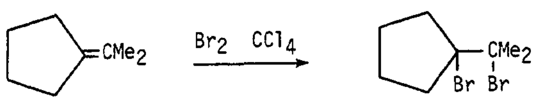
$C_5H_{11}CH{=}CH_2 \xrightarrow{Cl_2} C_5H_{11}CH(Cl)CH_2Cl$ 86%

Synth Comm (1972) 2 129

Cl_2, Pyr or Cl_2, $SbCl_3$ JOC (1959) 24 1621

Continued

Cl_2, $SbCl_5$	Chem Comm (1971) 1064 JACS (1951) 73 3329
$PhICl_2$	JOC (1959) 24 1621 (1971) 36 1024
NCS, HCl	JOC (1959) 24 1621 JACS (1959) 81 2191
SO_2Cl_2, Pyr	Rec Trav Chim (1971) 90 549 JOC (1971) 36 3566
NCl_3	Synthesis (1969) 135 JOC (1971) 36 3566
PCl_5	JOC (1971) 36 3566
$CuCl_2$	Bull Chem Soc Jap (1971) 44 1973 (1970) 43 1439
$TlCl_3$	Bull Chem Soc Jap (1972) 45 1482
$Pb(OAc)_4$, MeCOCl	Tetrahedron (1969) 25 1545



50%

	Rec Trav Chim (1964) 83 67 Org Synth (1943) Coll Vol 2 171
$Pyr{\cdot}HBr_3$	Org Synth (1966) 46 46 JACS (1972) 94 7118
$CuBr_2$	JOC (1971) 36 3324

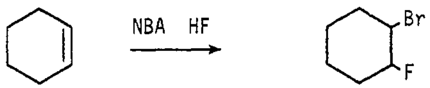
$$\mathrm{PrCH{=}CH_2} \xrightarrow{I_2} \mathrm{Pr}\underset{\mathrm{I}}{\mathrm{C}}\mathrm{HCH_2I}$$

Can J Chem (1964) 42 2710

$$\mathrm{BuCH{=}CH_2} \xrightarrow[\text{sulfolane}]{\text{NCS HF Pyr}} \mathrm{Bu}\underset{\mathrm{F}}{\mathrm{C}}\mathrm{HCH_2Cl}$$

40%

Synthesis (1973) 780



JACS (1959) 81 4107 2191
Org Synth (1966) 46 10

NBS, HF Synthesis (1973) 780

Br_2, AgF Can J Chem (1969) 47 361
Chem Ind (1967) 1787

$BuCH{=}CH_2 \xrightarrow[\text{sulfolane}]{\text{HF } I_2 \text{ } AgNO_3 \text{ Pyr}} BuCH(F)CH_2I$ 80%

Synthesis (1973) 780

I_2, AgF or NIS, HF Can J Chem (1969) 47 361
JACS (1960) 82 4007

$PhCH{=}CH_2 \xrightarrow[H_2O]{\text{NBA HCl}} PhCH(Cl)CH_2Br$ 36-44%

JACS (1951) 73 998
(1959) 81 2191
(1952) 74 4891

$t\text{-}BuCH{=}CH_2 \xrightarrow[\text{MeCN}]{I_2 \text{ } CuCl_2} t\text{-}BuCH(Cl)CH_2I$ 73%

JOC (1971) 36 3324 2088

I_2, $HgCl_2$ JACS (1948) 70 828

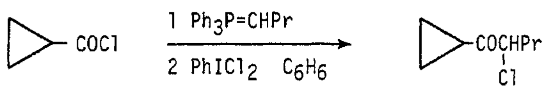
Section 369 Halide — Ketone

$PrC{\equiv}CMe \xrightarrow[\text{HOAc}]{Et_2NCl \text{ } H_2SO_4} PrCH(Cl)COMe$ 33%

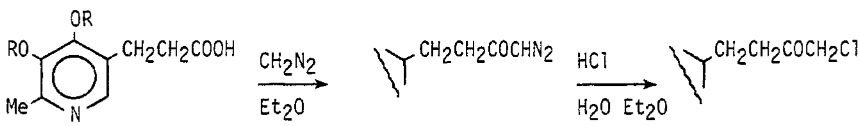
JOC (1967) 32 3263

$$C_5H_{11}C{\equiv}CH \xrightarrow[\text{2 } Br_2]{\text{1 EtMgBr} \quad Et_2O} C_5H_{11}C{\equiv}CBr \xrightarrow[\text{2 HCl} \quad H_2O]{\text{1 HgO} \quad BF_3} C_5H_{11}COCH_2Br$$

JACS (1937) 59 1307



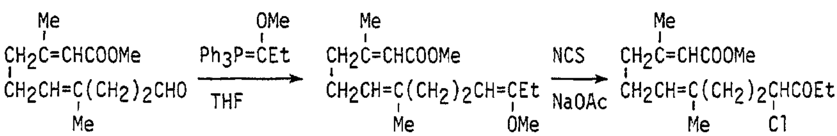
Tetrahedron (1969) 25 1871



J Med Chem (1971) 14 641
Org Synth (1955) Coll Vol 3 119

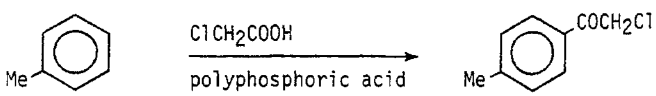
Bromoketones JOC (1970) 35 1381

Iodoketones via bromoketones JACS (1943) 65 1516



60%

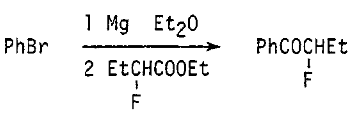
JACS (1972) 94 5374 5379



40%

Synth Comm (1972) 2 97

$ClCH_2COCl$, $AlCl_3$ Org Synth (1955) Coll Vol 3 183

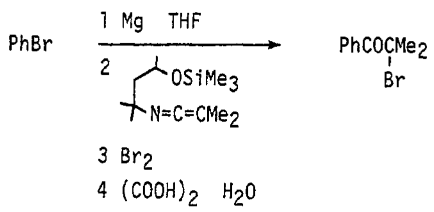


50%

Bull Soc Chim Fr (1970) 991

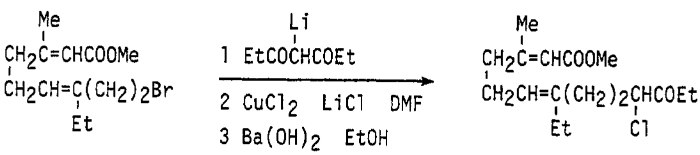
$BuBr \xrightarrow[2\ ClCH_2COCl]{1\ Mg\quad Et_2O} BuCOCH_2Cl$ 51%

Org React (1954) 8 28
JACS (1945) 67 1944

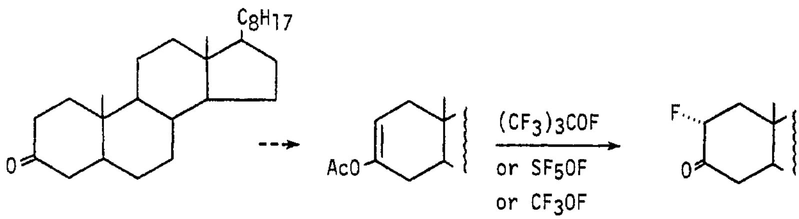


40%

JOC (1973) 38 2129



JACS (1968) 90 6225
(1944) 66 1132



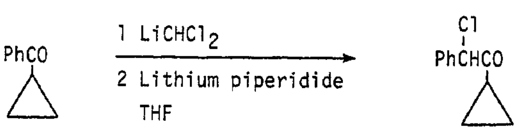
40-62%

Chem Comm (1972) 122

$FClO_3$ JCS Perkin I (1973) 2365

Via ethoxalyl derivative JACS (1960) 82 2312

Via enamine JOC (1958) 23 1406



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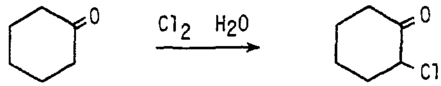
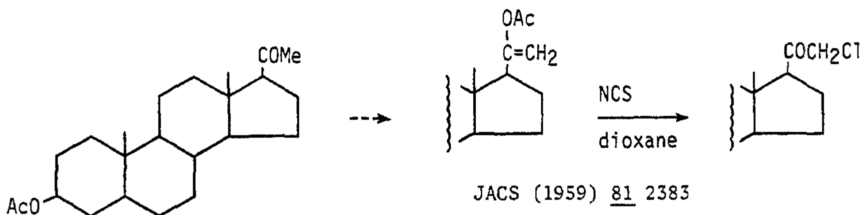
Tetr Lett (1972) 4117 4661
Ber (1973) 106 2626

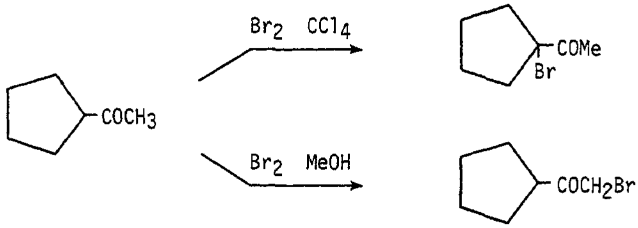


61-66%

	Org Synth (1955) Coll Vol 3 188
Cl_2, HOAc	JCS (1953) 3869
Pyr·HCl_3	JACS (1953) 75 3500
$CuCl_2$	JOC (1963) 28 630
SO_2Cl_2	Org Synth (1963) Coll Vol 4 162 JOC (1972) 37 2436
$SeOCl_2$	JOC (1963) 28 1128
PCl_5	Compt Rend (1963) 256 1996
t-BuOCl	JACS (1953) 75 3500
$Pb(OAc)_4$, MeCOCl	Tetrahedron (1969) 25 1545
Chlorination of imines	Tetrahedron (1970) 26 5191



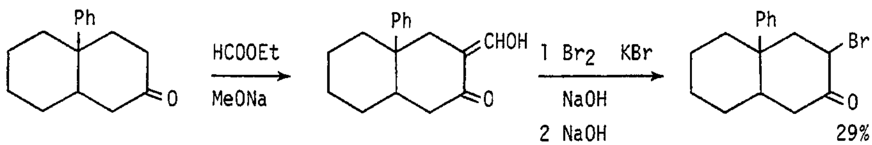
	JACS (1959) 81 2383
Cl_2	JOC (1961) 26 4569



