Compendium of Organic Synthetic Methods

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PREFACE

Compendium of Organic Synthetic Methods is a systematic listing of functional group transformations designed for use by bench chemists, persons planning syntheses, students attending courses on synthetic chemistry, and teachers of these courses. The idea for this compilation came from the observation that organic chemists spend a large proportion of their time searching a formidable original literature for these hard-to-find synthetic methods.

A key feature of this book is the classification of reactions on the basis of the functional group of the starting material and of the product, without reference to the reaction mechanism. We wished to produce as comprehensive a set of reactions as possible, covering all branches of organic chemistry. Reactions giving low yields or requiring exotic reagents are not omitted. Consequently reactions included cover the full range of methods from boiling in oil to treatment with fluorine or orange-peel enzymes.

The presentation of each synthetic method in the form of representative reactions without discussion follows the plan used successfully in *Steroid Reactions* (Djerassi, Holden-Day). The limitations of such compilations containing much information but few words are obvious; there is, however, a great need for a comprehensive one-volume listing of synthetic methods as an intermediary between the chemist and the literature. The reader interested in a detailed discussion of synthetic methods should consult *Reagents for Organic Synthesis* (Fieser and Fieser, Wiley) and *Survey of Organic Syntheses* (Buehler and Pearson, Wiley).

We apologize to authors for the space-saving anonymity of references and for referring in many instances not to papers by the originators of a reaction but rather to subsequent articles by other authors. We make no apology, however, for omitting unnecessary reference punctuation, and avoiding the use of *ibid.* and other sources of confusion.

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Palo Alto, California
March 1971

CONTENTS

ABBREVIATIONS

Ac	acetyl
Bu	butyl
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMA	dimethylacetamide
DMF	dimethylformamide
Et	ethyl
HMPA	hexamethylphosphoramide
Me	methyl
Ms	methanesulfonyl
NBA	*N*-bromoacetamide
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
Ni	Raney nickel
Ph	phenyl
Pr	propyl
Pyr	pyridine
THF	tetrahydrofuran
THP	tetrahydropyranyl
Ts	*p*-toluenesulfonyl

INDEX

Sections—heavy type
Pages—light type

PREPARATION OF →
FROM ↓

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** 1	**16** 16	**31** 75	**46** 132	**61** 177	**76** 203	**91** 230	**106** 271		**136** 329		**166** 379	**181** 457	**196** 479
Carboxylic acids, acid halides, anhydrides	**2** 2	**17** 18	**32** 76	**47** 132	**62** 178	**77** 204	**92** 230	**107** 272	**122** 309	**137** 329	**152** 357	**167** 380	**182** 457	**197** 482
Alcohols, phenols	**3** 3	**18** 26	**33** 78	**48** 137	**63** 180	**78** 208	**93** 232	**108** 280	**123** 310	**138** 331	**153** 359	**168** 386	**183** 459	**198** 484
Aldehydes	**4** 3	**19** 31	**34** 80	**49** 144	**64** 181	**79** 209	**94** 233	**109** 287	**124** 316	**139** 338	**154** 363	**169** 396	**184** 460	**199** 489
Alkyls, methylenes, aryls		**20** 36		**50** 146	**65** 182	**80** 210				**140** 338	**155** 365	**170** 400	**185** 464	**200** 493
Amides		**21** 39	**36** 85	**51** 148	**66** 184	**81** 211	**96** 236	**111** 289		**141** 338	**156** 366	**171** 403	**186** 464	**201** 495
Amines	**7** 5	**22** 41	**37** 86	**52** 150	**67** 184	**82** 213	**97** 240	**112** 290	**127** 318	**142** 339	**157** 367	**172** 404	**187** 465	**202** 496
Esters	**8** 6	**23** 42	**38** 87	**53** 152	**68** 185	**83** 218	**98** 249	**113** 291	**128** 318	**143** 342	**158** 368	**173** 406	**188** 467	**203** 498
Ethers, epoxides		**24** 46	**39** 92	**54** 154	**69** 186	**84** 220	**99** 249	**114** 293	**129** 320	**144** 343	**159** 369	**174** 408	**189** 467	**204** 501
Halides, sulfonates, sulfates	**10** 6	**25** 47	**40** 102	**55** 156	**70** 186	**85** 220	**100** 250	**115** 295	**130** 320	**145** 345	**160** 370	**175** 411	**190** 468	**205** 504
Hydrides (RH)		**26** 53	**41** 107	**56** 162	**71** 191	**86** 222	**101** 255	**116** 299	**131** 322	**146** 349	**161** 375	**176** 417	**191** 471	**206** 512
Ketones	**12** 10	**27** 56	**42** 110	**57** 164	**72** 193	**87** 223	**102** 258	**117** 302	**132** 323	**147** 353	**162** 375	**177** 419	**192** 473	**207** 513
Nitriles		**28** 62		**58** 166	**73** 198	**88** 225	**103** 262	**118** 304			**163** 376	**178** 433	**193** 474	**208** 520
Olefins	**14** 13	**29** 64	**44** 119	**59** 168	**74** 198	**89** 227	**104** 264	**119** 305	**134** 325	**149** 354	**164** 377	**179** 435	**194** 475	**209** 520
Miscellaneous compounds	**15** 13	**30** 68	**45** 122	**60** 172	**75** 202	**90** 229	**105** 266	**120** 307	**135** 328	**150** 356	**165** 377	**180** 442	**195** 476	**210** 526

PROTECTION

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

INTRODUCTION

Classification and Organization. *Compendium of Organic Synthetic Methods* contains approximately 3000 examples of published chemical transformations 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 by increases or decreases in the length of carbon chains. For example, the reactions *t*-BuOH → *t*-BuCOOH, $PhCH_2OH \rightarrow PhCOOH$, and $PhCH = CHCH_2OH \rightarrow PhCH = CHCOOH$ are all found in Section 18 on 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 → RCOOR (esters from alcohols, also esters from carboxylic acids)

Sulfonic esters are grouped with halides. Hydrazines are listed with amines and hydrazides with amides.

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

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

How to Use the Book. Examples of the preparation of one functional group from another are located via the index on p. xi, which gives the corresponding section and page. Thus Section 1 contains examples of the preparation of acetylenes from other acetylenes; Section 2, acetylenes from carboxylic acids; Section 3, acetylenes from alcohols; etc.

Sections giving examples of the reactions of a functional group are found in horizontal rows of the index. Thus Section 1 gives examples of the reactions of acetylenes forming other acetylenes; Section 16, reactions of acetylenes forming carboxylic acids; Section 31, reactions of acetylenes forming alcohols; etc.

Examples of alkylation, dealkylation, homologation, isomerization, transposition, etc. are found in Sections 1, 17, 33, and so forth, which lie close to a diagonal of the index. These sections correspond to the preparation of acetylenes from acetylenes, carboxylic acids from carboxylic acids, alcohols and phenols from alcohols and phenols, etc.

Examples of the protection of carboxylic acids, alcohols, phenols, aldehydes, amines, and ketones are also indexed on page xi.

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

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.

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

The references given usually yield a further crop of references to previous work. Subsequent publications can be found through Science Citation Index.

Reactions Included in the Book. Interconversions of monofunctional compounds form the major part of this compilation. Reactions of bifunctional compounds in which the two functions are identical and which give monofunctional

products are also included; for example, $R_2C(COOH)_2 \rightarrow R_2CO$ (ketones from carboxylic acids).

Examples of the removal of one functional group from bifunctional compounds and the preparation of functional groups from groups not listed on the index are included in the miscellaneous sections; for example, $RCH(Br)COR \rightarrow RCH_2COR$, $RCH(OH)COR \rightarrow RCH_2COR$ and $RCH=CHCOR \rightarrow RCH_2CH_2COR$ (ketones from miscellaneous compounds), $RCH_2NO_2 \rightarrow RCHO$ (aldehydes from miscellaneous compounds).

Reactions are included even when full experimental details are lacking from 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.

Reactions Not Included in the Book. Reactions forming bifunctional products are not included, for example, $RCH=CH_2 \rightarrow RCH(OH)CH_2OH$. Chain lengthening processes via unsaturated intermediates, for instance, $RCHO \rightarrow [RCH=CHCOOEt] \rightarrow RCH_2CH_2COOEt$, are only partially covered. Ring forming reactions and reactions that involve several functional centers (e.g., the Diels-Alder reaction) are represented by very few examples. These gaps will be filled by a second volume, presently under consideration, which will include reactions forming unsaturated and other bifunctional products.

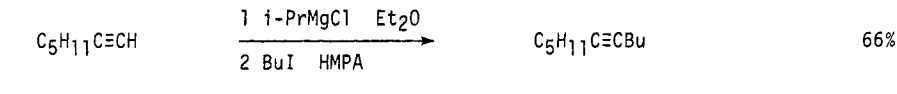
Reactions published after early 1971 are not included.

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 1 PREPARATION OF ACETYLENES

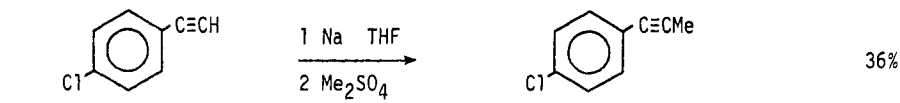
Section 1 Acetylenes from Acetylenes

Review: The Synthesis of Acetylenes Org React (1949) 5 1



Bull Soc Chim Fr (1964) 2000

JACS (1936) 58 796
JOC (1959) 24 840

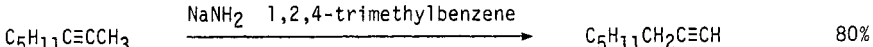


Bull Soc Chim Fr (1965) 1525

Further examples of the reaction $RC{\equiv}CH + R'X \rightarrow RC{\equiv}CR'$ are included in section 10 (Acetylenes from Halides, Sulfonates and Sulfates)

Bull Soc Chim Fr (1965) 1525
Tetrahedron (1958) 3 197

JACS (1951) 73 1273
Quart Rev (1970) 24 585



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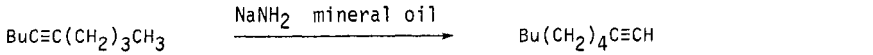
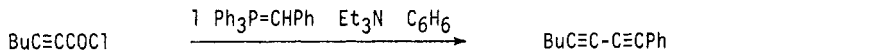
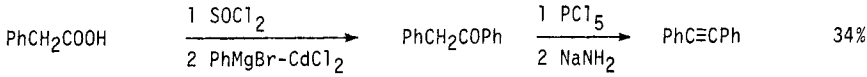


Org React (1949) 5 1

Section 2 Acetylenes from Carboxylic Acids and Acid Halides



JCS (1964) 543



Helv (1938) 21 1356

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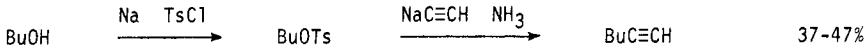
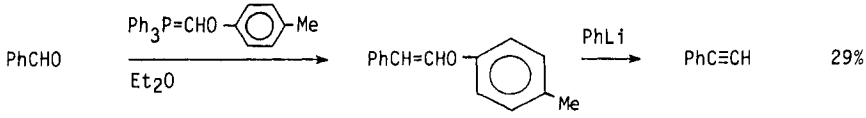
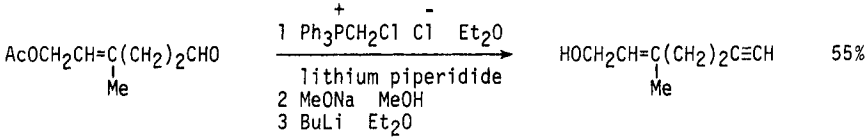


JACS (1937) 59 1490
Org React (1949) 5 1

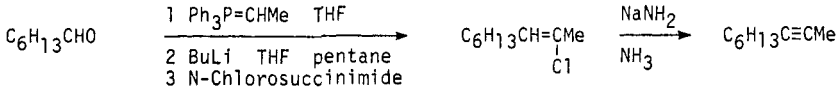
Section 4 Acetylenes from Aldehydes



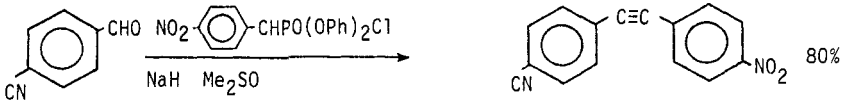
Ber (1962) 95 2514



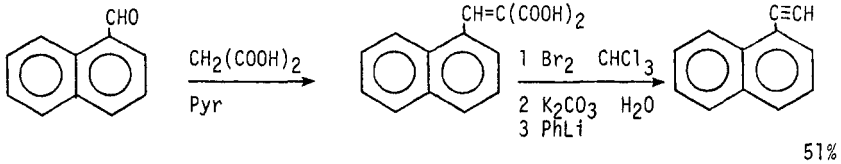
JACS (1969) 91 4318



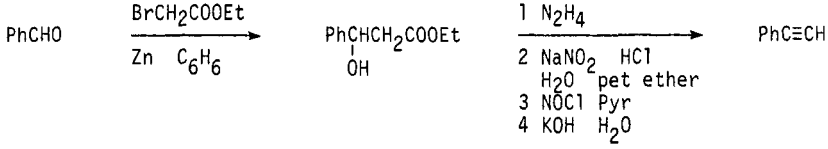
Tetr Lett (1970) 447



JACS (1965) 87 2777



Compt Rend (1949) 229 660



JACS (1951) 73 4199

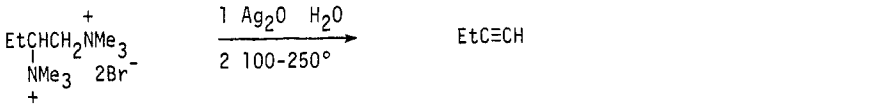
Section 5 Acetylenes from Alkyls, Methylenes and Aryls

No examples

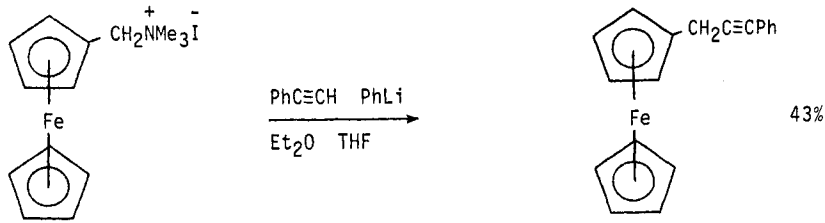
Section 6 Acetylenes from Amides

No examples

Section 7 Acetylenes from Amines

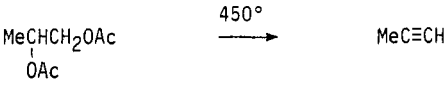


JACS (1939) 61 1943



JCS (1963) 2990

Section 8 Acetylenes from Esters



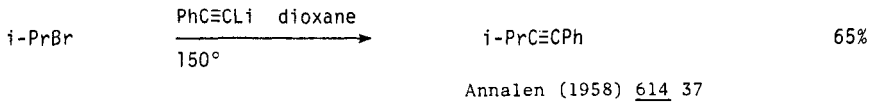
Izv (1959) 43
(Chem Abs 54 7547)

Section 9 Acetylenes from Ethers

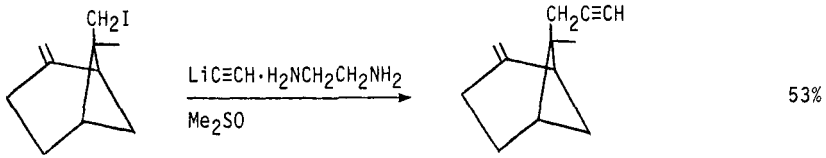
No examples

Section 10 Acetylenes from Halides, Sulfonates and Sulfates

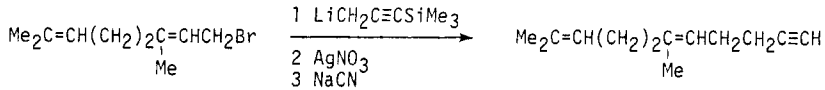
Review: The Synthesis of Acetylenes Org React (1949) 5 1



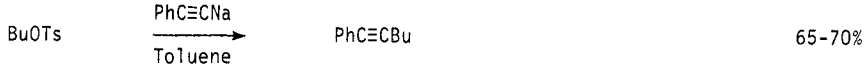
Annalen (1958) 614 37



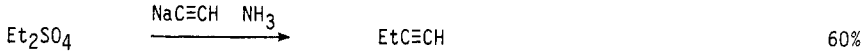
JACS (1969) 91 4771
Angew (1959) 71 245



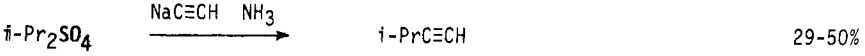
Tetr Lett (1968) 5041
(1970) 2247



Org React (1949) 5 1
JACS (1937) 59 1490



JACS (1931) 53 289



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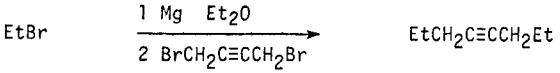
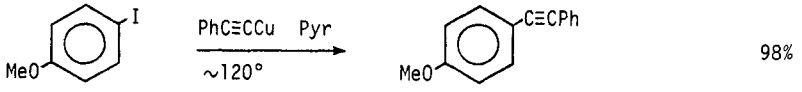


JCS (1946) 1009



JOC (1963) 28 3313
JACS (1964) 86 4358

$$PhCH{=}CHBr \xrightarrow{PhC{\equiv}CCu\ \ DMF} PhCH{=}CHC{\equiv}CPh \qquad 75\%$$

Chem Comm (1967) 1259

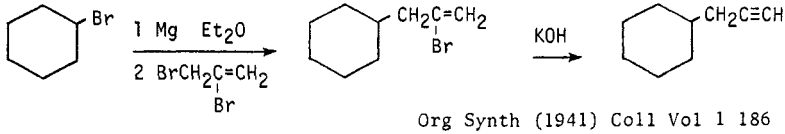
$$PhI \xrightarrow[2\ \text{Acid hydrolysis}\\ 3\ NaOH\ \ MeOH\ \ H_2O]{1\ CuC{\equiv}CCH(OEt)_2\ \ pyr} PhC{\equiv}CH$$

JCS C (1969) 2173

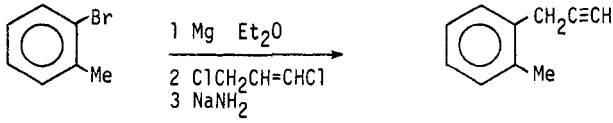
Further examples of the reaction RC≡CH + R'X → RC≡CR' are included in section 1 (Acetylenes from Acetylenes)

$$BuBr \xrightarrow[2\ PhC{\equiv}CBr\ \ CoCl_2]{1\ Mg\ \ Et_2O} BuC{\equiv}CPh \qquad 32\%$$

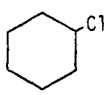
JCS (1954) 1704



Org Synth (1941) Coll Vol 1 186
Org React (1949) 5 1

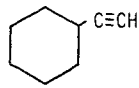


Compt Rend (1925) 181 555



1 CH_2=CHCl $AlCl_3$

2 $NaNH_2$ NH_3



36%

Rec Trav Chim (1965) 84 31

$EtCHCH_2Br$ (Br)

1 Me_3N

2 Ag_2O H_2O

3 100-250°

$EtC{\equiv}CH$ 9%

JACS (1939) 61 1943

$C_8H_{17}CH(Br)-CH_2Br$

$NaNH_2$ Me_2SO

$C_8H_{17}C{\equiv}CH$ 54%

Tetrahedron (1970) 26 2127
JACS (1934) 56 2120

$EtCH_2CH(Br)-CH_2Br$

KOH EtOH

$EtCH_2C{\equiv}CH$

Org React (1949) 5 1

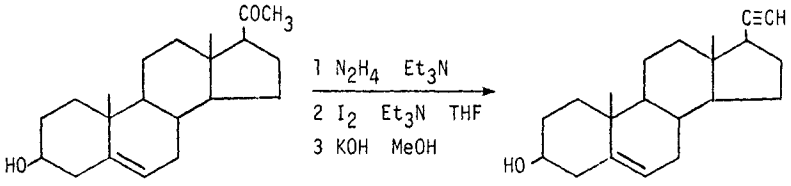
Further examples of the conversion of dibromides into acetylenes are included in section 14 (Acetylenes from Olefins)

Section 11 Acetylenes from Hydrides (RH)

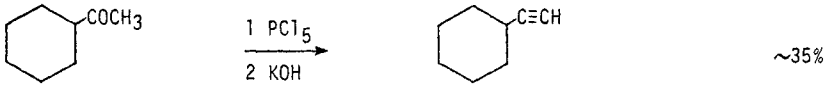
No examples

Section 12 Acetylenes from Ketones

Review: The Synthesis of Acetylenes Org React (1949) 5 1

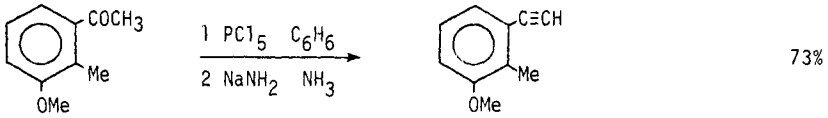


JOC (1969) 34 3502



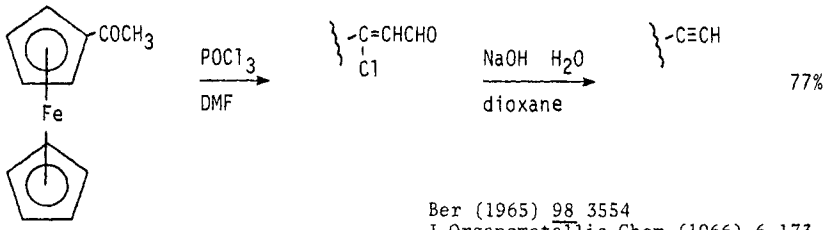
~35%

JACS (1932) 54 1184



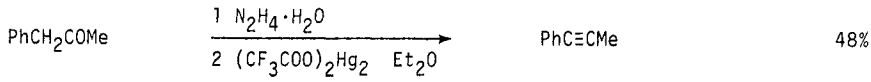
73%

Tetrahedron (1969) 25 4249

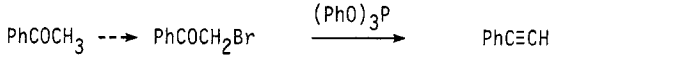


77%

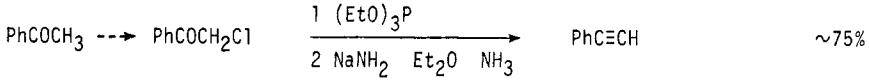
Ber (1965) 98 3554
J Organometallic Chem (1966) 6 173



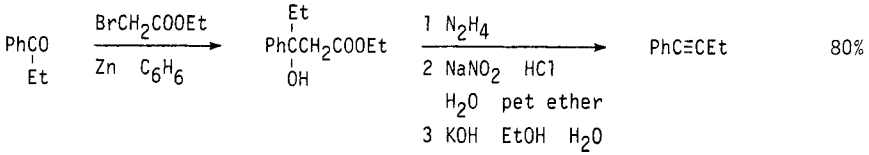
JOC (1966) 31 624



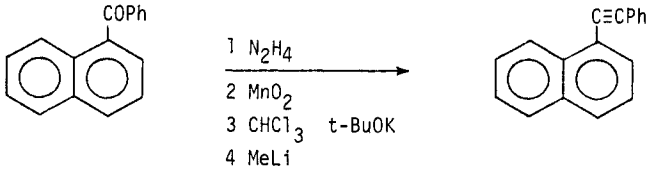
Dokl (1965) 163 656
(Chem Abs 63 11338)



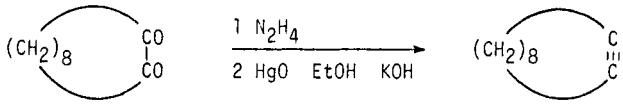
JCS (1963) 3712



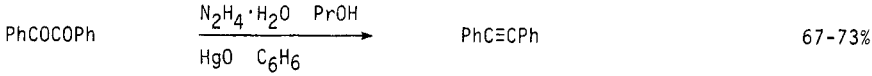
JACS (1951) 73 4199



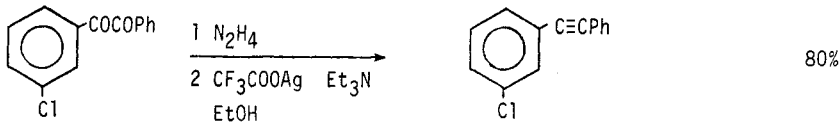
Chem Ind (1969) 1306



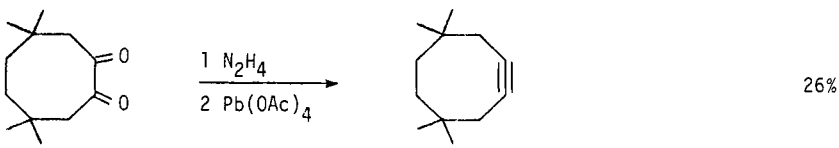
JACS (1952) 74 3636 3643



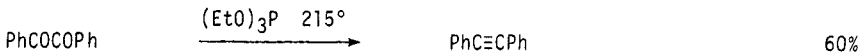
Org Synth (1963) Coll Vol 4 377



JOC (1958) 23 665



Tetr Lett (1968) 4511



JOC (1964) 29 2243

Section 13 Acetylenes from Nitriles

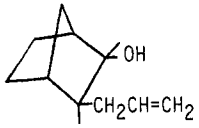
No examples

Section 14 Acetylenes from Olefins

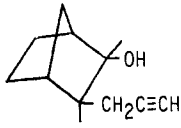
$BuCH{=}CH_2 \xrightarrow{Li\ \ THF} BuC{\equiv}CLi \xrightarrow{H_2O} BuC{\equiv}CH$

~65%

JOC (1967) 32 105



$\xrightarrow[2\ NaNH_2\ \ HMPA]{1\ Br_2\ \ CCl_4}$



48%

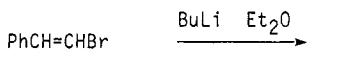
Tetr Lett (1970) 41
Tetrahedron (1970) 26 2127

$C_8H_{17}CH{=}CH(CH_2)_7COOH \xrightarrow[2\ NaNH_2\ \ NH_3\ \ Et_2O]{1\ Br_2} C_8H_{17}C{\equiv}C(CH_2)_7COOH$ 68%

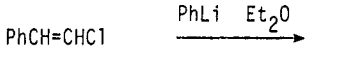
J Am Oil Chem Soc (1951) 28 27
(Chem Abs 45 8449)
Org Synth (1947) 27 76

Section 15 Acetylenes from Miscellaneous Compounds

Review: The Synthesis of Acetylenes Org React (1949) 5 1

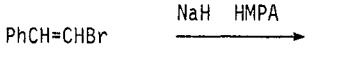


JACS (1940) 62 2327



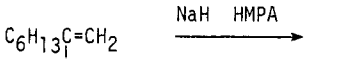
100%

Ber (1941) 74B 1474



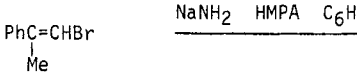
78%

Bull Soc Chim Fr (1966) 1293



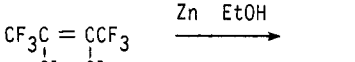
70%

Bull Soc Chim Fr (1966) 1293



40%

Bull Soc Chim Fr (1966) 1293

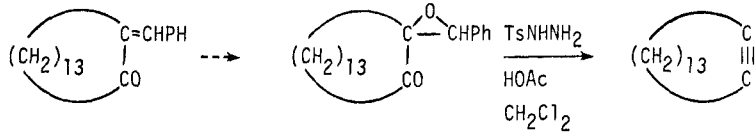


54%

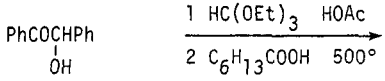
JACS (1949) 71 298

$PhCH{=}CClF \xrightarrow{BuLi} PhC{\equiv}CBu$ ~20%

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

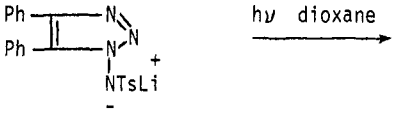


Helv (1967) 50 2101

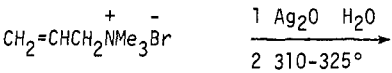


Chem Comm (1970) 206

Tetr Lett (1966) 1663



Angew (1964) 76 144
(Internat Ed 3 138)

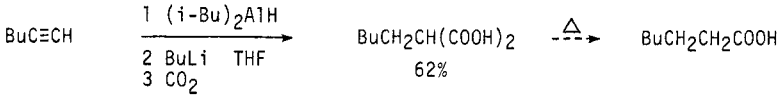


JOC (1949) 14 1

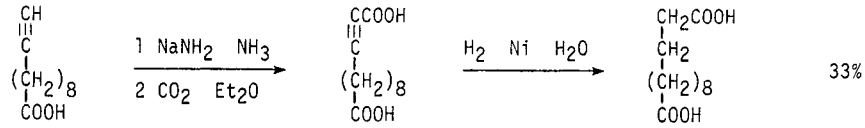
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 2 PREPARATION OF CARBOXYLIC ACIDS ACID HALIDES AND ANHYDRIDES

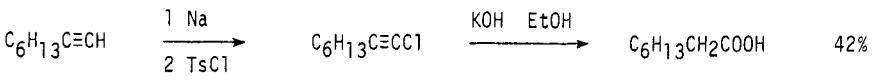
Section 16 Carboxylic Acids from Acetylenes



Tetr Lett (1966) 6021



JACS (1945) 67 1171



Annales de Chimie (1931) 16 309

$$BuC{\equiv}CH \xrightarrow[2\ \text{m-Chloroperbenzoic acid}\quad THF]{1\ \text{Dicyclohexylborane}\quad THF} BuCH_2COOH$$

JACS (1967) 89 291

$$PhC{\equiv}CH \xrightarrow[CH_2Cl_2]{CF_3CO_2H\quad Na_2HPO_4} \underset{25\%}{PhCOOH} + \underset{38\%}{PhCH_2COOH}$$

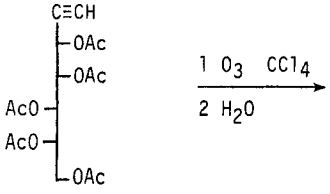
JACS (1964) 86 4866

$$C_8H_{17}C{\equiv}C(CH_2)_7COOH \xrightarrow[pH\ 12]{KMnO_4\quad H_2O} HOOC(CH_2)_7COOH \qquad 80\%$$

JOC (1952) 17 1063

$$BuC{\equiv}CBu \xrightarrow[2\ NaI]{1\ O_3\quad CCl_4\quad HOAc} BuCOOH \qquad 35\%$$

Annalen (1953) 583 29

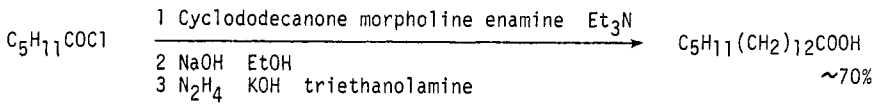


41%

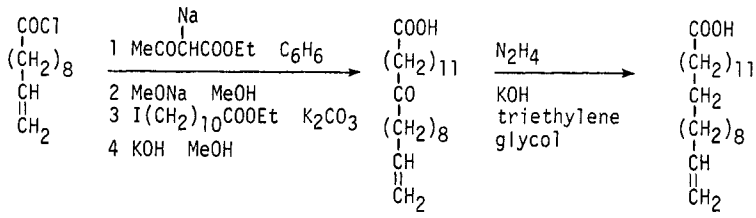
Carbohydrate Res (1966) 2 315

Carboxylic acids may also be prepared by conversion of acetylenes into esters or amides, followed by hydrolysis. See section 106 (Esters from Acetylenes) and section 76 (Amides from Acetylenes)

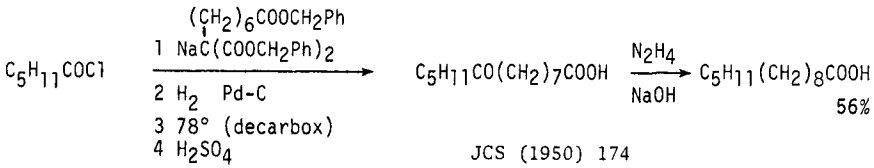
Section 17 Carboxylic Acids, Acid Halides and Anhydrides from Carboxylic Acids and Acid Halides



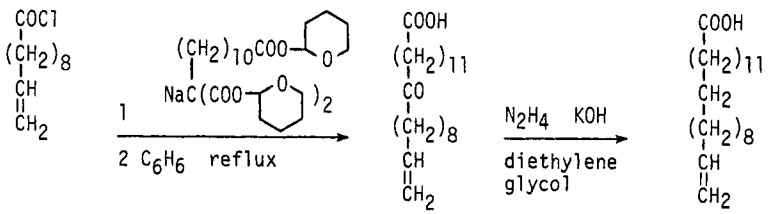
Ber (1967) 100 4010



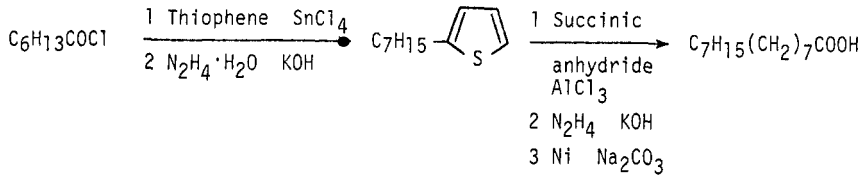
Arkiv Kemi (1949) 1 99
(Chem Abs 43 7414)



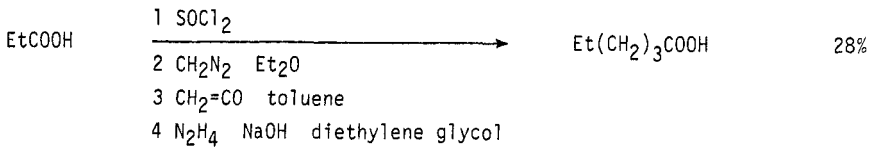
JCS (1950) 174



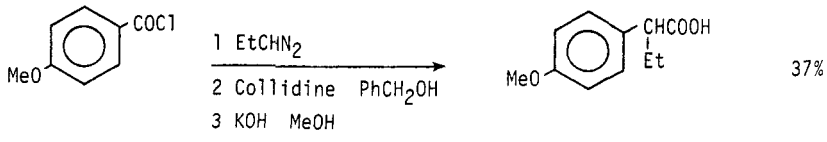
JCS (1952) 3945



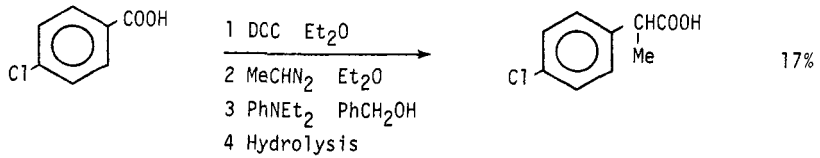
JCS (1954) 4162
(1962) 350



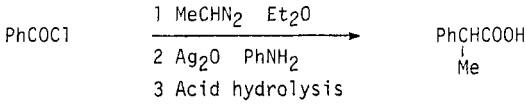
Annalen (1964) 678 113



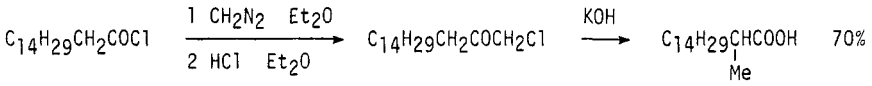
JOC (1948) 13 763



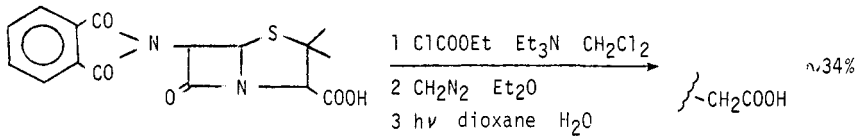
JCS C (1970) 971



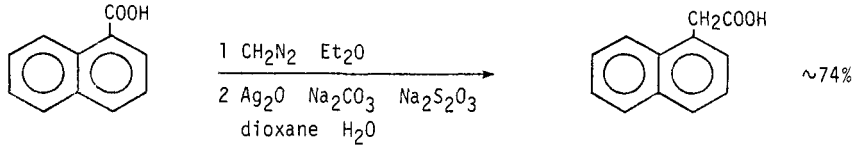
Chem Ind (1955) 1673



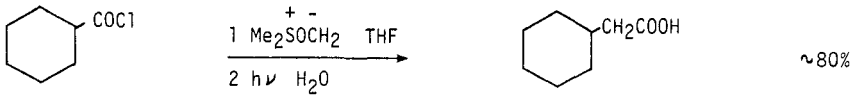
Chem Phys Lipids (1968) 2 213



JCS C (1969) 1319
Tetr Lett (1969) 4517



Org React (1942) 1 38
JCS (1950) 926



JACS (1964) 86 1640

$BuCH_2COOH$ —(1 NaH $(i\text{-}Pr)_2NH$ THF; 2 BuLi; 3 $C_6H_{13}Br$)→ $BuCHCOOH$ (C_6H_{13}) 86%

JACS (1970) 92 1397

$C_5H_{11}CH_2COOH$ —(1 BuLi $(i\text{-}Pr)_2NH$ hexane THF; 2 HMPA; 3 BuBr)→ $C_5H_{11}CHCOOH$ (Bu) 93%

JOC (1970) 35 262

$C_5H_{11}CHCOOH$ (Bu) —(1 BuLi $(i\text{-}Pr)_2NH$ hexane THF; 2 BuBr)→ $C_5H_{11}CCOOH$ (Bu, Bu) 50%

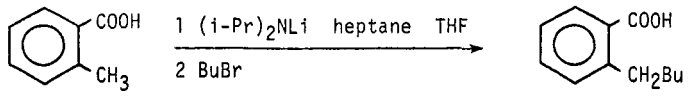
JOC (1970) 35 262

$PhCH_2COOH$ —(1 Sodium-naphthalene THF; 2 i-PrBr)→ $PhCHCOOH$ (i-Pr) 88%

JOC (1967) 32 2797

$PhCH_2COOH$ —(1 i-PrMgCl HMPA Et_2O; 2 EtI)→ $PhCHCOOH$ (Et)

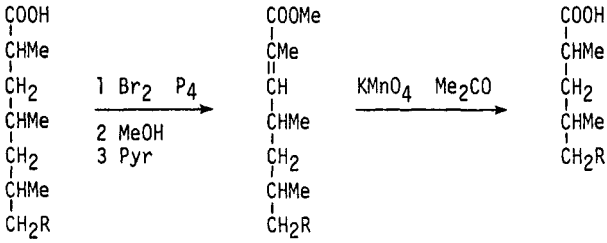
Bull Soc Chim Fr (1964) 2000



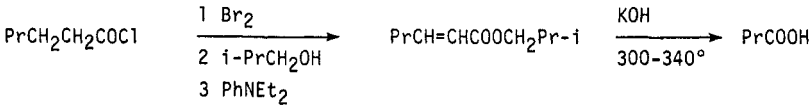
69-73%

JACS (1970) 92 1396

Alkylation of acids may also be accomplished via ester or amide intermediates. See section 113 (Esters from Esters) and section 81 (Amides from Amides)



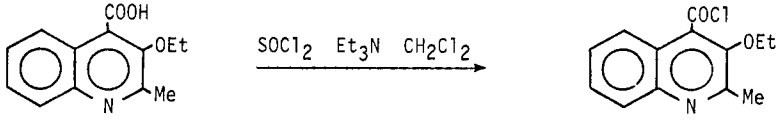
JCS (1963) 3081



Biochem J (1951) 50 163

89%

Helv (1959) 42 1653
Org Synth (1932) Coll Vol 1 12



JCS (1963) 491

$PhCH_2CH_2COOH \xrightarrow{(COCl)_2\ C_6H_6} PhCH_2CH_2COCl$ 98%

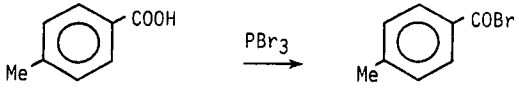
JACS (1920) 42 599
Can J Chem (1955) 33 1515

$t\text{-}BuCOOH \xrightarrow{PhCOCl} t\text{-}BuCOCl$ 92%

JACS (1938) 60 1325

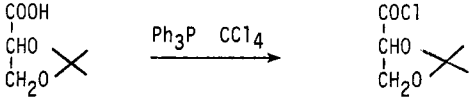
$PhCH_2COOH \xrightarrow{PCl_3} PhCH_2COCl$

Org Synth (1943) Coll Vol 2 156

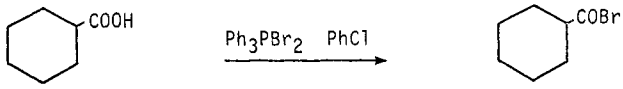


65%

JCS (1934) 1406



JACS (1966) 88 3440



Annalen (1966) 693 132

$C_{15}H_{31}COOH$ —(NN'-Carbonyldiimidazole; HCl $CHCl_3$)→ $C_{15}H_{31}COCl$ 68%

Annalen (1966) 694 78

PhCOOH —(PCl_3)→ PhCOCl 77%

Ber (1963) 96 1387

MeCH=CHCOOH —($MeCCl_2OEt$)→ MeCH=CHCOCl 79%

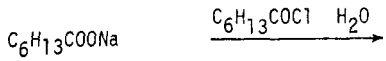
Rec Trav Chim (1957) 76 969

$C_{17}H_{35}COOH$ —(Ac_2O)→ $(C_{17}H_{35}CO)_2O$ 50-80%

JACS (1941) 63 699

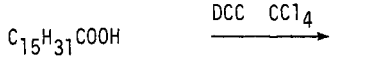
PhCOOH —(TsCl pyr)→ $(PhCO)_2O$ 97%

JACS (1955) 77 6214



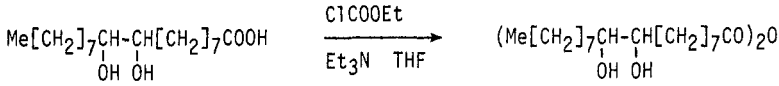
60%

JCS (1964) 755

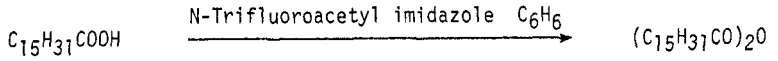


85%

J Lipid Res (1966) 7 174

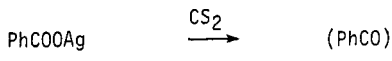


JOC (1963) 28 1905



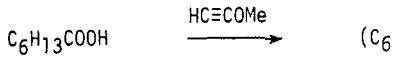
54%

Ber (1962) 95 2073



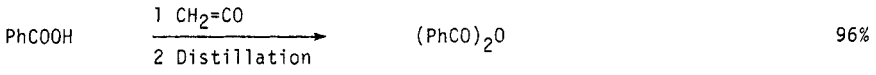
98%

Proc Chem Soc (1957) 20

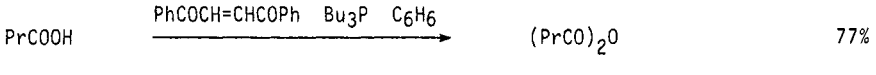


67%

JCS (1954) 1860

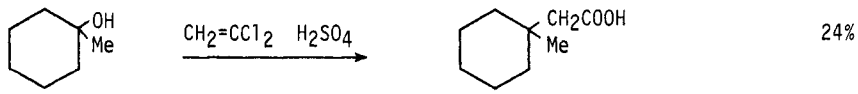


JACS (1932) 54 3427

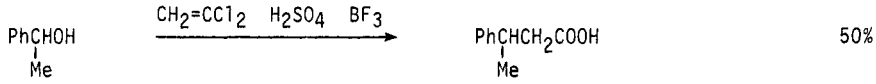


JOC (1964) 29 1385

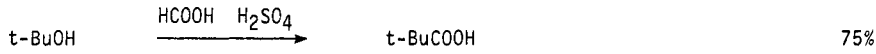
Section 18 Carboxylic Acids from Alcohols and Phenols



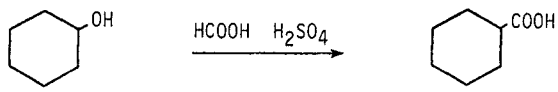
Ber (1967) 100 978



Angew (1965) 77 967
(Internat Ed 4 956)

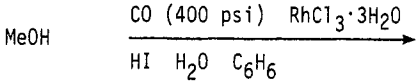


Org Synth (1966) 46 72
JACS (1961) 83 3980



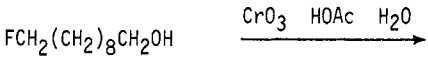
75%

Ber (1966) 99 1149



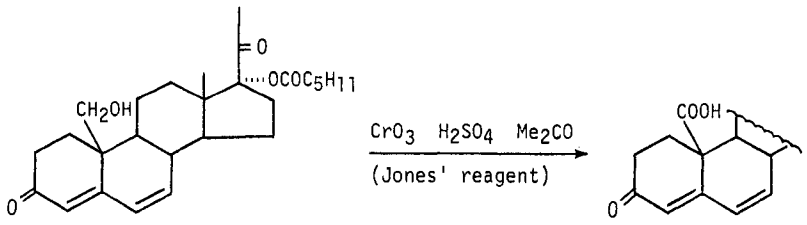
99%

Chem Comm (1968) 1578



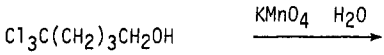
93%

JACS (1956) 78 2255
(1960) 82 6147



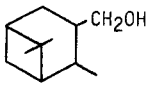
77%

Helv (1967) 50 269
J Med Chem (1970) 13 926

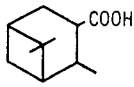


92%

Bull Chem Soc Jap (1963) 36 1264



$KMnO_4$ Na_2CO_3 H_2O



66%

Bull Acad Polon (1964) 12 15
(Chem Abs 61 1895)
JACS (1950) 72 2953

$Br(CH_2)_5CH_2OH$ $\xrightarrow{HNO_3}$ $Br(CH_2)_5COOH$

JACS (1950) 72 5137

$C_9H_{19}CH_2OH$ $\xrightarrow{N_2O_4}$ $C_9H_{19}COOH$

Ber (1956) 89 202

$C_5H_{11}CH_2OH$ $\xrightarrow{RuO_4 \quad CCl_4}$ $C_5H_{11}COOH$ 10%

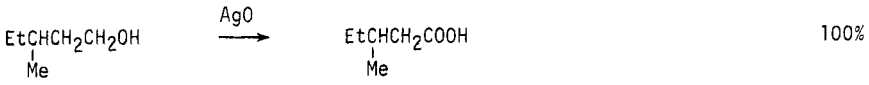
JACS (1958) 80 6682

$Ph(CH_2)_2CH_2OH$ $\xrightarrow[NaOH \quad H_2O]{\text{Nickel peroxide}}$ $Ph(CH_2)_2COOH$ 70%

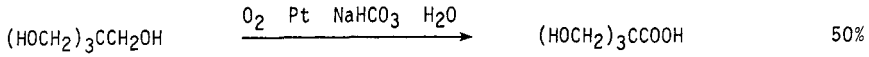
JOC (1962) 27 1597

$PhCH{=}CHCH_2OH$ $\xrightarrow[NaOH \quad H_2O]{\text{Nickel peroxide}}$ $PhCH{=}CHCOOH$ 81%

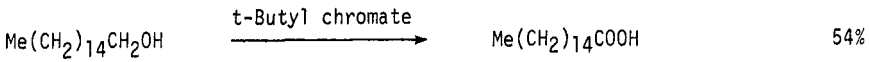
JOC (1962) 27 1597



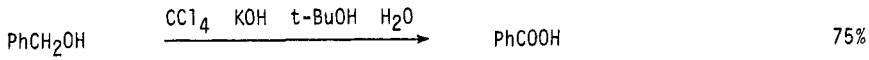
Tetr Lett (1968) 5685



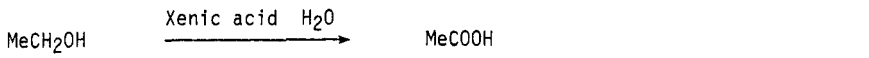
Ber (1956) 89 1648
Angew (1957) 69 600



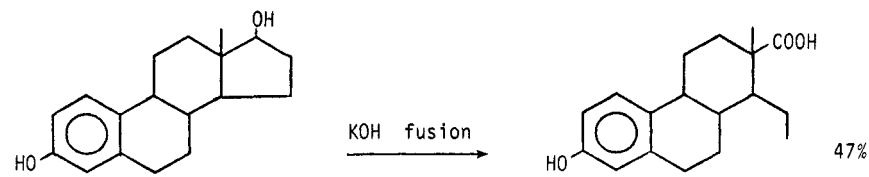
Bull Chem Soc Jap (1965) 38 893



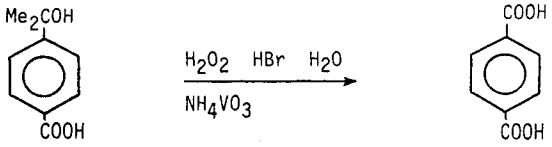
JACS (1969) 91 7510



JACS (1964) 86 2078



Helv (1944) 27 1727
JACS (1948) 70 3485



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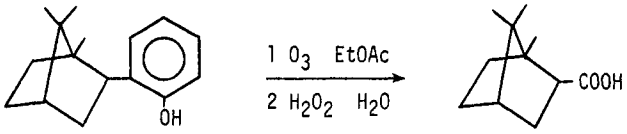
JCS (1961) 4082



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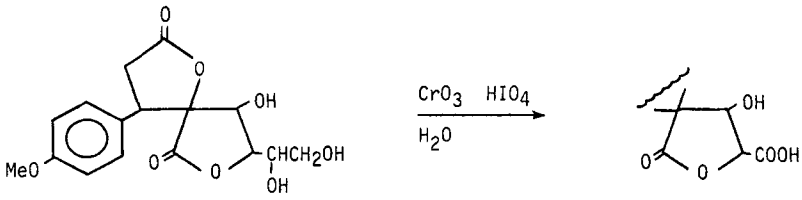
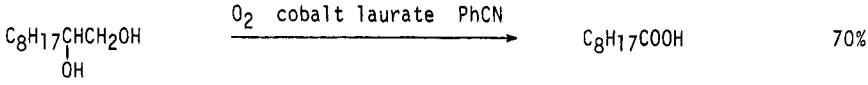
Zh Org Khim (1967) 3 1636
(Chem Abs 68 29874)
Tetr Lett (1967) 4729



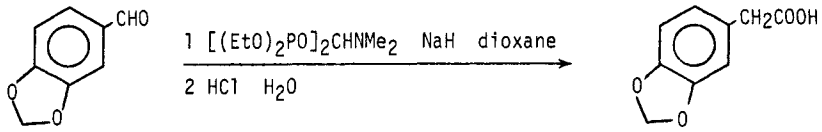
JCS C (1966) 1918



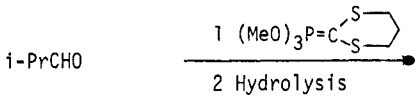
70%

Tetr Lett (1968) 5689

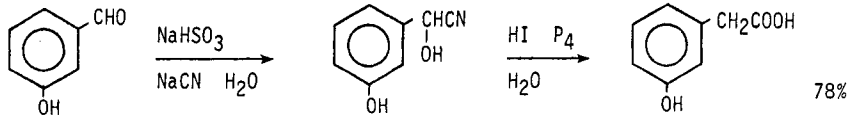
Section 19 Carboxylic Acids and Acid Halides from Aldehydes



Angew (1968) 80 364
(Internat Ed 7 391)

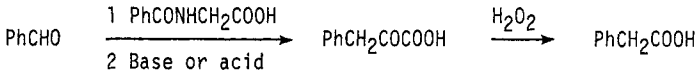


Tetr Lett (1967) 3201

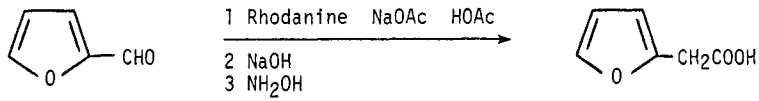


78%

JOC (1956) 21 1149

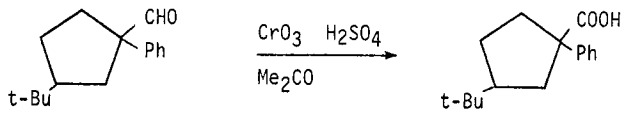


Org React (1942) 1 210



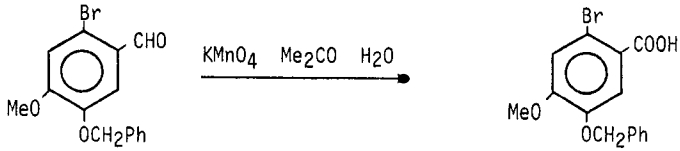
74%

JACS (1940) 62 1512
Org React (1942) 1 210

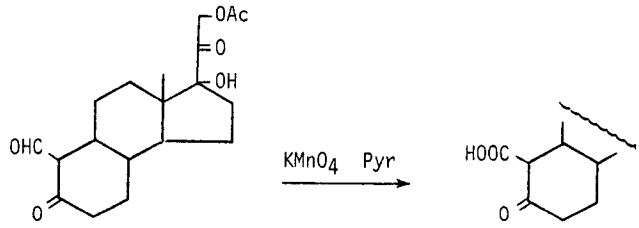


85%

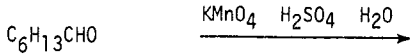
JCS C (1970) 1168



JCS C (1970) 1208

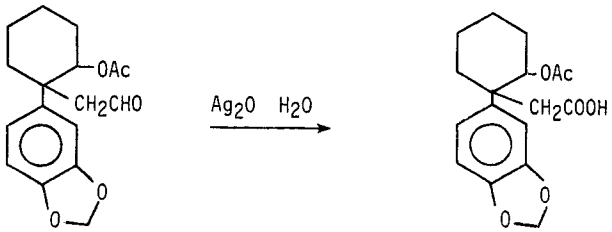


Steroids (1964) 3 639



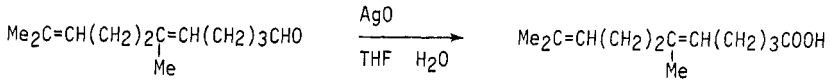
76-78%

Org Synth (1943) Coll Vol 2 315



93%

Tetrahedron (1968) 24 6583



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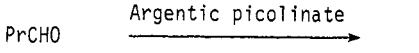
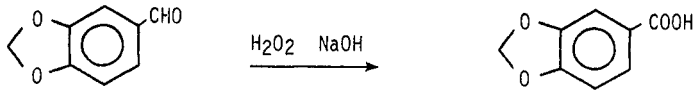
Tetr Lett (1969) 1837
JACS (1968) 90 5617

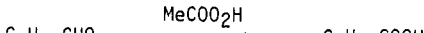


Tetr Lett (1967) 415



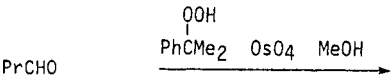
90%

Monatsh (1955) 86 325

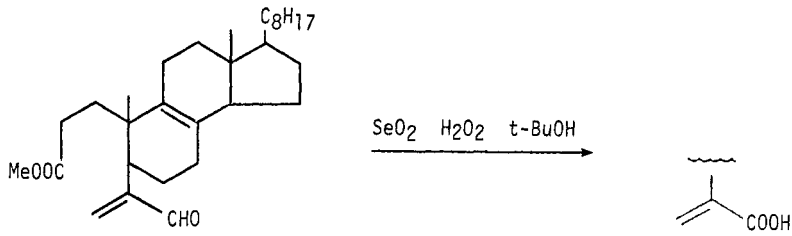


88%

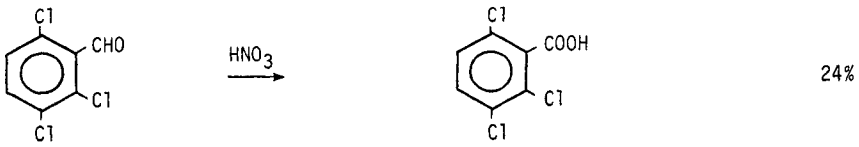
Org React (1957) 9 73



JCS (1950) 2169

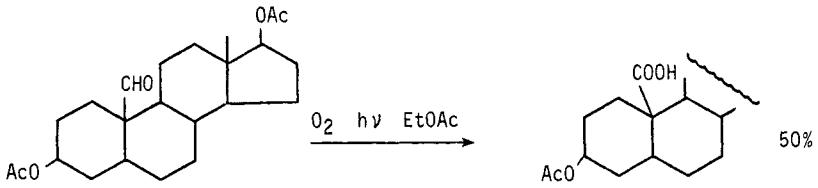


Chem Comm (1969) 945



24%

JCS (1951) 1208



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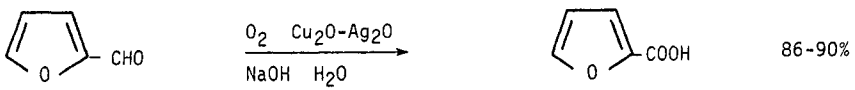
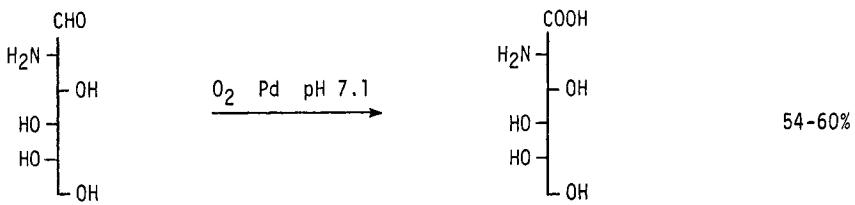
Tetr Lett (1966) 2507



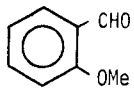
86-90%

Org Synth (1963) Coll Vol 4 493

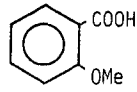


54-60%

Helv (1957) 40 2383



$\xrightarrow{KOH \quad H_2O}$



34%

Org React (1944) 2 94
Org Synth (1963) Coll Vol 4 974

$\xrightarrow{NaOH \quad H_2O}$

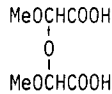
20%

Helv (1951) 34 1211

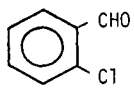
i-PrCHO $\xrightarrow[2\ KOH \quad diethylene\ glycol]{1\ NH_2OH\cdot HCl \quad NaOAc \quad EtOH \quad H_2O}$ i-PrCOOH 88%

JOC (1962) 27 629

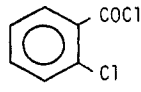
$\xrightarrow[KHCO_3 \quad H_2O]{I_2 \quad KI \quad K_2CO_3}$



JACS (1954) 76 3188



$\xrightarrow{Cl_2}$



70%

Org Synth (1941) Coll Vol 1 155

i-PrCH$_2$CHO $\xrightarrow{Benzoyl\ peroxide \quad CCl_4}$ i-PrCH$_2$COCl 60%

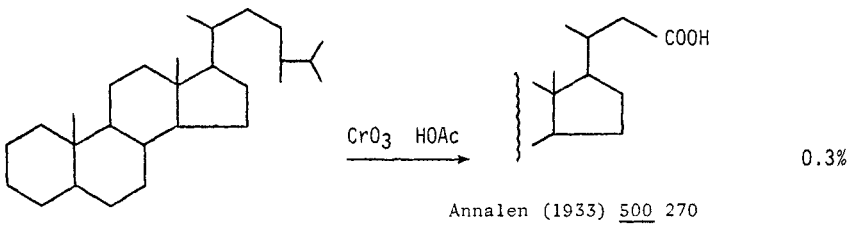
JACS (1947) 69 2916

Carboxylic acids may also be prepared by conversion of aldehydes into esters, followed by hydrolysis. See section 109 (Esters from Aldehydes). Some of the methods listed in section 27 (Carboxylic Acids from Ketones) may also be applied to the preparation of carboxylic acids from aldehydes

Section 20 Carboxylic Acids from Alkyls, Methylenes and Aryls

25%

J Med Chem (1970) 13 254



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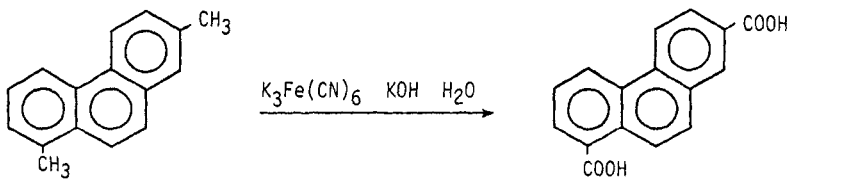
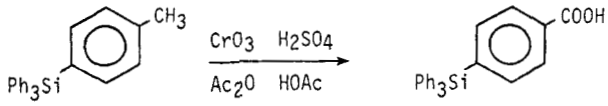
Annalen (1933) 500 270

76-78%

Org Synth (1943) Coll Vol 2 135

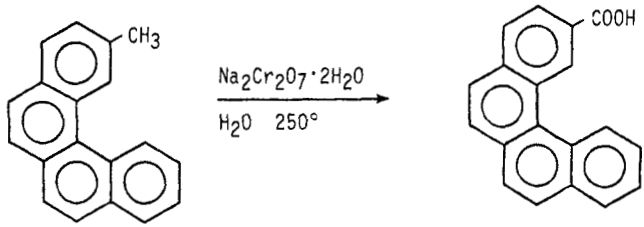


Helv (1931) 14 233



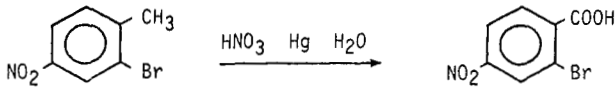
81%

JACS (1956) 78 1689



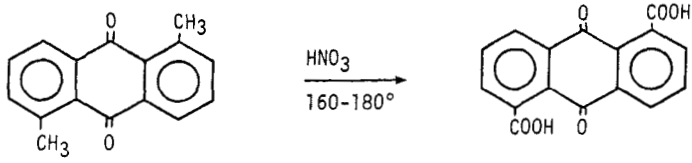
64%

JOC (1961) 26 1759

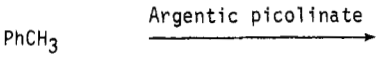


76%

Ber (1961) 94 834



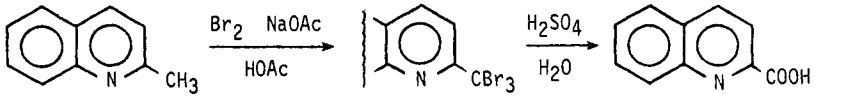
JCS (1960) 341
JOC (1960) 25 668



Tetr Lett (1967) 415

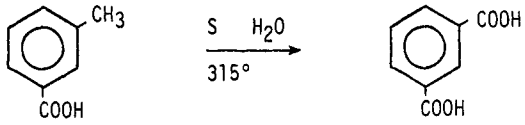
$PhCH_3 \xrightarrow{Cl_2} PhCCl_3 \xrightarrow{TiO_2} PhCOCl \dashrightarrow PhCOOH$

JACS (1958) 80 3483



~70%

JACS (1946) 68 1840



100%

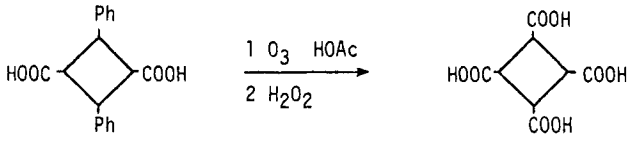
JOC (1961) 26 2929

$PhCHMe_2 \xrightarrow[315°]{SO_2\ H_2O} PhCOOH$ 24%

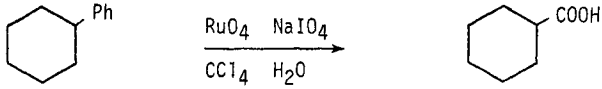
JOC (1961) 26 2929

$PhCH_2Me \xrightarrow[H_2O]{H_2O_2\ NH_4VO_3\ HBr} PhCOOH$ 40%

JCS (1961) 4082



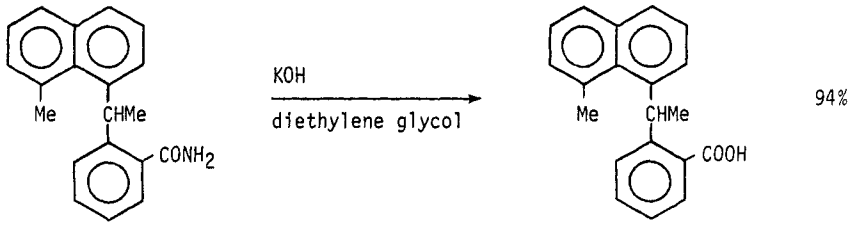
Ber (1960) 93 2521



25%

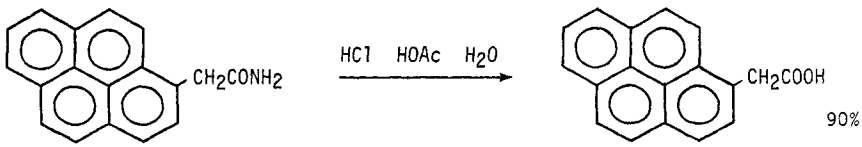
Tetr Lett (1967) 4729
Chem Comm (1970) 1420

Section 21 Carboxylic Acids from Amides



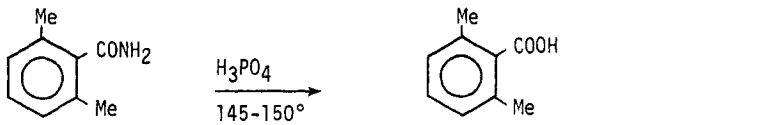
94%

JOC (1950) 15 617



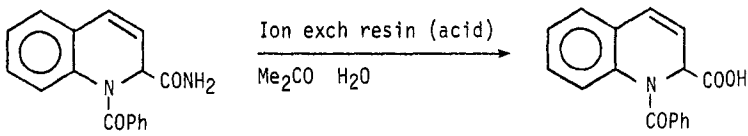
90%

JACS (1941) 63 2494



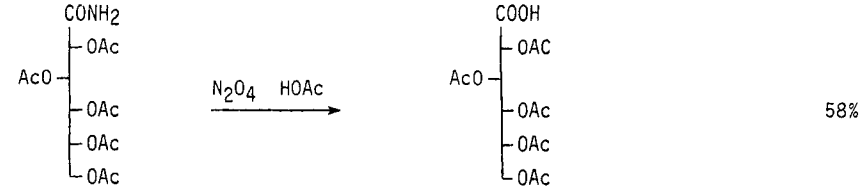
70%

Rec Trav Chim (1927) 46 600



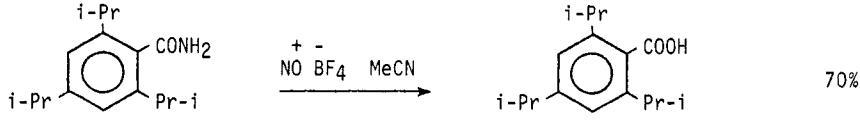
61%

Chem Ind (1957) 736



58%

JACS (1938) 60 235

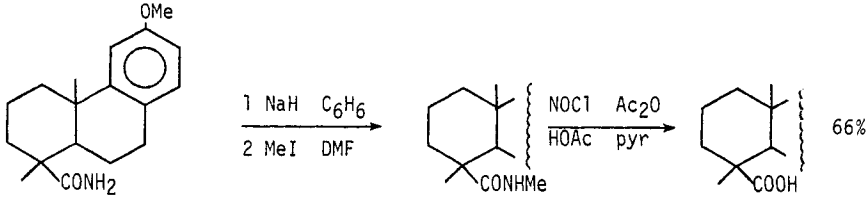


70%

JOC (1965) 30 2386

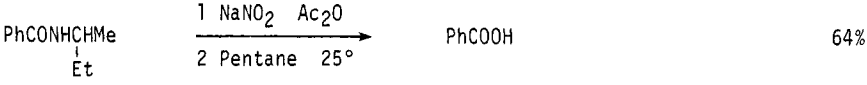
79%

JACS (1948) 70 3091
J Med Chem (1966) 9 603



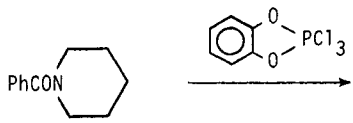
66%

JACS (1961) 83 1492



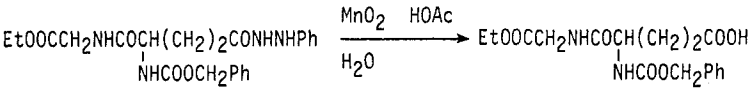
64%

JACS (1955) 77 6011



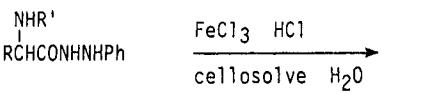
67%

Ber (1963) 96 1387



82%

JOC (1963) 28 453

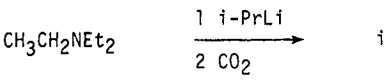


85%

JACS (1957) 79 637 645

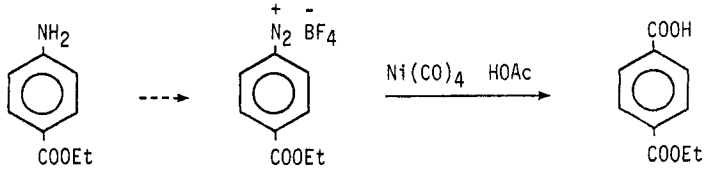
Carboxylic acids may also be prepared by conversion of amides into esters, followed by hydrolysis. See section 111 (Esters from Amides)

Section 22 Carboxylic Acids from Amines



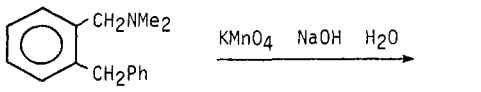
25%

JACS (1969) 91 6362



52%

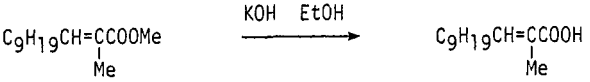
JCS (1962) 686



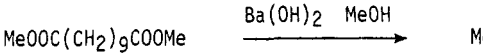
27%

JACS (1951) 73 4122

Section 23 Carboxylic Acids and Acid Halides from Esters

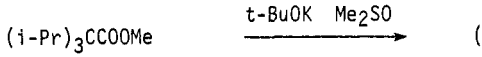


Org Synth (1963) Coll Vol 4 608



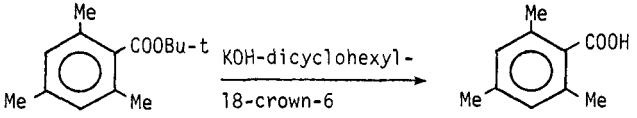
60%

Org Synth (1963) Coll Vol 4 635



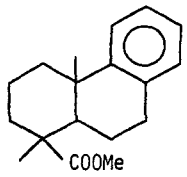
100%

Tetr Lett (1964) 2969
JCS (1965) 1290

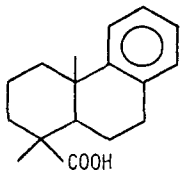


94%

JACS (1967) 89 7017



Li NH_3 THF



59%

JACS (1958) 80 217

PhCOOMe $\xrightarrow{Me_3N\ MeOH}$ PhCOOH

JACS (1933) 55 4079

MeCOOPh $\xrightarrow{\text{Guanidine}\ H_2O\ EtOH}$ MeCOOH

Bull Chem Soc Jap (1966) 39 852
JACS (1964) 86 837

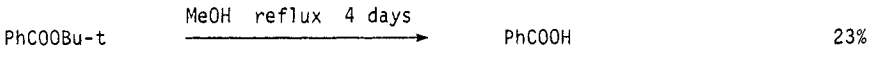
$BrCH_2CHCOOMe$ (Br) $\xrightarrow{HBr\ H_2O}$ $BrCH_2CHCOOH$ (Br) 72%

JACS (1940) 62 3495

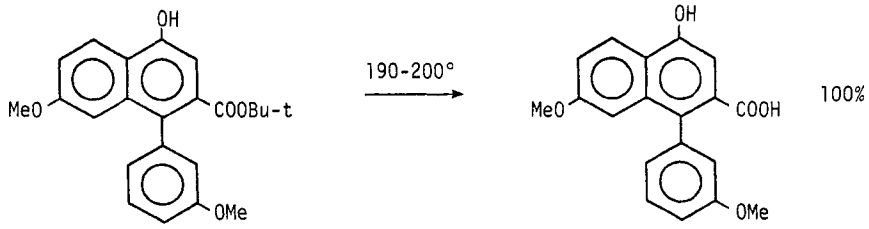
$MeCOOC_5H_{11}$ $\xrightarrow{\text{Ion exch resin (acid)}\ H_2O}$ MeCOOH

JCS (1952) 1607

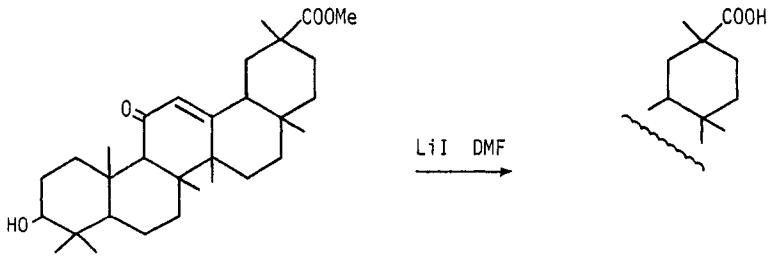
Further examples of the reaction RCOOR' → RCOOH + R'OH are included in section 38 (Alcohols from Esters) and section 30A (Protection of Carboxylic Acids)



JACS (1941) 63 3382

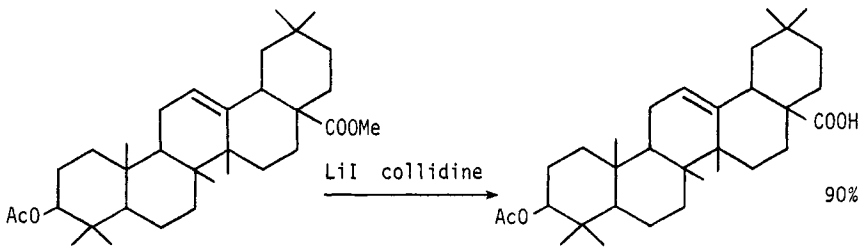


JOC (1962) 27 519



JCS (1965) 6655

For cleavage of ethyl esters see JOC (1963) 28 2184



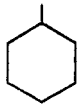
Helv (1960) 43 113

$(i\text{-}Pr)_3CCOOMe \xrightarrow{PrSLi\ \ HMPA} (i\text{-}Pr)_3CCOOH$ 99%

Tetr Lett (1970) 4459

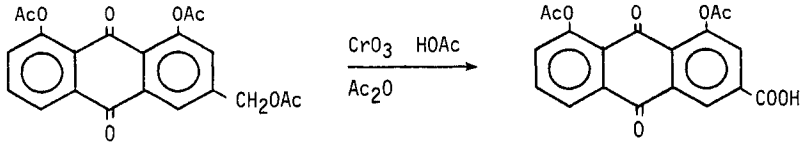
$PhCOOCH_2Ph \xrightarrow{H_2\ \ Pd\ \ Et_2O} PhCOOH$

JOC (1958) 23 1700
Org React (1953) 7 263

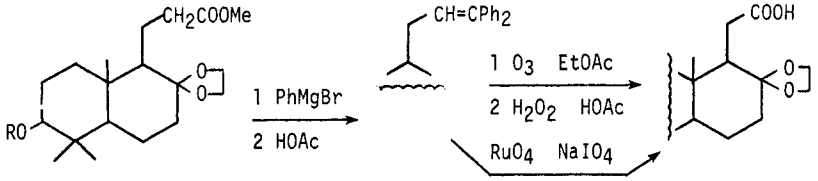
PhCOOCHPh  $\xrightarrow{H_2\ \ Pd\ \ Et_2O}$ PhCOOH

JOC (1958) 23 1700

Further examples of the cleavage of benzyl esters are included in section 30A (Protection of Carboxylic Acids)



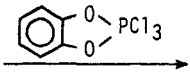
JOC (1961) 26 979



JACS (1963) 85 3419

$C_7H_{15}COOC(Me)=CH_2$ —(HF, Et_2O)→ $C_7H_{15}COF$ 50%

JOC (1969) 34 2486

PhCOOBu —()→ PhCOCl 91%

Ber (1963) 96 1387

Section 24 Carboxylic Acids from Ethers

CH_3CH_2OEt —(1 i-PrLi, Et_2O; 2 CO_2)→ i-$PrCH_2CH_2COOH$ 5%

JACS (1953) 75 1771
(1955) 77 2806

$CH_2=CHCH_2OPh$ —(1 Mg, $BrCH_2CH_2Br$, THF; 2 CO_2)→ $CH_2=CHCH_2COOH$ 63%

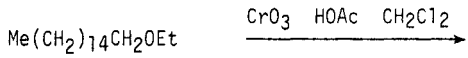
J Organometallic Chem (1969) 18 249

$(EtCH_2)_2O$ —(Br_2, H_2O)→ EtCOOH 100%

JACS (1967) 89 3550

$(PhCH_2)_2O$ —(Br_2, H_2O)→ PhCOOH 55%

JACS (1967) 89 3550

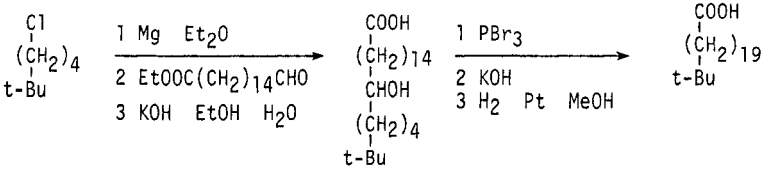


55%

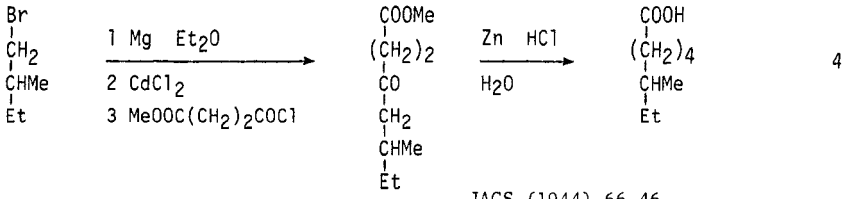
Chem Comm (1966) 752

Carboxylic acids may also be prepared by oxidation of ethers to esters, followed by hydrolysis. See section 114 (Esters from Ethers)

Section 25 Carboxylic Acids and Acid Halides from Halides

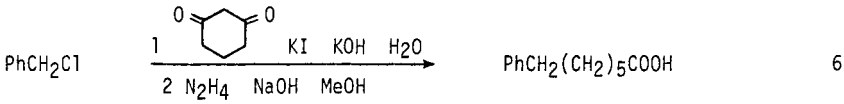


JACS (1950) 72 5139



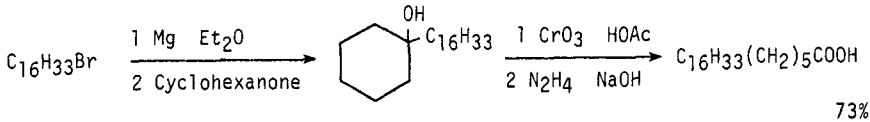
46%

JACS (1944) 66 46



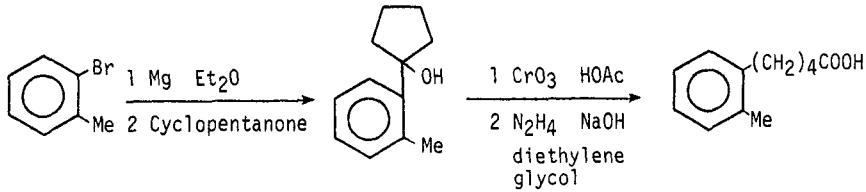
69%

Ber (1952) 85 61 1061

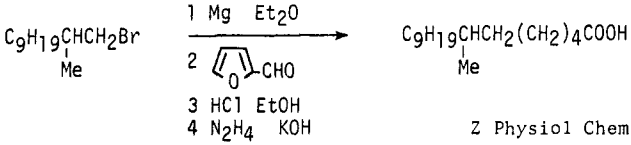


73%

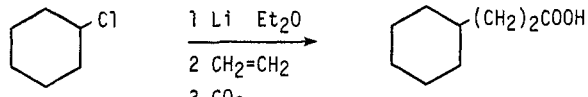
JACS (1948) 70 3352



JOC (1958) 23 584

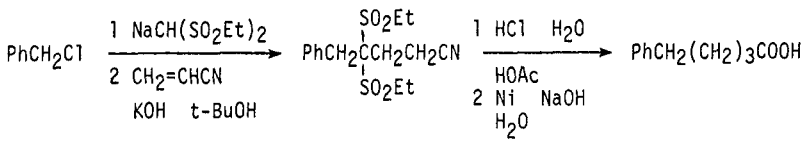


Z Physiol Chem (1951) 287 65

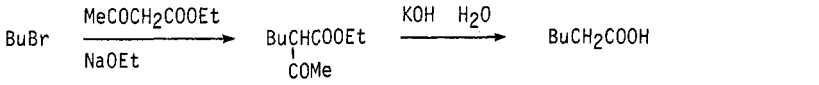


47%

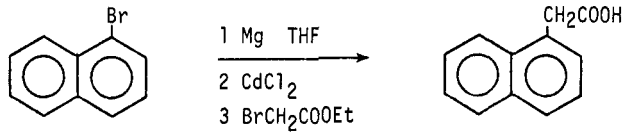
JACS (1969) 91 6362



JACS (1952) 74 1225

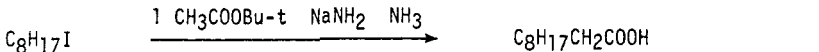


Org Synth (1941) Coll Vol 1 248
JACS (1930) 52 5005



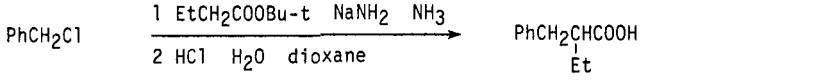
62%

JOC (1968) 33 1675



70%

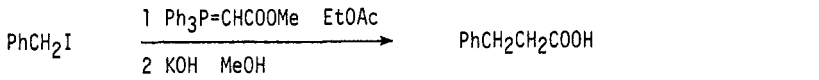
JACS (1959) 81 5817



92%

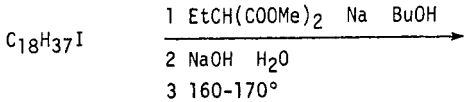
JACS (1959) 81 5817

Further examples of the alkylation of esters with halides are included in section 113 (Esters from Esters). Examples of the alkylation of acids with halides are included in section 17 (Carboxylic Acids from Carboxylic Acids)