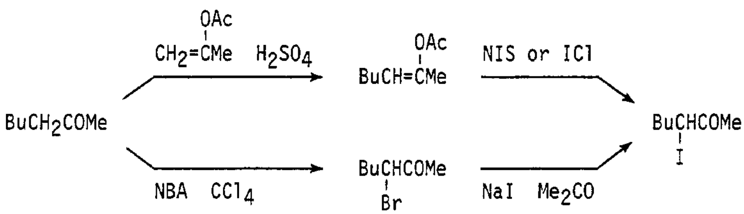
	Tetrahedron (1970) 26 5611
Br_2, HBr, HOAc or dioxane·Br_2	JCS (1954) 3257
Pyrrolidone·HBr_3	Can J Chem (1969) 47 706
$CuBr_2$	JOC (1964) 29 3459 JACS (1968) 90 6218
NBS, benzoyl peroxide	JCS Perkin I (1972) 50 Angew (1959) 71 349

continued

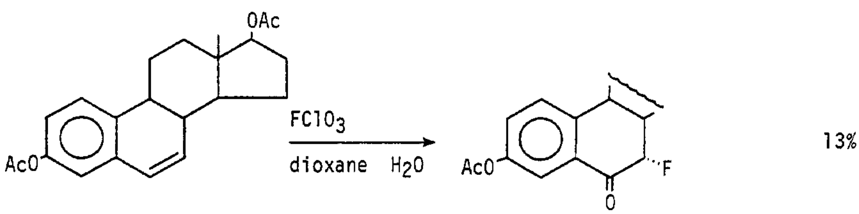
$Ph\overset{+}{N}Me_3\ \overset{-}{Br_3}$	JOC (1971) 36 4124 Bull Soc Chim Fr (1962) 90
Bromination of Ketals	Tetrahedron (1963) 19 861 Bull Soc Chim Fr (1962) 90 JACS (1965) 87 817
Bromination of enol acetates	Chem Pharm Bull (1969) 17 1585 (1972) 20 2156
Bromination of lithium enolates	JOC (1973) 38 2576
Bromination of enol ethers	JOC (1959) 24 1564 Tetr Lett (1972) 4055
Bromination of imines	Tetrahedron (1970) 26 5191



JOC (1970) 35 753

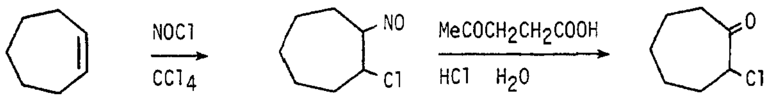


	JACS (1953) 75 3493
I_2, CaO	JOC (1960) 25 1966
1,3-Diiodo-5,5-dimethylhydantoin	JOC (1965) 30 1101
Via oxalyl derivative	JACS (1952) 74 4974



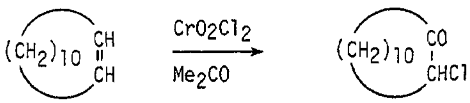
JCS Perkin I (1973) 1462

NOF Chem Ind (1965) 1929



93%

JOC (1967) 32 4136



79%

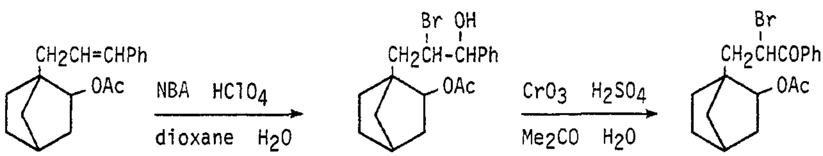
JOC (1973) 38 185

$$BuCH{=}CH_2 \xrightarrow[\text{2 i-PrCOCHN}_2]{\text{1 }B_2H_6\text{ THF}} BuCH_2CH_2\underset{\displaystyle Br}{CH}COPr\text{-}i$$

3 NBS

4 NaOH H_2O

Can J Chem (1972) 50 2387



JACS (1972) 94 5386
(1956) 78 3749
Helv (1944) 27 821

$$Me\underset{\displaystyle Cl}{CH}COCl \xrightarrow[\text{2 }C_6H_6\text{ (reflux)}]{\text{1 }C_6H_{13}CH(COOTHP)_2\text{ Na }C_6H_6} Me\underset{\displaystyle Cl}{CH}COCH_2C_6H_{13}$$

JCS (1952) 3945

$$PhH \xrightarrow[AlCl_3\ \ CS_2]{BrCH_2CH_2COCl} BrCH_2CH_2COPh$$

<93%

JACS (1940) 62 1435

$$I(CH_2)_{10}COCl \xrightarrow[Et_2O]{Bu_2CuLi} I(CH_2)_{10}COBu \qquad 93\%$$

JACS (1972) 94 5106

Section 370 Halide — Nitrile

Halonitriles

$$PhNH_2 \dashrightarrow Ph\overset{+}{N}_2\ \overset{-}{Cl} \xrightarrow{CH_2{=}CHCN\quad Cu^{2+}} PhCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCN \qquad \sim 60\%$$

Proc Chem Soc (1962) 117
Org React (1960) 11 189

$$Me_2\underset{\displaystyle OH}{\underset{|}{C}}CN \xrightarrow{PCl_5\quad C_6H_6} Me_2\underset{\displaystyle Cl}{\underset{|}{C}}CN \qquad 38\%$$

JACS (1945) 67 690
$POCl_3$, lutidine JACS (1950) 72 1753

$$EtCH{=}CH_2 \xrightarrow[\text{2 } Cl_2CHCN \text{ potassium 2,6-di-t-butylphenoxide THF}]{\text{1 9-BBN}} EtCH_2CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCN \qquad 75\%$$

JACS (1970) 92 5790

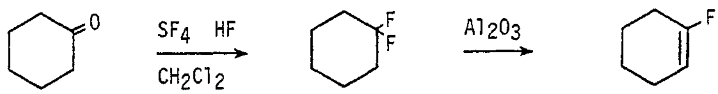
Section 371 Halide — Olefin

Vinylic halides, allylic halides, homoallylic halides and other olefinic halides.

For the conversion of allylic alcohols to allylic halides see section 138 vol 1 and vol 2 (Halides from Alcohols)
For allylic halogenation with NBS etc. see section 146 vol 1 and vol 2 (Halides from Hydrides)

$$C_5H_{11}CHO \xrightarrow[\text{THF}]{Ph_3P{=}CHF} C_5H_{11}CH{=}CHF$$ 35%

Synthesis (1969) 75



44%

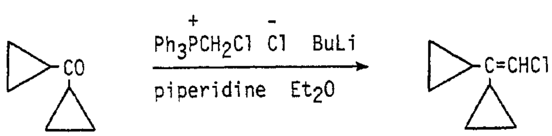
JOC (1971) 36 818

$$PhC{\equiv}CH \xrightarrow[CH_2Cl_2]{PhCH_2Cl \quad ZnCl_2} PhC(Cl){=}CHCH_2Ph$$ 95%

JCS Perkin I (1973) 2491

$$BuC{\equiv}CH \xrightarrow[2\ Me_3SiCl]{1\ EtMgBr \quad Et_2O} BuC{\equiv}CSiMe_3 \xrightarrow[\substack{2\ HOAc \\ 3\ H_2O_2 \quad \text{base} \\ 4\ X_2 \\ 5\ MeONa}]{1\ \text{Dicyclohexylborane}} \underset{\text{trans}}{BuCH{=}CHX}$$ X=Cl or Br

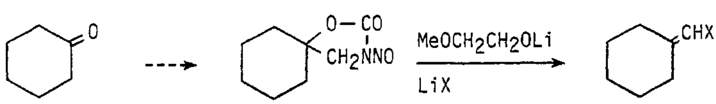
Tetr Lett (1974) 543



81%

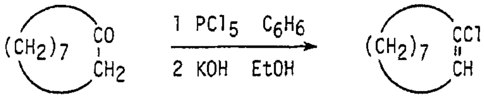
Ber (1972) 105 1683
Org React (1965) 14 270

$PhHgCHClBr, Ph_3P$ J Organometallic Chem (1965) 3 337



X=Cl or I

JACS (1970) 92 4309



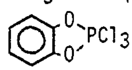
32%

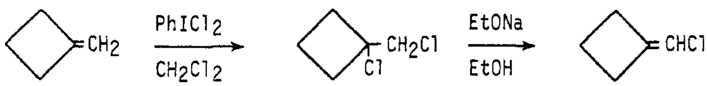
JACS (1952) 74 3643

Ph_3PCl_2 Annalen (1959) 626 26

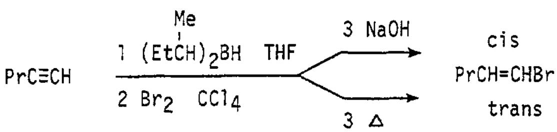
Cl_2CHOMe, $ZnCl_2$ Ber (1959) 92 83

Ph_3P, CCl_4 Chem Comm (1972) 443

 Ber (1963) 96 1387



JOC (1971) 36 1024



JACS (1967) 89 4531
(1973) 95 6456

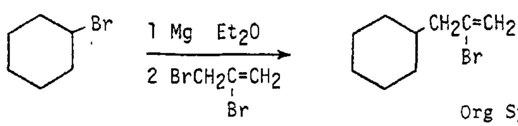
78%

Helv (1964) 47 194

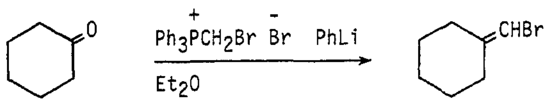
BuC≡CH $\xrightarrow{\text{HBr peroxides}}$ BuCH=CHBr

Org React (1963) 13 150 234

74%

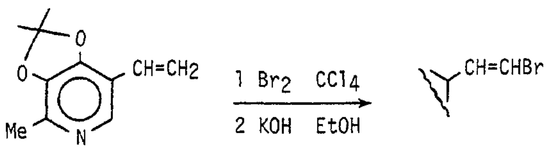


Org Synth (1932) Coll Vol 1 186



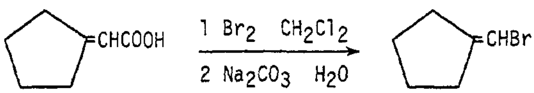
89%

JOC (1965) 30 2208
Org React (1965) 14 270



J Med Chem (1972) 15 1262

t-BuOK	JOC (1965) 30 2208
$NaNH_2$, t-BuOK	Chem Comm (1972) 1289
$Bu_4\overset{+}{N}\ \overset{-}{Br}$, CH_2CH_2 (O)	Ber (1973) 106 1648



85%

JOC (1965) 30 2208
JCS C (1971) 2352

BuC≡CX $\xrightarrow[\text{2 HOAc}]{\text{1 Dicyclohexylborane THF}}$ BuCH=CHX <95% (X=Br)
cis <85% (X=I)

JACS (1967) 89 5086

BuC≡CH $\xrightarrow[\text{2 } X_2 \text{ THF; 3 } H_2SO_4\ H_2O]{\text{1 } (i\text{-}Bu)_2AlH \text{ heptane}}$ BuCH=CHX 72% (X=Br)
trans 74% (X=I)

JACS (1967) 89 2753

$C_6H_{13}C{\equiv}CH$ $\xrightarrow[\text{2 } H_2O\text{; 3 NaOH } H_2O\ Et_2O\text{; 4 } I_2]{\text{1 Catecholborane}}$ $C_6H_{13}CH{=}CHI$ 71%

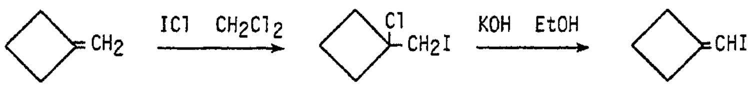
JACS (1973) 95 5786
Tetr Lett (1974) 543

$$\underset{\text{OTHP}}{C_5H_{11}CHC{\equiv}CH} \xrightarrow[2\ I_2]{1\ BuLi\quad Et_2O} \underset{\text{OTHP}}{C_5H_{11}CHC{\equiv}CI} \xrightarrow[HOAc\quad MeOH]{KOOCN{=}NCOOK} \underset{\text{OTHP}}{C_5H_{11}CHCH{=}CHI}\ \text{cis} \qquad \sim 65\%$$

JACS (1972) 94 9256

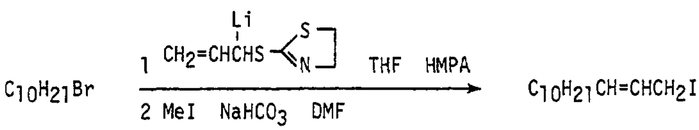
$$PhCOCH_2Me \xrightarrow[2\ I_2\quad Et_3N\quad Et_2O]{1\ N_2H_4{\cdot}H_2O\quad EtOH} PhC(I){=}CHMe \qquad 60\text{-}65\%$$

Aust J Chem (1971) 24 1425
(1970) 23 989
JCS (1962) 470
JOC (1969) 34 3502



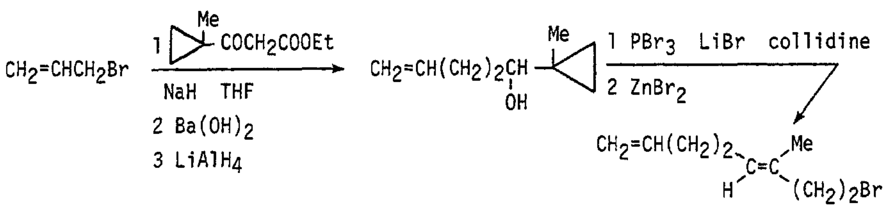
27%

JOC (1971) 36 1024



50%

Tetr Lett (1972) 2743



JACS (1968) 90 2882 6225

$$I(CH_2)_3Cl \xrightarrow{EtC(Me){=}CHCu} EtC(Me){=}CH(CH_2)_3Cl \qquad 46\%$$

Tetr Lett (1973) 2407

Also via: Acetylenic halides (Section 308)

Section 372 Ketone — Ketone

$$\mathrm{BuC{\equiv}CBu} \xrightarrow[\mathrm{CCl_4\quad H_2O}]{\mathrm{RuO_2\quad NaIO_4}} \mathrm{BuCOCOBu} \qquad 70\%$$

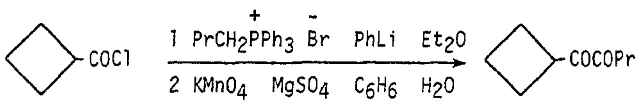
Tetr Lett (1971) 2941

NBS Can J Chem (1971) 49 1099

HNO_3 JACS (1956) 78 2518 2522

$KMnO_4$ JOC (1952) 17 1063

$Tl(NO_3)_3$ JACS (1973) 95 1296



Tetrahedron (1968) 24 2419
Ber (1969) 102 2259

$$\mathrm{C_6H_{13}\overset{OH}{C}H\text{-}\overset{OH}{C}HC_7H_{15}} \xrightarrow[\mathrm{H_2O}]{\mathrm{NBS\quad EtOAc}} \mathrm{C_6H_{13}COCOC_7H_{15}} \qquad 35\%$$

JCS C (1968) 2617

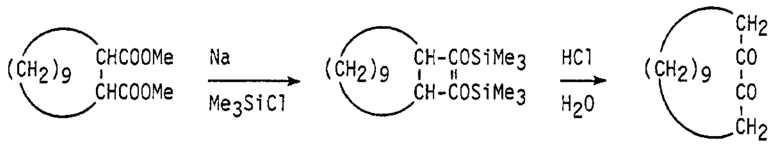
$(Ph_3P)_3RuCl_2$, PhCH=CHCOMe JOC (1972) 37 1832

$$\mathrm{PhCHO} \xrightarrow[\mathrm{ZnCl_2}]{\mathrm{PhSH}} \mathrm{PhCH(SPh)_2} \xrightarrow[\text{2 Hydrolysis}]{\text{1 NaH\quad PhCOCl\quad DMF}} \mathrm{PhCOCOPh}$$

JOC (1963) 28 961

$$\mathrm{PhCHO} \dashrightarrow \mathrm{PhCH{=}NPh} \xrightarrow[\text{2 HCl\quad H}_2\text{O}]{\text{1 NaCN\quad DMF}} \mathrm{PhCOCOPh} \qquad 71\%$$

JOC (1972) 37 135

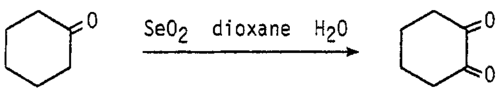


71%

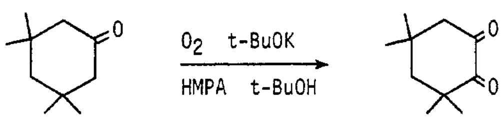
Can J Chem (1969) 47 3266

BuBr $\dashrightarrow$ Bu_2Cd $\xrightarrow[\text{THF}]{(COCl)_2 \quad \text{LiBr}}$ BuCOCOBu 37%

JCS A (1966) 456



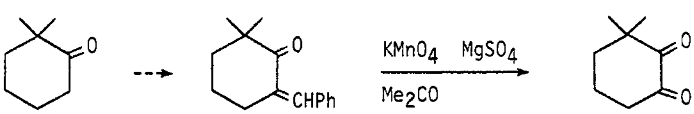
Org Synth (1963) Coll Vol 4 229
Annalen (1962) 659 64
Synthesis (1971) 215



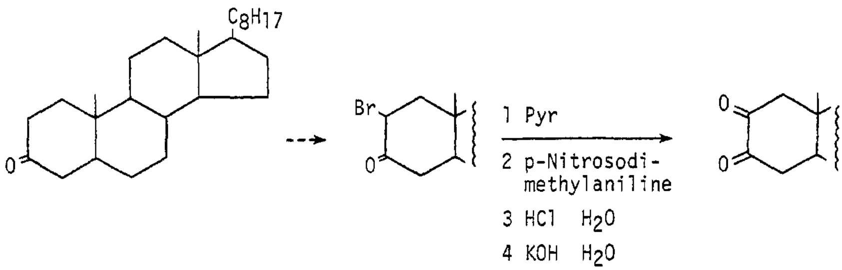
Bull Soc Chim Fr (1967) 3742
Tetr Lett (1961) 554

$BuCH_2COMe$ $\xrightarrow[Et_2O \quad H_2O]{\text{MeONO} \quad \text{HCl}}$ BuCCOMe (=NOH) $\xrightarrow[]{H_2SO_4 \quad H_2O}$ BuCOCOMe

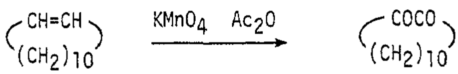
JOC (1959) 24 1726
Org Synth (1955) Coll Vol 3 20



JACS (1964) 86 3068
Via hydroxymethylene derivative Chem Comm (1968) 1055

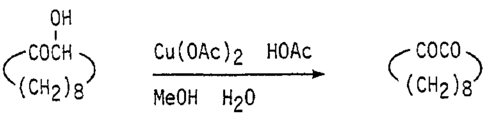


Helv (1944) 27 524
JOC (1964) 29 1677



48%

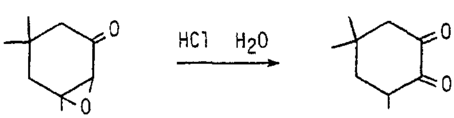
JACS (1971) 93 3303



88-89%

Org Synth (1963) Coll Vol 4 838
JOC (1964) 29 1677

Air, $CuSO_4$, Pyr	Org Synth (1932) Coll Vol 1 87
CrO_3, H_2SO_4, Me_2CO	Chem Ind (1972) 807
Ac_2O, Me_2SO	JOC (1967) 32 3204
MnO_2	JOC (1966) 31 615
Bi_2O_3	JACS (1956) 78 2518 JCS (1951) 793
TlOEt	JCS (1952) 2771
$HgCl_2$	JCS B (1966) 366
$Na[Sb(OAc)_6]$	Ber (1964) 97 124
$Ph_3P\cdot Br_2$	Synthesis (1972) 697
$(Ph_3P)_3RuCl_2$, PhCH=CHCOMe	JOC (1972) 37 1832
NBS	JCS C (1968) 2617



65%

JOC (1959) 24 719
Helv (1962) 45 2575

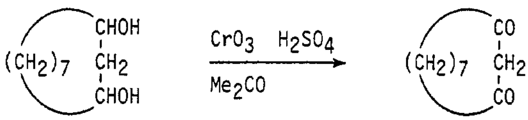
$$BuC{\equiv}CH \xrightarrow[2\ MeOH]{1\ MeCOOH\quad (CF_3CO)_2O} BuCOCH_2COMe \qquad 20\%$$

JCS (1953) 3628

$\overset{+}{RCO}\ \overset{-}{BF_4}$ Tetr Lett (1972) 4935
(1971) 3101

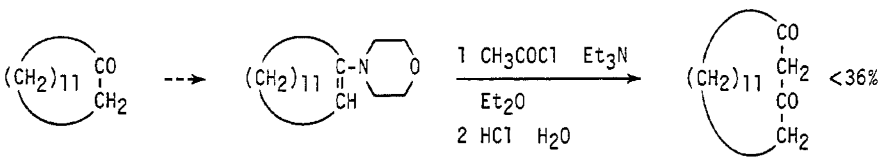
$$(EtCH_2CO)_2O \xrightarrow[2\ (BuCO)_2O]{1\ BF_3} EtCH_2COCHEt(COBu) \qquad 80\%$$

Annalen (1963) <u>668</u> 15

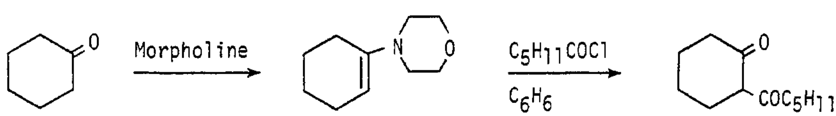


JCS Perkin I (1972) 1509

Review: The Acylation of Ketones to Form β-Diketones or β-Keto Aldehydes
Org React (1954) <u>8</u> 59



Ber (1972) <u>105</u> 2216

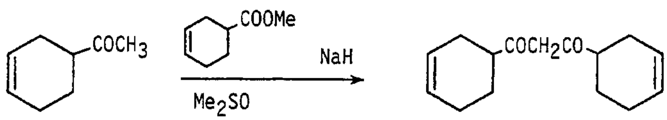


JACS (1963) <u>85</u> 207

$BuCH_2COMe \xrightarrow{Ac_2O\ \ TsOH} BuCH{=}C(OAc)Me \xrightarrow[Ac_2O]{AcOH \cdot BF_3} BuCH(COMe)COMe$ 64-77%

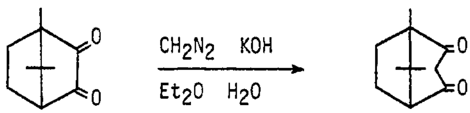
Org Synth (1971) 51 90
JACS (1953) 75 5030
Tetrahedron (1966) 22 2039
JOC (1969) 34 1425