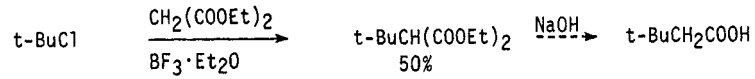
75%

Tetr Lett (1960) (4) 5
Ber (1962) 95 2921

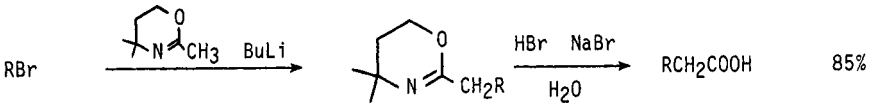


83%

JCS (1953) 3031
Org React (1957) 9 107

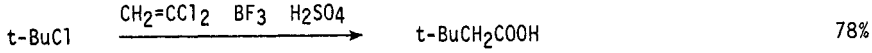


Naturwiss (1964) 51 288



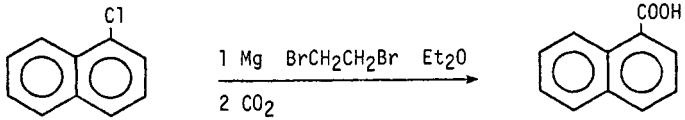
85%

JACS (1969) 91 5886



78%

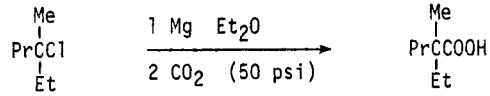
Angew (1965) 77 967
(Internat Ed 4 956)



56%

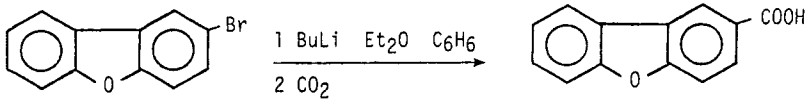
(Procedure for unreactive halides)

JOC (1959) 24 504



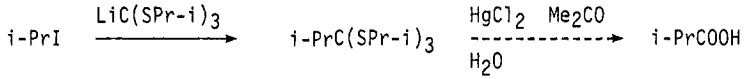
25%

JACS (1949) 71 1877

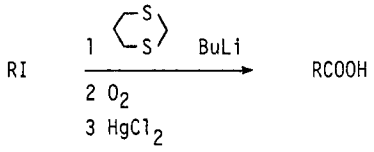


58%

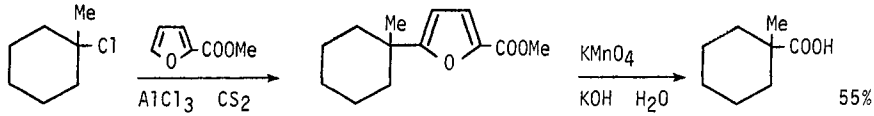
JACS (1939) 61 1371



Angew (1967) 79 468
(Internat Ed 6 442)

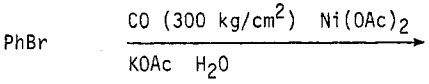


Angew (1965) 77 1134
(Internat Ed 4 1075)

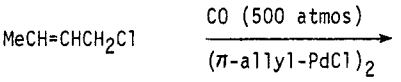


55%

Helv (1935) 18 721

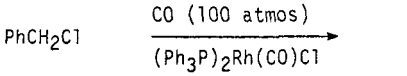


Bull Chem Soc Jap (1967) 40 2203

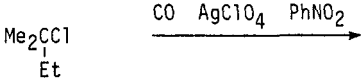


81%

JCS (1964) 1588



Tetr Lett (1966) 4713
JACS (1968) 90 99



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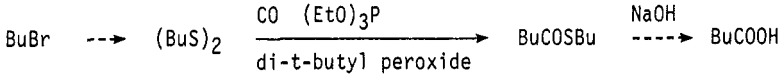
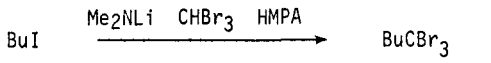
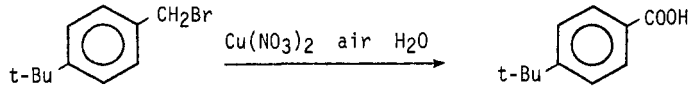
JACS (1960) 82 1261



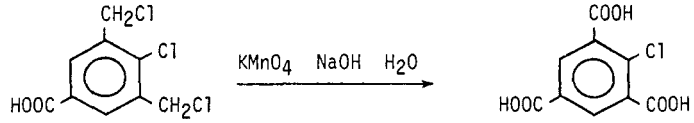
JACS (1960) 82 2181



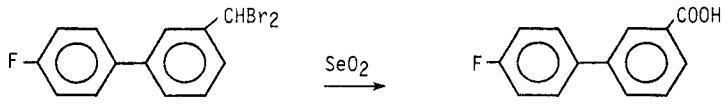
Compt Rend (1967) C 264 1609



JCS (1935) 1847



J Pharm Soc Jap (1950) 70 538



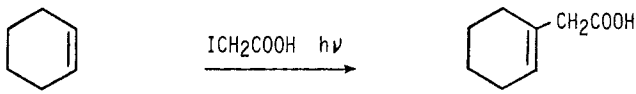
13%

JACS (1966) 88 3318
JCS (1962) 186

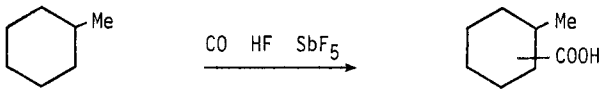
Carboxylic acids may also be prepared by conversion of halides into esters or amides followed by hydrolysis. See section 115 (Esters from Halides) and section 85 (Amides from Halides)

Section 26 Carboxylic Acids from Hydrides (RH)

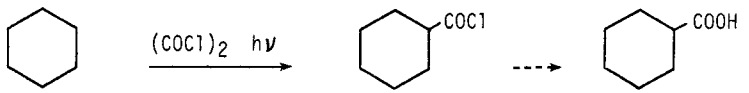
Reactions in which a hydrogen is replaced by carboxyl or a carboxyl containing chain, e.g. RH → RCOOH or RCH_2COOH (R=alkyl, vinyl or aryl), are included in this section. For reactions in which alkyl or aryl groups are oxidized to carboxyl, e.g. RCH_3 → RCOOH, see section 20 (Carboxylic Acids from Alkyls, Methylenes and Aryls)



ACS Div Petr Chem (1966) 11 241
(Chem Abs 66 104510)



Ber (1967) 100 984



63%

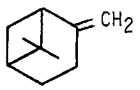
JCS (1963) 3918

$C_8H_{17}H$ —(1 $(i\text{-}Bu)_2Hg\text{-}K$, 2 CO_2)→ $C_8H_{17}COOH$ 24-35%

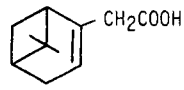
Monatsh (1967) 98 763

$PhCH_3$ —(1 Na PhCl, 2 CO_2)→ $PhCH_2COOH$ 77%

JACS (1940) 62 1514
Chem Rev (1957) 57 867



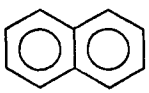
—(1 $CO(CN)_2$, 2 H_2O dioxane)→



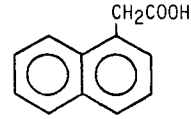
Chem Ind (1961) 1116

PhH —($(CH_2)_nCOO$, $AlCl_3$)→ $Ph(CH_2)_nCOOH$ 44% (n=3) 51% (n=4)

JACS (1952) 74 1591

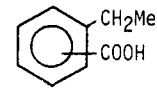


—($ClCH_2COOH$ Fe_2O_3 KBr)→

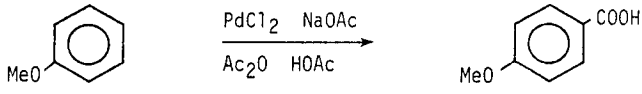


<45%

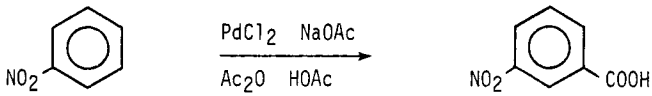
JACS (1950) 72 4302
Synthesis (1970) 628

$PhCH_2Me$ —(1 $BuLi\cdot Me_2NCH_2CH_2NMe_2$, 2 CO_2)→ $PhCH(Me)COOH$ + 

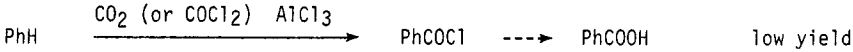
JOC (1970) 35 10
Chimia (1970) 24 109



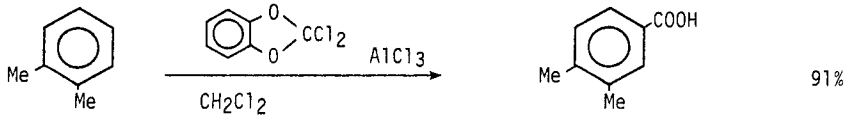
Tetr Lett (1969) 1019



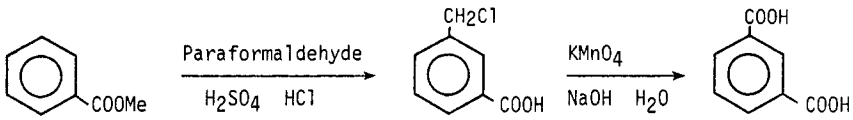
Tetr Lett (1969) 1019



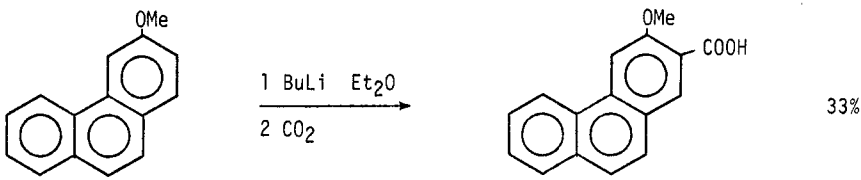
Chem Rev (1955) 55 229



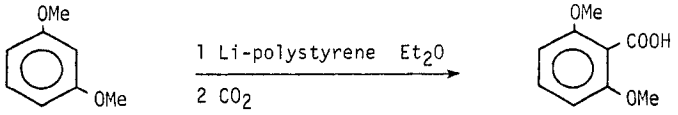
Ber (1963) 96 1382



J Pharm Soc Jap (1950) 70 535



JOC (1970) 35 10
Org React (1954) 8 258

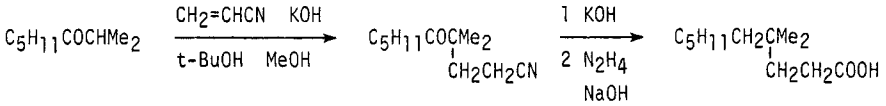


60%

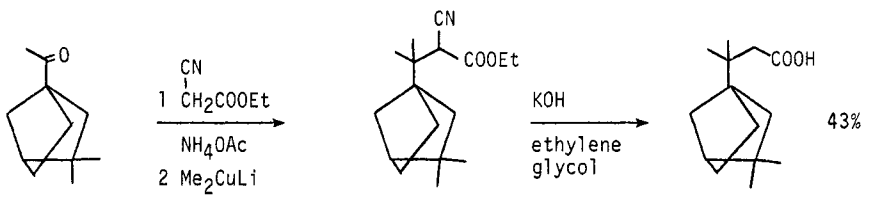
Ber (1964) 97 3098

Carboxylic acids may also be prepared by conversion of hydrides (RH) into esters or amides, followed by hydrolysis. See section 116 (Esters from Hydrides) and section 86 (Amides from Hydrides)

Section 27 Carboxylic Acids from Ketones

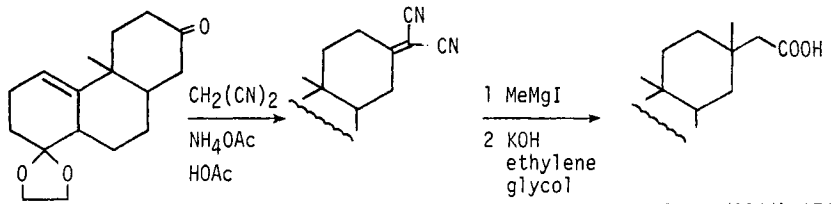


JCS (1948) 1741

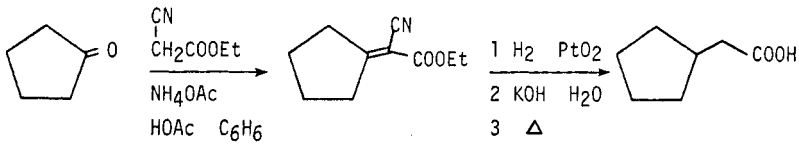


43%

Tetr Lett (1967) 2893

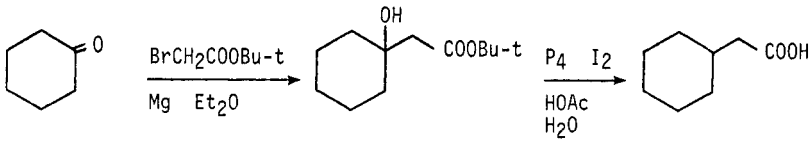


Tetr Lett (1964) 1763

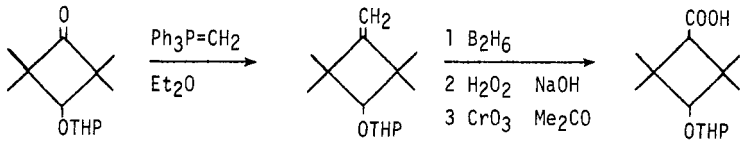


57%

JACS (1948) 70 497
(1959) 81 5397



JOC (1966) 31 983
JACS (1946) 68 2339



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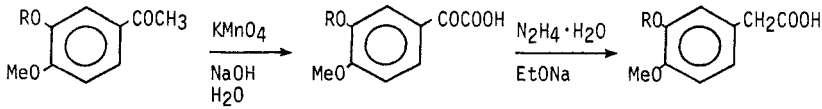
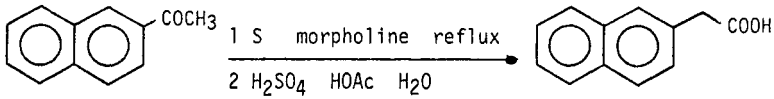
Chem Comm (1968) 206
JACS (1960) 82 2498

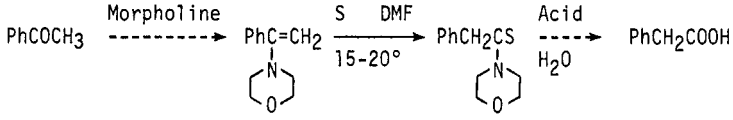


Monatsh (1952) 83 883

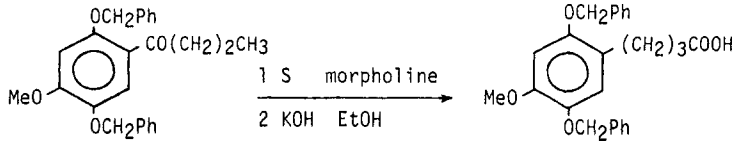


76%

Org React (1946) 3 83



Angew (1964) 76 861
(Internat Ed 3 705)



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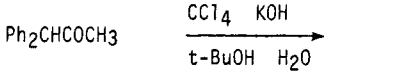
Helv (1964) 47 1996



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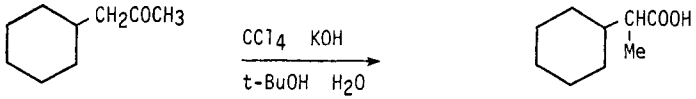
JACS (1969) 91 7510



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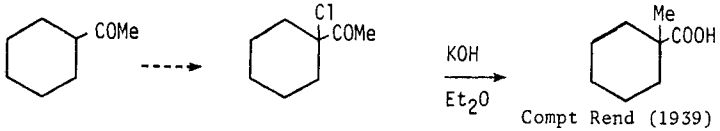
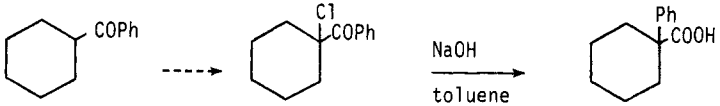
JACS (1969) 91 7510



Compt Rend (1939) 208 1020
JACS (1960) 82 4307
Org React (1960) 11 261



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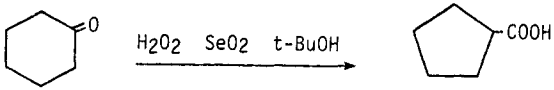
JACS (1952) 74 5352



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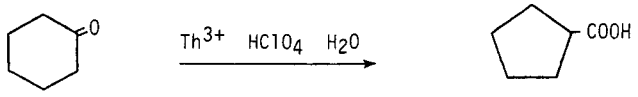
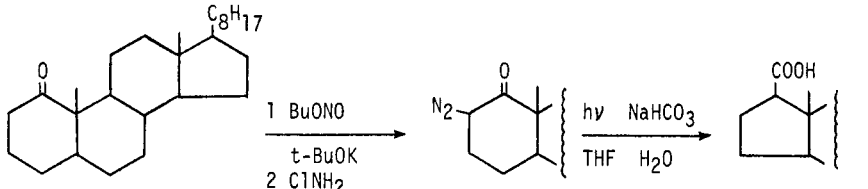
JOC (1957) 22 1680
Compt Rend C (1967) 265 578
Annalen (1965) 681 30



Tetr Lett (1966) 1779



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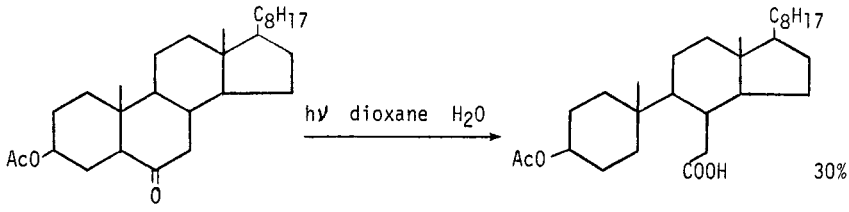
Tetr Lett (1964) 2813



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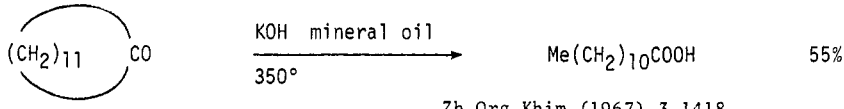
Ber (1964) 97 958
Angew (1965) 77 229
(Internat Ed 4 211)



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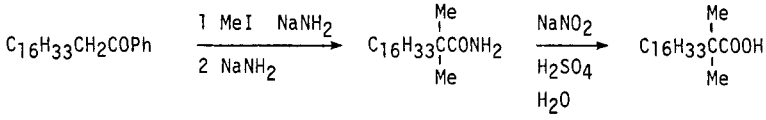
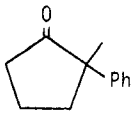
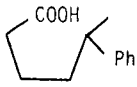
Zh Org Khim (1967) 3 1418
(Chem Abs 67 116618)



JCS (1942) 488

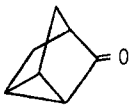


t-BuOK t-BuOH
165°

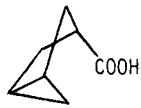


43%

JACS (1969) 91 1009



t-BuOK Me_2SO H_2O
room temp



65%

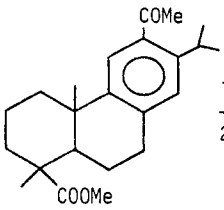
Tetr Lett (1964) 3251

Ph_2CO — t-BuOK monoglyme H_2O, 30° → PhCOOH — 90%

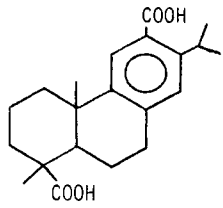
JACS (1967) 89 946

t-BuCOMe — CCl_4 KOH, t-BuOH H_2O → t-BuCOOH — 80%

JACS (1969) 91 7510

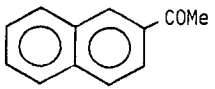


1 I_2 Pyr
2 KOH
diethylene glycol
H_2O

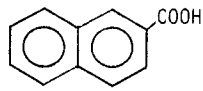


60-70%

JACS (1951) 73 3803

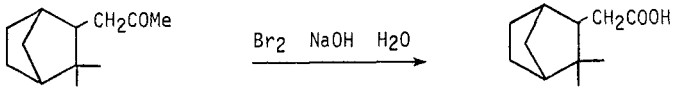


Cl_2 NaOH H_2O



87%

Org Synth (1943) Coll Vol 2 428



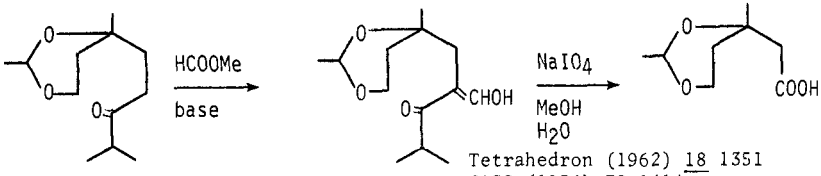
Aust J Chem (1967) 20 2033

PhCOPr —(1 NaOBr H2O; 2 NaOH)→ PhCOOH 48%

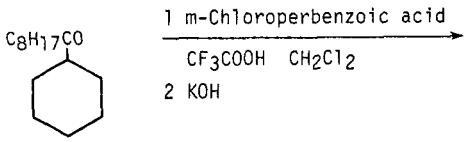
JACS (1950) 72 1642

Et_3CCOEt —(HNO_3 H_2O)→ Et_3CCOOH 71%

Bull Soc Chim Fr (1967) 2011
JACS (1942) 64 2421

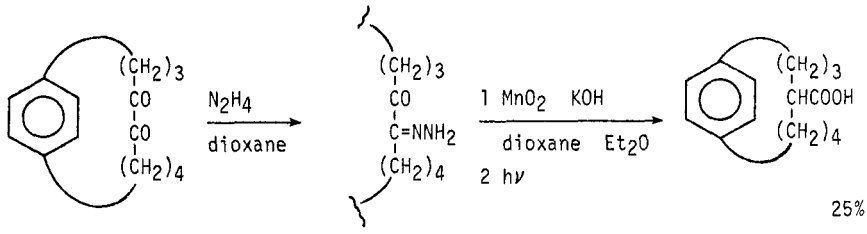


Tetrahedron (1962) 18 1351
JACS (1956) 78 1414



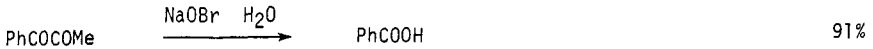
79%

JACS (1967) 89 4530

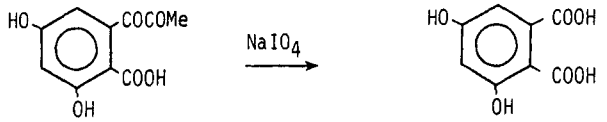


25%

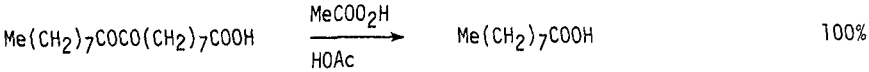
JACS (1963) 85 1171



JACS (1950) 72 1642



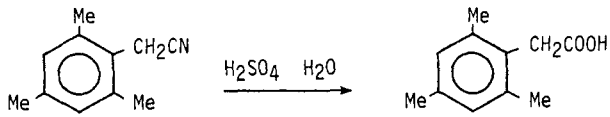
JCS (1935) 1467
Org React (1944) 2 341



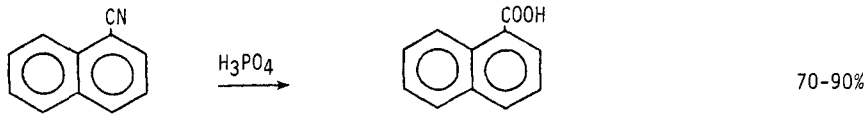
Org React (1957) 9 73

Carboxylic acids may also be prepared by conversion of ketones into esters or amides, followed by hydrolysis. See section 117 (Esters from Ketones) and section 87 (Amides from Ketones)

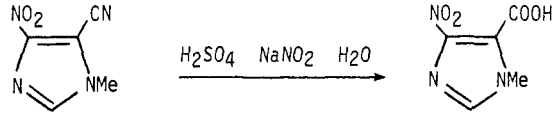
Section 28 Carboxylic Acids from Nitriles



Org Synth (1955) Coll Vol 3 557

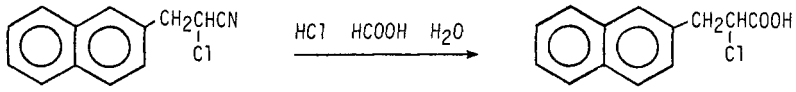


Rec Trav Chim (1927) 46 600



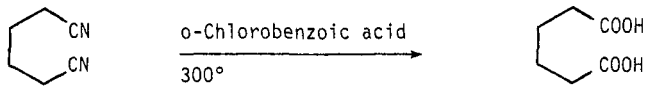
92%

JCS (1945) 751



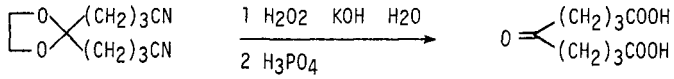
80%

Proc Chem Soc (1962) 117



97%

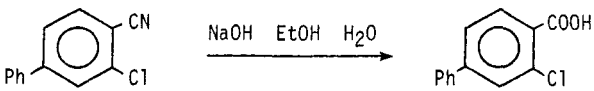
Annalen (1968) 716 78



85%

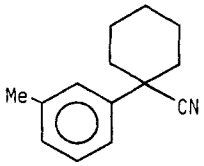
JCS (1962) 4722

Ber (1890) 23 158
JOC (1951) 16 131

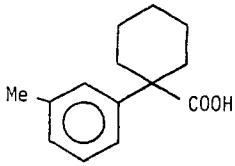


81-90%

JCS C (1966) 840



KOH H_2O
diethylene glycol



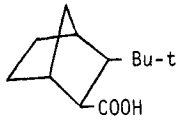
93%

Chem Pharm Bull (1969) 17 1564

Carboxylic acids may also be prepared by conversion of nitriles into esters or amides, followed by hydrolysis. See section 118 (Esters from Nitriles) and section 88 (Amides from Nitriles)

Section 29 Carboxylic Acids from Olefins

1 t-BuLi Et_3N
2 CO_2



30-45%

JOC (1965) 30 917
JACS (1969) 91 6362

$Me_2C{=}CH_2$ $\xrightarrow{CH_2{=}CCl_2\ \ BF_3\ \ H_2SO_4}$ Me_3CCH_2COOH 75%

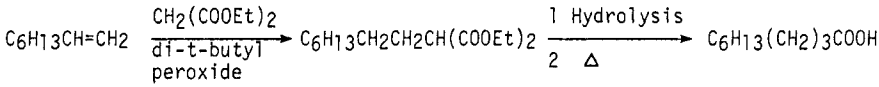
Angew (1965) 77 967
(Internat Ed 4 956)

$C_6H_{13}CH{=}CH_2$ $\xrightarrow[\text{di-t-butyl peroxide}]{CH_3COOH}$ $C_6H_{13}(CH_2)_3COOH$ ~70%

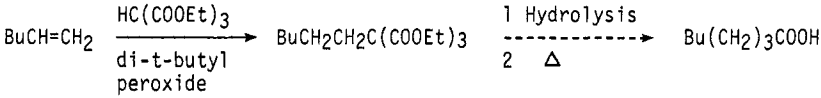
JCS (1965) 1918

$BuCH{=}CH_2$ $\xrightarrow{BrCH_2COOH\ \ h\nu}$ $Bu(CH_2)_3COOH$ 80%

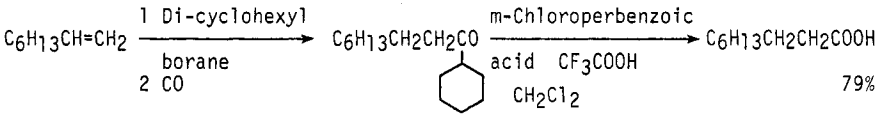
Chem Comm (1967) 435



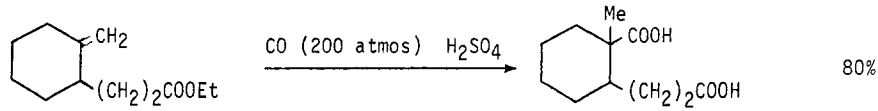
Chem Ind (1961) 830



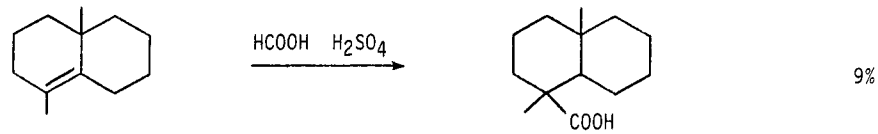
Synthesis (1970) 124



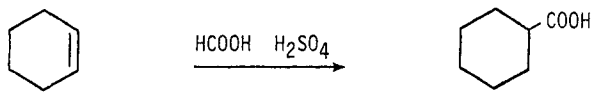
JACS (1967) 89 4530



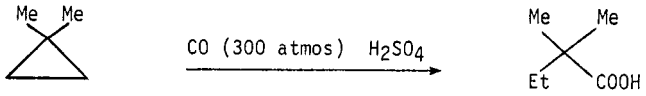
JACS (1960) 82 1261



Tetrahedron (1965) 21 2641

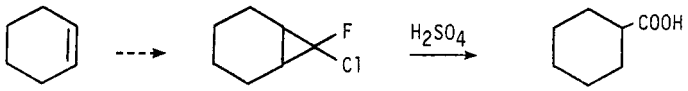


Ber (1966) 99 1149



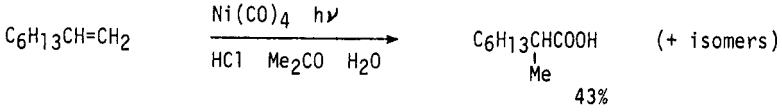
60%

Ber (1964) 97 3088

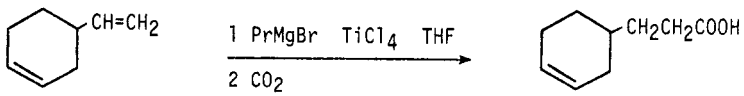


90%

Ber (1968) 101 1291

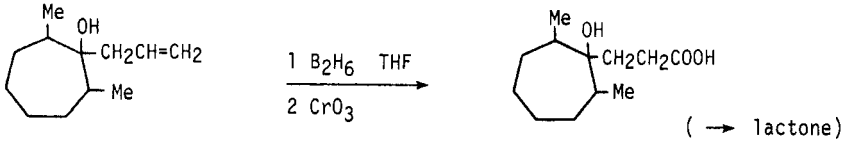


Angew (1965) 77 813
(Internat Ed 4 790)

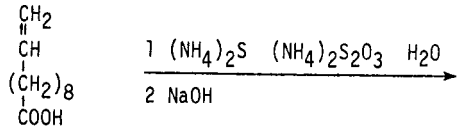


49%

JOC (1970) 35 392

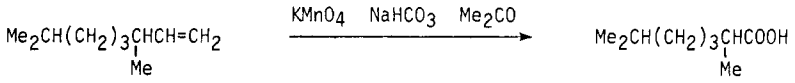


Chem Comm (1968) 122



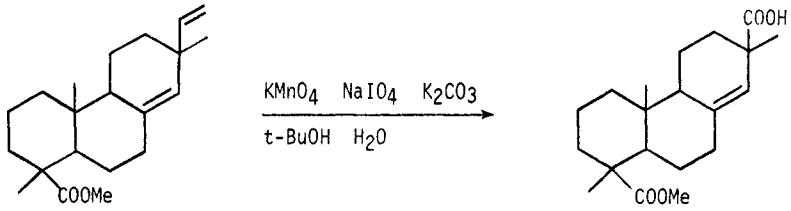
35%

JACS (1946) 68 2033

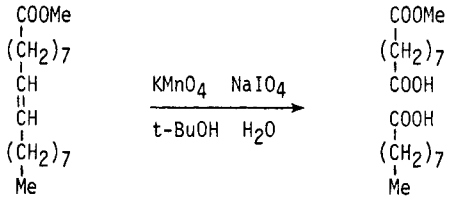


45%

JACS (1943) 65 745

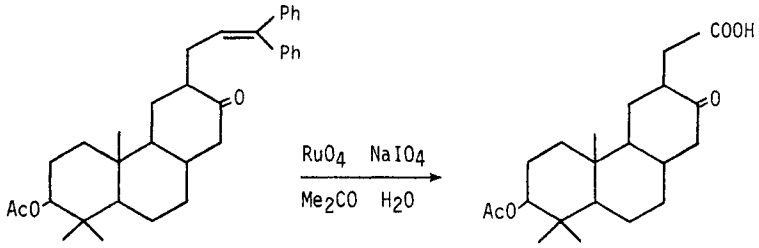


Can J Chem (1967) 45 1439



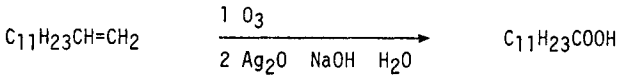
98-99%

Can J Chem (1956) 34 1413
JACS (1961) 83 4819

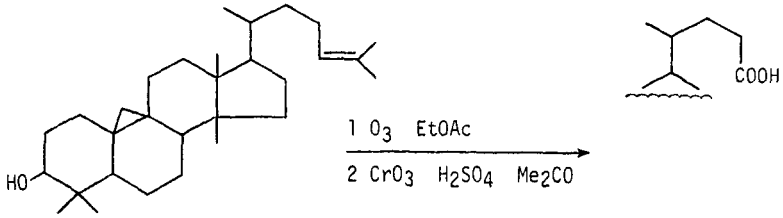


89%

JACS (1963) 85 3419



Ber (1942) 75B 656

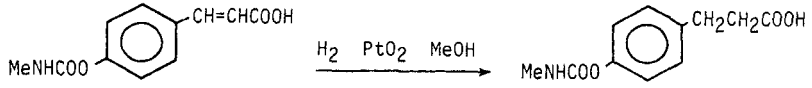


80%

Tetr Lett (1969) 1733

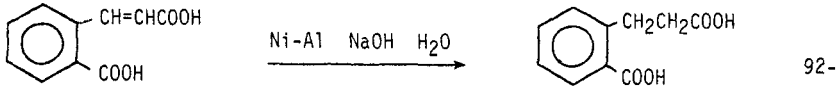
Carboxylic acids may also be prepared by conversion of olefins into esters or amides, followed by hydrolysis. See section 119 (Esters from Olefins) and section 89 (Amides from Olefins)

Section 30 Carboxylic Acids from Miscellaneous Compounds



70%

Chem Pharm Bull (1970) 18 243



92-95%

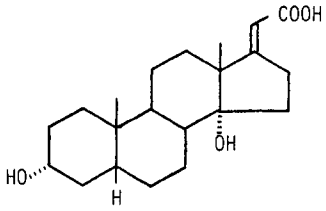
Org Synth (1963) Coll Vol 4 136

85%

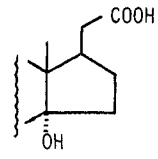
Act Chem Scand (1961) 15 1200

$PhCH{=}CHCOOH \xrightarrow{H_2\ (Ph_3P)_3RhCl} PhCH_2CH_2COOH$ 75%

Compt Rend C (1966) 263 251
Chem Comm (1969) 1365



$\xrightarrow{K\ NH_3\ dioxane}$



95%

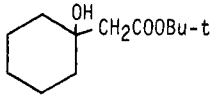
JACS (1969) 91 1228
Compt Rend (1969) C 268 640

$PhCH{=}CHCOOH \xrightarrow{P_4\ KI\ H_3PO_4} PhCH_2CH_2COOH$ 80%

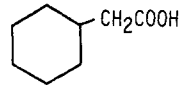
Helv (1939) 22 601

$PhCHCOOH \xrightarrow[OH]{P_4\ KI\ H_3PO_4} PhCH_2COOH$ 90%

Helv (1939) 22 601
Org Synth (1932) Coll Vol 1 224



$\xrightarrow[HOAc\ \ H_2O]{P_4\ \ I_2}$



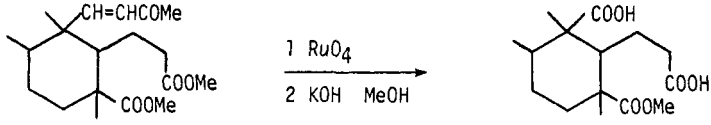
JOC (1966) 31 983

$PhCHCOOH \xrightarrow[tetralin]{H_2\ \ Pd\text{-}BaSO_4} PhCH_2COOH$
(OAc)

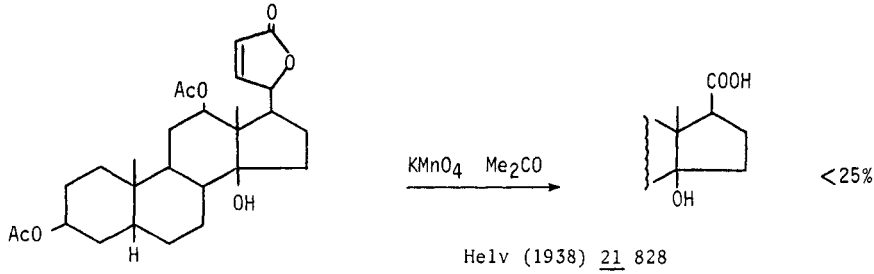
Org React (1953) 7 263

$PrCH_2NO_2 \xrightarrow{H_2SO_4\ \ H_2O} PrCOOH$ ~90%

Ind Eng Chem (1939) 31 118



Tetr Lett (1968) 2681



<25%

Helv (1938) 21 828

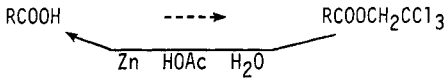
$C_8H_{17}COCH(CH_2)_7COOH$ (OH) $\xrightarrow{KIO_4\ \ H_2SO_4\ \ EtOH}$ $C_8H_{17}COOH$ 92%

JCS (1936) 1788
(1935) 1467

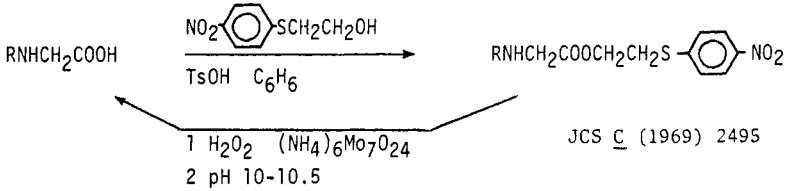
PhCHCOOH (OH) $\xrightarrow[NaOH\ \ H_2O]{\text{Nickel peroxide}}$ PhCOOH 90%