Acylation of ketals JACS (1963) 85 3901



83%

JOC (1962) 27 2742
Org Synth (1955) Coll Vol 3 251 291



90%

Annalen (1962) 659 64

$C_6H_{13}CH{=}CH_2 \xrightarrow[\text{peroxides}]{MeCOCH_2COMe} C_6H_{13}CH_2CH_2CH(COMe)COMe$

Proc Chem Soc (1964) 142

$C_{17}H_{35}COOC(CH_3){=}CH_2 \xrightarrow{AlCl_3\ \ \text{Hexane}} C_{17}H_{35}COCH_2COC_{17}H_{35}$ 65-70%

Tetr Lett (1969) 2553
JOC (1971) 36 1447

$EtCOCH_2Br \xrightarrow[Et_2O]{PrCOSH\ \ Et_3N} EtCOCH_2SCOPr \xrightarrow[\text{propyl]-phenylphosphine LiBr MeCN}]{\text{Bis-[3-dimethylamino-}} EtCOCH_2COPr$ ~86%

Helv (1971) 54 710

$$RCOCH_2COR \xrightarrow[\text{base}]{RX} \underset{\textstyle R}{RCOCHCOR}$$

Base:

K_2CO_3	Org Synth (1973) Coll Vol 5 785
TlOEt	JACS (1968) <u>90</u> 2421
NaH	JOC (1961) <u>26</u> 4112
$NaNH_2$	Org Synth (1967) <u>47</u> 92

$$C_6H_{13}C{\equiv}CH \xrightarrow[\substack{2\ (C_6H_{13})_3B\quad \text{diglyme} \\ 3\ BrCH_2COMe \\ 4\ H_2O_2\quad NaOAc\quad H_2O}]{1\ \text{BuLi}\quad \text{hexane}} \underset{\textstyle C_6H_{13}}{C_6H_{13}COCHCH_2COMe} \qquad 75\%$$

Tetr Lett (1973) 4491

$$EtCOCl \dashrightarrow EtCOCHN_2 \xrightarrow[\substack{\text{cuprous acetylacetonate} \\ 2\ \text{Base}}]{1\ CH_2{=}\overset{\textstyle Me}{C}OAc} EtCOCH_2CH_2COMe$$

Tetr Lett (1971) 2575

$$PhCHO \xrightarrow[\text{DMF}]{PhCH{=}CHCOMe\quad KCN} \underset{\textstyle Ph}{PhCOCHCH_2COMe} \qquad 67\%$$

Angew (1973) <u>85</u> 89
(Internat Ed <u>12</u> 81)
Tetr Lett (1973) 1461

$$C_6H_{13}CHO \dashrightarrow C_6H_{13}CH(SPh)_2 \xrightarrow[\substack{2\ CuI \\ 3\ CH_2{=}CHCOMe \\ 4\ CuCl\quad CuO \\ Me_2CO\quad H_2O}]{1\ \text{BuLi}\quad \text{THF}\quad \text{hexane}} C_6H_{13}COCH_2CH_2COMe \qquad 72\%$$

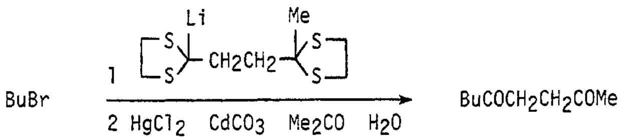
JACS (1972) <u>94</u> 8641

$$C_6H_{13}OTs \xrightarrow[\substack{2\ \text{BuLi} \\ 3\ CH_2{=}CHCOMe \\ 4\ HgCl_2\quad HCl}]{1\ EtSOCH_2SMe\quad \text{BuLi}\quad \text{HMPA}} C_6H_{13}COCH_2CH_2COMe \qquad 76\%$$

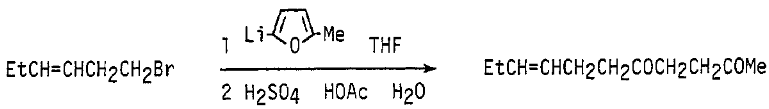
Tetr Lett (1973) 3275 3271

$$PhBr \dashrightarrow PhLi \xrightarrow[]{\overset{CONMe_2}{(CH_2)_N CONMe_2} \quad Et_2O} PhCO(CH_2)_N COPh \qquad N=2 \text{ or } 3$$

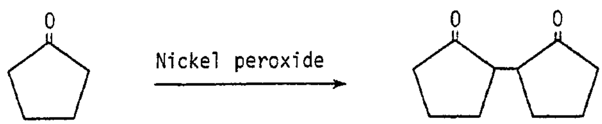
JOC (1973) <u>38</u> 901



Chem Comm (1972) 529

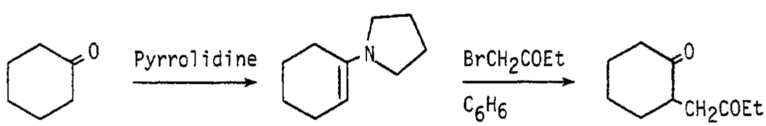


JOC (1966) <u>31</u> 977

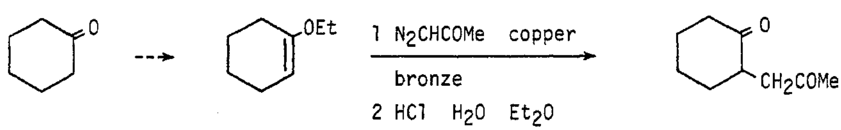


<80%

JCS Perkin I (1974) 280



JACS (1963) <u>85</u> 207



Synth Comm (1973) <u>3</u> 255

$PhCOCHO \xrightarrow{Ph_3P=CHCOPh} PhCOCH=CHCOPh \xrightarrow[HOAc\quad H_2O]{SnCl_2\quad HCl} PhCOCH_2CH_2COPh$ <85%

Aust J Chem (1971) 24 2137

$BuC{\equiv}C(CH_2)_NCOMe \xrightarrow[MeOH\quad H_2O]{HgSO_4\quad H_2SO_4} BuCH_2CO(CH_2)_NCOMe$ 85% (N=2) 93% (N=3)

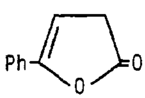
JACS (1964) 86 935

$Me_2C=CHCOMe \xrightarrow[pentane]{Ni(CO)_4\quad BuLi} BuCOC(Me)_2CH_2COMe$ 89%

Synthesis (1971) 55

$EtCH_2NO_2 \xrightarrow[(i\text{-}Pr)_2NH]{CH_2=CHCOMe} EtCH(NO_2)CH_2CH_2COMe \xrightarrow[glyme]{TiCl_3\quad H_2O} EtCOCH_2CH_2COMe$ 64%

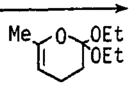
JACS (1971) 93 5309
Tetr Lett (1972) 1331
JOC (1974) 39 259



$\xrightarrow[2\ HCl\quad H_2O\quad HOAc]{1\ Et_2NC{\equiv}CMe\quad MeCN} PhCOCH_2CH_2COCH_2Me$ 56%

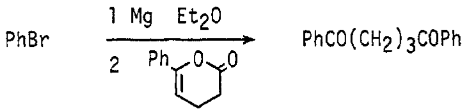
Tetr Lett (1971) 1565 1569

$MeI \xrightarrow{1\ Mg}$ 2

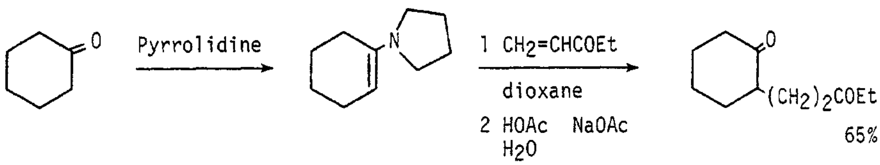


$MeCO(CH_2)_3C(Me)(OEt)_2 \dashrightarrow MeCO(CH_2)_3COMe$ < 20%

Bull Soc Chim Fr (1970) 4429



Zh Org Khim (1969) 5 83
(Chem Abs 70 87453)



JACS (1963) 85 207

$$BuCOOH \xrightarrow[THF]{CH_2=CHMgCl \quad CuCl} BuCO(CH_2)_4COBu \qquad 53\%$$

Can J Chem (1972) 50 2786

$$COCl(CH_2)_4COCl \xrightarrow{R_2CuLi \quad Et_2O} COR(CH_2)_4COR$$

92% (R=Me)
90% (R=Bu)

JACS (1972) 94 5106

$$COCl(CH_2)_4COCl \xrightarrow{PhH \quad AlCl_3} COPh(CH_2)_4COPh \qquad 75\text{-}81\%$$

Org Synth (1943) Coll Vol 2 169

$$MeCO(CH_2)_2COOH \xrightarrow[MeONa \quad MeOH]{Electrolysis} MeCO(CH_2)_4COMe \qquad 21\text{-}26\%$$

Annalen (1953) 580 125

Section 373 Ketone — Nitrile

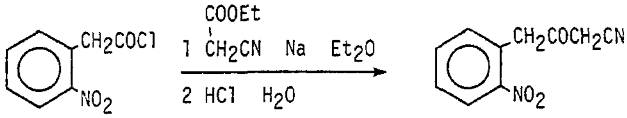
α, β, γ, δ and ε-ketonitriles

$BuC{\equiv}CH \dashrightarrow (BuC{\equiv}C)_2Hg \xrightarrow{NOCl} BuCOCN$

Proc Chem Soc (1963) 13

$PhCOCl \xrightarrow{CuCN} PhCOCN$ 60-65%

Org Synth (1955) Coll Vol 3 112
Can J Chem (1971) 49 919

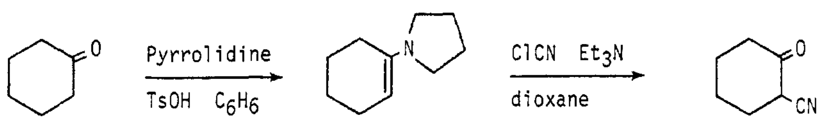


40%

JOC (1960) 25 736

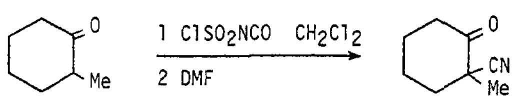
$PrCOOEt \xrightarrow[Et_2O]{CH_3CN \quad Ph_3CNa} PrCOCH_2CN$

JACS (1942) 64 2720



<93%

JACS (1959) 81 5400



69%

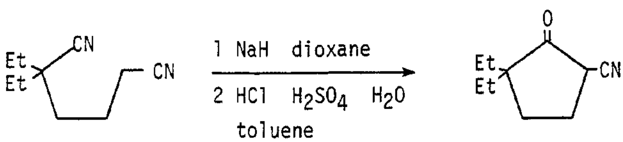
Synthesis (1973) 682

$$PhCH_2CN \xrightarrow[EtOH]{MeCOOEt \quad EtONa} PhCH(COMe)CN$$ 66-73%

Org Synth (1943) Coll Vol 2 487
(1963) Coll Vol 4 174

$$PhCN \xrightarrow[2\ HCl \quad EtOH \quad H_2O]{1\ CH_3CN \quad NaNH_2 \quad Et_2O} PhCOCH_2CN$$

Ber (1949) 82 254

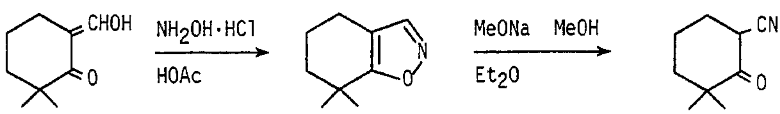


46%

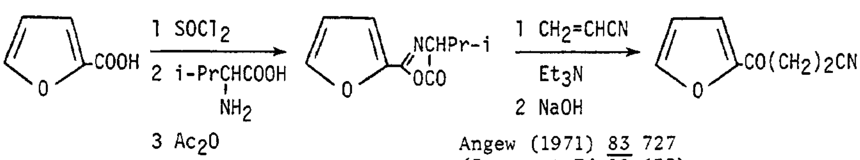
Can J Chem (1965) 43 2512

$$PhCOCH_2Br \xrightarrow{LiCN \quad DMF} PhCOCH_2CN$$

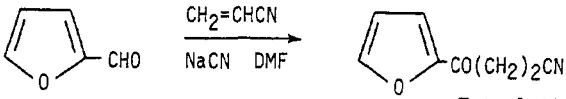
JOC (1964) 29 1970
JACS (1947) 69 990



Tetrahedron (1968) 24 5959

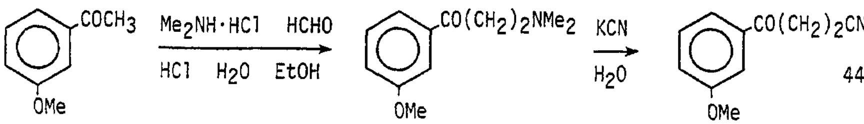


Angew (1971) 83 727
(Internat Ed 10 655)



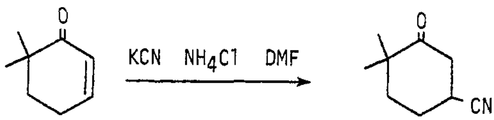
32%

Tetr Lett (1973) 1461
Angew (1973) 85 89
(Internat Ed 12 81)



44%

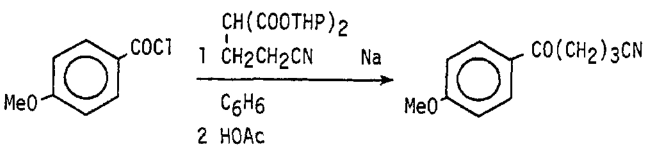
JCS (1947) 1190



JOC (1972) 37 268
Org Synth (1943) Coll Vol 2 498
JOC (1959) 24 879
JCS Perkin I (1972) 2765

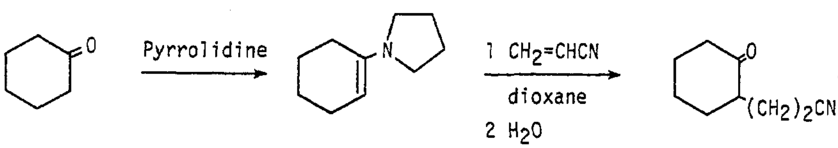
HCN, Et_3Al Org Synth (1972) 52 100
JACS (1972) 94 4635 4654

$Me_2C(OH)CN$ JCS (1958) 4193
Bull Soc Chim Fr (1963) 2471
Tetr Lett (1973) 141



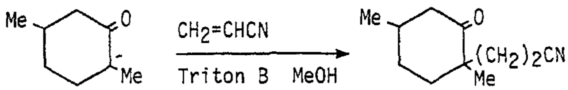
80%

Bull Soc Chim Fr (1969) 4437

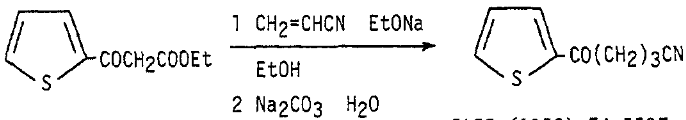


80%

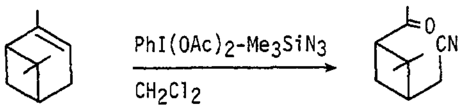
JACS (1963) 85 207



JACS (1964) 86 465
Org React (1949) 5 79



JACS (1952) 74 5597



65%

Synthesis (1972) 285

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)

Annelation reactions are not listed

$$PrCH_2C\equiv CBu \xrightarrow{MeCOO_2H} PrCH=CHCOBu$$

Ber (1954) 87 1478

$$PrC{\equiv}CH \xrightarrow[\text{2 MeONa; 3 } H_2O_2 \text{ NaOAc}]{\text{1 } BuC{\equiv}CCl \quad i\text{-}PrC(Me)_2BH_2} PrCH{=}CHCOCH_2Bu \qquad 48\%$$

Chem Comm (1973) 606

$$C_5H_{11}C{\equiv}CH \xrightarrow[\text{2 } (i\text{-}Pr)_3B\text{; 3 MeCOCl; 4 } CrO_3 \ H_2SO_4 \ Me_2CO]{\text{1 RLi THF}} C_5H_{11}C(COMe){=}C(Pr\text{-}i)_2 \qquad 42\%$$

Tetr Lett (1973) 795

$$PhCOOLi \xrightarrow{Me_2C{=}CHLi \quad Et_2O} PhCOCH{=}CMe_2 \qquad 40\%$$

JCS (1950) 2012
Advances in Org Chem (1960) 2 1

$$EtCH(Me)COCl \xrightarrow[\text{2 } PhNEt_2]{\text{1 } CH_2{=}CH_2 \quad AlCl_3 \quad PhNO_2} EtCH(Me)COCH{=}CH_2$$

Gazz (1967) 97 610
(Chem Abs 68 12401)

$$PhCOOH \xrightarrow{HOCH_2C{\equiv}CH} PhCOOCH_2C{\equiv}CH \xrightarrow[\text{(vapor phase)}]{660°} PhCOCH{=}CH_2 \qquad <80\%$$

JACS (1972) 94 5086

$$PhCH_2OH \xrightarrow[\text{2 } Me_2CO]{\text{1 MeMgI}} PhCH{=}CHCOMe$$

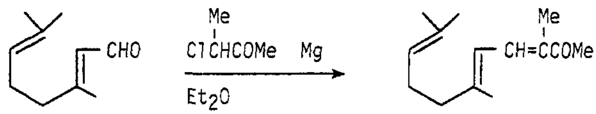
Tetr Lett (1964) 3481

$$PhCHO \xrightarrow{CH_3COMe \quad NaOH \quad H_2O} PhCH{=}CHCOMe \qquad 65\text{-}78\%$$

Org Synth (1932) Coll Vol 1 77 78 81 283
Org React (1968) 16 1

$$PrCHO \xrightarrow[\text{2 TsOH}]{\text{1 } CH_2(COMe)COOBu\text{-}t \text{ piperidine EtOH}} PrCH{=}CHCOMe \qquad 73\%$$

Acta Chem Scand (1963) 17 2216

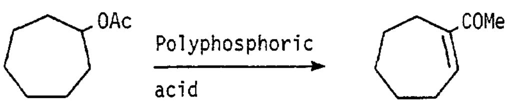


Rec Trav Chim (1950) 69 307

$$Me_2CH_2CHO \xrightarrow[\text{NaH } MeOCH_2CH_2OMe]{(EtO)_2POCH_2COMe} Me_2CH_2CH{=}CHCOMe \qquad 76\%$$

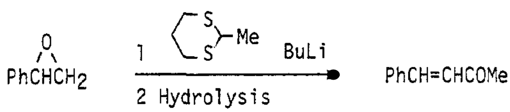
Bull Soc Chim Fr (1967) 2477
JACS (1969) 91 5675
Org React (1965) 14 270

$Ph_3P{=}CHCOR$ Ber (1962) 95 1513



25%

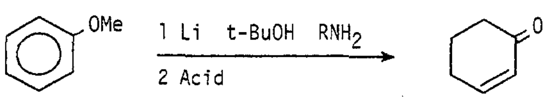
Tetrahedron (1968) 24 553



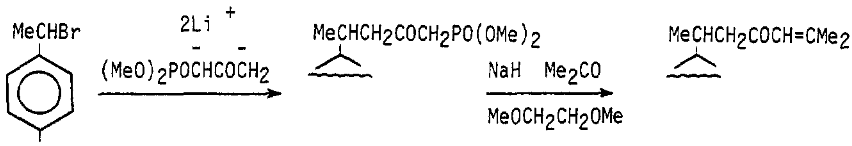
<70%

Angew (1965) 77 1134
(Internat Ed 4 1075)

$EtSCH{=}CH_2$, RLi JACS (1973) 95 2694



Synthesis (1972) 391
Advances in Org Chem (1972) 8 1

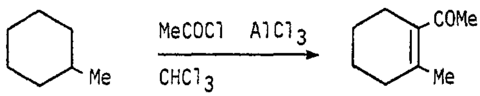


JOC (1973) 38 2909

$$PrBr \xrightarrow[\text{2 } Et_2NCH{=}CHCOMe]{\text{1 Mg}} PrCH{=}CHCOMe$$

Bull Soc Chim Fr (1960) 515
(1966) 287

ArOC=CHCOR' (R on C) Compt Rend (1964) 258 5234

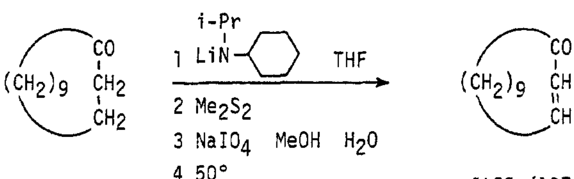


Tetr Lett (1968) 5455

$$PhCOCH_2Me \xrightarrow[\text{2 } PhCH_2SCH_2Br \quad \text{3 } NaIO_4 \quad \text{4 Toluene (reflux)}]{\text{1 } LiN(Pr\text{-}i)_2} PhCOC(Me){=}CH_2$$

52%

Chem Comm (1974) 135

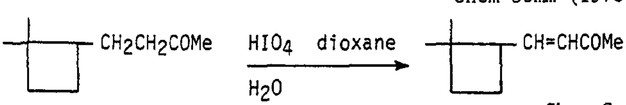


JACS (1973) 95 6840

$PhSeCl, H_2O_2$ JACS (1973) 95 6137

$PhSeBr, NaIO_4$ JACS (1973) 95 5813

Chem Comm (1973) 695



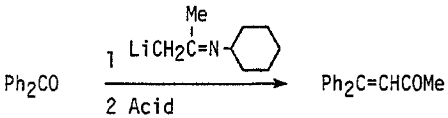
Chem Comm (1973) 746

O_2, palladium acetylacetonate JOC (1971) 36 752

Review: The Aldol Condensation Org React (1968) <u>16</u> 1

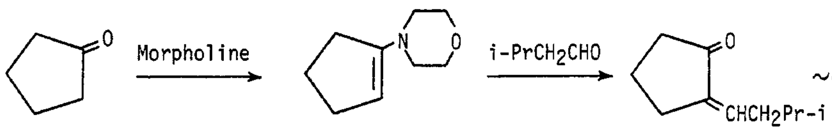
$$i\text{-}PrCH_2COCH_3 \xrightarrow[2\ (COOH)_2]{1\ MeCHO\quad KOH\quad i\text{-}PrOH} i\text{-}PrCH_2COCH{=}CHMe$$