Chem Pharm Bull (1964) 12 403

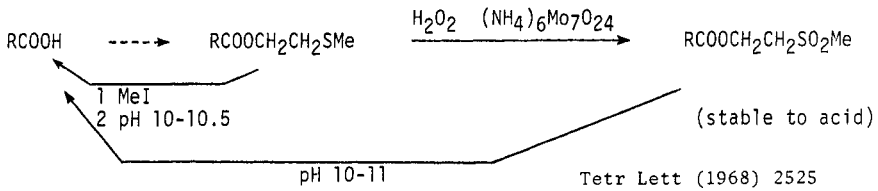
Section 30A Protection of Carboxylic Acids



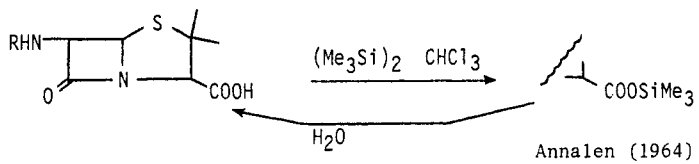
JACS (1966) 88 852



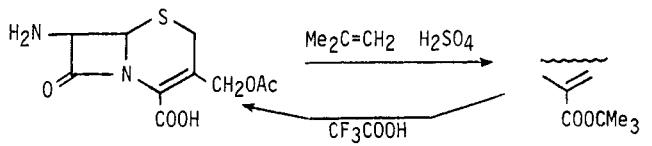
JCS C (1969) 2495



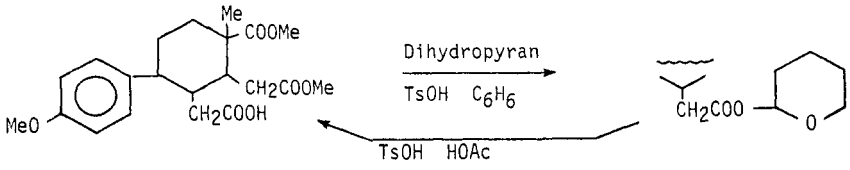
Tetr Lett (1968) 2525



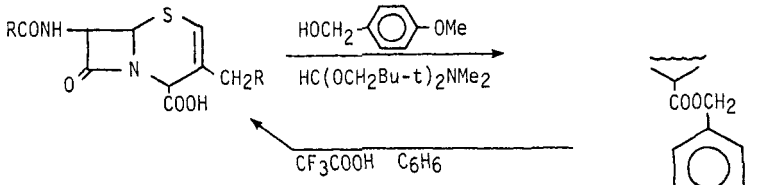
Annalen (1964) 673 166
JACS (1966) 88 3390



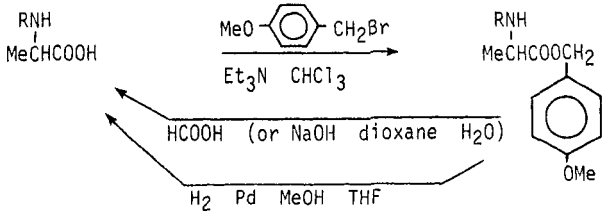
J Med Chem (1966) 9 444



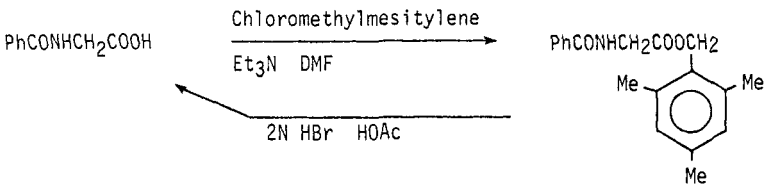
JACS (1957) 79 1995
JCS (1952) 3945



JACS (1969) 91 5674

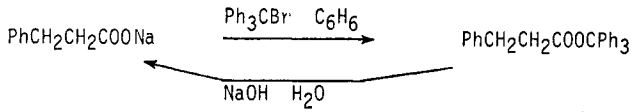


JCS C (1970) 964

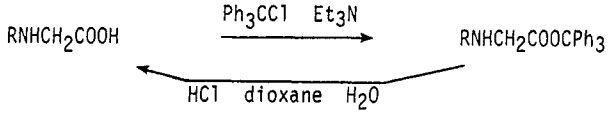


Aust J Chem (1966) 19 1067
(1967) 20 2243

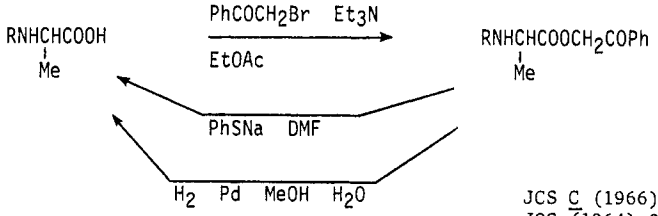
Further examples of the preparation and cleavage of benzyl esters are included in section 107 (Esters from Carboxylic Acids) and section 23 (Carboxylic Acids from Esters)



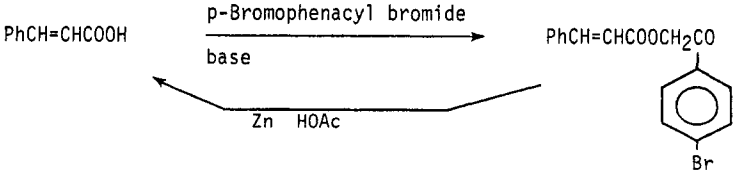
JOC (1962) 27 3595



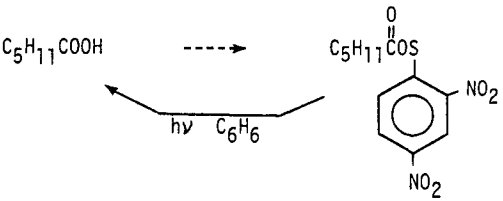
JCS C (1966) 1191



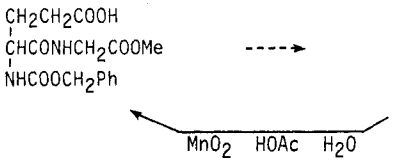
JCS C (1966) 1191
JOC (1964) 29 2006



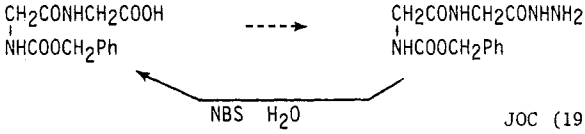
Tetr Lett (1970) 343



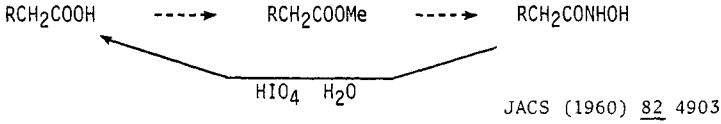
JCS (1965) 3571
JACS (1970) 92 6333



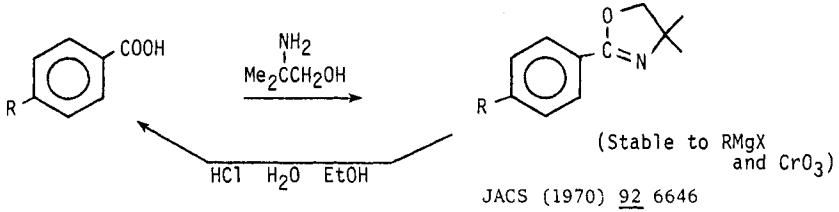
JOC (1963) 28 453



JOC (1965) 30 315



JACS (1960) 82 4903



(Stable to RMgX and CrO_3)

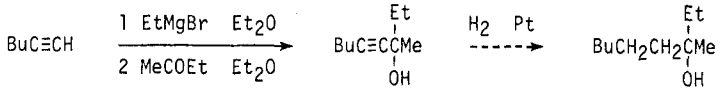
JACS (1970) 92 6646

Other reactions useful for the protection of carboxylic acids are included in section 107 (Esters from Carboxylic Acids), section 23 (Carboxylic Acids from Esters), section 77 (Amides from Carboxylic Acids) and section 21 (Carboxylic Acids from Amides)

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

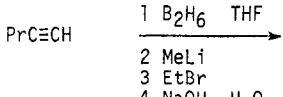
Chapter 3 PREPARATION OF ALCOHOLS AND PHENOLS

Section 31 Alcohols from Acetylenes



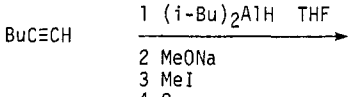
92%

JACS (1941) 63 186
Tetr Lett (1965) 1619



90%

Tetr Lett (1966) 2535
JACS (1967) 89 291



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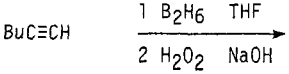
Tetr Lett (1966) 6021



80%

JACS (1967) 89 291

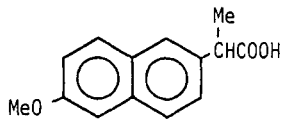
Section 32 Alcohols and Phenols from Carboxylic Acids, Acid Chlorides and Anhydrides

$PhCOOH \xrightarrow[H_2O]{H_2\ (205\ atmos)\ \ ReO_3} PhCH_2OH$ 43%

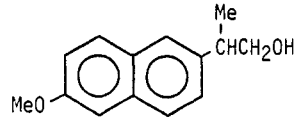
JOC (1963) 28 2345

$C_9H_{19}COOH \xrightarrow{H_2\ (173\ atmos)\ \ Rh_2O_7} C_9H_{19}CH_2OH$ 100%

JOC (1959) 24 1847

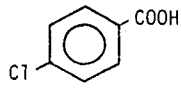


$\xrightarrow{B_2H_6\ \ THF}$

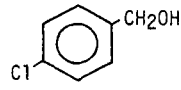


87%

J Med Chem (1970) 13 203

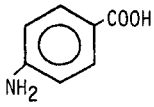


$\xrightarrow[diglyme]{NaBH_4\ \ AlCl_3}$

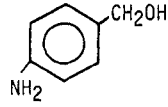


64%

JACS (1956) 78 2582

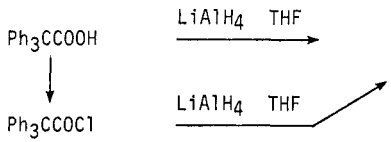


$\xrightarrow[H_2SO_4\ \ H_2O]{Electrolysis}$

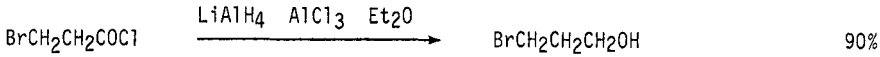


56%

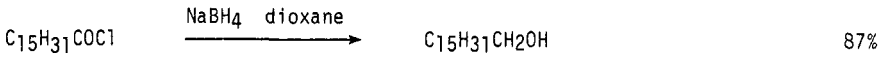
JCS (1942) 98



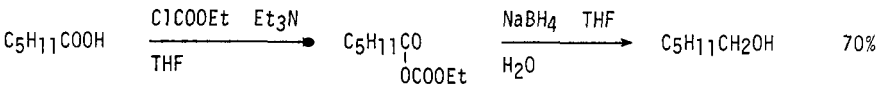
Org React (1951) 6 469



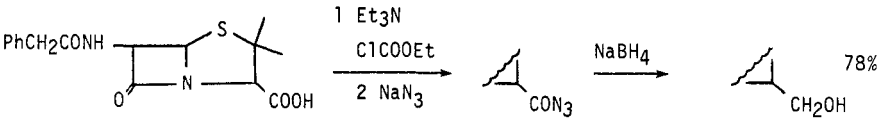
JACS (1959) 81 610



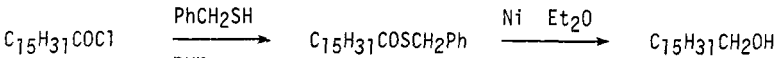
JACS (1949) 71 122



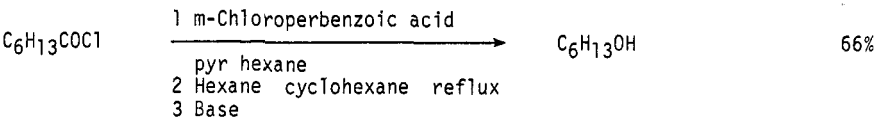
Chem Pharm Bull (1968) 16 492



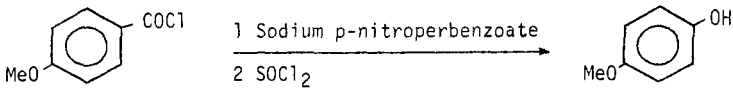
J Med Chem (1964) 7 483



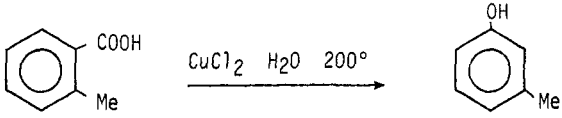
Helv (1946) 29 684



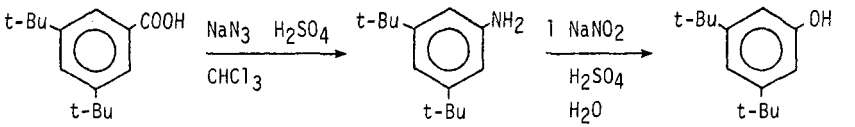
JOC (1965) 30 3760



JACS (1950) 72 67



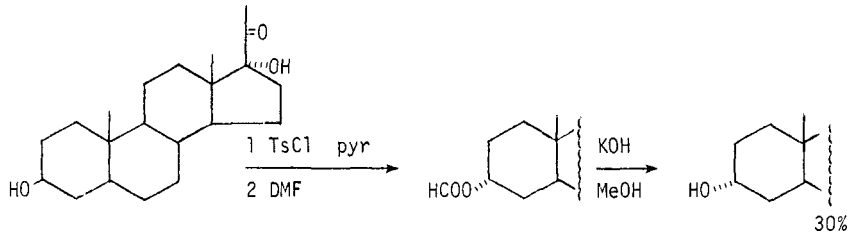
JOC (1961) 26 3144



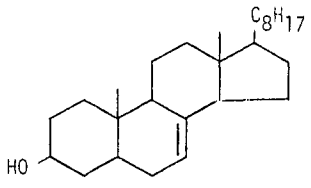
Can J Chem (1963) 41 1653

Alcohols may also be prepared by esterification of carboxylic acids followed by reduction. See section 38 (Alcohols from Esters)

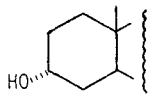
Section 33 Alcohols from Alcohols and Phenols



Steroids (1964) 3 359

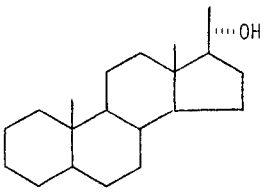


1 TsCl Pyr
2 Bu_4NOAc Me_2CO
3 $LiAlH_4$

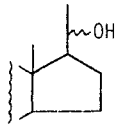


92%

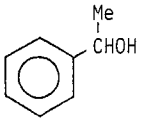
JCS C (1969) 1605



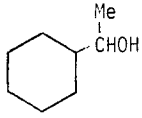
Ph_2CO $C_5H_{11}ONa$



JCS C (1969) 969

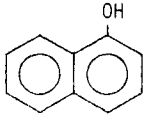


H_2 Rh-Al_2O_3
MeOH HOAc

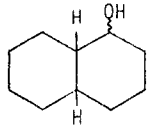


80%

JOC (1962) 27 2288

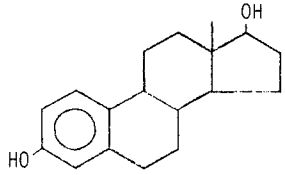


H_2 Rh-Al_2O_3 HOAc

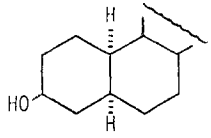


90%

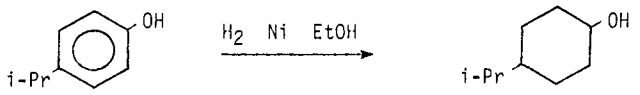
JOC (1964) 29 3427



H_2 RuO_2

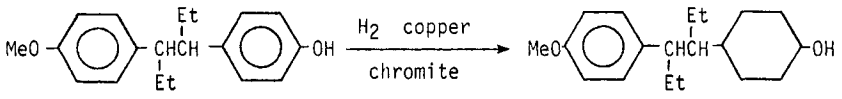


JOC (1958) 23 1404



96%

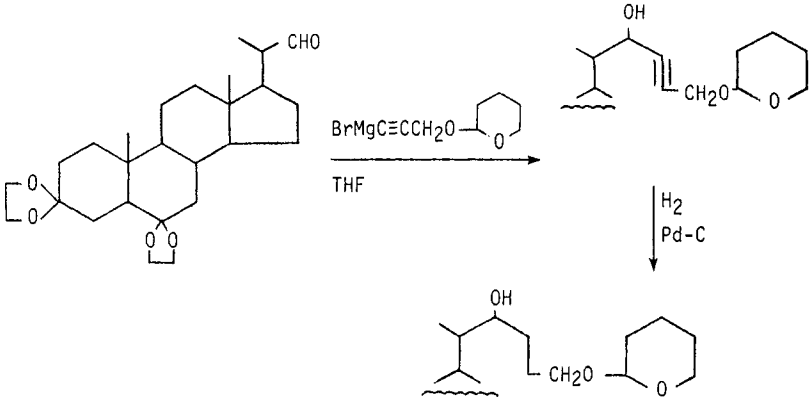
JACS (1949) 71 3889



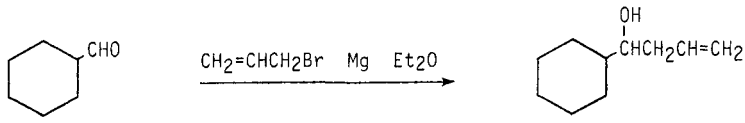
~52%

JACS (1948) 70 4127

Section 34 Alcohols and Phenols from Aldehydes



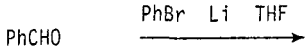
Chem Pharm Bull (1969) 17 690
Tetr Lett (1966) 3457



72%

(Procedure for unstable Grignard reagents)

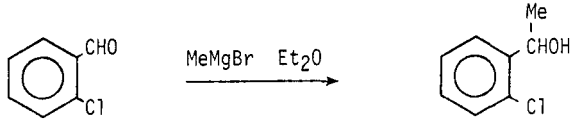
JOC (1963) 28 3269



96%

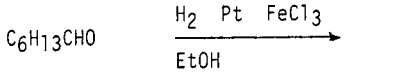
(One-step procedure)

Chem Comm (1970) 1160

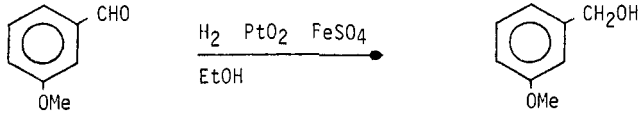


76%

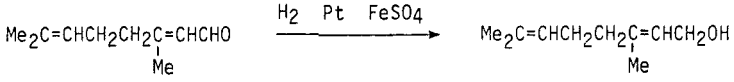
JACS (1944) 66 1295



JACS (1923) 45 1071



JACS (1940) 62 1478



100%

JACS (1926) 48 477
(1925) 47 3061

$C_6H_{13}CHO \xrightarrow{H_2\ (50\ atmos)\quad RhCl_3(Ph_3P)_3} C_6H_{13}CH_2OH$ 100%

Chem Comm (1965) 17

$PrCHO \xrightarrow[RhCl_3 \cdot 3H_2O]{H_2\ \ CO\ (240\ atmos)} PrCH_2OH$ 70%

Ber (1966) 99 1086

$C_6H_{13}CHO \xrightarrow{Fe\ \ HOAc\ \ H_2O} C_6H_{13}CH_2OH$ 75-81%

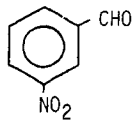
Org Synth (1932) Coll Vol 1 304
JACS (1939) 61 2134

$C_6H_{13}CHO \xrightarrow{LiAlH_4\ \ Et_2O} C_6H_{13}CH_2OH$ 86%

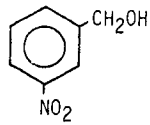
Org React (1951) 6 469
JACS (1947) 69 1197

$PhCHO \xrightarrow{LiAl(OBu\text{-}t)_3H\ \ Et_2O} PhCH_2OH$

JACS (1958) 80 5372



$\xrightarrow{NaBH_4\ \ MeOH}$



82%

JACS (1949) 71 122

$PhCHO \xrightarrow{LiBH_3CN \quad MeOH} PhCH_2OH$ 78%

JACS (1969) 91 3996

$PrCHO \xrightarrow{B_2H_6 \quad THF} PrCH_2OH$

JACS (1960) 82 681

$PhCH{=}CHCHO \xrightarrow{C_5H_5NBH_3 \quad C_6H_6} PhCH{=}CHCH_2OH$ 84%

JOC (1958) 23 1561

$PhCHO \xrightarrow{Ph_3SnH} PhCH_2OH$ 85%

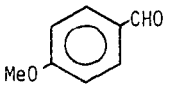
JACS (1961) 83 1246

$MeCH{=}CHCHO \xrightarrow{Bu_2SnH_2 \quad Et_2O} MeCH{=}CHCH_2OH$ 59%

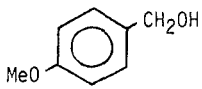
JACS (1961) 83 1246

$PrCHO \xrightarrow{(i\text{-}PrO)_3Al \quad C_6H_6} PrCH_2OH$ 36%

Org React (1944) 2 178

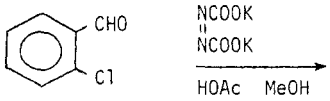


$\xrightarrow[MeOH \quad H_2O]{HCHO \quad NaOH}$



85-90%

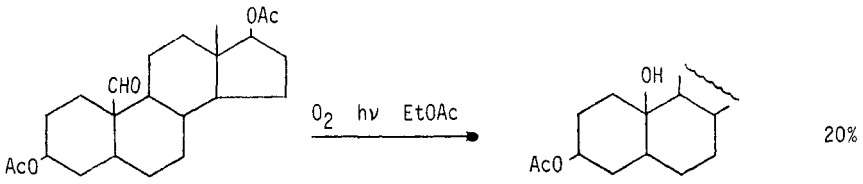
JACS (1935) 57 905
Org React (1944) 2 94



75%

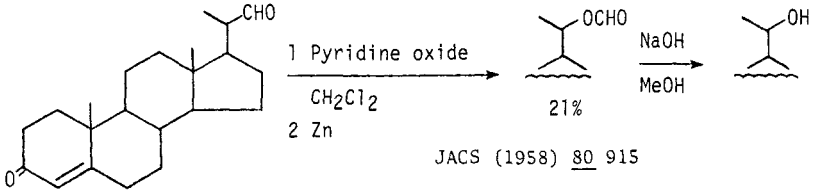
(Rate of reduction ArC=O > AliphC=O)

JCS C (1967) 1120



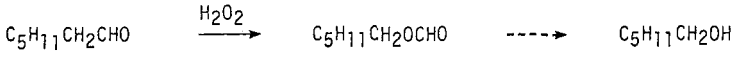
20%

Tetr Lett (1966) 2507

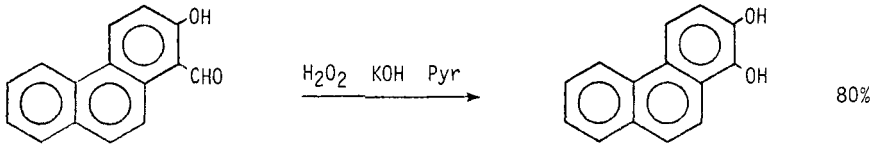


21%

JACS (1958) 80 915



Org React (1957) 9 73
Ber (1941) 74B 1552



80%

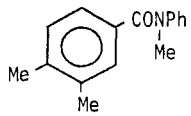
Org React (1957) 9 73
Ber (1940) 73B 935

Alcohols may also be prepared from aldehydes by some of the methods listed in section 42 (Alcohols and Phenols from Ketones)

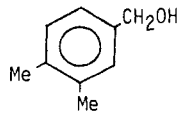
Section 35 Alcohols and Phenols from Alkyls, Methylenes and Aryls

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

Section 36 Alcohols from Amides

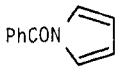


$LiAlH_4$ THF



96%

Ber (1955) 88 301



$LiAlH_4$ Et_2O

$PhCH_2OH$ 80%

JOC (1953) 18 1190

$C_{11}H_{23}CONH_2$ — H_2 (200-300 atmos) 250°, Copper chromite EtOH → $C_{11}H_{23}CH_2OH$

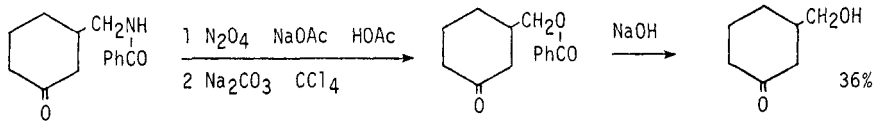
JACS (1934) 56 2419

$C_{13}H_{27}CONH_2$ — Electrolysis LiCl $MeNH_2$ → $C_{13}H_{27}CH_2OH$ 92%

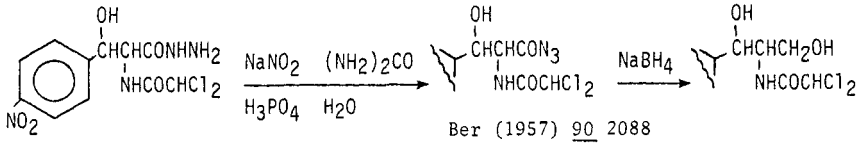
JOC (1970) 35 1210

$PhCONHC_6H_{13}$ — Electrolysis Me_4NCl MeOH → $PhCH_2OH$ 69%

Ber (1965) 98 3462



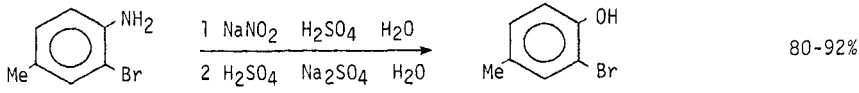
JOC (1969) 34 3834



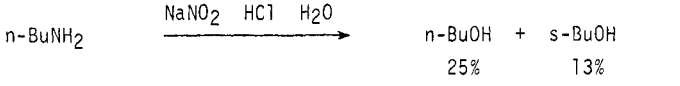
Ber (1957) 90 2088

Alcohols may also be prepared by conversion of amides into esters, followed by hydrolysis. See section 111 (Esters from Amides)

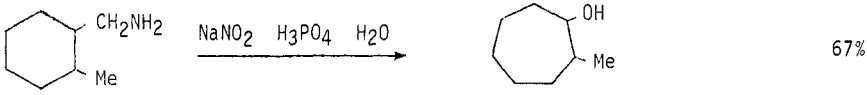
Section 37 Alcohols and Phenols from Amines



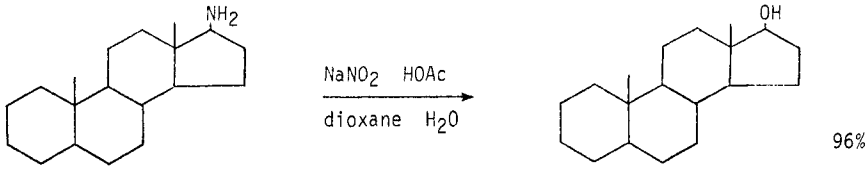
Org Synth (1955) Coll Vol 3 130



JACS (1932) 54 3441

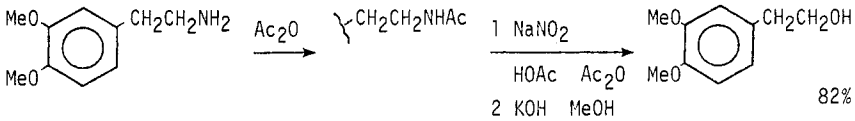


JOC (1965) 30 350



96%

JCS (1959) 345

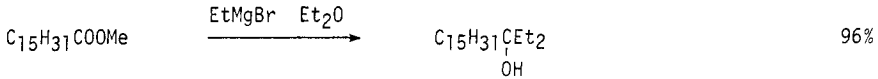


82%

Chem Pharm Bull (1960) 8 266

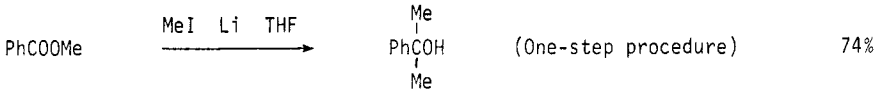
Section 111 contains further examples of the conversion of N-acyl amines into esters from which alcohols can be prepared by hydrolysis

Section 38 Alcohols and Phenols from Esters



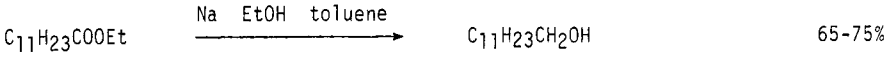
96%

JACS (1945) 67 2239



74%

Chem Comm (1970) 1160



65-75%

Org Synth (1943) Coll Vol 2 372

$C_7H_{15}COOEt$ —(Na, NaOAc, HOAc; H_2O, Et_2O)→ $C_7H_{15}CH_2OH$ > 90%

Rec Trav Chim (1923) 42 1050

$C_5H_{11}COOMe$ —(H_2 (200 atmos), copper chromite; 250°)→ $C_5H_{11}CH_2OH$ 92%

JACS (1932) 54 1145
Org React (1954) 8 1

$PrCOOBu$ —(H_2 (205 atmos), ReO_3; 218°)→ $PrCH_2OH$ 85%

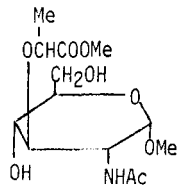
JOC (1963) 28 2345

$PhCOOEt$ —(Electrolysis, Me_4NCl, MeOH)→ $PhCH_2OH$ 89%

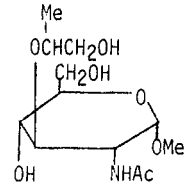
Ber (1965) 98 3462

$C_{15}H_{31}COOEt$ —($LiAlH_4$, Et_2O)→ $C_{15}H_{31}CH_2OH$ 98%

JACS (1947) 69 1197
Org React (1951) 6 469

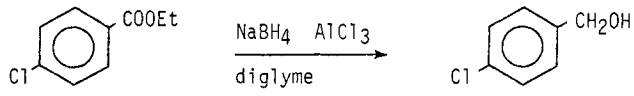


—($LiBH_4$, THF)→



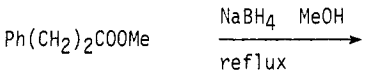
91%

Carbohydrate Res (1967) 4 504



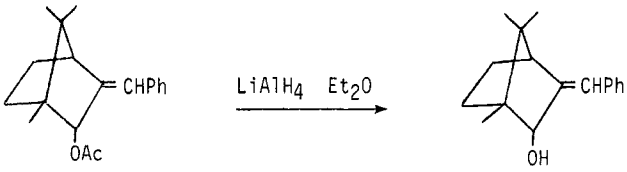
84%

JACS (1956) 78 2582



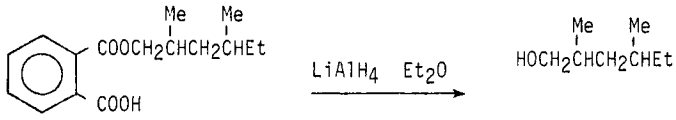
73%

JOC (1963) 28 3261



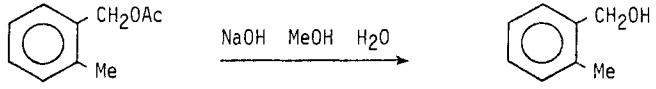
92%

Tetrahedron (1970) 26 395



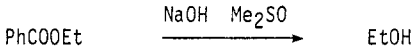
~80%

JACS (1950) 72 147

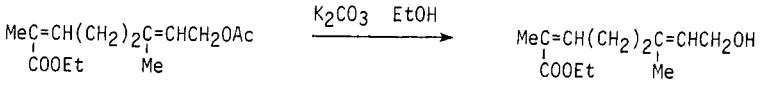


95-97%

Org Synth (1963) Coll Vol 4 582

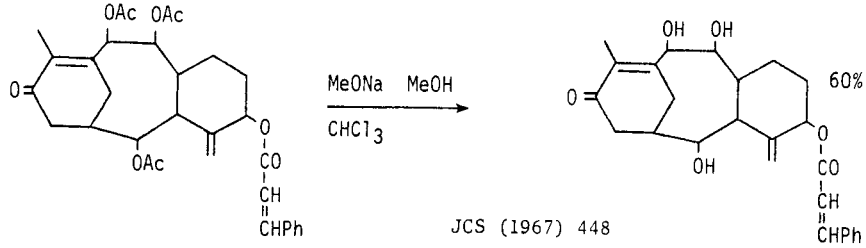


JCS (1965) 1290



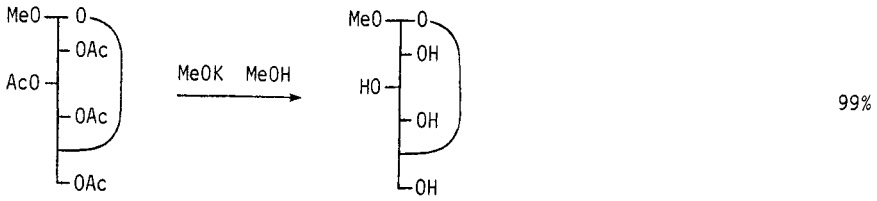
98%

JACS (1969) 91 4318



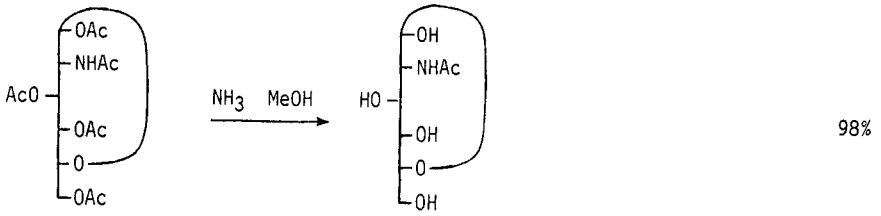
60%

JCS (1967) 448



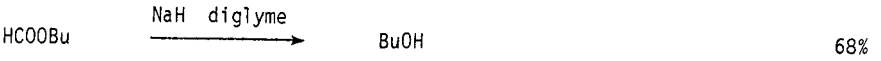
99%

JACS (1948) 70 314



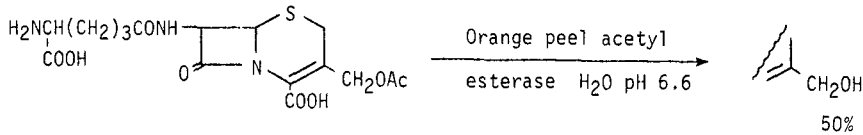
98%

JCS (1956) 2042



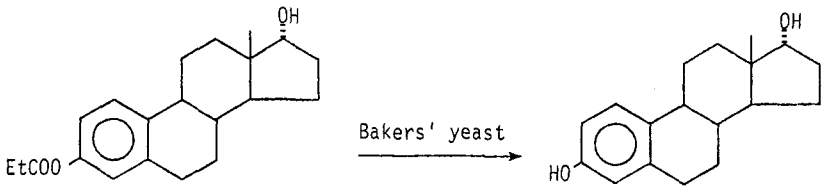
68%

Tetr Lett (1965) 1713

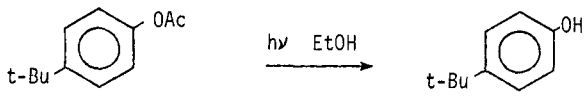


50%

Biochem J (1961) 81 591

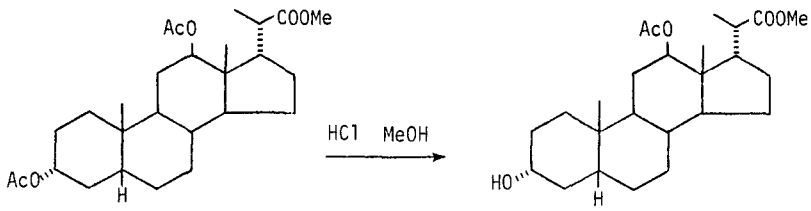


Ber (1938) 71B 2696



34%

JCS (1965) 5162

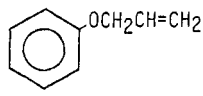


88%

Helv (1944) 27 713

Further examples of the hydrolysis and cleavage of esters are included in section 23 (Carboxylic Acids from Esters) and section 45A (Protection of Alcohols and Phenols)

Section 39 Alcohols and Phenols from Ethers and Epoxides



73%

Org React (1944) 2 1

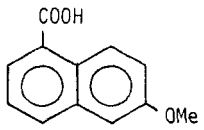
$PhCH_2OMe \xrightarrow{PhLi \quad Et_2O} PhCHOH(Me)$ 35%

Annalen (1942) 550 260
JOC (1962) 27 1933

$Me_2C{=}CHCH_2OCH_2CH{=}CMe_2 \xrightarrow{t\text{-}BuLi \quad THF} Me_2C{=}CHCH(OH)C(Me)CH_2$ 31%

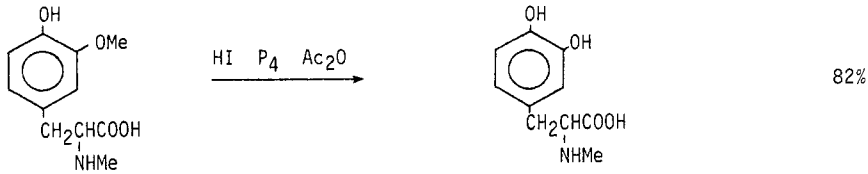
Tetr Lett (1970) 353

Review: The Cleavage of Ethers Chem Rev (1954) 54 615



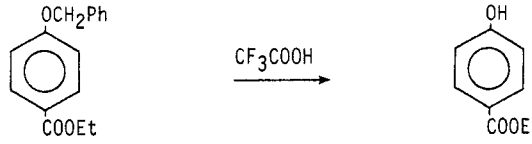
90%

JOC (1941) 6 852

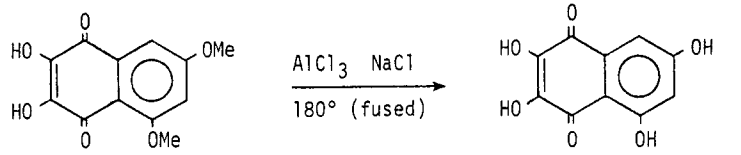


82%

Org Synth (1955) Coll Vol 3 586

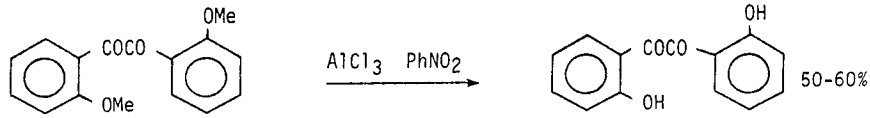


JOC (1965) 30 2491



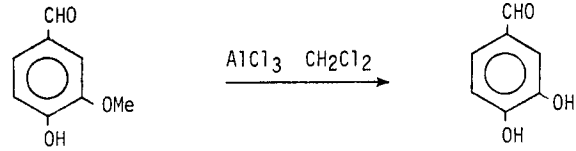
Low yield

JCS (1961) 1008



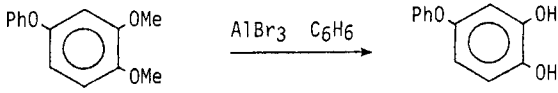
50-60%

Ber (1943) 76B 900



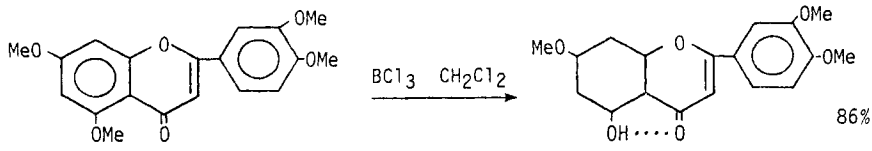
87%

JOC (1962) 27 2037

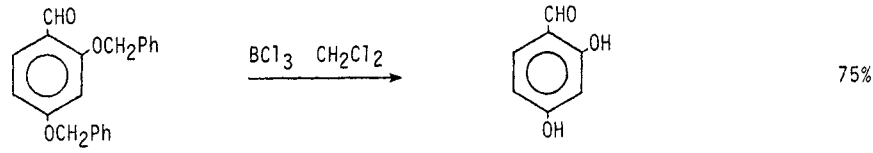


87%

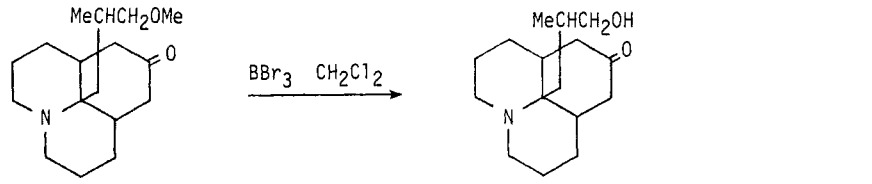
Ber (1960) 93 2761



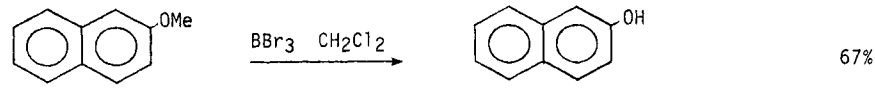
Tetr Lett (1966) 4153
JCS (1962) 1260



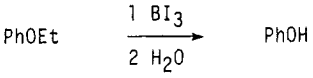
Tetr Lett (1966) 4155



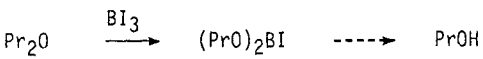
JACS (1968) 90 1648



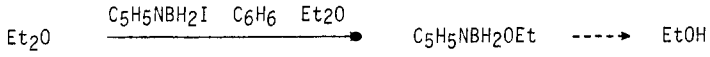
Tetrahedron (1968) 24 2289



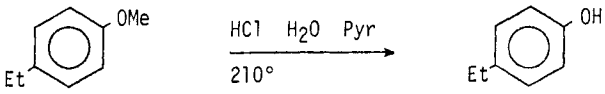
Tetr Lett (1967) 4131



Tetr Lett (1967) 4131

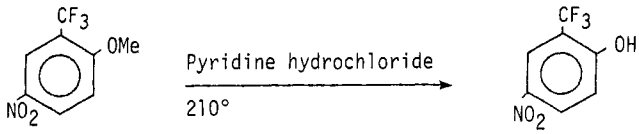


JACS (1968) 90 6260



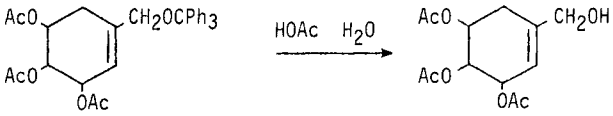
97%

Chem Ind (1967) 1138



75%

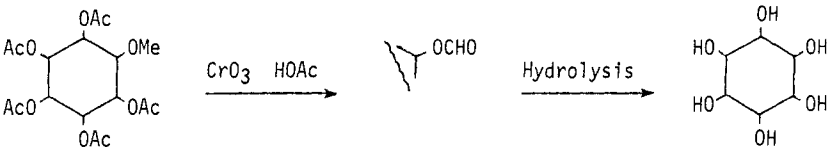
JOC (1962) 27 4660



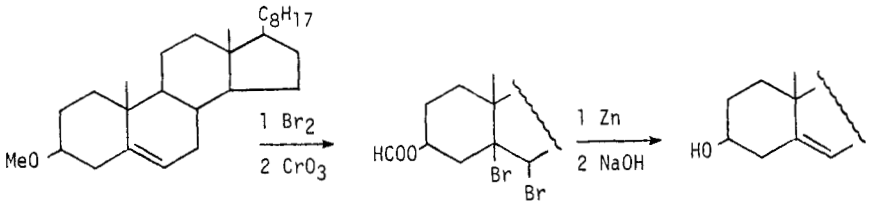
80%

Ber (1956) 89 898

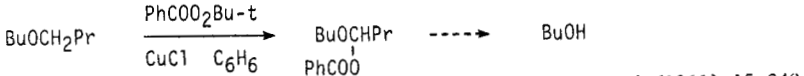
Further examples of the cleavage of triphenylmethyl ethers are included in section 45A (Protection of Alcohols and Phenols)