JCS <u>C</u> (1970) 1469



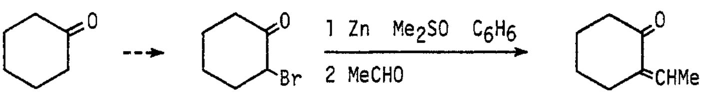
50%

Angew (1968) <u>80</u> 8
(Internat Ed <u>7</u> 7)



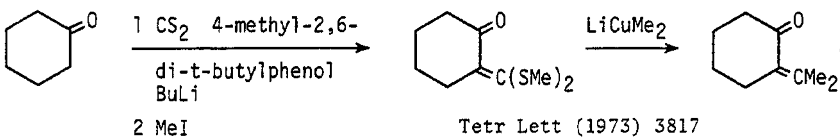
~86%

Ber (1962) <u>95</u> 1493



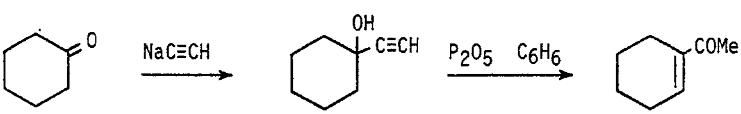
57%

JACS (1967) <u>89</u> 5727



83%

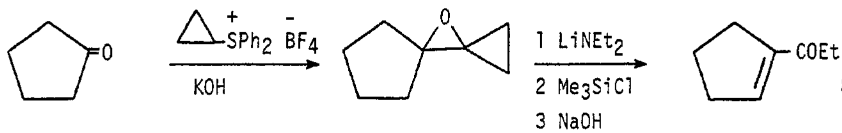
Tetr Lett (1973) 3817



Org Synth (1955) Coll Vol 3 22
JACS (1953) <u>75</u> 4740

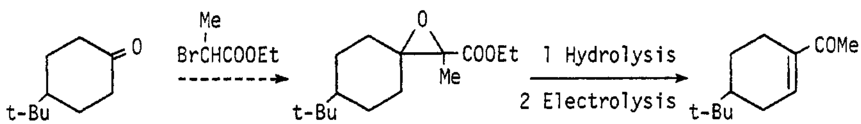
$$Ph_2CO \xrightarrow[NaH\quad THF]{Ph_2POCH=\overset{NHBu}{\overset{|}{C}}Ph} Ph_2C=CHCOPh \qquad 62\%$$

Tetr Lett (1971) 1401 1419
JOC (1971) 36 2892

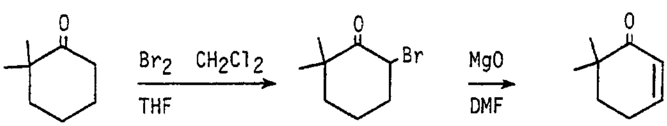


88%

JACS (1973) 95 289



JOC (1971) 36 3232

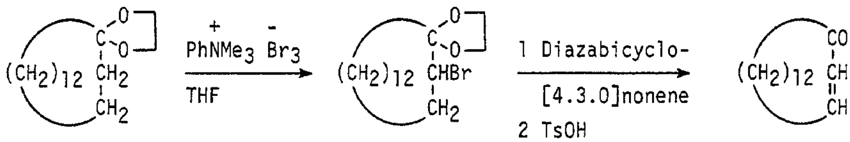


JOC (1972) 37 268

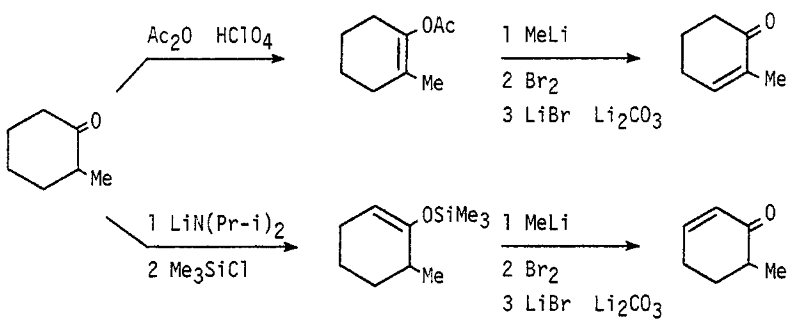
Dehydrohalogenation with: $CaCO_3$, DMA	JCS (1961) 2532
LiBr, Li_2CO_3, Me_2SO	JCS Perkin I (1972) 50
LiBr, Li_2CO_3, DMF	Tetrahedron (1973) 29 2575
LiCl, DMF	JOC (1972) 37 2436
HMPA	Tetr Lett (1968) 2105
Collidine	JCS (1961) 1583
$PhNEt_2$	Izv (1953) 889 (Chem Abs 49 1082)
Pyr	Helv (1942) 25 821
$NH_2NHCONH_2$	JACS (1952) 74 483; JCS (1961) 2532
$NH_2NHCOOEt$	JCS (1959) 1691

continued

2,4-Dinitrophenylhydrazine	JACS (1952) 74 3951
	(1950) 72 2290
$(MeO)_2PO_2^{-}\ \overset{+}{N}Me_4$	Bull Soc Chim Fr (1971) 2962 2551
$AgNO_3$	JACS (1960) 82 130



JOC (1971) 36 4124 ~65%



JOC (1973) 38 2576

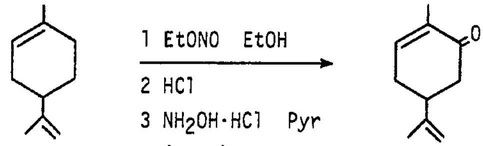
$$EtCH{=}CH_2 \xrightarrow[\text{2 HC≡CCOMe; 3 Air}]{\text{1 } B_2H_6 \text{ THF}} EtCH_2CH_2CH{=}CHCOMe \qquad 72\%$$

JACS (1970) 92 3503

$$MeCH{=}CH_2 \xrightarrow[\text{2 Quinoline}]{\text{1 MeCOCl } AlCl_3 \text{ } CH_2Cl_2} MeCH{=}CHCOMe$$

Org Synth (1971) 51 115

$MeCOOH, (CF_3CO)_2O$ JCS (1953) 3628



~60%

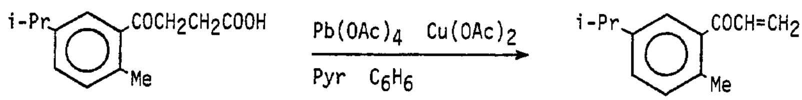
JACS (1951) 73 5856

NOF JOC (1968) 33 3699

$C_5H_{11}C{\equiv}CCH_2OMe$ → $C_5H_{11}C(Me){=}CHCOMe$

1 BuLi $Me_2NCH_2CH_2NMe_2$
2 Me_2SO_4
3 BuLi
4 MeI
5 Acid

Tetr Lett (1973) 2585



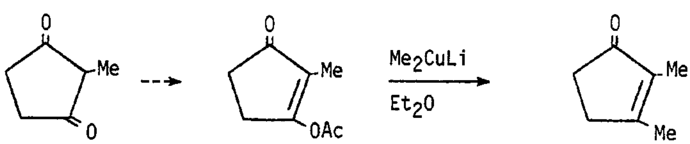
31%

Synthesis (1973) 541
JOC (1968) 33 2008

$C_6H_{13}COCH(Me)COOMe$ → $C_6H_{13}COC(Me){=}CH_2$ 52%

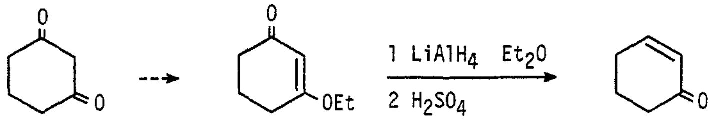
1 HCHO Me_2NH
HCl dioxane
2 MeI
3 DMF 75°

Tetr Lett (1973) 5037



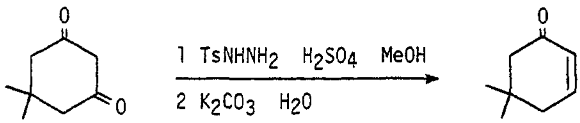
Tetr Lett (1973) 2071

Via enol ether Chem Comm (1973) 907



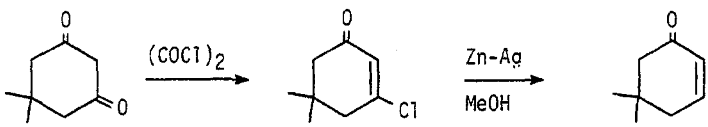
62-75%

Org Synth (1973) Coll Vol 5 294



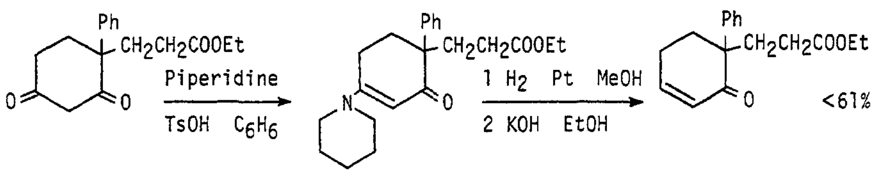
52%

JOC (1973) 38 3637



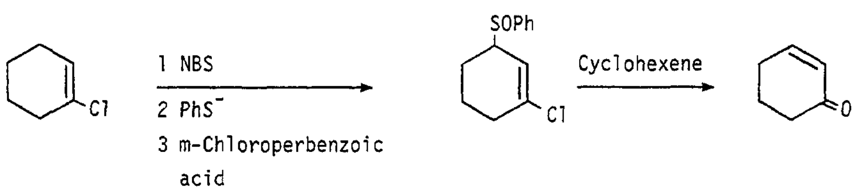
75%

JOC (1973) 38 3658



<61%

Ber (1964) 97 1723



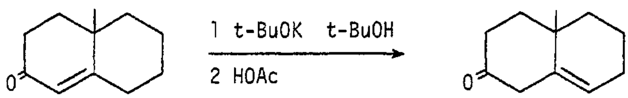
Chem Comm (1974) 21

$C_6H_{13}C{\equiv}CH \xrightarrow[\text{2 } (C_6H_{13})_3B \text{ diglyme; 3 } BrCH_2COMe\text{; 4 HOAc}]{\text{1 BuLi hexane}} (C_6H_{13})(H)C{=}C(C_6H_{13})(CH_2COMe)$ 75%

Tetr Lett (1973) 4491

$EtCH_2COPr \xrightarrow{Ph_3P{=}C{=}C(Ph)OLi} EtCH{=}C(Pr)CH_2COPh$ 52%

Tetr Lett (1972) 933

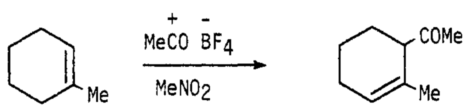


Tetr Lett (1962) 669
Steroids (1964) 3 183

Via enol trichloroacetate Tetrahedron (1969) 25 1717

$Me_2CHCH{=}CHCOMe \xrightarrow{h\nu \;\; Et_2O} Me_2C{=}CHCH_2COMe$ 75%

Tetr Lett (1964) 1203
JCS C (1966) 571

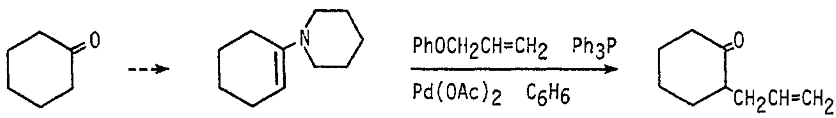


70%

Tetr Lett (1971) 3101

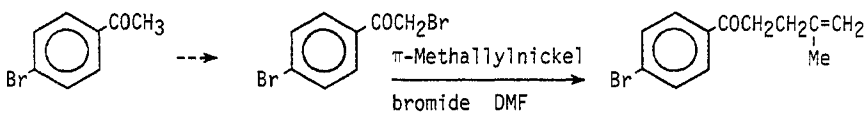
$PhCOOH \xrightarrow[THF]{ClMgCH{=}CH_2} PhCOCH_2CH_2CH{=}CH_2$ 84%

Synthesis (1970) 189

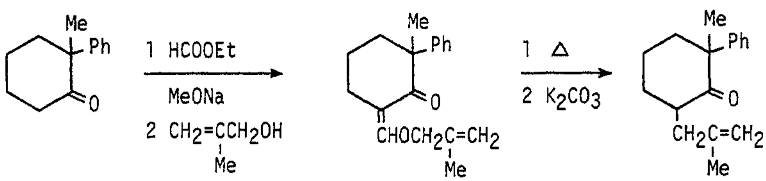


70%

Tetr Lett (1973) 121



JACS (1967) 89 2755



62%

JOC (1970) 35 570

$Me_2C(OH)CH{=}CH_2 \xrightarrow[]{CH_2{=}C(Me)OMe \quad H_3PO_4} Me_2C{=}CHCH_2CH_2COMe$ 94%

Helv (1967) 50 2091 2095
Tetr Lett (1969) 3243
JACS (1973) 95 553

$EtC(OH)(Me)CH{=}CH_2 \xrightarrow[MeONa]{Diketene} MeCOCH_2COO\text{-}C(Et)(Me)CH{=}CH_2 \xrightarrow{Al(OPr\text{-}i)_3} EtC(Me){=}CHCH_2CH_2COMe$

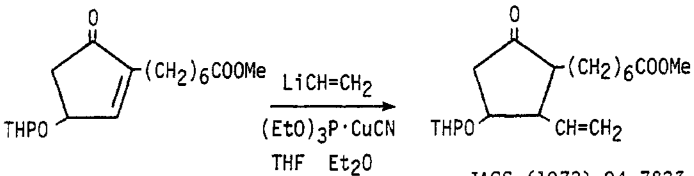
Tetrahedron (1969) 25 1667

$CH_2{=}C(Me)CH_2Cl \xrightarrow[K_2CO_3 \quad EtOH]{MeCOCH_2COMe} CH_2{=}C(Me)CH_2CH_2COMe$

Org Synth (1973) Coll Vol 5 767

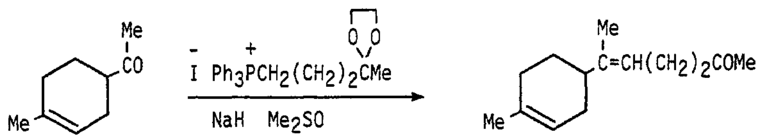
$$MeC{\equiv}CCH_2CH_2COMe \xrightarrow[EtOAc]{H_2 \quad Pd\text{-}CaCO_3} MeCH{=}CHCH_2CH_2COMe \qquad 78\%$$

JCS (1951) 2445
JACS (1972) 94 507



JACS (1972) 94 7823
Can J Chem (1970) 48 1626
Helv (1971) 54 1939
Org React (1972) 19 1

$(i\text{-}Bu)_2AlCH{=}CHR$ Tetr Lett (1972) 4083



JCS Perkin I (1972) 2653

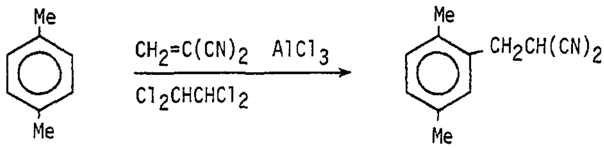
		Section
Also via:	Acetylenic ketones	309
	β-Hydroxyketones	330

Section 375 Nitrile — Nitrile

Dinitriles

$$PhCH_2Cl \xrightarrow[Me_2SO]{CH_2(CN)_2 \quad NaH} (PhCH_2)_2C(CN)_2 \qquad 75\%$$

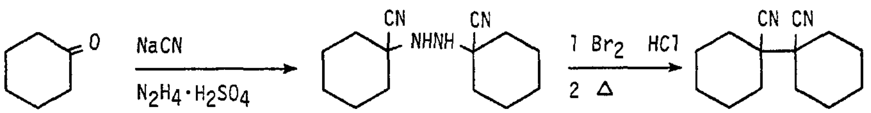
JOC (1961) 26 4112



JACS (1954) 76 1076

$$PhCHO \xrightarrow[MeOH \quad H_2O]{PhCH_2CN \quad NaCN} \underset{CN}{PhCH}-\underset{CN}{CHPh}$$

JACS (1958) 80 1752



~40%

Org Synth (1963) Coll Vol 4 273 274 66
JACS (1965) 87 4403

$$PhCH_2CN \xrightarrow{CH_2=CHCN \quad EtONa} \underset{CH_2CH_2CN}{PhCHCN} \qquad 20\text{-}30\%$$

JACS (1943) 65 437
Org React (1949) 5 79

$$MeCH=CHCN \xrightarrow[DMF]{Electrolysis \quad Et_4\overset{+}{N}\ \overset{-}{O}Ts} \begin{array}{l} MeCHCH_2CN \\ | \\ MeCHCH_2CN \end{array}$$

Compt Rend C (1967) 265 751

$$\underset{CN}{Me_2C}(CH_2)_2COOH \xrightarrow[Na_2CO_3 \quad MeOH]{Electrolysis} \underset{CN}{Me_2C}(CH_2)_4\underset{CN}{CMe_2} \qquad 60\%$$

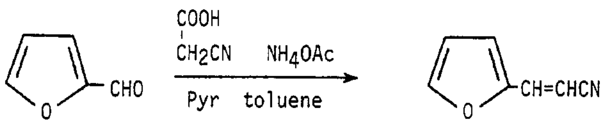
Bull Soc Chim Fr (1970) 183
Z Naturforsch (1947) 2b 185

Section 376 Nitrile — Olefin

αβ, βγ, and higher olefinic nitriles

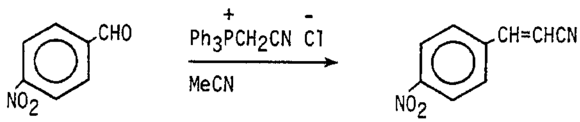
$$BuC\equiv CH \xrightarrow[\text{2 MeLi } Et_2O \quad \text{3 } (CN)_2]{\text{1 } (i\text{-}Bu)_2AlH \text{ hexane}} BuCH{=}CHCN \qquad 87\%$$

JACS (1968) 90 7139



74-78%

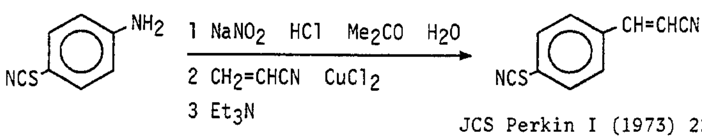
Org Synth (1973) Coll Vol 5 585
JCS Perkin I (1973) 2241
JACS (1949) 71 3562



42%

$(Ph_3\overset{+}{P})_2CHCN\ 2\overset{-}{Br}$, NaOH

Ber (1970) 103 2077
JOC (1971) 36 2026

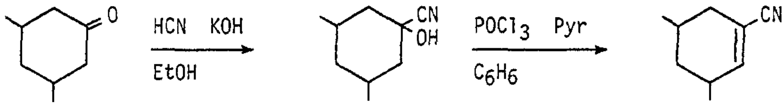


60%

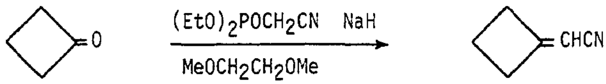
JCS Perkin I (1973) 2241
Org React (1960) 11 189

$$PhH \xrightarrow[HOAc]{CH_2{=}CHCN \quad Pd(OAc)_2} PhCH{=}CHCN$$

Tetrahedron (1969) 25 4819



JOC (1972) 37 2201
Tetrahedron (1968) 24 3127
Can J Chem (1969) 47 3266



75%

JOC (1971) 36 1024
(1965) 30 505

$Ph_2CO \xrightarrow[2\ H_3PO_4\quad H_2O]{1\ CH_3CN\quad BuLi\quad THF\quad hexane} Ph_2C{=}CHCN$ 58%

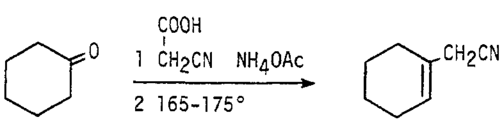
JOC (1968) 33 3402
Angew (1972) 84 767
(Internat Ed 11 722)

$PhCH_2CN \xrightarrow[EtOH]{HCHO\quad PhCH_2\overset{+}{N}Me_3\ \overset{-}{O}H} PhC(CN){=}CH_2$ 86%

JACS (1950) 72 5645

$EtCHO \xrightarrow[t\text{-}BuOH]{CH_2{=}CHCN\quad Ph_3P} EtCH{=}CHCH_2CN$ 44%

Tetr Lett (1967) 2401
(1964) 1653



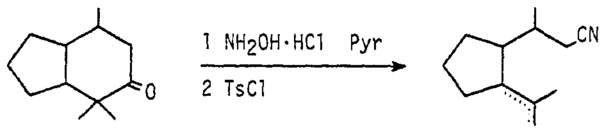
76-91%

Org Synth (1963) Coll Vol 4 234
(1973) Coll Vol 5 585

Via enamine Chem Pharm Bull (1973) 21 1601

$$\underset{\displaystyle Ph}{EtCHCN} \xrightarrow[NaOH \quad Me_2SO]{HC{\equiv}CH \quad PhCH_2\overset{+}{N}Et_3 \ \overset{-}{Cl}} \underset{\displaystyle Ph}{\overset{\displaystyle CH{=}CH_2}{EtCCN}} \qquad 80\%$$

Tetr Lett (1966) 5489



64%

JOC (1970) 35 186
(1962) 27 1961 1965
Coll Czech (1962) 27 377

Also via: Acetylenic nitriles (Section 310)