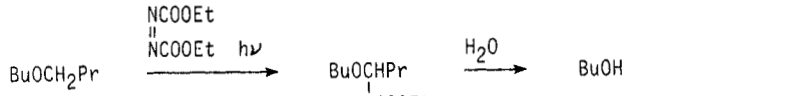
Carbohydrate Res (1970) 12 147



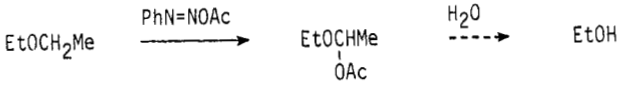
Chem Comm (1966) 752



Acta Chem Scand (1961) 15 249
Tetr Lett (1960) (2) 4
Arkiv Kemi (1960) 16 287

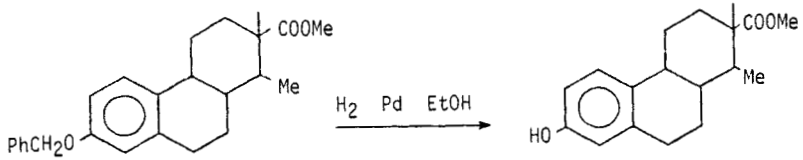


Chem Comm (1965) 259

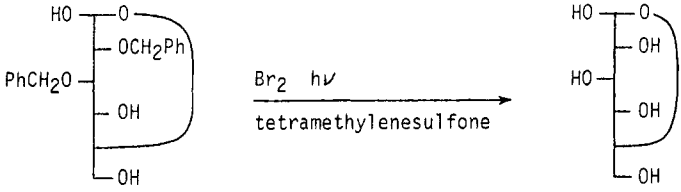


JACS (1964) 86 3180

Org React (1953) 7 263
JACS (1954) 76 3188

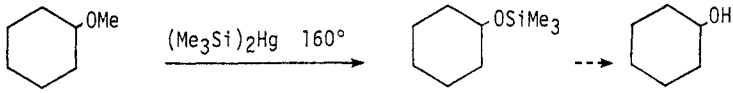


J Med Chem (1969) 12 192

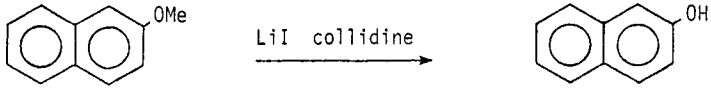


97%

JOC (1968) 33 4292



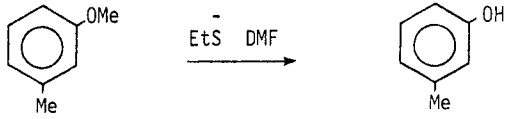
JCS C (1967) 2188



100%

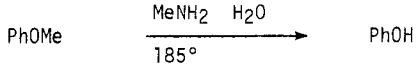
Chem Comm (1969) 616
JACS (1950) 72 3396

For cleavage with KCN see Ber (1933) 66B 1623

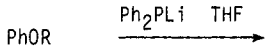


94%

Tetr Lett (1970) 1327

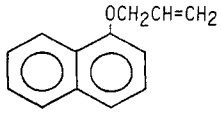


Chem Ind (1970) 1230
Aust J Chem (1970) 23 2539

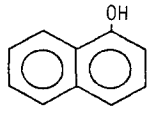


83% (R=Me)
88% (R=PhCH2)
No reaction (R=Et, i-Pr)

JCS (1965) 4120
Tetr Lett (1967) 3661
JACS (1970) 92 7232



$LiAlH_4$ $NiCl_2$ / THF



76%

JACS (1957) 79 5463

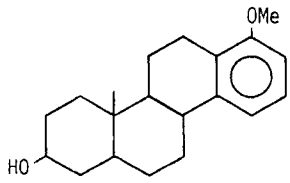
PhOMe — Lithium diphenyl THF → PhOH 80%

JOC (1963) 28 707

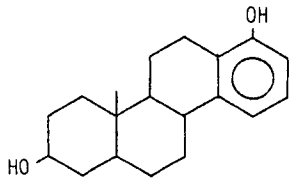
PhOR — BuMgBr $CoCl_2$ Et_2O → PhOH

86% ($R=PhCH_2$)
43% (R=Ph)
No reaction (R=Me)

JOC (1952) 17 669

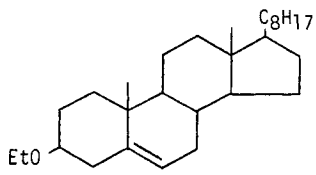


MeMgI / 175°

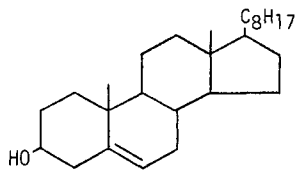


90%

JACS (1956) 78 6322

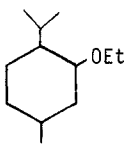


Na $C_5H_{11}Cl$ / hexane

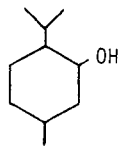


74%

JACS (1951) 73 1263



EtNa Et_4Pb / cyclohexane



72%

J Prakt Chem (1938) 151 61

$PhOCH_2CH{=}CH_2$ —(1 Mg, THF; 2 CO_2)→ PhOH 86%

J Organometallic Chem (1969) 18 249

PhOR —($NaNH_2$, piperidine)→ PhOH 82% (R=Me) 90% ($R=PhCH_2$)

Chem Ind (1957) 80
JACS (1951) 73 1437

$PhCH_2OEt$ —(Li, THF)→ EtOH

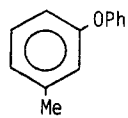
JOC (1961) 26 3723

PhOMe —(K, HMPA)→ PhOH 76-80%

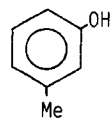
Bull Soc Chim Fr (1966) 3344

PhOMe —(Na, Pyr)→ PhOH 94%

Ber (1943) 76B 156



—(Na, NH_3)→

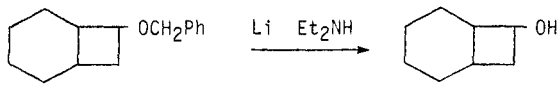


+ PhOH

JACS (1937) 59 1488

PhOMe —(Li, $H_2NCH_2CH_2NH_2$)→ PhOH 54%

JOC (1957) 22 891

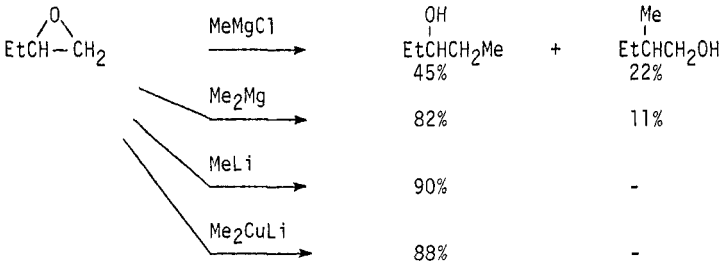


<94%

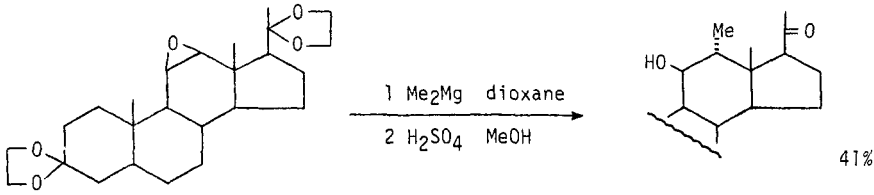
JACS (1970) 92 553

Alcohols and phenols may also be prepared by conversion of ethers into esters, followed by hydrolysis. See section 114 (Esters from Ethers)

Further methods for the cleavage of ethers to alcohols are included in section 45A (Protection of Alcohols and Phenols)

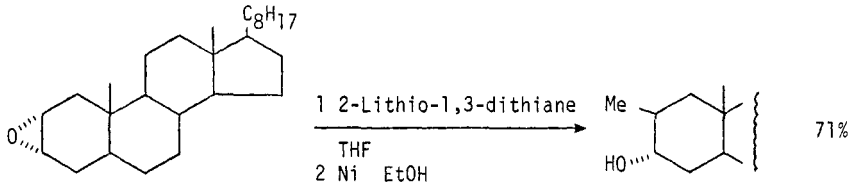


JACS (1970) 92 4979
Chem Rev (1951) 49 413



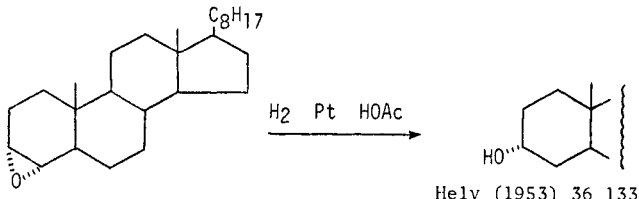
41%

JACS (1960) 82 3995
Bull Soc Chim Fr (1969) 4414



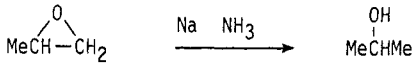
71%

Chem Comm (1970) 141 741

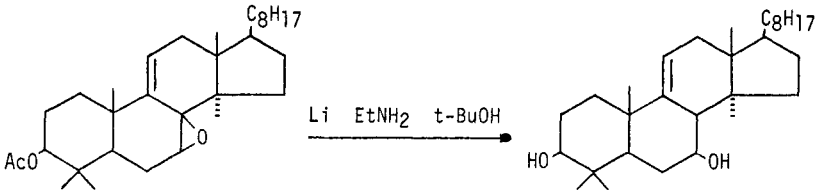


81%

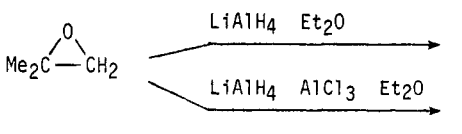
Helv (1953) 36 1332
(1943) 26 562



Quart Rev (1958) 12 17



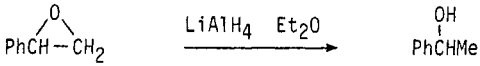
JCS C (1968) 1581



26%

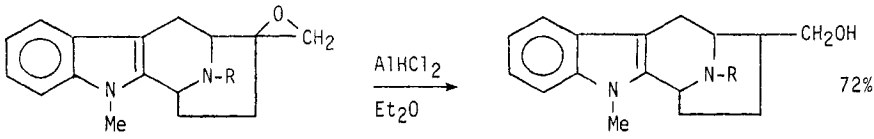
55%

JACS (1956) 78 3226
Org React (1951) 6 469

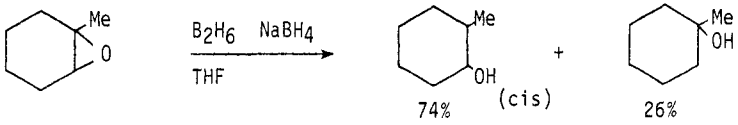


94%

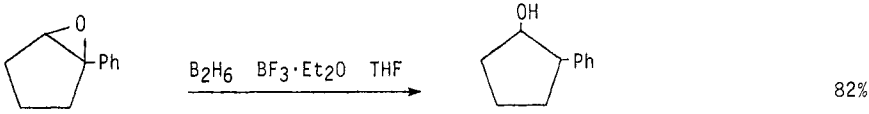
JACS (1948) 70 3738



Tetr Lett (1969) 901

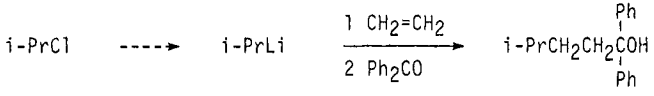


JACS (1968) 90 2686

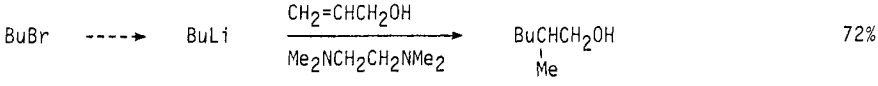


Chem Comm (1968) 1549

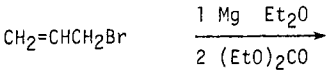
Section 40 Alcohols and Phenols from Halides and Sulfonates



JACS (1969) 91 6362

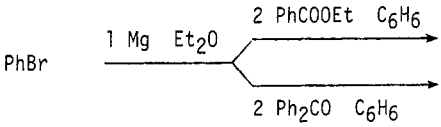


Tetr Lett (1969) 325



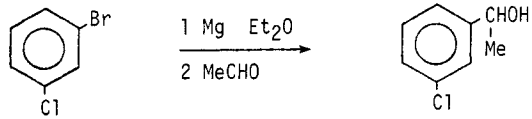
30%

Compt Rend (1968) C 267 773
Org Synth (1943) Coll Vol 2 602



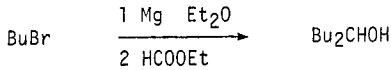
89-93%

Org Synth (1955) Coll Vol 3 839



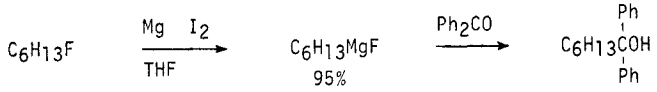
82-88%

Org Synth (1955) Coll Vol 3 200

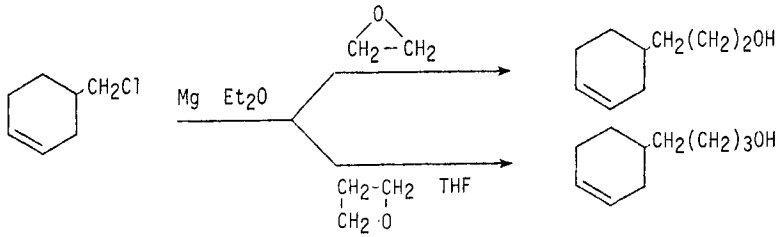


83-85%

Org Synth (1943) Coll Vol 2 179



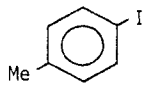
JACS (1970) 92 433



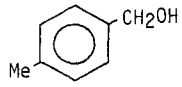
59%

37%

JOC (1968) 33 2991
Org Synth (1932) Coll Vol 1 306



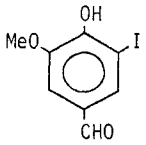
1 Li Et_2O
2 Paraformaldehyde



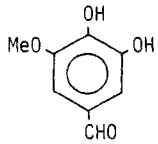
95%

Rec Trav Chim (1965) 84 1200

For Grignard reaction with HCHO gas see JACS (1933) 55 1119
and JOC (1968) 33 3408



$NaOH$ $CuSO_4$ H_2O



68%

Can J Chem (1962) 40 2175
JOC (1939) 4 318

PhBr — 1 Mg Et_2O; 2 O_2 → PhOH 46%

JACS (1955) 77 6032

$C_6H_{13}CHClMe$ — 1 Mg Et_2O; 2 O_2 → $C_6H_{13}CHOOHMe$ (91%) ----→ $C_6H_{13}CHOHMe$

JACS (1955) 77 6032
(1943) 65 501

t-BuCl — 1 Mg Et_2O; 2 $HgCl_2$ → t-BuHgCl — O_3 CH_2Cl_2 → t-BuOH 50%

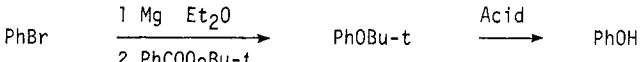
Tetr Lett (1970) 2679

PhCl — 1 Mg Et_2O; 2 $(MeO)_3B$; 3 H_2O_2 H_2O → PhOH 78%

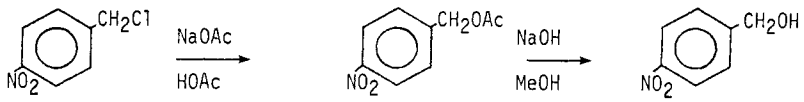
JOC (1957) 22 1001

PhBr — 1 Mg Et_2O; 2 t-BuOOH → PhOH 98%

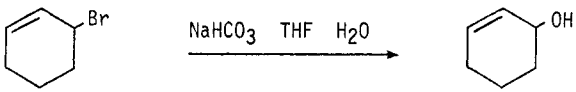
JACS (1959) 81 4230



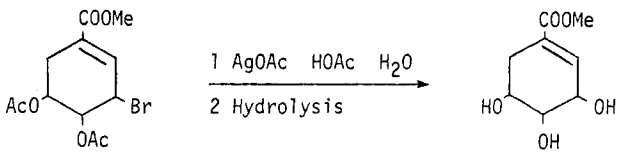
Arkiv Kemi (1961) 17 393
Org Synth (1963) 43 55



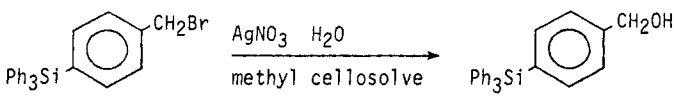
Org Synth (1955) Coll Vol 3 650 652



JACS (1961) 83 198
(1946) 68 751

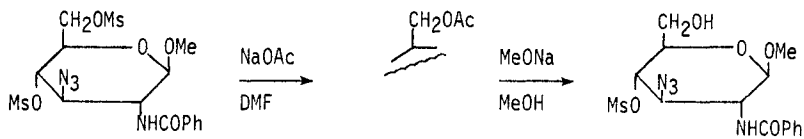


Ber (1964) 97 443



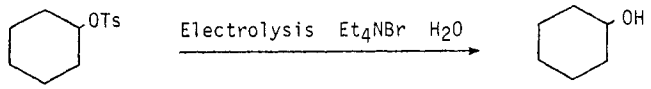
76%

JACS (1956) 78 1689
J Biol Chem (1946) 164 569



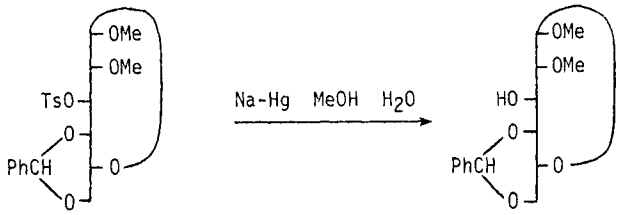
77%

Ber (1970) 103 37



96%

JOC (1968) 33 2716



88%

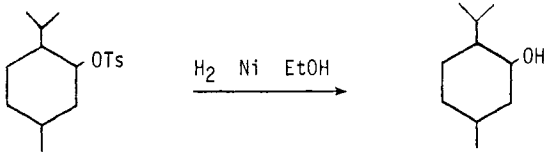
Helv (1945) 28 1164

PhOTs —Sodium-naphthalene THF→ PhOH 99%

JACS (1966) 88 1581

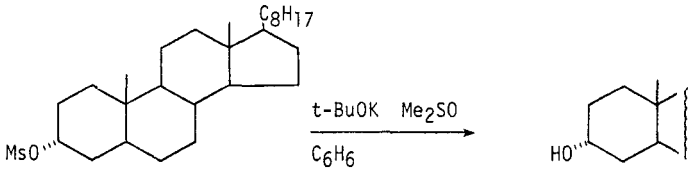
$C_8H_{17}OTs$ —Na NH_3 Et_2O→ $C_8H_{17}OH$ 56%

JOC (1956) 21 479



86%

JCS (1949) S178

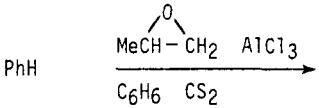


87%

Tetr Lett (1964) 305

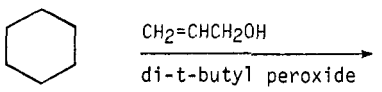
Further examples of the cleavage of sulfonates to alcohols and phenols are included in section 45A (Protection of Alcohols and Phenols)

Section 41 Alcohols and Phenols from Hydrides (RH)



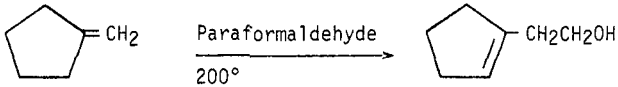
56%

Bull Chem Soc Jap (1967) 40 2980



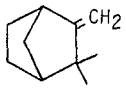
38%

Neftekhimiya (1965) 5 554
(Chem Abs 63 16223)

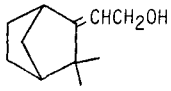


38%

JACS (1950) 72 2871
Chem Rev (1952) 51 505



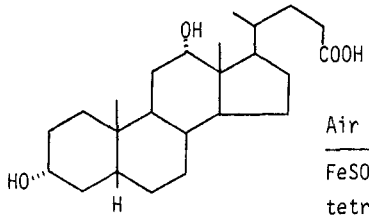
Paraformaldehyde Ac_2O
220°



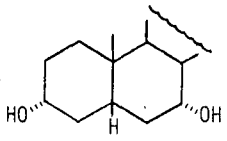
Aust J Chem (1967) 20 2033

C_7H_{16} — 1 $(CF_3COO)_4Pb$, 2 NaOH H_2O → $C_7H_{15}OH$ (isomer mixture) ~45%

JACS (1967) 89 3662

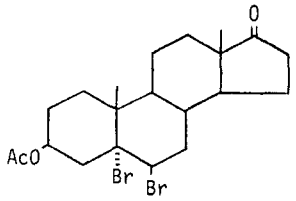


Air ascorbic acid
$FeSO_4$ ethylenediaminetetraacetic acid EtOH
EtOAc pH 5.5

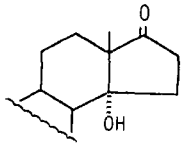


~61%

Steroids (1965) 5 451



CrO_3 HOAc
H_2O



30%

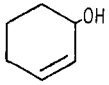
Tetr Lett (1969) 1157
JCS C (1968) 2346
JACS (1948) 70 3237

$Na_2Cr_2O_7$ $HClO_4$
HOAc H_2O

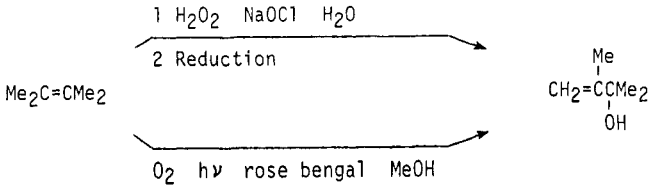
6%

JACS (1961) 83 423
Tetrahedron (1968) 24 4667

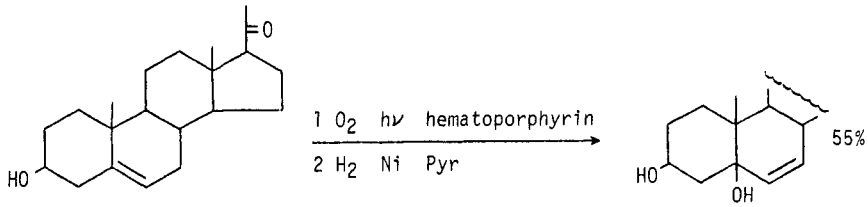
H_2O_2 V_2O_5 Me_2CO



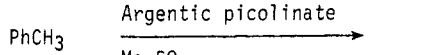
JOC (1963) 28 2057



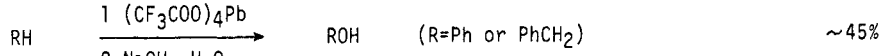
JACS (1968) 90 975



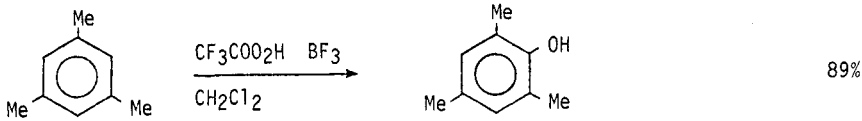
Annalen (1958) 618 194 185



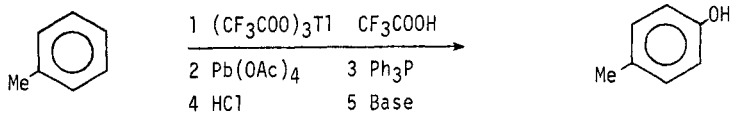
Tetr Lett (1967) 415



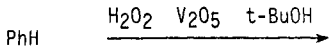
JACS (1967) 89 3662



JOC (1964) 29 2397
(1966) 31 153

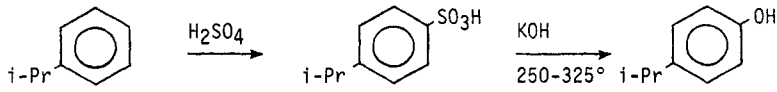


JACS (1970) 92 3520



30%

JACS (1937) 59 2342
Tetrahedron (1968) 24 3475

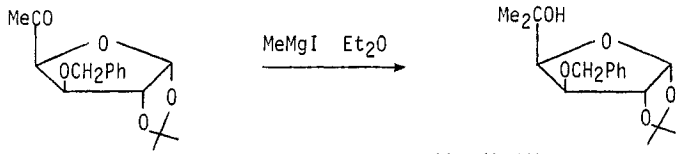


35%

JACS (1949) 71 3889
Org React (1946) 3 141

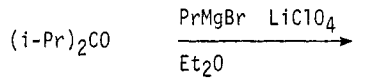
Alcohols may also be prepared by conversion of hydrides into esters, followed by hydrolysis. See section 116 (Esters from Hydrides)

Section 42 Alcohols and Phenols from Ketones



71%

JOC (1962) 27 2107



70%

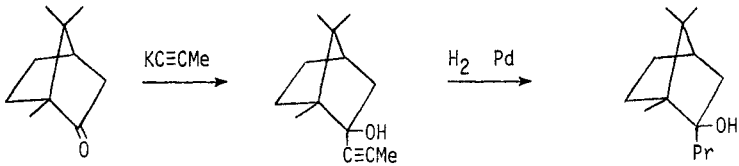
(Procedure for hindered ketones)

Chem Comm (1970) 470

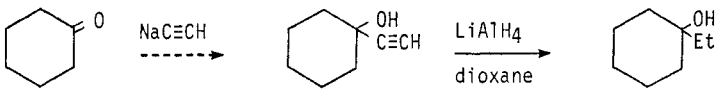
Me_2CO —(PhBr Li THF)→ $Me_2C(Ph)OH$ 34%

(One-step procedure)

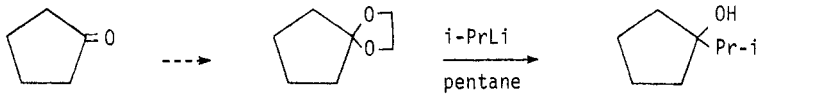
Chem Comm (1970) 1160



Tetr Lett (1965) 1619
JOC (1969) 34 3754



JCS (1954) 1854



64%

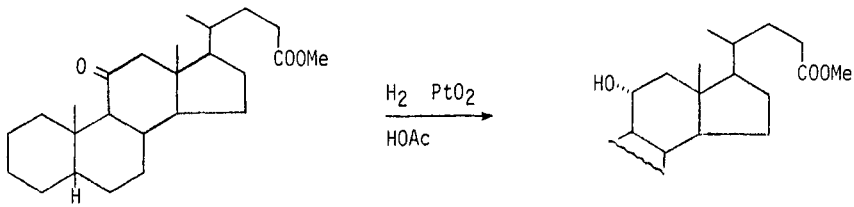
J Heterocyclic Chem (1969) 6 139

$i\text{-}PrCH_2COMe$ —(H_2 Pd-C)→ $i\text{-}PrCH_2CH(OH)Me$

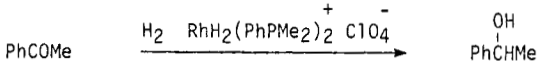
(Pt Rh or Ru catalysts may also be used)

JOC (1959) 24 1855

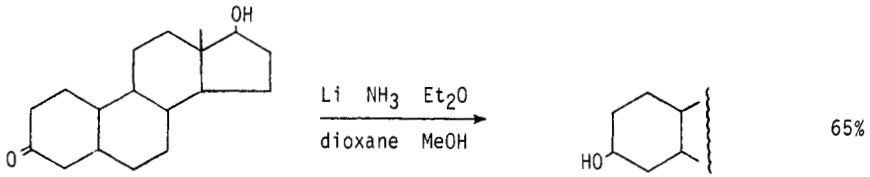
For stereochemistry see Chem Rev (1957) 57 895



Helv (1943) 26 562
JCS (1954) 2487

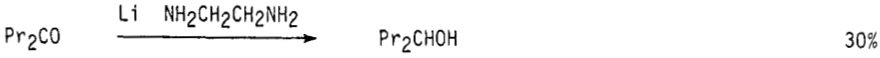


Chem Comm (1970) 567



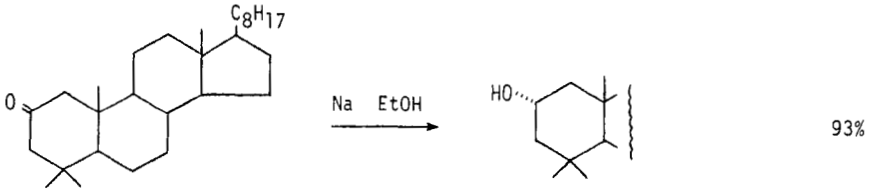
65%

JACS (1958) 80 6115
(1968) 90 6486



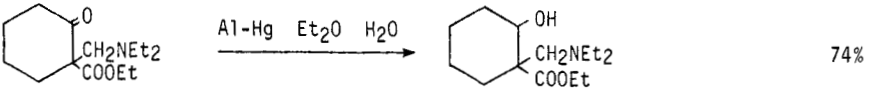
30%

JOC (1957) 22 891



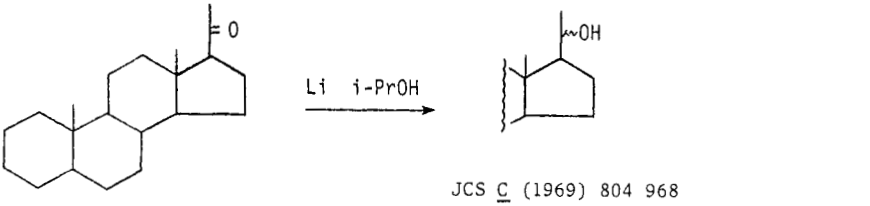
93%

Bull Soc Chim Fr (1964) 2236
JCS C (1969) 968

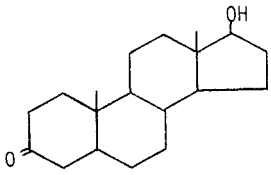


74%

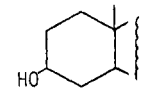
Arch Pharm (1942) 280 361



JCS C (1969) 804 968

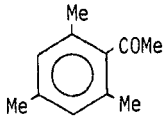


Electrolysis
Bu_4NCl

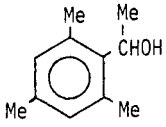


100%

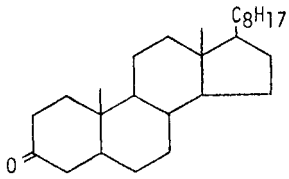
JOC (1961) 26 1738
(1970) 35 261



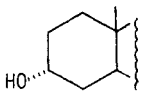
$LiAlH_4$ Et_2O



JACS (1947) 69 1197
Org React (1951) 6 469

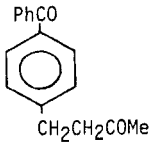


$LiAlH_4$ $AlCl_3$ isoborneol
Et_2O

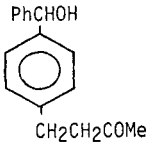


70%

JOC (1965) 30 3809

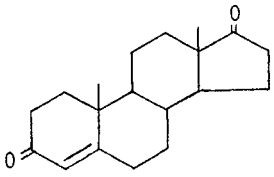


$LiAlH_4$ Pyr

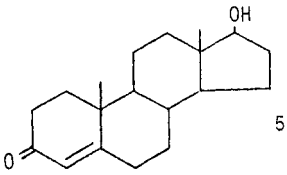


56%

JACS (1962) 84 1756

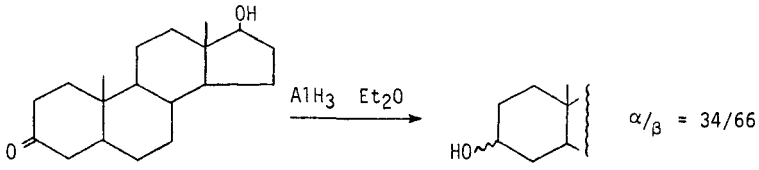


$LiAl(OBu\text{-}t)_3H$
THF

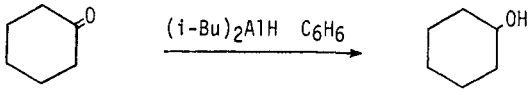


55%

Coll Czech (1959) 24 2284



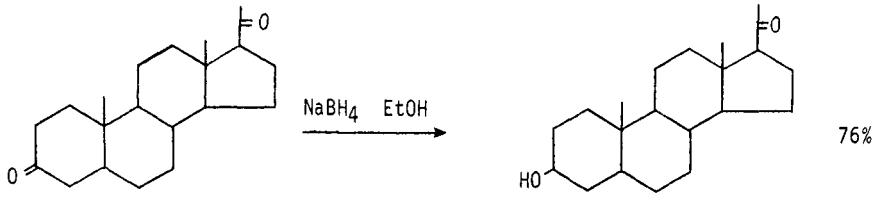
JCS B (1967) 581



83%

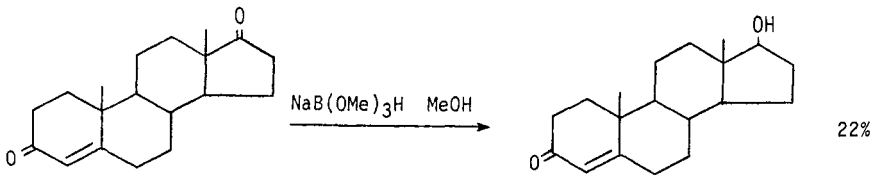
JOC (1959) 24 627

For reduction of unsaturated ketones see Chem Comm (1970) 213



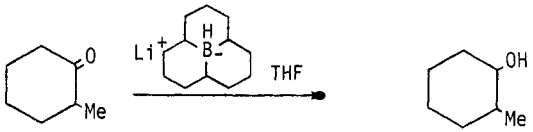
76%

JACS (1953) 75 1286



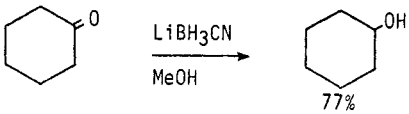
22%

JCS (1955) 3426



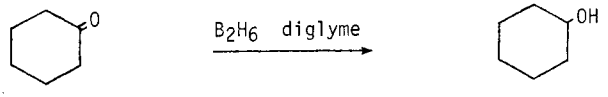
cis/trans=99/1

JACS (1970) 92 709

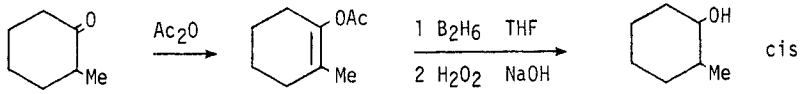


(LiBH3CN is stable to pH 3)

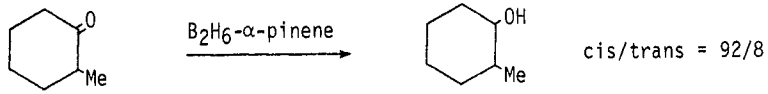
JACS (1969) 91 3996



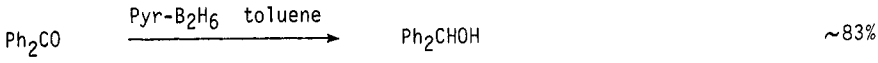
JACS (1960) 82 681



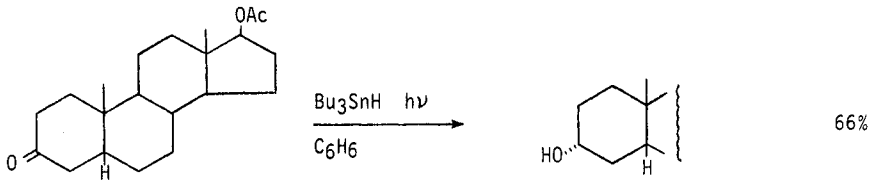
Tetr Lett (1968) 4937



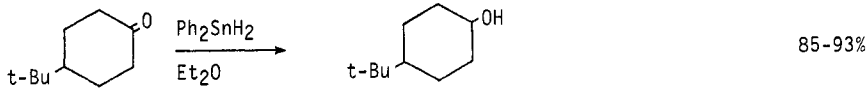
JACS (1961) 83 3166



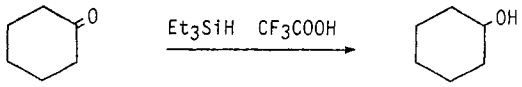
JOC (1958) 23 1561



Helv (1967) 50 2259
Tetr Lett (1968) 5385



JACS (1958) 80 3798
(1961) 83 1246

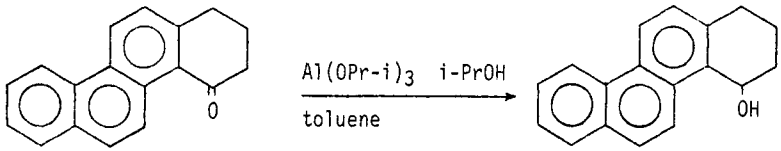


74%

Tetrahedron (1967) 23 2235

Ph_2CO —(NaH, xylene)→ Ph_2CHOH 83%

JACS (1946) 68 2647

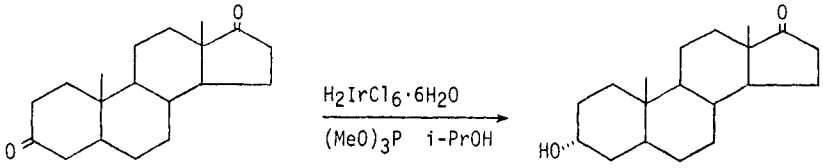


76%

JOC (1939) 4 456
Org React (1944) 2 178

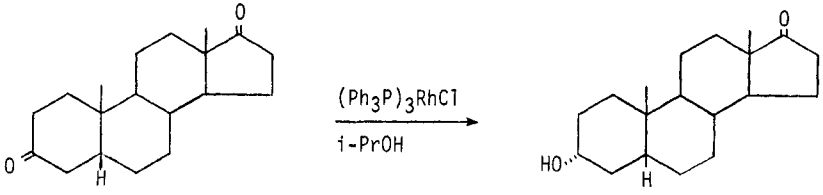
PhCOMe —(i-PrOLi, i-PrOH)→ PhCHOH(Me) > 90%

JCS C (1969) 804



85%

JCS C (1969) 1653
(1970) 785
Chem Comm (1970) 162

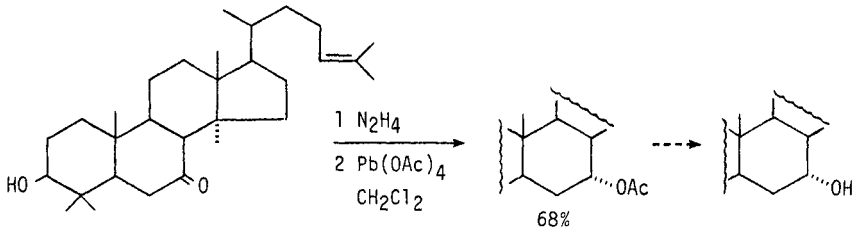


100%

Chem Comm (1970) 162

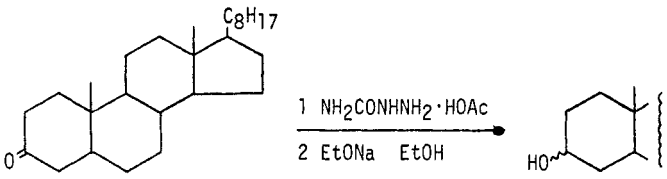
Ph_2CO —(KOH, $HOCH_2CH_2OH$)→ Ph_2CHOH 93%

JOC (1967) 32 840
(1960) 25 1707



68%

Chem Comm (1969) 450



90%

JACS (1939) 61 1992

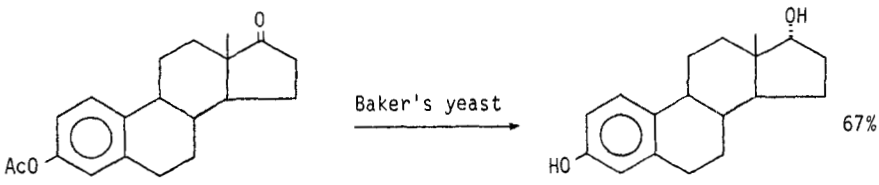
PhCOMe —(NCOONa = NCOONa, HOAc, MeOH)→ PhCHOH(Me) 31%

(Rate of reduction ArC=O > AliphC=O)

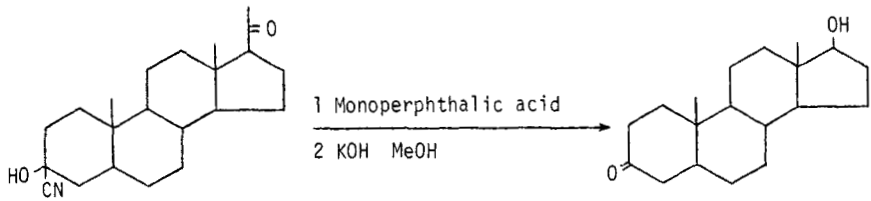
Chem Comm (1965) 71

Ph_2CO —(PhLi-Pyr, Et_2O)→ Ph_2CHOH 62%

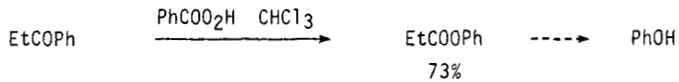
Can J Chem (1963) 41 1961



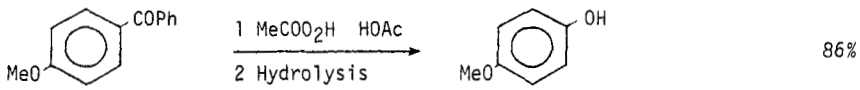
Ber (1938) 71B 2696



Gazz (1961) 91 1250
(Chem Abs 56 10211)



JACS (1949) 71 14



JACS (1950) 72 5515

Further examples of the Baeyer-Villiger degradation of ketones to alcohols and phenols via esters are included in section 117 (Esters from Ketones)

Some of the methods listed in section 34 (Alcohols and Phenols from Aldehydes) may also be applied to the preparation of alcohols from ketones

Section 43 Alcohols and Phenols from Nitriles

No examples

Section 44 Alcohols from Olefins

$C_6H_{13}CH{=}CH_2$ —(1 $NaBH_4$ BF_3 diglyme; 2 CO; 3 H_2O_2 NaOH H_2O)→ $(C_6H_{13}CH_2CH_2)_3COH$ 90%

JACS (1967) 89 2737
(1970) 92 6648

$C_5H_{11}CH{=}CH_2$ —(Di-t-butyl peroxide; $MeCH_2OH$)→ $C_5H_{11}CH_2CH_2CHOH$ (Me) 40-60%

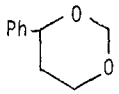
Izv (1964) 894
(Chem Abs 61 5510)

$PrCH{=}CH_2$ —(1 B_2H_6 THF; 2 $MeOCHCl_2$ MeLi Et_2O; 3 H_2O_2 NaOH H_2O)→ $(PrCH_2CH_2)_2CHOH$ (21%) + $PrCH_2CH(OH)CH_2CH_2Pr$ (28%)

Tetr Lett (1969) 2955

$C_6H_{13}CH{=}CH_2$ —(1 B_2H_6 THF; 2 CO $LiBH_4$; 3 KOH EtOH; 4 H_2O_2)→ $C_6H_{13}(CH_2)_3OH$ 70%

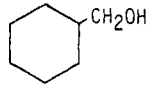
JACS (1967) 89 2740

$PhCH{=}CH_2$ —(HCHO; H_2SO_4)→  —(H_2 (2,600 psi); copper chromite)→ $Ph(CH_2)_3OH$ ~74%

JACS (1950) 72 5314
Chem Rev (1952) 51 505

$C_5H_{11}CH=CH_2$ —(CO H_2 (240 atmos), $RhCl_3 \cdot 3H_2O$)→ $C_5H_{11}(CH_2)_3OH$ 73%

Ber (1966) 99 1086

—(CO H_2 (450 atmos), Co)→ 

56%

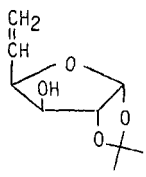
JACS (1952) 74 4496

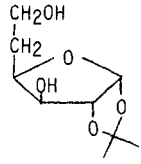
$BuCH=CH_2$ —(1 B_2H_6; 2 $CH_2=SMe_2$ Me_2SO; 3 H_2O_2 NaOH H_2O)→ $Bu(CH_2)_3OH$ + $Bu(CH_2)_2OH$

Chem Comm (1967) 505

$i\text{-}PrCH_2CH=CH_2$ —(1 $NaBH_4$ $BF_3 \cdot Et_2O$ THF; 2 H_2O_2 NaOH H_2O)→ $i\text{-}Pr(CH_2)_3OH$ 80%

Org React (1963) 13 1



—(1 $LiBH_4$ H_2SO_4 THF; 2 H_2O_2 NaOH H_2O)→ 

22%

JOC (1963) 28 3551

$CH_2=CH(CH_2)_8COOH$ —(1 $(i\text{-}PrCH(Me))_2BH$ THF; 2 H_2O_2)→ $HOCH_2CH_2(CH_2)_8COOH$ 82%

JACS (1961) 83 486

$Me_2C=CHMe$ —(1  THF; 2 H_2O_2 NaOH H_2O)→ $Me_2CHCHMe$ (OH) ~95%

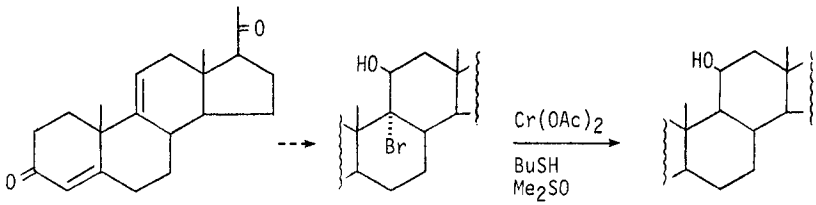
JACS (1968) 90 5281

$C_{10}H_{21}CH{=}CHC_{11}H_{23}$ — 1 $NaBH_4$ $BF_3{\cdot}Et_2O$; bis-2-ethoxyethyl ether, 185-190°; 2 H_2O_2 NaOH H_2O → $C_{22}H_{45}CH_2OH$ 51%

JOC (1961) 26 3657
JACS (1967) 89 561 567

PhCH=CHMe — 1 Et_2AlCl; 2 H_2O_2 NaOH → $PhCH_2CHMe$ (OH) 75%

Tetr Lett (1970) 3471



JACS (1966) 88 3016

$MeCO(CH_2)_2CH{=}CMe_2$ — 1 HCOOH; 2 $NaHCO_3$ MeOH → $MeCO(CH_2)_2CH_2C(OH)Me_2$ 80-95%

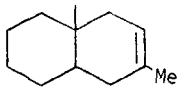
Bol Inst Quim Univ Nac Aut Mex (1965) 17 181
(Chem Abs 65 8963)
JACS (1953) 75 6212

$MeCO(CH_2)_2CH{=}CMe_2$ — 1 H_2SO_4 H_2O; 2 NaOH H_2O → $MeCO(CH_2)_2CH_2C(OH)Me_2$ 85%

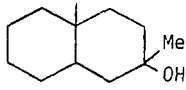
JACS (1955) 77 1617

BuCH=CH_2 — 1 $Hg(OAc)_2$ THF H_2O; 2 NaOH H_2O; 3 $NaBH_4$ NaOH H_2O → BuCHMe (OH) 96%

JACS (1967) 89 1522
JOC (1970) 35 1844

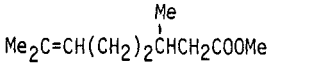


H_2O $h\nu$ xylene / $MeOCH_2CH_2OMe$

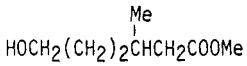


50%

JACS (1967) 89 6788
Acc Chem Res (1969) 2 33



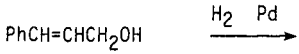
1 O_3 MeOH / 2 $NaBH_4$



72%

JACS (1968) 90 3525
Helv (1967) 50 2445

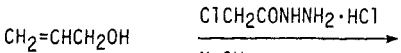
Section 45 Alcohols from Miscellaneous Compounds



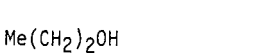
H_2 Pd

55%

Annalen (1924) 439 276

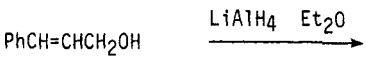


$ClCH_2CONHNH_2 \cdot HCl$ / NaOH



70%

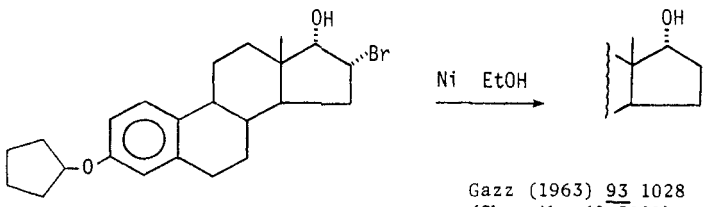
Chem Ind (1964) 839



$LiAlH_4$ Et_2O

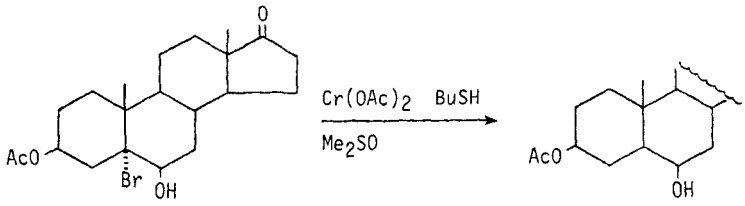
93%

JACS (1948) 70 3484



Ni EtOH

Gazz (1963) 93 1028
(Chem Abs 60 3029)
JACS (1953) 75 1700

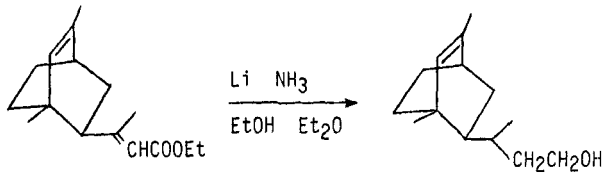


65%

JACS (1966) 88 3016

PhCH=CHCHO $\xrightarrow{H_2\ Pt}$ $Ph(CH_2)_3OH$

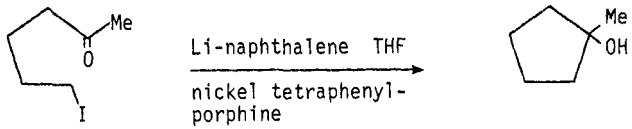
JACS (1925) 47 3061



Tetr Lett (1970) 3219

MeCH=CHCOOH $\xrightarrow{B_2H_6}$ $Me(CH_2)_3OH$

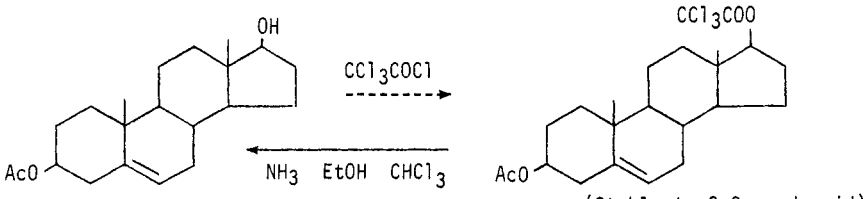
Hua Hsueh Hsueh Pao (1965) 31 376
(Chem Abs 64 8022)



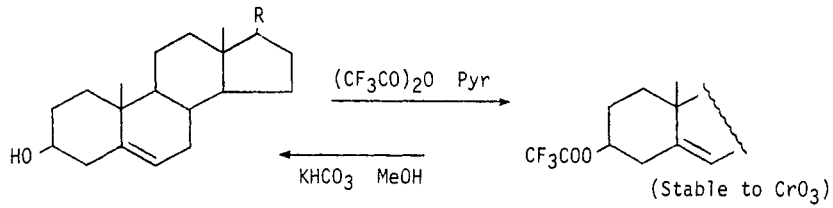
61%

JACS (1970) 92 395

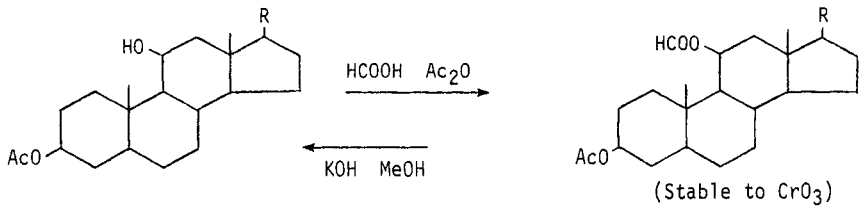
Section 45A Protection of Alcohols and Phenols



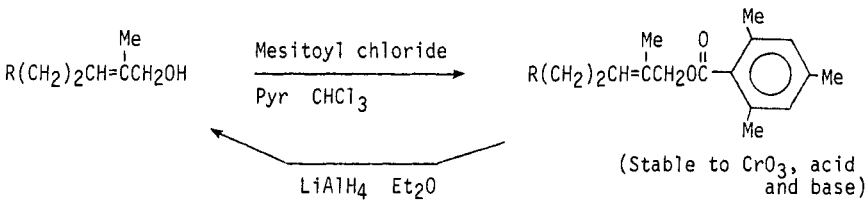
Coll Czech (1962) 27 2567
Tetr Lett (1968) 4681



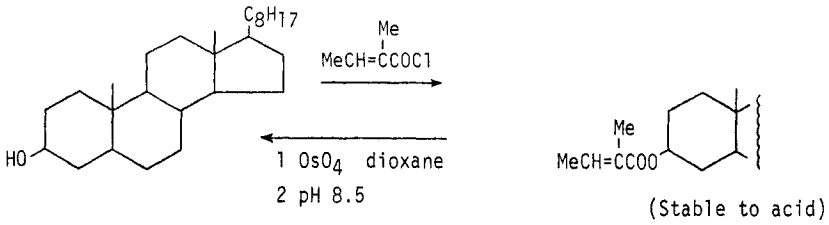
Helv (1954) 37 388



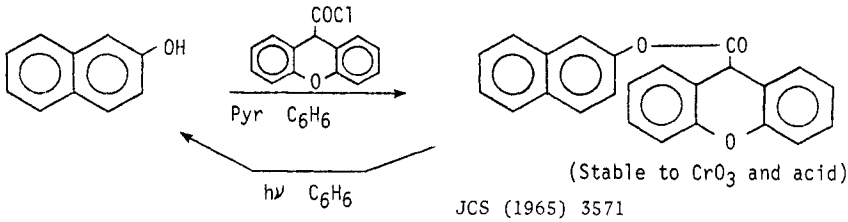
Helv (1954) 37 443



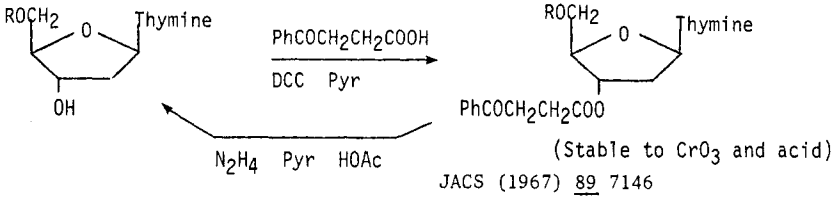
JACS (1969) 91 4318
(1967) 89 2758



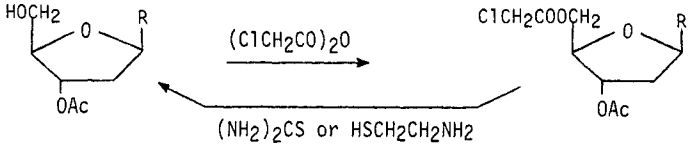
JOC (1962) 27 3103



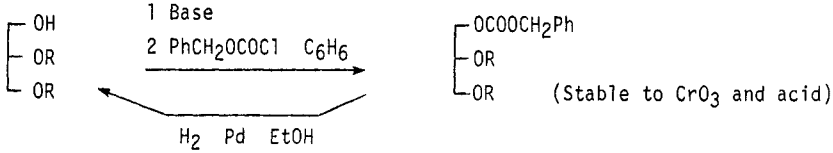
JCS (1965) 3571



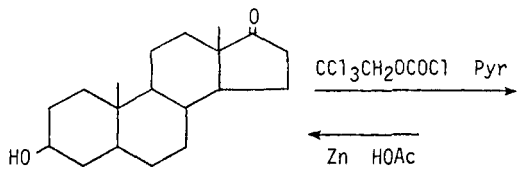
JACS (1967) 89 7146



JOC (1970) 35 1940



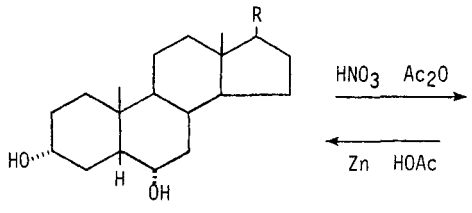
JACS (1939) 61 3328



(Stable to CrO_3 and acid)

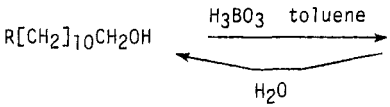
Tetr Lett (1967) 2555
JOC (1968) 33 3589

Further examples of the preparation and cleavage of esters are included in section 108 (Esters from Alcohols and Phenols) and section 38 (Alcohols and Phenols from Esters)



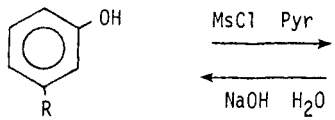
(Stable to CrO_3, acid and base)

Ber (1962) 95 1094
Chem Rev (1955) 55 485



(Stable to Wittig reagents, acid and base)

Rec Trav Chim (1953) 72 411
Tetr Lett (1969) 4155

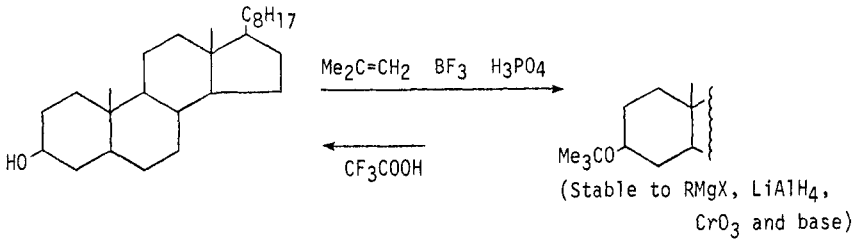


(Stable to CrO_3 and acid)

JACS (1957) 79 717

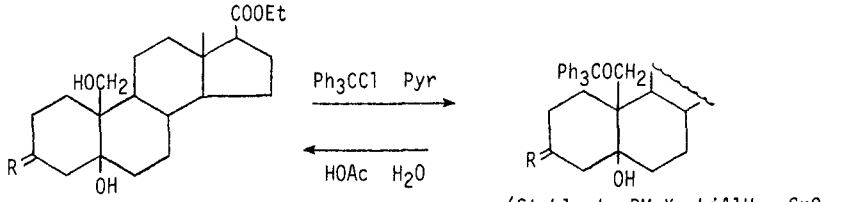
For cleavage of mesylates with PhLi see JCS C (1968) 2283

Further examples of the preparation and cleavage of sulfonates are included in section 138 (Halides and Sulfonates from Alcohols and Phenols) and section 40 (Alcohols and Phenols from Halides and Sulfonates)



(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

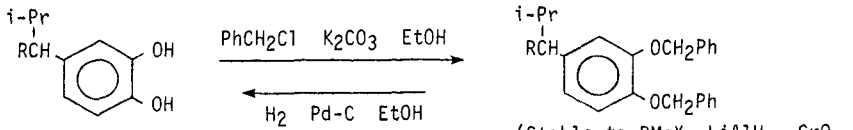
JCS (1963) 755



(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

JOC (1951) 16 349
(1950) 15 264

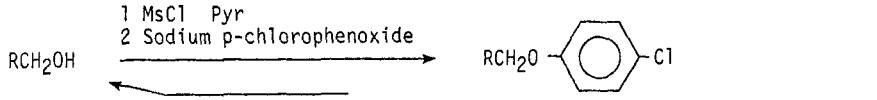
For hydrogenolysis of trityl ethers see Rec Trav Chim (1942) 61 373



(Stable to RMgX, $LiAlH_4$, CrO_3 acid and base)

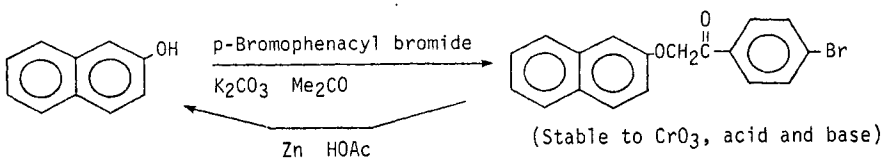
J Med Chem (1967) 10 262
JACS (1954) 76 3188
Org React (1953) 7 263

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

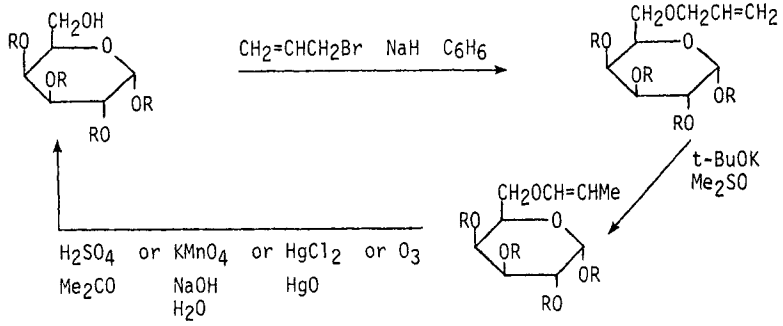


(Stable to RMgX, $LiAlH_4$, CrO_3 acid and base)

JACS (1968) 90 1090

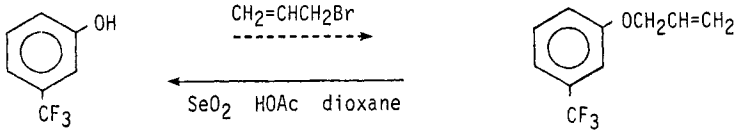


Tetr Lett (1970) 343

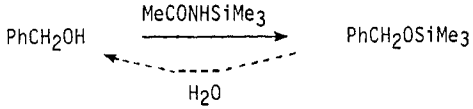


JCS (1965) 2205
(1968) 1903

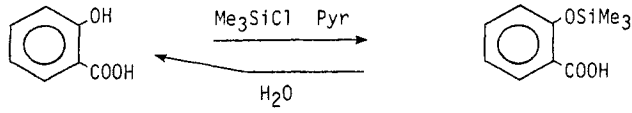
Further examples of the cleavage of ethers are included in section 39 (Alcohols and Phenols from Ethers and Epoxides)



Tetr Lett (1970) 2885

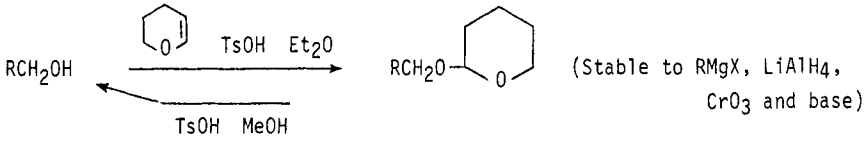


Ber (1964) 97 2196
For trimethylsilyl ethers of 3ry alcohols see Chem Comm (1968) 466



JOC (1957) 22 592

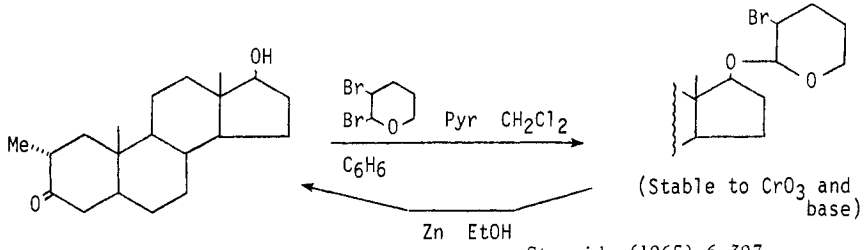
For trimethylsilyl ethers of hindered phenols see JACS (1966) 88 3390



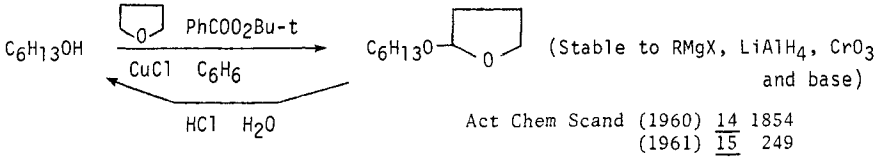
JACS (1969) 91 4318

For tetrahydropyranyl ethers of 3ry alcohols see Tetrahedron (1961) 13 241

and Steroids (1964) 4 229

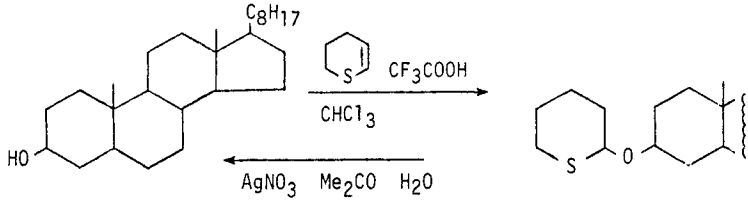


Steroids (1965) 6 397

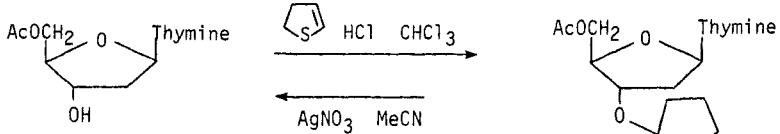


Act Chem Scand (1960) 14 1854

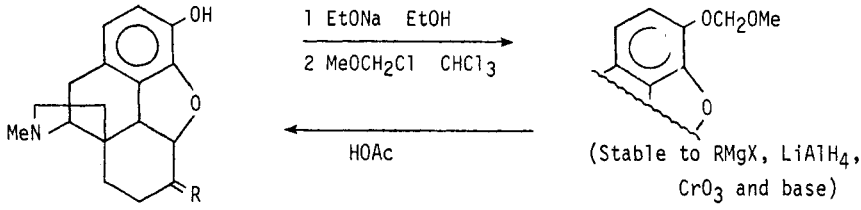
(1961) 15 249



JOC (1966) 31 2333

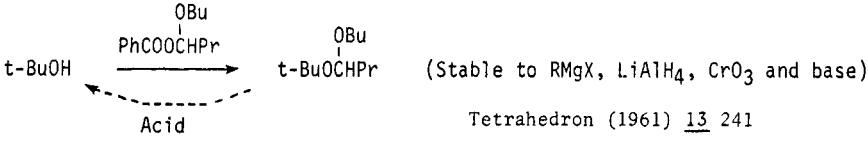


JOC (1966) 31 2333



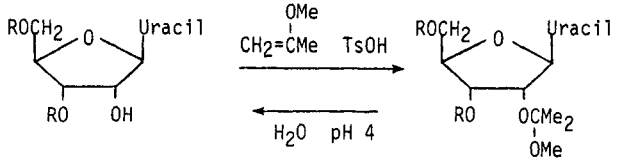
(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

J Med Chem (1966) 9 1
JACS (1957) 79 5792

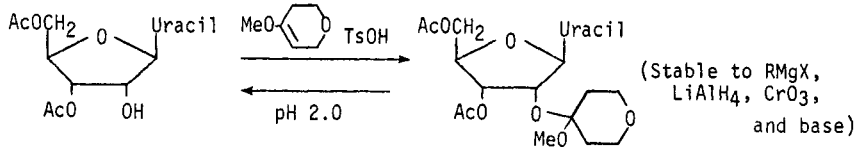


(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

Tetrahedron (1961) 13 241

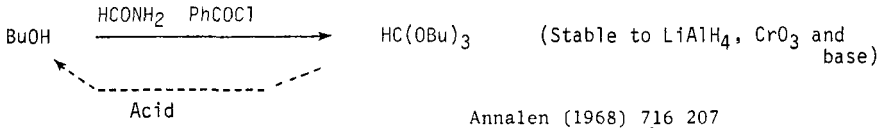


JACS (1967) 89 3366
Tetrahedron (1970) 26 1023

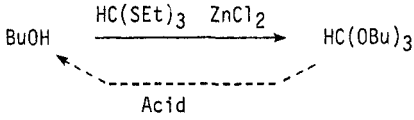


(Stable to RMgX, $LiAlH_4$, CrO_3, and base)

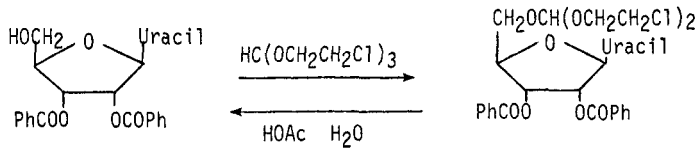
JACS (1967) 89 3366
Tetrahedron (1970) 26 1023



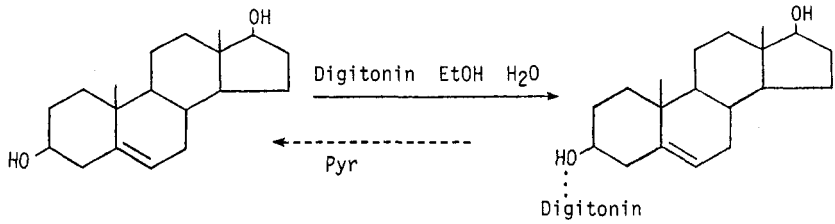
Annalen (1968) 716 207
Rec Trav Chim (1969) 88 897



JACS (1948) 70 2268



Tetr Lett (1969) 4443



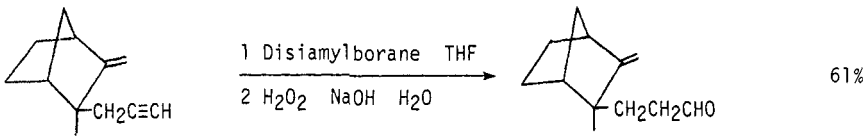
(Stable to CrO_3)

JACS (1960) 82 1257

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

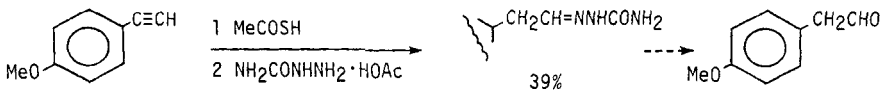
Chapter 4 PREPARATION OF ALDEHYDES

Section 46 Aldehydes from Acetylenes



61%

Tetr Lett (1970) 41
JACS (1969) 91 4771
Org React (1963) 13 1

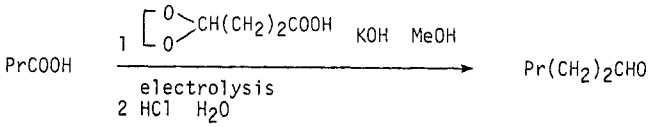


JCS (1949) 619

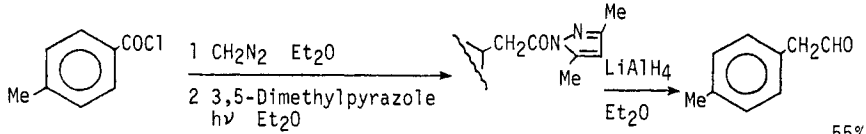
Section 47 Aldehydes from Carboxylic Acids, Acid Halides and Anhydrides

Review: The Synthesis of Aldehydes from Carboxylic Acids

Org React (1954) 8 218

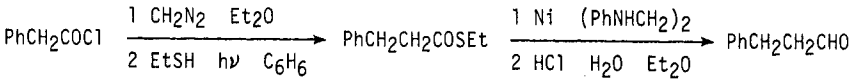


Bull Chem Soc Jap (1965) 38 922

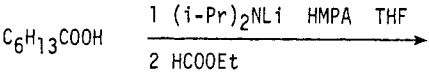


55%

Annalen (1961) 642 121

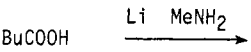


Ber (1959) 92 528
Org React (1954) 8 218



65%

Tetr Lett (1970) 699



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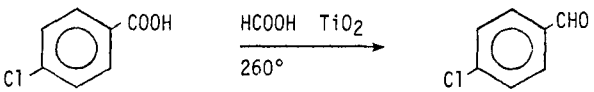
JACS (1970) 92 5774

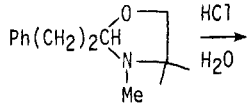


36%

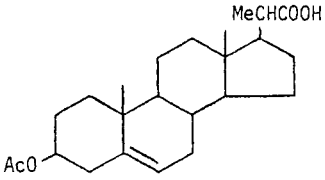
JCS (1943) 84
JOC (1963) 28 3029

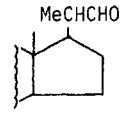
$C_8H_{17}COOH$ —(Na-Hg H_3BO_3 $NaHSO_3$ / Na_2CO_3 H_2O)→ $C_8H_{17}CHO$ 36%

J Soc Chem Ind (1943) 62 128

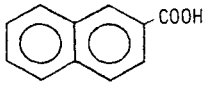
$Ph(CH_2)_2COOH$ —(1 Me_2CCH_2OH (NH_2) / 2 MeI $MeNO_2$ / 3 $NaBH_4$ MeOH / 4 NaOH H_2O)→  —(HCl / H_2O)→ $Ph(CH_2)_2CHO$

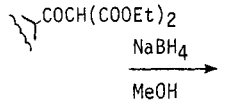
J Heterocyclic Chem (1966) 3 531

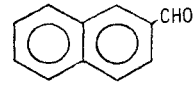


—(1 N,N-Carbonyl diimidazole / THF / 2 $LiAl(OBu\text{-}t)_3H$ THF)→ 

JOC (1970) 35 458
Annalen (1962) 654 119

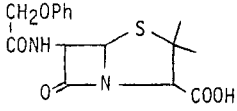


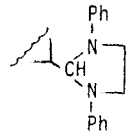
—(1 ClCOOEt NEt_3 / C_6H_6 / 2 $EtOMgCH(COOEt)_2$ / EtOH)→ 

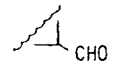
—($NaBH_4$ / MeOH)→ 

79%

Ber (1965) 98 3040

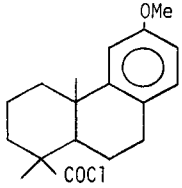


—(1 ClCOOEt NEt_3 / 2 NaSH / 3 Ni $(PhNHCH_2)_2$ / HOAc THF)→ 

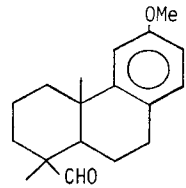
—(TsOH / CH_2Cl_2)→ 

<47%

JOC (1966) 31 1922



H_2 Pd-$BaSO_4$ / xylene



80%

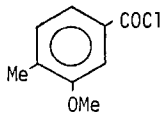
JACS (1942) 64 928
(1940) 62 49
Org React (1948) 4 362

PhCOCl $\xrightarrow{Bu_3SnH}$ PhCHO

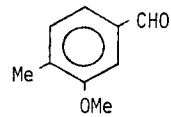
JOC (1960) 25 284

PhCOBr $\xrightarrow{h\nu\ \ Et_2O}$ PhCHO 80%

Angew (1965) 77 169
(Internat Ed 4 146)



$LiAl(OBu\text{-}t)_3H$ / diglyme



62%

J Med Chem (1970) 13 26
JACS (1956) 78 252

t-BuCOCl $\xrightarrow[Et_3N\ \ C_6H_6]{NH,\ CH_2\text{-}CH_2}$ t-BuCON(CH$_2$)CH$_2$ $\xrightarrow[Et_2O]{LiAlH_4}$ t-BuCHO

JACS (1961) 83 4549

$C_{15}H_{31}COCl \xrightarrow[2\ HOAc]{1\ CH_2N_2\ \ Et_2O} C_{15}H_{31}COCH_2OAc \xrightarrow[2\ Pb(OAc)_4\ HOAc]{1\ Al(OPr\text{-}i)_3\ \ i\text{-}PrOH} C_{15}H_{31}CHO$ 56%

Org React (1954) 8 218

$PhCOCl \xrightarrow{EtSH\ \ Pyr} PhCOSEt \xrightarrow[H_2O]{Ni\ \ EtOH} PhCHO$ <62%

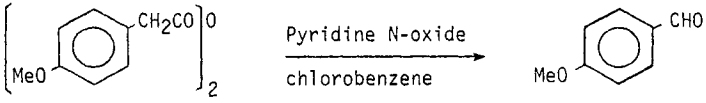
JACS (1946) 68 1455
Tetr Lett (1964) 1763
Org React (1954) 8 218

$PhCOCl \xrightarrow{N_2H_4} PhCONHNH_2 \xrightarrow[2\ Na_2CO_3\ \ ethylene\ glycol]{1\ PhSO_2Cl\ \ Pyr} PhCHO$ ~60%

Org React (1954) 8 218
JOC (1961) 26 3664

$BuCOCl \xrightarrow[2\ H_2SO_4\ \ H_2O]{1\ Quinoline\ \ HCN\ \ C_6H_6} BuCHO$ 62%