Section 377 Olefin — Olefin

$$EtC{\equiv}CEt \xrightarrow[2\ I_2 \quad NaOH]{1\ B_2H_6 \quad THF} EtCH{=}\underset{\displaystyle Et}{C}{-}\overset{\displaystyle Et}{C}{=}CHEt \qquad 68\%$$

cis trans

JACS (1968) 90 6243
JOC (1973) 38 1617

$$BuC{\equiv}CH \dashrightarrow BuC{\equiv}CCl \xrightarrow[2\ PrC{\equiv}CH]{1\ i\text{-}Pr\underset{Me}{\overset{Me}{C}}BH_2} BuCH{=}CHCH{=}CHPr \qquad 45\%$$

3 MeONa
4 i-PrCOOH

trans trans

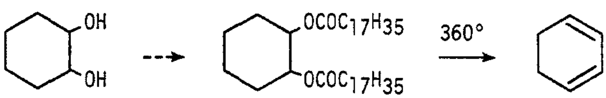
Chem Comm (1973) 606

BuC≡CC≡CBu $\xrightarrow[\text{2 HOAc; 3 } H_2O_2 \text{ NaOH } H_2O]{\text{1 Dicyclohexylborane THF}}$ BuCH=CHCH=CHBu (cis cis) 79%

JACS (1970) 92 4068

BuC≡CH $\xrightarrow[\text{2 CuCl THF; 3 } H_2SO_4 \text{ } H_2O]{\text{1 } (i\text{-Bu})_2AlH \text{ hexane}}$ BuCH=CHCH=CHBu (trans trans) 73%

JACS (1970) 92 6678
Annalen (1960) 629 222



42%

JACS (1953) 75 384

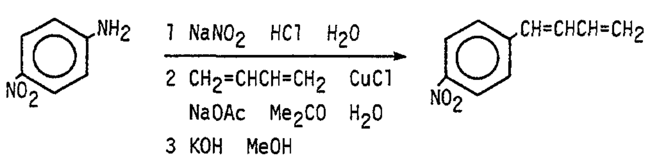
$$\begin{array}{c} CH_3 \\ | \\ MeCOH \\ | \\ MeCOH \\ | \\ CH_3 \end{array} \xrightarrow{HBr \quad H_2O} \begin{array}{c} MeC{=}CH_2 \\ | \\ MeC{=}CH_2 \end{array}$$

Org Synth (1955) Coll Vol 3 312

Me_2SO 160° JOC (1964) 29 123

PhCHO $\xrightarrow[\text{EtOLi EtOH}]{PhCH=CHCH_2\overset{+}{P}Ph_3 \ \overset{-}{Cl}}$ PhCH=CHCH=CHPh ~60%

Org Synth (1973) Coll Vol 5 499

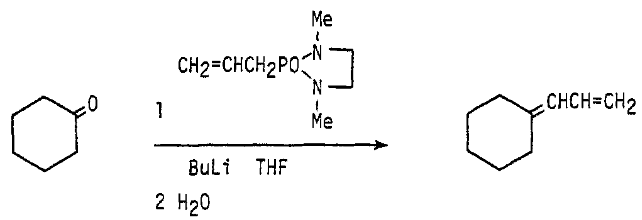


57-62%

Org Synth (1963) Coll Vol 4 727
Org React (1960) 11 189

$$PrBr \xrightarrow[2\ CH_2{=}CHCH{=}CHCH_2Br]{1\ Mg\quad THF} PrCH_2CH{=}CHCH{=}CH_2$$

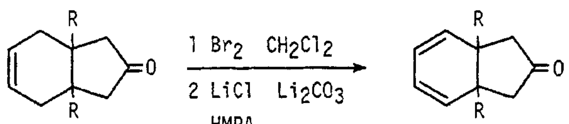
Bull Soc Chim Fr (1964) 2485



2 H_2O

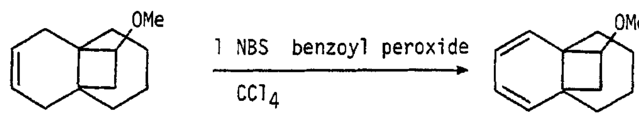
3 110-120°

JOC (1969) 34 3053



JACS (1972) 94 2155

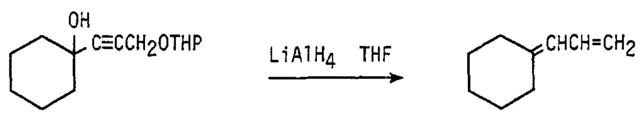
Org Synth (1973) Coll Vol 5 285



2 t-BuOK THF

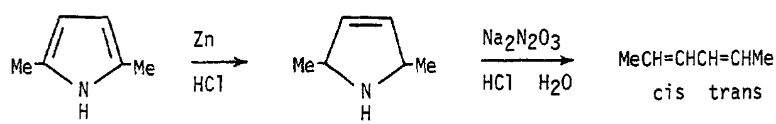
59%

JACS (1972) 94 7118

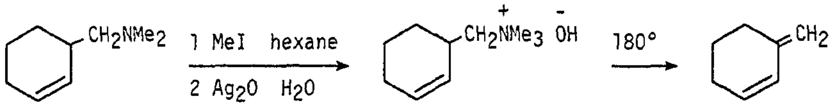


52%

Acta Chem Scand (1972) 26 2540

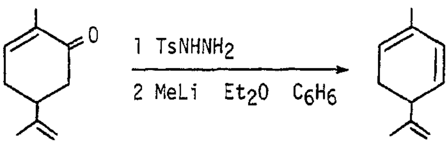


JACS (1966) 88 1335 2858



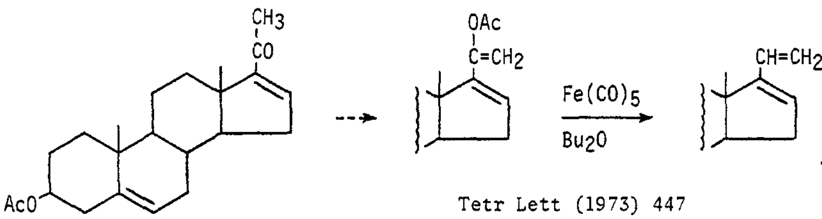
57%

JOC (1972) 37 2201



80%

JACS (1968) 90 4762



<40%

Tetr Lett (1973) 447

$$PhCH{=}CHBr \xrightarrow[2\ SOCl_2]{1\ Mg\quad THF} PhCH{=}CHCH{=}CHPh$$

JOC (1972) 37 3749

Mg; CuCl Angew (1967) 79 101 (Internat Ed 6 85)

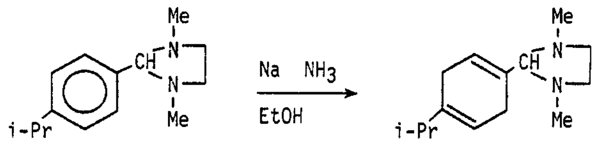
$K_4[Ni_2(CN)_6]$ Tetr Lett (1970) 4567

$$C_6H_{13}C{\equiv}CCH_2C{\equiv}C(CH_2)_6Cl \xrightarrow[\text{heptane}]{(i\text{-}Bu)_2AlH} C_6H_{13}CH{=}CHCH_2CH{=}CH(CH_2)_6Cl$$ 82%

JOC (1963) 28 1254

Reviews: Reductions by Metal-Ammonia Solutions and Related Reagents
Advances in Org Chem (1972) 8 1

A Comparison of Methods Using Lithium/Amine and Birch Reduction Systems
Synthesis (1972) 391



Aust J Chem (1955) 8 512

Electrolytic reduction JOC (1969) 34 3970

$$CH_2{=}CHCH_2Br \xrightarrow[\substack{2\ BrCH_2CH(Br)OEt \\ 3\ Zn\ \ ZnCl_2 \\ BuOH}]{1\ Mg\ \ Et_2O} CH_2{=}CHCH_2CH{=}CH_2 \qquad <59\%$$

Org Synth (1963) Coll Vol 4 748

$$CH_2{=}CHOBu \xrightarrow{(CH_2{=}C(Me){-}CH_2)_3B} CH_2{=}CHCH_2C(Me){=}CH_2 \qquad 80\text{-}90\%$$

Tetr Lett (1971) 2127

$$CH_2{=}CHCH_2Br \xrightarrow[\substack{1{,}4\text{-diazabicyclo}[2{,}2{,}2]\text{octane} \\ 2\ Li\ \ EtNH_2}]{1\ PhSCH_2CH{=}CH_2\ \ BuLi\ \ THF} CH_2{=}CHCH_2CH_2CH{=}CH_2$$

Tetr Lett (1968) 5629
(1969) 3707

$$(MeO)_2CHCH_2CH_2C(Me){=}CHCH_2Cl \xrightarrow[THF\ \ HMPA]{CH_2{=}C(Me)CH_2MgCl} (MeO)_2CHCH_2CH_2C(Me){=}CHCH_2CH_2C(Me){=}CH_2$$

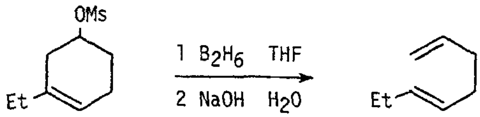
Tetr Lett (1969) 1393
Org Synth (1955) Coll Vol 3 121
Bull Soc Chim Fr (1964) 2485
Tetr Lett (1972) 1471

$$PhH \xrightarrow{ClCO(CH_2)_8COCl} PhCO(CH_2)_8COPh \xrightarrow[MeO(CH_2)_4OMe]{h\nu} CH_2{=}CH(CH_2)_2CH{=}CH_2 \qquad <53\%$$

JOC (1971) 36 1838

$$Me_2C{=}CHCH_2CH_2C(Me){=}CHCH_2OH \xrightarrow[MeOCH_2CH_2OMe]{MeLi \quad TiCl_3} \begin{array}{l} Me_2C{=}CHCH_2CH_2C(Me){=}CHCH_2 \\ Me_2C{=}CHCH_2CH_2C(Me){=}CHCH_2 \end{array}$$

JACS (1968) 90 209



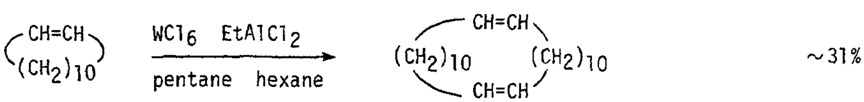
Synthesis (1971) 229

$$PrC{\equiv}C(CH_2)_4C{\equiv}CCONHBu\text{-}i \xrightarrow[EtOAc]{H_2 \quad Pd\text{-}CaCO_3} PrCH{=}CH(CH_2)_4CH{=}CHCONHBu\text{-}i$$

JCS (1950) 115

$$CH_2{=}CH(CH_2)_4Br \dashrightarrow CH_2{=}CH(CH_2)_4MgBr \xrightarrow[FeCl_3 \quad THF]{CH_2{=}CHBr} CH_2{=}CH(CH_2)_4CH{=}CH_2$$

Synthesis (1971) 303



Synthesis (1972) 134

$$CH_2{=}CH(CH_2)_8COONa \xrightarrow[MeOH]{Electrolysis} CH_2{=}CH(CH_2)_{16}CH{=}CH_2$$

JCS (1953) 2393