JACS (1941) 63 2021
Org React (1954) 8 218



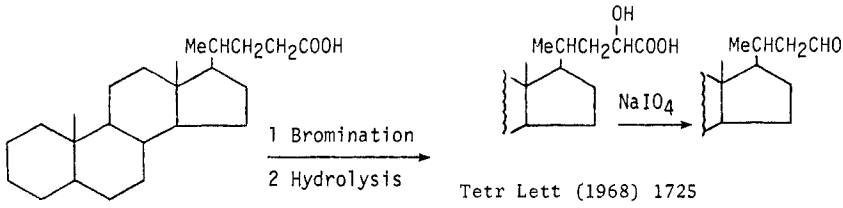
69%

Tetr Lett (1965) 233

$C_6H_{13}CH_2COCl \xrightarrow[C_6H_6\ \ 2\ HCl]{1\ BuSH\ \ ZnCl_2} C_6H_{13}CH{=}C(SBu)_2 \xrightarrow[2\ N_2H_4\ \ MeOH]{1\ Perphthalic\ acid\ \ Et_2O}$

$C_6H_{13}CH{=}NNH_2 \dashrightarrow C_6H_{13}CHO$

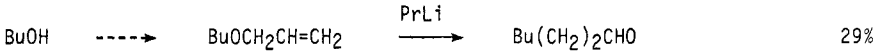
Rec Trav Chim (1959) 78 354



Tetr Lett (1968) 1725

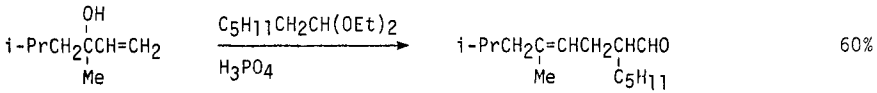
Aldehydes may also be prepared from carboxylic acids via amide or ester intermediates. See section 51 (Aldehydes from Amides) and section 53 (Aldehydes from Esters)

Section 48 Aldehydes from Alcohols



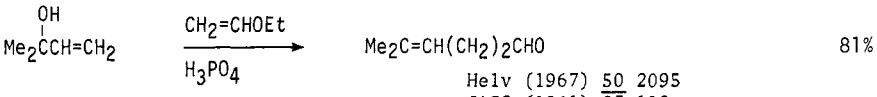
29%

Tetr Lett (1969) 821



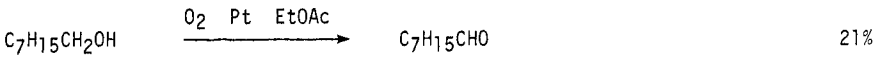
60%

Helv (1967) 50 2095
Tetr Lett (1961) 493



81%

Helv (1967) 50 2095
JACS (1961) 83 198



21%

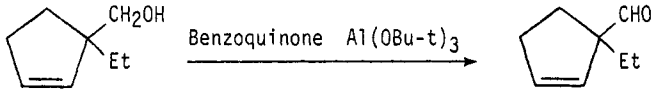
JACS (1955) 77 190
Angew (1957) 69 600

For application to allylic alcohols see Helv (1957) 40 265

$BuCH_2OH \xrightarrow{Li\ \ NH_2CH_2CH_2NH_2} BuCHO$ 66%

Applicable to benzylic alcohols

JOC (1962) 27 2662

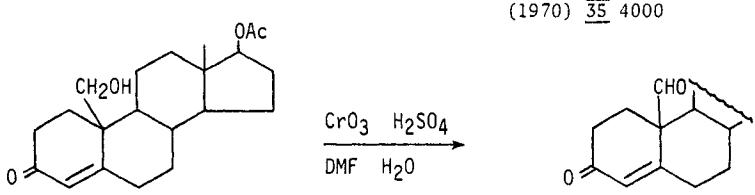


Chem Comm (1969) 799

$C_6H_{13}CH_2OH \xrightarrow{CrO_3\text{-}Pyr\ \ CH_2Cl_2} C_6H_{13}CHO$ 93%

Applicable to allylic and benzylic alcohols

Tetr Lett (1968) 3363
JOC (1961) 26 4814
(1970) 35 4000



80%

Helv (1968) 51 772

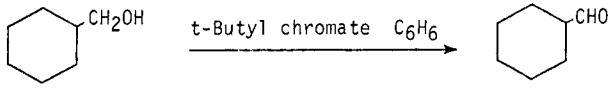
$PhCH{=}CHCH_2OH \xrightarrow[Pyr\cdot HCl\ \ Pyr]{Na_2Cr_2O_7} PhCH{=}CHCHO$ 80%

Chem Ind (1969) 1594

$EtCH_2OH \xrightarrow{K_2Cr_2O_7\ \ H_2SO_4\ \ H_2O} EtCHO$ 45-49%

Org Synth (1943) Coll Vol 2 541

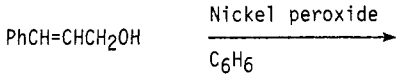
For application to allylic alcohols see Bull Soc Chim Fr (1933) 53 301
and Ber (1947) 80 137



40%

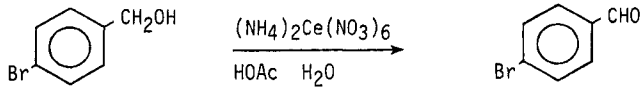
Applicable to allylic and benzylic alcohols

Bull Chem Soc Jap (1965) 38 1503 893 1141



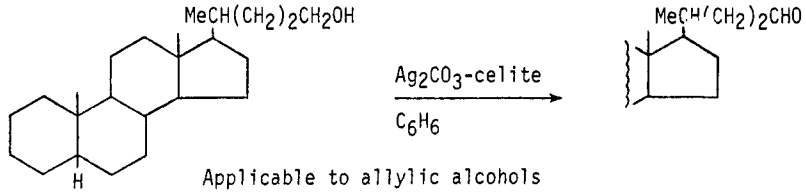
86%

JOC (1962) 27 1597
JCS (1969) C 2173



93%

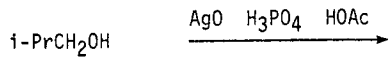
JCS (1965) 5777
JOC (1967) 32 2349 3865



95%

Applicable to allylic alcohols

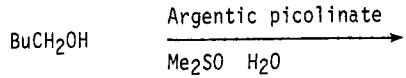
Compt Rend (1968) C 267 900



30%

Applicable to allylic alcohols

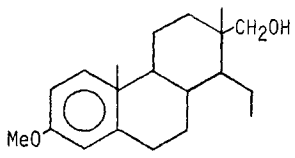
Tetr Lett (1967) 4193



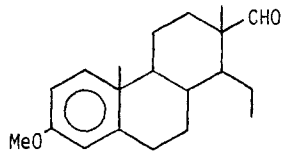
74%

Applicable to benzylic alcohols

Can J Chem (1969) 47 1649



MnO_2 MeCN



76%

Proc Chem Soc (1964) 110
Chem Comm (1966) 121

$PhCH{=}CHCH_2OH \xrightarrow{MnO_2 \quad CCl_4} PhCH{=}CHCHO$

JCS (1952) 1094
JACS (1955) 77 4399

$PrCH_2OH \xrightarrow{Pb(OAc)_4 \quad Pyr} PrCHO$ 70%

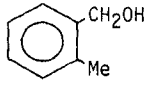
Applicable to allylic and benzylic alcohols

Tetr Lett (1964) 3071

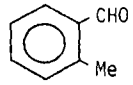
$C_5H_{11}CH_2OH \xrightarrow{INO_3\text{-}Pyr \quad CHCl_3} C_5H_{11}CHO$ 20%

Applicable to benzylic alcohols

JCS C (1970) 676

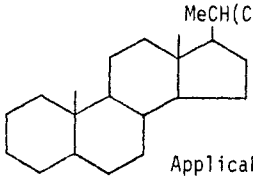


N_2O_4 CCl_4

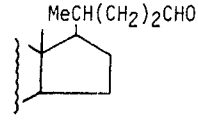


95%

JCS (1955) 1110



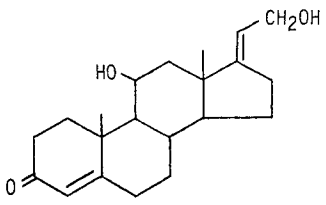
DCC CF_3COOH
Me_2SO Pyr C_6H_6



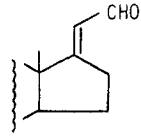
85%

Applicable to benzylic alcohols

JACS (1965) 87 5670
Chem Rev (1967) 67 247



$SO_3 \cdot Pyr$ Me_2SO / Et_3N



70%

JACS (1967) 89 5505

$C_7H_{15}CH_2OH$ ----> $C_7H_{15}CH_2OTs$ $\xrightarrow{NaHCO_3\ \ Me_2SO}$ $C_7H_{15}CHO$ ~78%

Applicable to benzylic alcohols

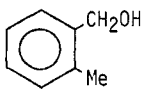
JACS (1959) 81 4113

$C_5H_{11}CH_2OH$ $\xrightarrow{COCl_2\ \ Et_2O}$ $C_5H_{11}CH_2OCOCl$ $\xrightarrow[2\ Et_3N]{1\ Me_2SO}$ $C_5H_{11}CHO$ 68%

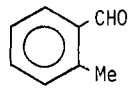
JCS (1964) 1855

$PhCH_2OH$ $\xrightarrow{KOCl\ \ MeOH\ \ H_2O}$ PhCHO 77%

JOC (1961) 26 1046



N-Chlorosuccinimide / Pyr



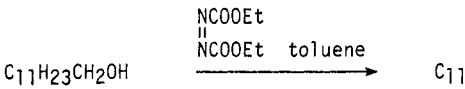
71%

Bull Soc Chim Belg (1951) 60 54
Compt Rend (1954) 238 2538
Chem Rev (1963) 63 21

i-$PrCH_2OH$ $\xrightarrow{K_2S_2O_8\ \ AgNO_3\ \ H_2O}$ i-PrCHO 31%

JACS (1954) 76 6345

For application to benzylic alcohols see JCS (1960) 1332



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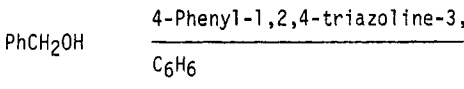
Applicable to benzylic alcohols

JOC (1967) 32 727



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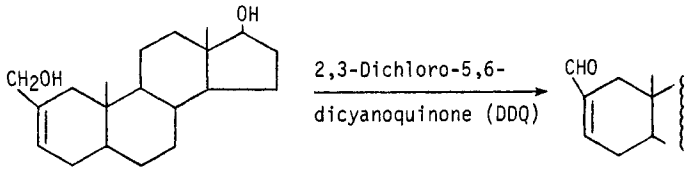
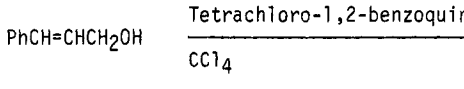
Chem Comm (1966) 744
JCS C (1969) 1474



Applicable only to allylic and benzylic alcohols

J Med Chem (1962) 5 409
Chem Rev (1967) 67 153



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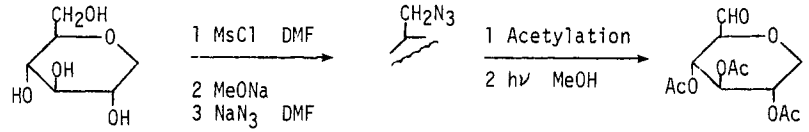
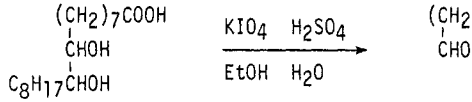
Applicable only to allylic and benzylic alcohols

JCS (1956) 3070

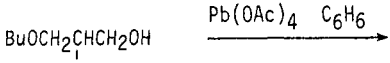


Carbohydrate Res (1968) 8 366



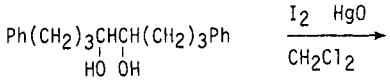
76%

Org React (1944) 2 341



57%

JACS (1945) 67 39
JOC (1970) 35 249



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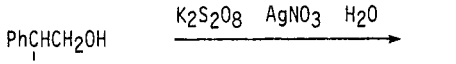
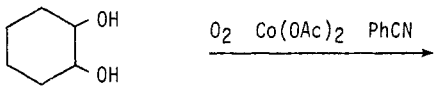
JCS C (1969) 383

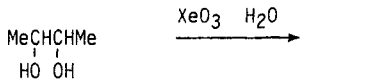


61%

JACS (1954) 76 6345

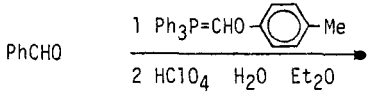


Tetr Lett (1968) 5689



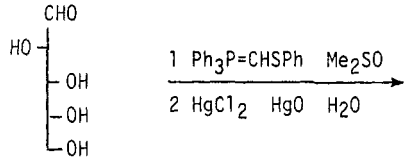
JACS (1964) 86 2078

Section 49 Aldehydes from Aldehydes



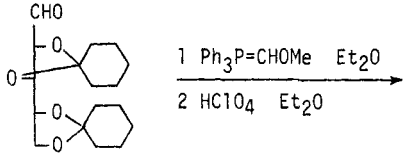
55%

Ber (1962) 95 2514



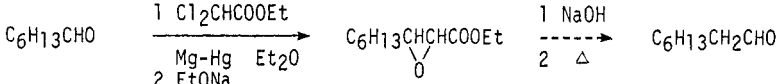
36%

Tetr Lett (1969) 3665

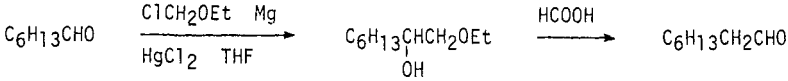


28%

Carbohydrate Res (1969) 10 184

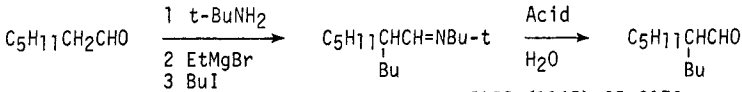


Compt Rend (1937) 204 272
Org React (1949) 5 413



10%

Bull Soc Chim Fr (1959) 459



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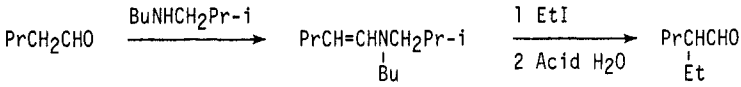
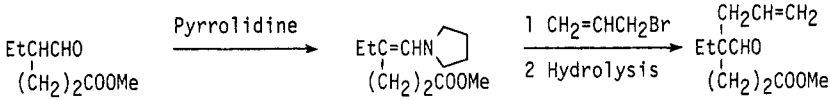
JACS (1963) 85 2178

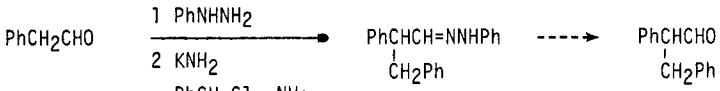


78%

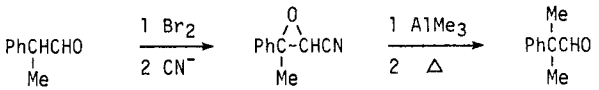
Chem Comm (1967) 510



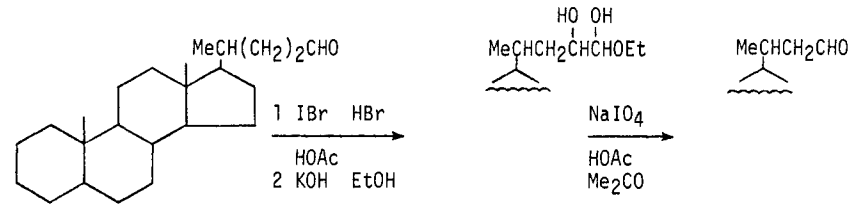
Chem Comm (1965) 197
JACS (1963) 85 207
Angew (1960) 72 169



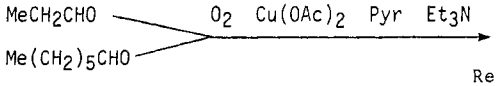
JACS (1967) 89 463



Tetr Lett (1970) 2947



Chem Comm (1968) 851
Tetr Lett (1970) 5229

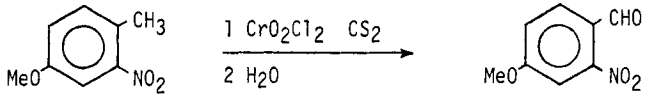


Rec Trav Chim (1966) 85 437

Some of the methods included in section 57 (Aldehydes from Ketones) may also be applied to the preparation of aldehydes from aldehydes

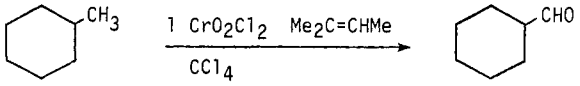
Section 50 Aldehydes from Alkyls

Reactions in which methyl groups are converted into aldehyde (RMe → RCHO) are included in this section. For reactions in which a hydrogen is replaced by aldehyde, RH → RCHO (R=alkyl, vinyl or aryl), see section 56 (Aldehydes from Hydrides)



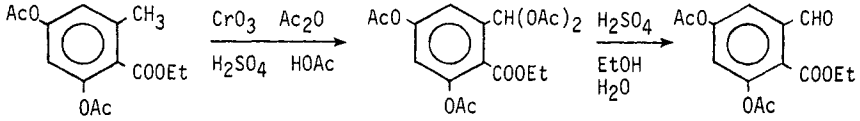
50%

JCS (1949) S230

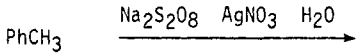


25%

JACS (1951) 73 221

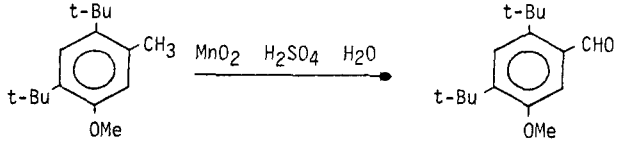


JOC (1968) 33 4176
Org Synth (1943) Coll Vol 2 441



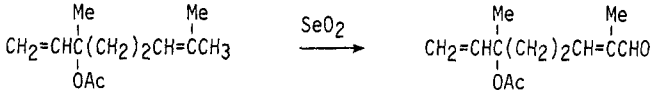
50%

JCS (1960) 1332

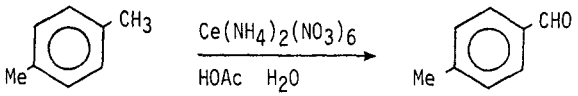


23%

JOC (1951) 16 586

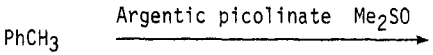


Chem Comm (1968) 1277
Org React (1949) 5 331

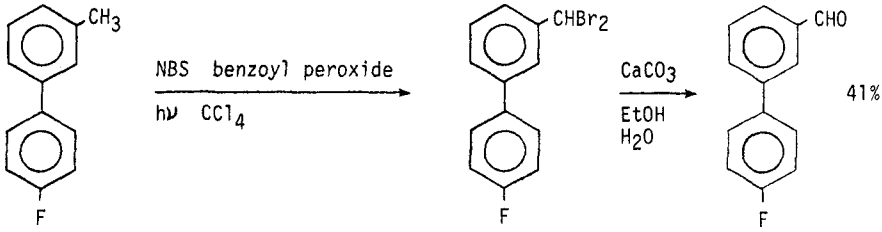


73%

JOC (1966) 31 2033
JCS C (1970) 1630



Tetr Lett (1967) 415



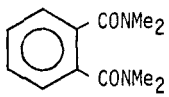
41%

JACS (1966) 88 3318
(1956) 78 1689
Org React (1954) 8 197

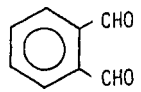
Section 51 Aldehydes from Amides

$C_{15}H_{31}CONMe_2 \xrightarrow{NaAlH_4\ THF} C_{15}H_{31}CHO$ 78%

Tetrahedron (1969) 25 5555

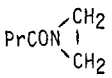


$\xrightarrow{LiAlH_4\ THF\ Et_2O}$



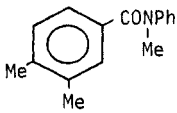
~70%

Ber (1951) 84 625

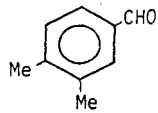


$\xrightarrow{LiAlH_4\ Et_2O}$ PrCHO 88%

JACS (1961) 83 4549

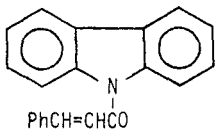


$\xrightarrow{LiAlH_4\ THF}$



57%

Ber (1955) 88 301
Org React (1954) 8 218

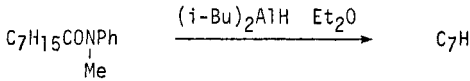


$\xrightarrow{LiAlH_4\ Et_2O}$ PhCH=CHCHO 45%

JOC (1953) 18 1190

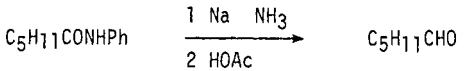
$BuCONMe_2 \xrightarrow{LiAl(OEt)_3H\ Et_2O} BuCHO$ 92%

JACS (1964) 86 1089



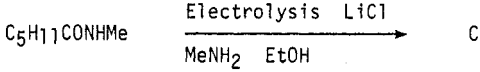
56%

Izv (1959) 2146
(Chem Abs 54 10932)



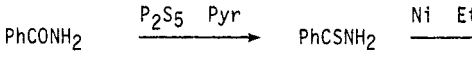
53%

Aust J Chem (1955) 8 512

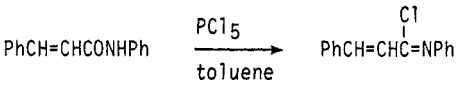


50%

JOC (1970) 35 1210

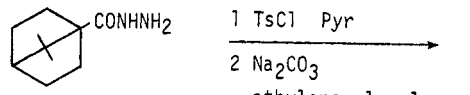


JACS (1952) 74 3936
Org React (1962) 12 356



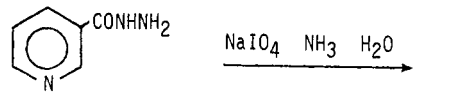
92%

Org React (1954) 8 218



60%

JOC (1961) 26 3664
Org React (1954) 8 218



60-70%

JACS (1952) 74 5796

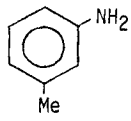
$PhCH_2NHAc$ —(Argentic picolinate, Me_2SO)→ $PhCHO$

Tetr Lett (1967) 415

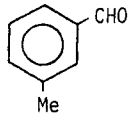
$EtNHAc$ —($K_2S_2O_8$, K_2HPO_4, H_2O)→ $MeCHO$ 48%

JOC (1964) 29 3632

Section 52 Aldehydes from Amines



1 $NaNO_2$ NaOAc HCl H_2O
2 HCH=NOH NaOAc $CuSO_4$ Na_2SO_3
3 HCl H_2O



41%

JCS (1954) 1297

$PhCH_2NH_2$ —(1 2,4-Dinitrobenzaldehyde Pyr; 2 HCl H_2O)→ $PhCHO$ 63%

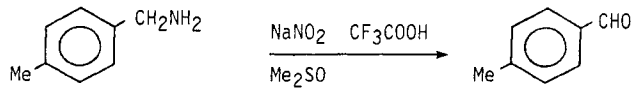
JCS (1954) 209

$C_{11}H_{23}CH_2NH_2$ —(1 3,5-Dinitromesitylglyoxal C_6H_6; 2 Diazabicyclononene Me_2SO THF; 3 $(COOH)_2$ MeOH THF)→ $C_{11}H_{23}CHO$ 34%

JACS (1969) 91 1429

$C_5H_{11}CH_2NH_2$ —(Hexamine HCHO; HOAc H_2O)→ $C_5H_{11}CHO$ 42%

JCS (1953) 1737
Org React (1954) 8 197



60%

Angew (1965) 77 811
(Internat Ed 4 787)

$PhCH_2NEt_2$ $\xrightarrow[HOAc\ \ H_2O]{NaNO_2\ \ NaOAc}$ PhCHO

JACS (1967) 89 1147

$MeCH_2NH_2$ $\xrightarrow{OF_2\ \ freon\ 11}$ MeCH=NOH ⟶ MeCHO 44%

JACS (1964) 86 1392

$(PrCH_2)_3N$ $\xrightarrow{O_3\ \ H_2O}$ PrCHO 47%

JCS (1964) 711

$(PrCH_2)_3N$ $\xrightarrow{Br_2\ \ H_2O\ \ pH\ 5}$ PrCHO 84%

JACS (1968) 90 3502

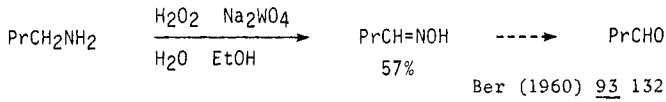
$(EtCH_2)_3N$ $\xrightarrow{NBS\ \ dioxane\ \ H_2O}$ EtCHO 68%

JCS (1957) 4905
Chem Rev (1963) 63 21

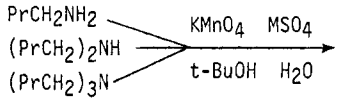
$PhCH_2CH_2NH_2$ $\xrightarrow[NaHCO_3\ \ Et_2O]{1\ t\text{-Butyl hypochlorite}}$ $PhCH_2CHO$ 39%

2 EtONa EtOH
3 H_2SO_4 H_2O

JACS (1954) 76 5554

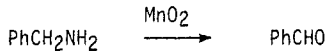


Ber (1960) 93 132



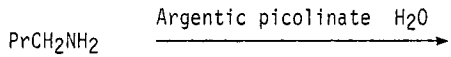
(M=Ca or Zn)

JOC (1967) 32 3129



34%

JACS (1955) 77 4399

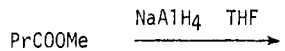


14%

JCS (1965) 4962
Tetr Lett (1967) 415

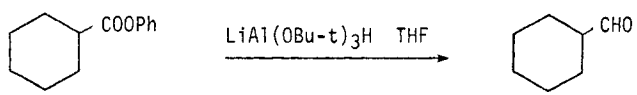
Aldehydes may also be prepared by oxidation of N-acyl amines. See section 51 (Aldehydes from Amides)

Section 53 Aldehydes from Esters



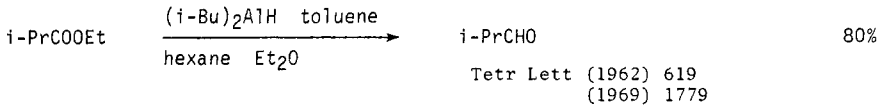
81%

Tetr Lett (1963) 2087

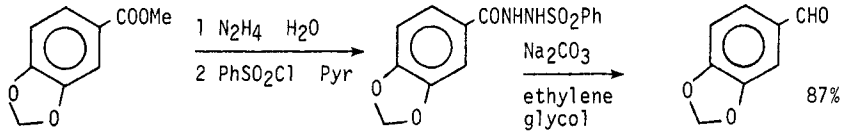


70%

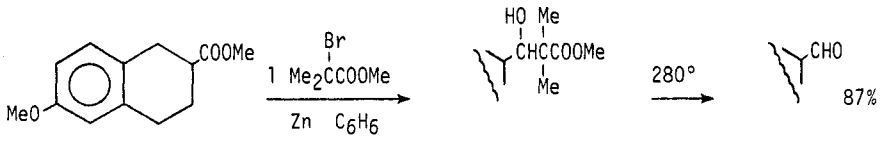
JOC (1966) 31 283



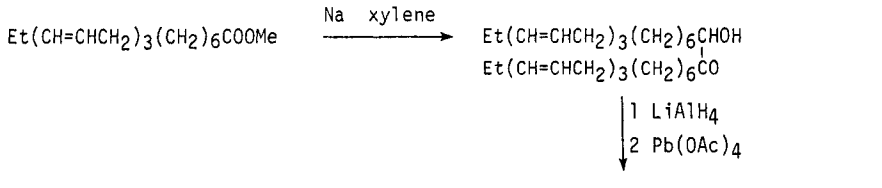
Tetr Lett (1962) 619
(1969) 1779



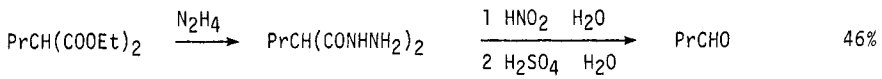
JCS (1936) 584
JOC (1961) 26 3664
Org React (1954) 8 218



Bull Soc Chim Fr(1965) 1864

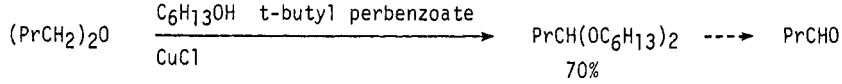


J Am Oil Chem Soc (1960) 37 425
(Chem Abs 54 23373)

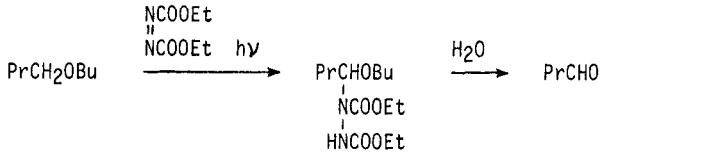


Org React (1946) 3 337

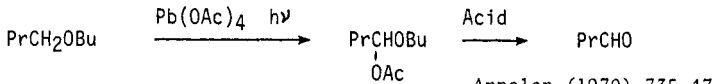
Section 54 Aldehydes from Ethers and Epoxides



Angew Chem (1961) 73 65
Act Chem Scand (1961) 15 249
Tetrahedron (1961) 13 241

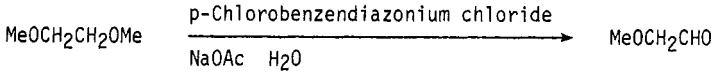


Chem Comm (1965) 259



Annalen (1970) 735 47

JACS (1964) 86 3180

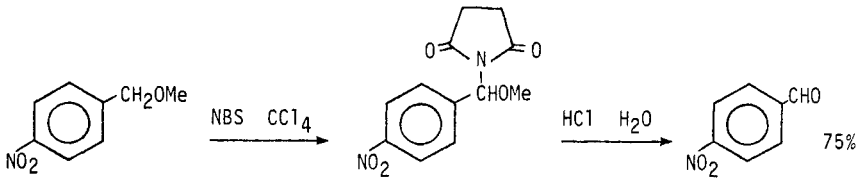


Angew (1958) 70 211

Annalen (1969) 728 12

$PhCH_2OMe \xrightarrow{Br_2\ HOAc\ H_2O} PhCHO$ 83%

JACS (1967) 89 3550



JOC (1958) 23 1490
Angew (1959) 71 349

$PhCH{=}CHCH_2OMe \xrightarrow{SeO_2\ HOAc\ dioxane} PhCH{=}CHCHO$ 66%

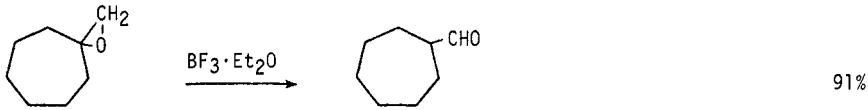
Tetr Lett (1970) 2885

$PrCH_2OMe \xrightarrow[2\ Acid]{1\ O_2\ Ph_2CO\ h\nu} PrCHO$ 55%

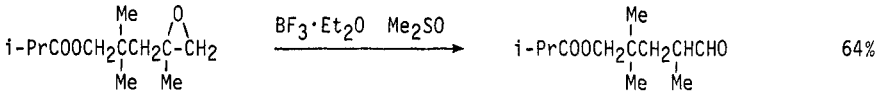
Ber (1963) 96 509

$MeCH_2OCPh_3 \xrightarrow{262^\circ} MeCHO$

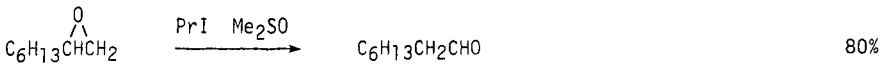
JACS (1930) 52 753
(1924) 46 2580



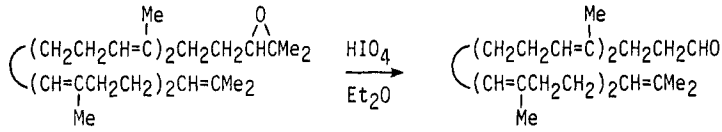
JACS (1962) 84 867
Chem Rev (1959) 59 737



JOC (1965) 30 3480

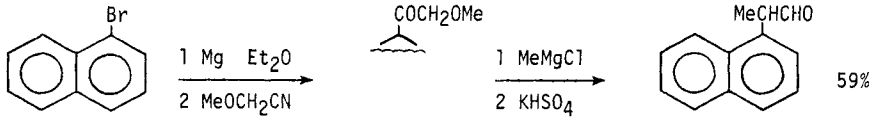


Chem Comm (1968) 227

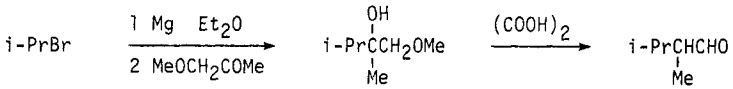


Chem Comm (1968) 1067

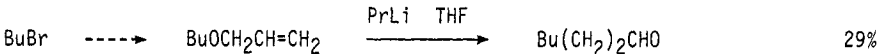
Section 55 Aldehydes from Halides and Sulfonates



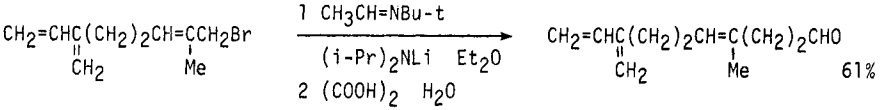
JACS (1939) 61 2134



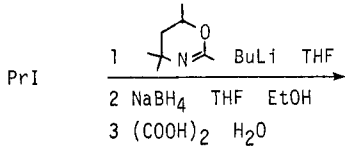
JACS (1946) 68 2339



Tetr Lett (1969) 821

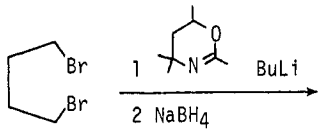


Helv (1967) 50 2440



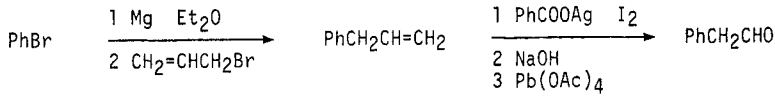
65%

JACS (1969) 91 763 5886
(1970) 92 6676

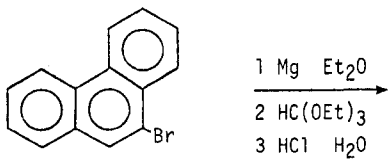


36%

JACS (1969) 91 765

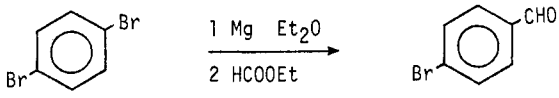


Helv (1934) 17 351



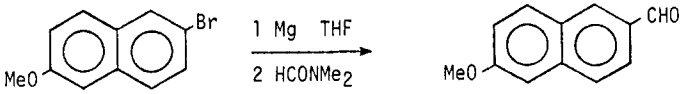
40-42%

Org Synth (1955) Coll Vol 3 701
(1943) Coll Vol 2 323
Ber (1970) 103 643



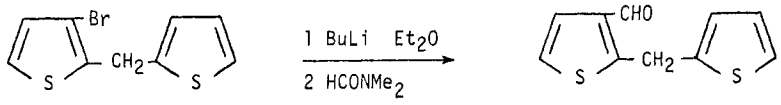
40%

Annalen (1912) 393 215

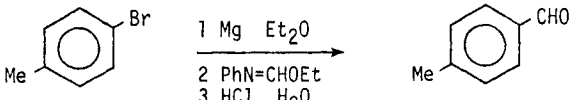


80%

Chimia (1964) 18 141
JCS (1956) 4691

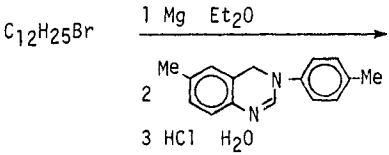


JOC (1970) 35 711



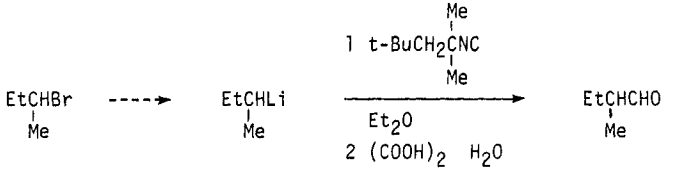
82%

JOC (1941) 6 489



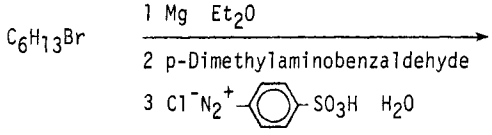
73%

JACS (1955) 77 5118



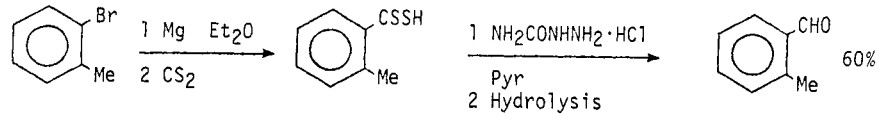
92%

JACS (1969) 91 7778
(1970) 92 6675

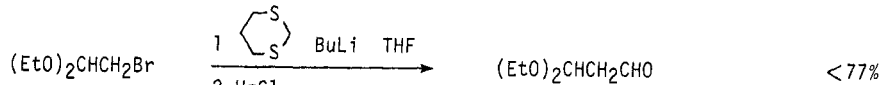


75%

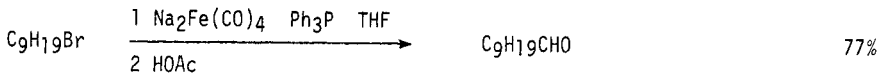
JOC (1960) 25 1691
(1962) 27 279



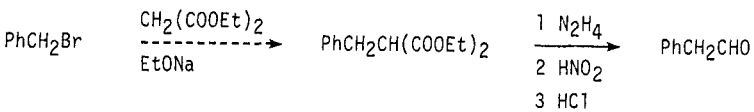
JOC (1941) 6 489



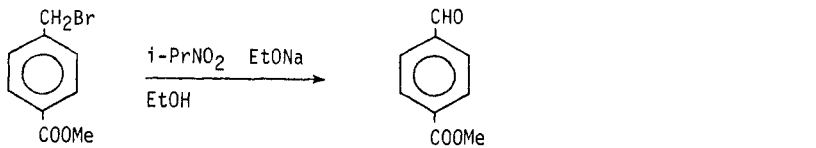
Angew (1965) 77 1134
(Internat Ed 4 1075)



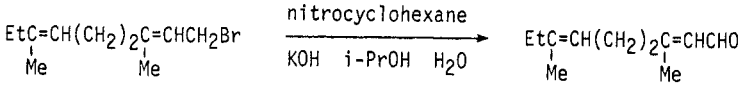
JACS (1970) 92 6080



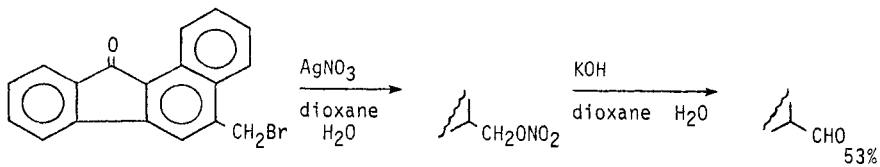
Org React (1946) 3 337



JACS (1949) 71 1767
Org Synth (1963) Coll Vol 4 932



Zh Obshch Khim (1959) 29 3965
(Chem Abs 54 21170)



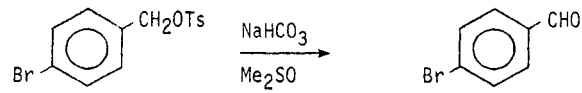
JACS (1961) 83 193

$C_7H_{15}CH_2X \xrightarrow[CHCl_3]{Me_3\overset{+}{N}\overset{-}{O}} C_7H_{15}CHO$ 50% (X=I) 55% (X=OTs)

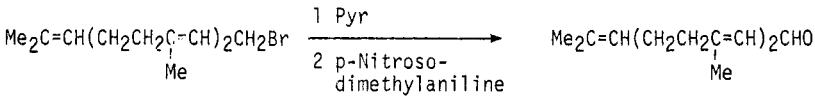
Ber (1961) 94 1360

$C_6H_{13}CH_2Br \xrightarrow[MeCN]{AgOTs} C_6H_{13}CH_2OTs \xrightarrow[Me_2SO]{NaHCO_3} C_6H_{13}CHO$ 74%

JACS (1959) 81 4113



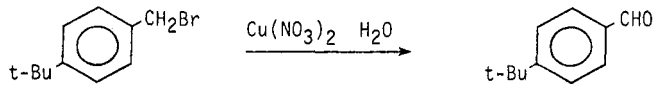
JACS (1959) 81 4113
Chem Rev (1967) 67 247



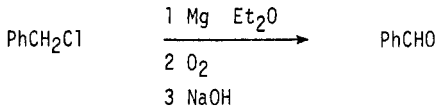
Helv (1941) 24 1039

$C_6H_{13}CH_2I \xrightarrow[2\ HOAc]{1\ Hexamine,\ CHCl_3} C_6H_{13}CHO$ 41%

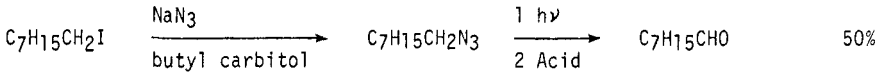
Org React (1954) 8 197



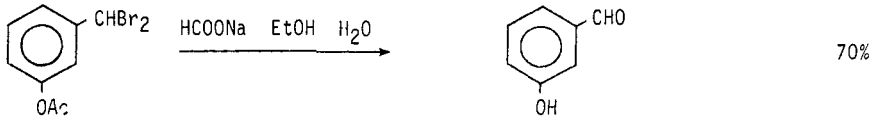
JCS (1935) 1847



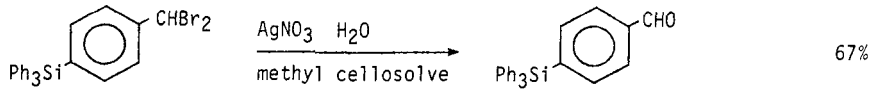
JACS (1955) 77 6032



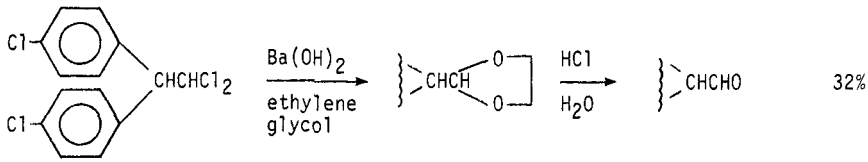
Tetrahedron (1965) 21 2877



JCS (1955) 1628



JACS (1956) 78 1689



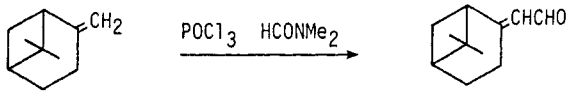
Ber (1959) 92 900

75%

JACS (1933) 55 1136

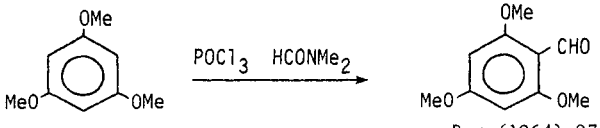
Section 56 Aldehydes from Hydrides (RH)

Reactions in which a hydrogen is replaced by CHO, e.g. RH ⟶ RCHO (R=vinyl, ethinyl or aryl), are included in this section. For reactions in which alkyl groups are oxidized to aldehyde, e.g. RCH_3 ⟶ RCHO, see section 50 (Aldehydes from Alkyls)

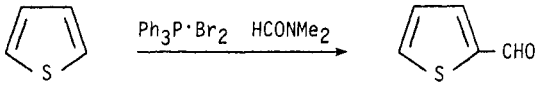


41%

Z Chem (1967) 7 346
Tetrahedron (1969) 25 4535

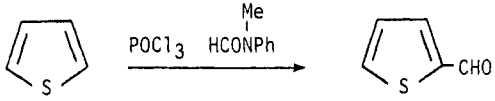


Ber (1964) 97 1252
JCS C (1969) 913



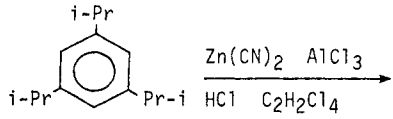
45%

Annalen (1968) 718 24



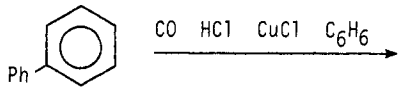
71%

Org Synth (1963) Coll Vol 4 915
(1955) Coll Vol 3 98



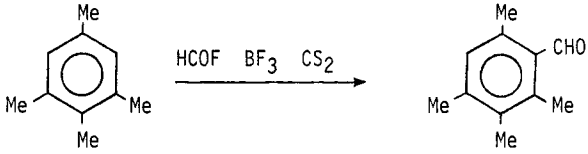
66%

JACS (1942) 64 30



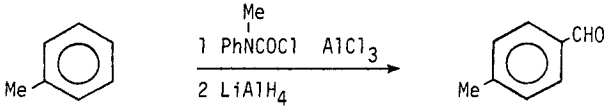
73%

Org React (1949) 5 290
Org Synth (1943) Coll Vol 2 583

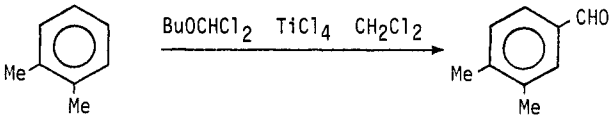


72%

JACS (1960) 82 2380



Ber (1955) 88 301



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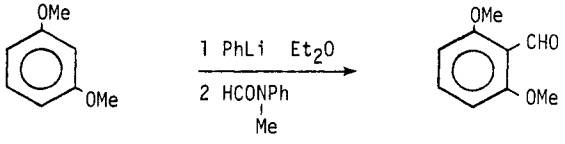
Ber (1960) 93 88

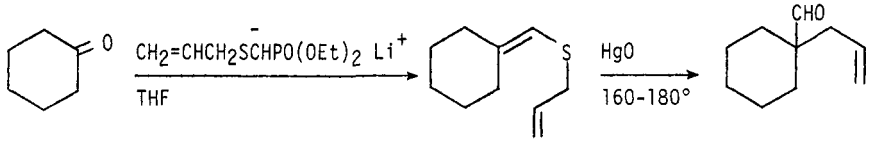


Org React (1954) 8 258

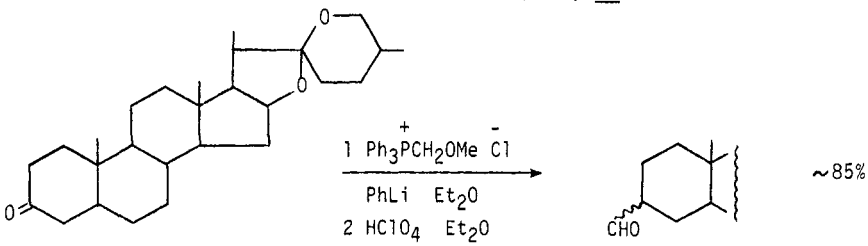
$Me(CH_2)_3C{\equiv}CH \xrightarrow[2\ HCONMe_2]{1\ EtMgBr} Me(CH_2)_3C{\equiv}CCHO$

JCS (1958) 1054

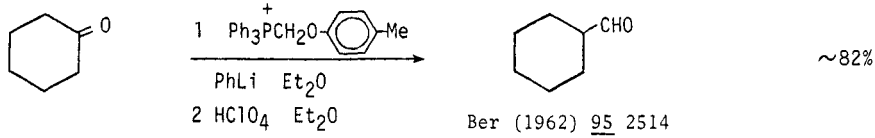
Section 57 Aldehydes from Ketones



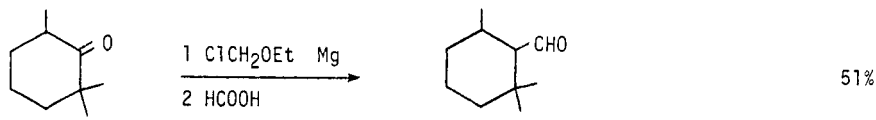
JACS (1970) 92 5522



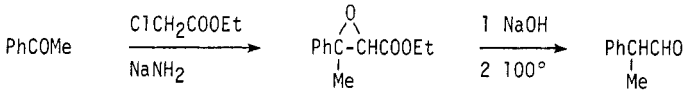
JACS (1958) 80 6150
Org React (1965) 14 270



Ber (1962) 95 2514

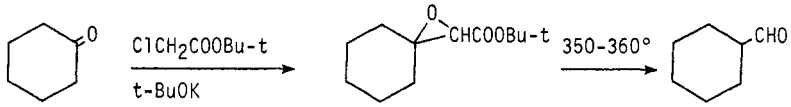


JACS (1968) 90 3282
Compt Rend (1963) 256 1996



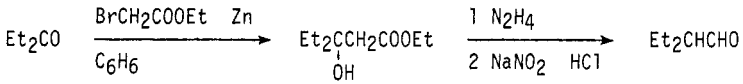
42%

Org React (1949) 5 413
JOC (1970) 35 1600
Chem Rev (1955) 55 283



39%

JACS (1963) 85 955



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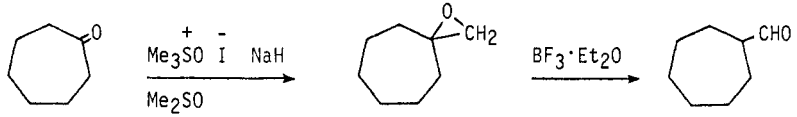
JACS (1951) 73 4199



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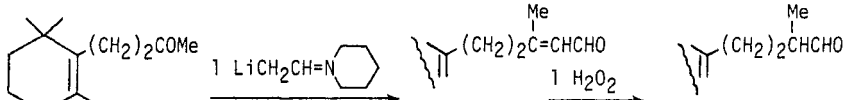
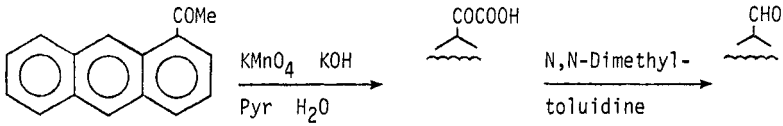
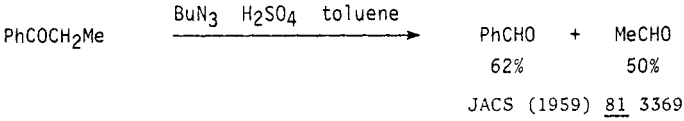
JACS (1962) 84 867



Tetr Lett (1970) 381



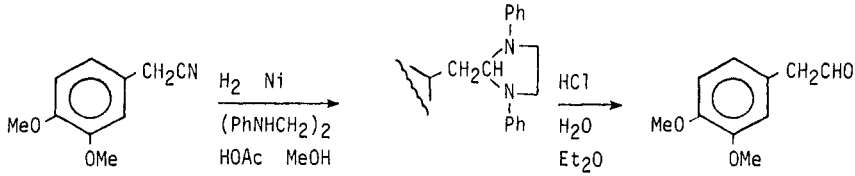
JACS (1965) 87 1247



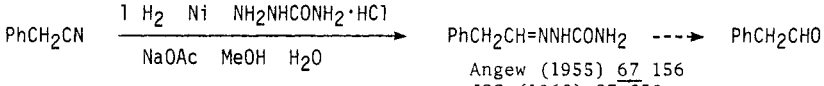
JACS (1959) 81 3369

Some of the methods included in section 49 (Aldehydes from Aldehydes) may also be applied to the preparation of aldehydes from ketones

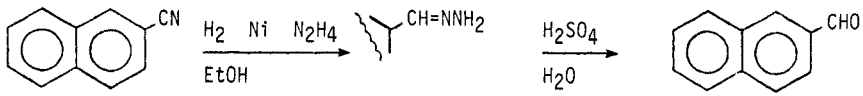
Section 58 Aldehydes from Nitriles



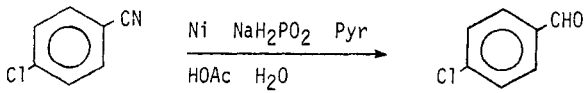
Ber (1957) 90 617



Angew (1955) 67 156
JOC (1962) 27 850

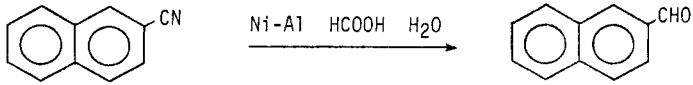


Gazz (1955) 85 1705
(Chem Abs 50 10037)



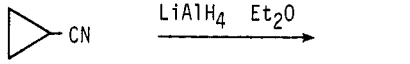
80%

JCS (1962) 3961



95%

JCS (1965) 5775
(1964) 5880



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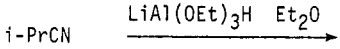
JACS (1951) 73 4047
Org React (1954) 8 252



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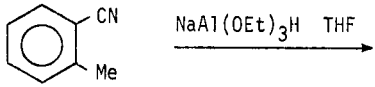
JACS (1964) 86 1085



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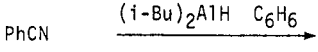
Annalen (1957) 607 24



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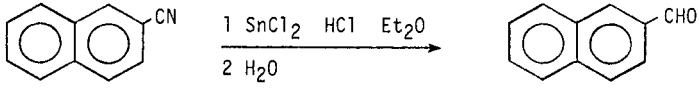
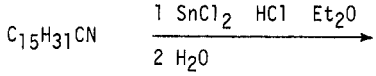
JOC (1959) 24 627

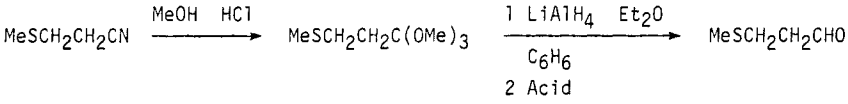


73-80%

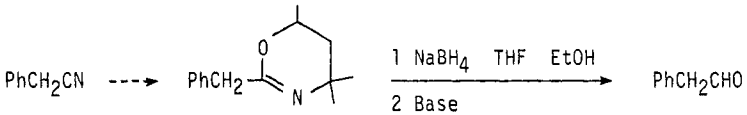
Org Synth (1955) Coll Vol 3 626



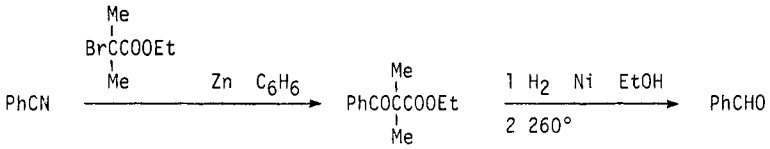
JCS (1925) 127 1874



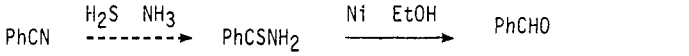
JACS (1951) 73 5005



Chem Comm (1967) 1163

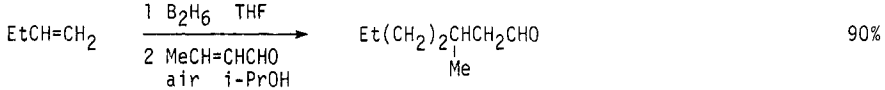


Compt Rend (1953) 236 826



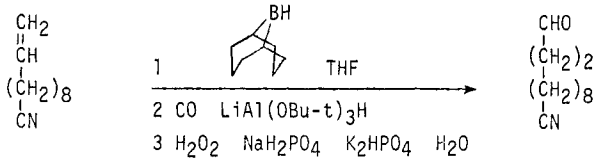
JACS (1952) 74 3936

Section 59 Aldehydes from Olefins



90%

JACS (1970) 92 714



JACS (1969) 91 4606

$Me_2C{=}CH_2$ —(1 B_2H_6 THF; 2 CO $LiAl(OMe)_3H$)→ Me_2CHCH_2CHO 91%

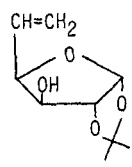
JACS (1968) 90 499 818

$C_6H_{13}CH{=}CH_2$ —(CO H_2 (100 psi) Rh-C; $(PhO)_3P$ toluene)→ $C_6H_{13}(CH_2)_2CHO$ 89%

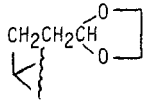
JOC (1969) 34 327
Chem Comm (1967) 305
(1965) 17

$PrCH(Me)CH{=}CH_2$ —(CO H_2 (200 atmos); $Co_2(CO)_8$ C_6H_6)→ $PrCH(Me)(CH_2)_2CHO$ ~62%

JACS (1968) 90 6847

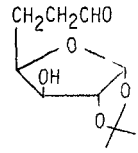


—( ; hν; Me_2CO)→

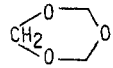


45%

—(Acid)→

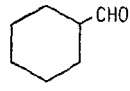


Tetr Lett (1969) 43
JOC (1968) 33 805

$C_6H_{13}CH{=}CH_2$ —(1  di-t-butyl peroxide; 2 HCl H_2O)→ $C_6H_{13}(CH_2)_2CHO$ ~20%

Tetr Lett (1968) 4339

—($Tl(NO_3)_2$ MeOH)→

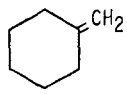


86%

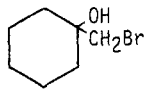
Acc Chem Res (1970) 3 338
Tetr Lett (1970) 5275

$(t\text{-}BuCH_2)_2C{=}CH_2$ —(1 $CrOCl_2$ CH_2Cl_2; 2 Zn)→ $(t\text{-}BuCH_2)_2CHCHO$ 80%

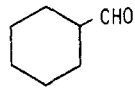
JOC (1968) 33 3970



(1 $Hg(OAc)_2$ Me_2CO; 2 NaBr; 3 Br_2 CCl_4)→



(i-PrMgBr; Et_2O C_6H_6)→



JOC (1968) 33 3953

$PhCH_2CH{=}CH_2$ —(DDQ C_6H_6)→ PhCH=CHCHO 50%

Chem Comm (1969) 773

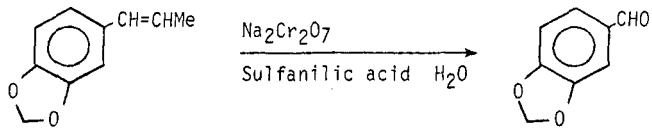
$C_8H_{17}CH{=}CH(CH_2)_7COOMe$ —(1 O_3 MeOH; 2 H_2 Pd-C MeOH EtOAc (or Zn HOAc))→ $C_8H_{17}CHO$ 78%

JOC (1960) 25 618
JACS (1953) 75 4952

For reduction of ozonides with tetracyanoethylene see Ber (1963) 96 1564
" " " " " $(MeO)_3P$ " JOC (1960) 25 1031
" " " " " $(Me_2N)_3P$ " Helv (1967) 50 2387
" " " " " Ph_3P " JOC (1968) 33 787
" " " " " Me_2S " Helv (1967) 50 2445
" " " " " dinitrophenylhydrazine see JACS (1956) 78 5601
" " " " " Na_2SO_3 see JOC (1961) 26 4912
" selective ozonolysis " JACS (1958) 80 915
(1969) 91 4318
(1958) 80 915

$PhCH{=}CH_2$ —(Bistriphenylsilyl chromate; CCl_4)→ PhCHO

JOC (1970) 35 774

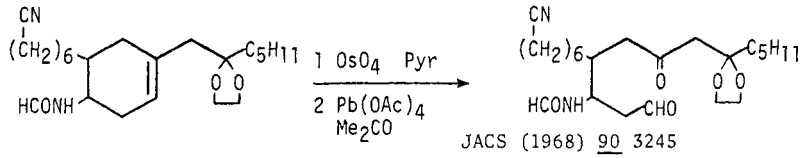


86%

J Soc Chem Ind (1943) 62 90
JCS (1937) 369
Org React (1959) 10 1

12%

JACS (1958) 80 6682

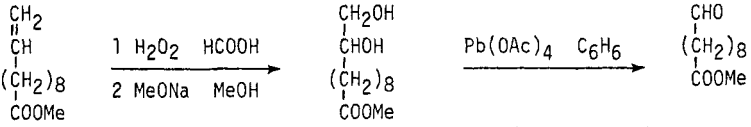


43%

JACS (1968) 90 3245

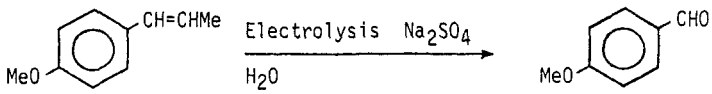
68%

JOC (1956) 21 478
Tetrahedron (1968) 24 3095



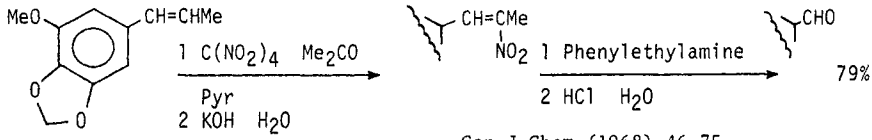
51%

J Med Chem (1969) 12 911



52%

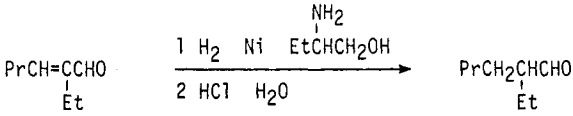
Helv (1925) 8 332



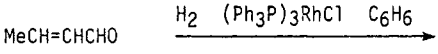
79%

Can J Chem (1968) 46 75

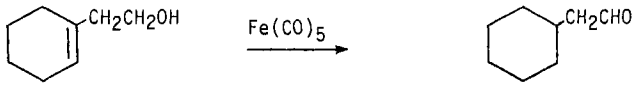
Section 60 Aldehydes from Miscellaneous Compounds



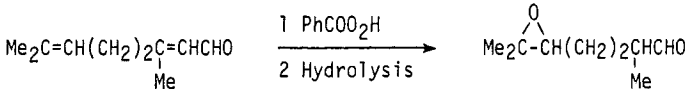
JACS (1955) 77 359



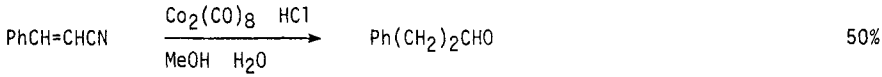
JCS C (1967) 270



Chem Comm (1968) 97



Org React (1957) 9 73
Tetr Lett (1970) 381

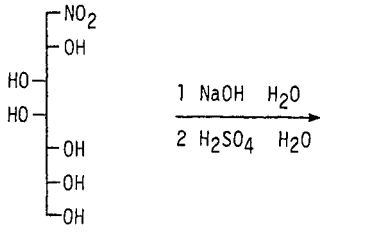


50%

Chem Comm (1967) 1140

$PhCH{=}CHCONH_2 \xrightarrow[2\ Acid\ \ H_2O]{1\ NaOCl\ \ MeOH} PhCH_2CHO$ ~70%

Org React (1946) 3 267



70%

JACS (1951) 73 4662
JOC (1943) 8 10
Chem Rev (1955) 55 137

$PrCH_2NO_2 \xrightarrow[MgSO_4\ \ H_2O]{KMnO_4\ \ KOH} PrCHO$ 97%

JOC (1962) 27 3699

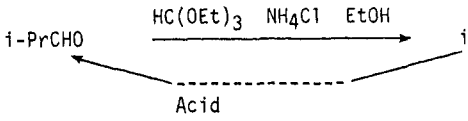
$C_{10}H_{21}CH(OH)COOH \xrightarrow{190\text{-}200^\circ} C_{10}H_{21}CHO$ 96%

J Soc Chem Ind (1943) 62 128

$PhCH(OEt)COOH \xrightarrow{Electrolysis\ \ MeOH} PhCH(OEt)OMe\ (71\%) \xrightarrow{HCl\ \ H_2O} PhCHO$

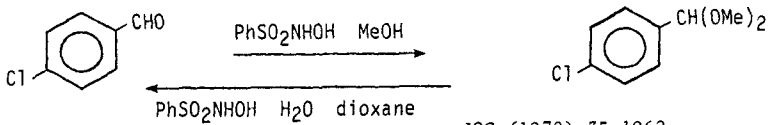
JOC (1962) 27 281

Section 60A Protection of Aldehydes

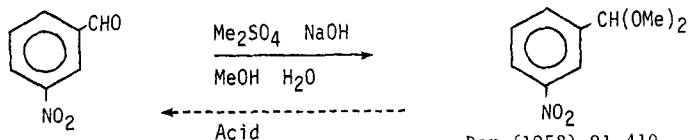


(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

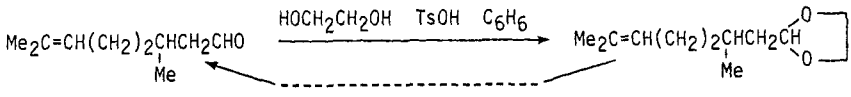
Bull Soc Chim Fr (1965) 1007



JOC (1970) 35 1962

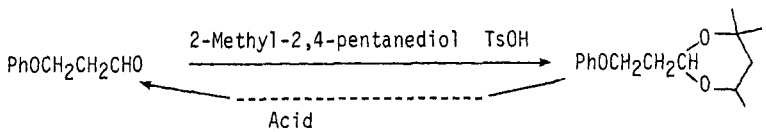


Ber (1958) 91 410

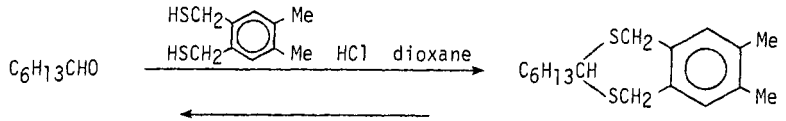


(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

Tetrahedron (1959) 6 217

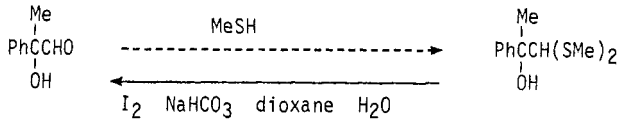


JOC (1963) 28 594



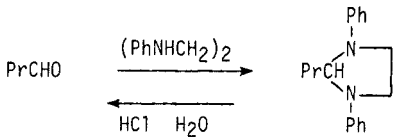
(Stable to $LiAlH_4$ and base)

JCS C (1966) 1005

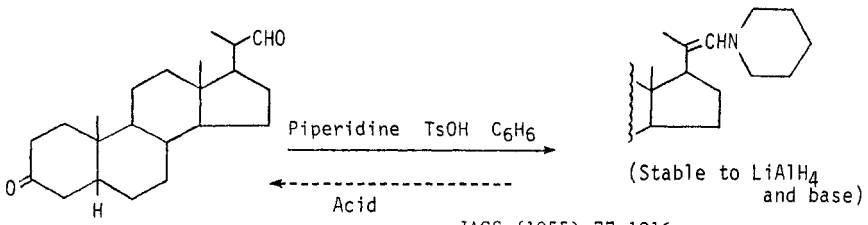


JOC (1969) 34 3618

For cleavage of thioketals with $HgCl_2$ see Ber (1958) 91 1043

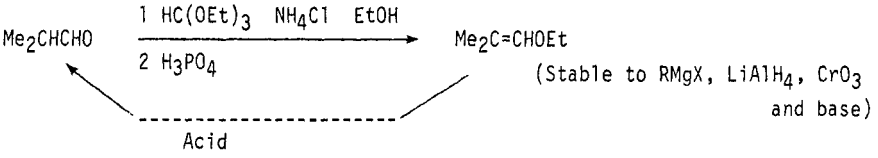


Ber (1953) 86 1463



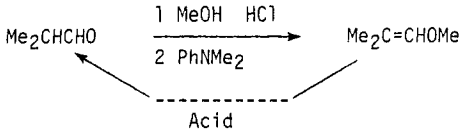
(Stable to $LiAlH_4$ and base)

JACS (1955) 77 1216

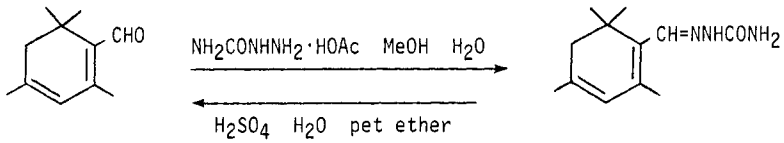


(Stable to RMgX, $LiAlH_4$, CrO_3 and base)

Bull Soc Chim Fr (1965) 1007

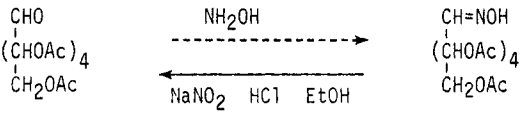


Ber (1956) 89 1468



JCS (1950) 3361

For cleavage of semicarbazones with HNO_2 see JACS (1934) 56 1794

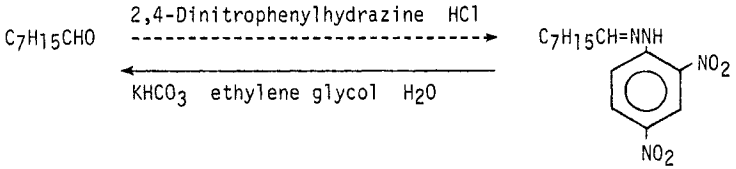


JACS (1934) 56 1794

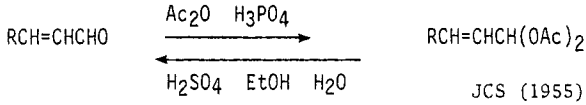
For cleavage of oximes with $(NH_4)_2Ce(NO_3)_6$ see Can J Chem (1969) 47 145

" " " " " $NaHSO_3$ " JOC (1966) 31 3446

" " " " " $Fe(CO)_5$ " JOC (1967) 32 2938



Aust J Chem (1968) 21 271



JCS (1955) 1384

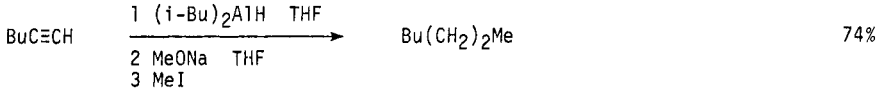
Some of the methods included in section 180A (Protection of Ketones) may also be applied to the protection of aldehydes

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

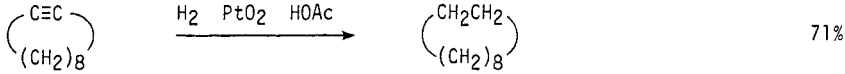
Chapter 5 PREPARATION OF ALKYLS METHYLENES AND ARYLS

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

Section 61 Alkyls and Methylenes from Acetylenes



Tetr Lett (1966) 6021



JACS (1952) 74 3636

For hydrogenation with Ni catalyst see JCS (1952) 5032
" " " Ru " " JOC (1959) 24 708
" " " Re_2S_7 " " JACS (1954) 76 1519
and JACS (1959) 81 3587

$BuC{\equiv}CH \xrightarrow[Ph_3P \quad MeOH]{H_2 \quad Rh_2(COOMe)_4} BuCH_2Me$

Chem Comm (1969) 825
(1965) 131

$C_5H_{11}C{\equiv}CH \xrightarrow{Li \quad NH_2CH_2CH_2NH_2} C_5H_{11}CH_2Me$

JOC (1957) 22 891

$EtC{\equiv}CEt \xrightarrow{Na \quad HMPA \quad t\text{-}BuOH} EtCH_2CH_2Et$ 79%

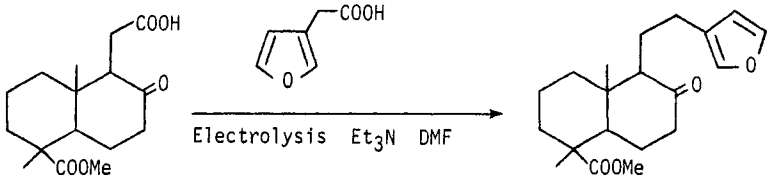
JOC (1970) 35 3565

$PhC{\equiv}CPh \xrightarrow{N_2H_4 \quad air \quad Cu^{2+} \quad MeOH} PhCH_2CH_2Ph$ 80%

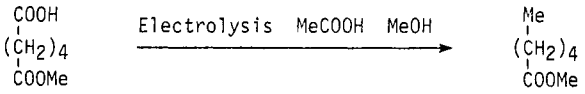
Tetr Lett (1961) 347

Section 62 Alkyls from Carboxylic Acids

Reactions in which carboxyl groups are converted into alkyl e.g. $RCOOH \longrightarrow RCH_3$, are included in this section. For the conversion $RCOOH \longrightarrow RH$ see section 152 (Hydrides from Carboxylic Acids)

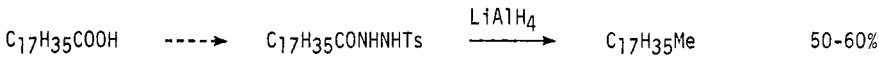


Chem Comm (1967) 96
Advances in Org Chem (1960) 1 1



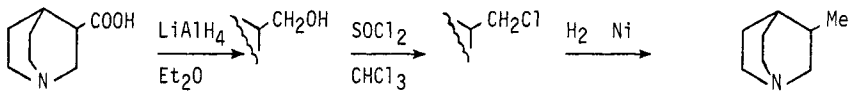
40%

JCS (1950) 3326

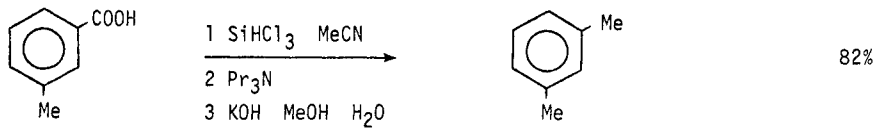


50-60%

Tetrahedron (1966) 22 487
Chim Ind (Milan) (1965) 47 62
(Chem Abs 62 10388)

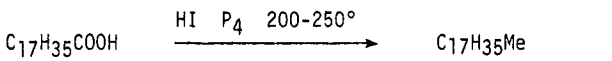


Helv (1954) 37 1689
(1946) 29 360

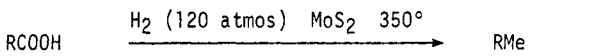


82%

JACS (1970) 92 3232



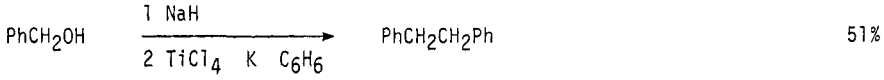
Ber (1882) 15 1687



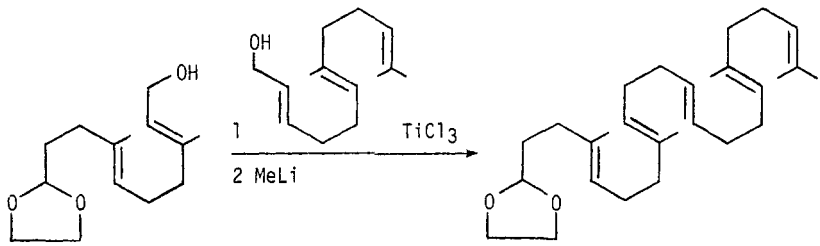
Chem Listy (1956) 50 569
(Chem Abs 50 13854)

Section 63 Alkyls and Aryls from Alcohols

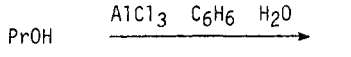
Reactions in which hydroxyl groups are replaced by alkyl or aryl e.g. ROH → RPh, are included in this section. For the conversion ROH → RH see section 153 (Hydrides from Alcohols and Phenols)



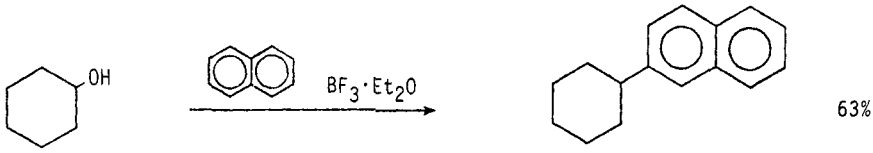
JACS (1965) 87 3277



JACS (1968) 90 3284
Chem Comm (1969) 53



JOC (1940) 5 253
JACS (1942) 64 1576



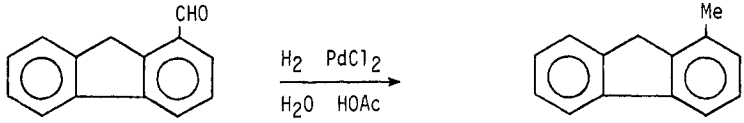
Org React (1946) 3 1

Section 64 Alkyls from Aldehydes

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

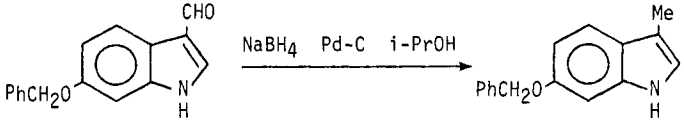
$C_6H_{13}CHO \xrightarrow{H_2\ WS_2\ 320\text{-}330°} C_6H_{13}Me$ 38%

Chem Listy (1956) 50 565
(Chem Abs 50 13831)



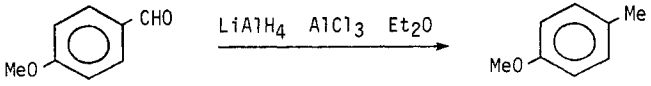
86%

JCS (1954) 4676
JACS (1956) 78 3769



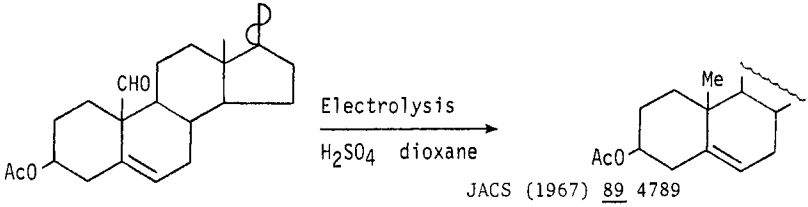
89%

Can J Chem (1964) 42 514



78%

JCS (1957) 3755
Tetr Lett (1967) 1849

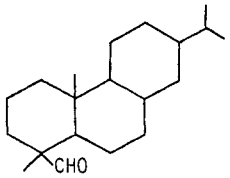


90%

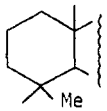
JACS (1967) 89 4789

$C_6H_{13}CHO \xrightarrow{Zn\ HCl\ H_2O} C_6H_{13}Me$ 72%

Org React (1942) 1 155



1 $N_2H_4 \cdot HCl$ N_2H_4
ethylene glycol
2 KOH

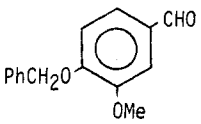


48%

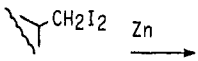
Tetrahedron (1969) 25 1335
Org React (1948) 4 378

$C_{11}H_{23}CHO$ —(1 $TsNHNH_2$; 2 $NaBH_4$ MeOH)→ $C_{11}H_{23}Me$

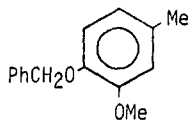
Chem Ind (1964) 153 1689
Tetrahedron (1963) 19 1127



1 N_2H_4 Et_3N
2 I_2 Et_3N THF



Zn
HOAc



JCS (1962) 470

$C_5H_{11}CHO$ —(EtSH $ZnCl_2$ Na_2SO_4)→ $C_5H_{11}CH(SEt)_2$ —(Ni EtOH)→ $C_5H_{11}Me$ 40%

JACS (1944) 66 909
JOC (1968) 33 3551
Org React (1962) 12 356

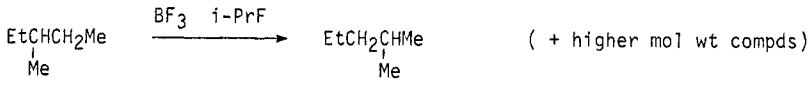
Further examples of the conversion C=O → CH_2 are included in section 72 (Alkyls and Methylenes from Ketones)

Section 65 Alkyls and Aryls from Alkyls and Aryls

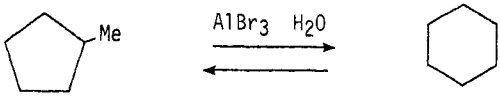
The conversion RR' → ArR (R,R'=alkyl), the epimerization, isomerization and transposition of alkyl groups and the hydrogenation of aryl groups are included in this section. For the conversions RR' → RH and ArR → ArH (R,R'=alkyl) see section 155 (Hydrides from Alkyls)

t-$BuCH_2Pr$-i —(PhH $AlCl_3$)→ t-BuPh

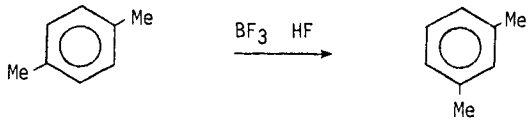
JACS (1935) 57 2415



JACS (1951) 73 5013
JOC (1964) 29 94

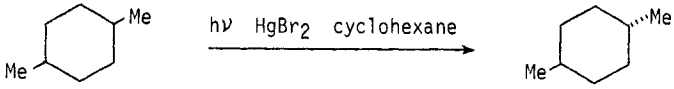


JACS (1948) 70 2773

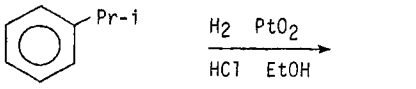


100%

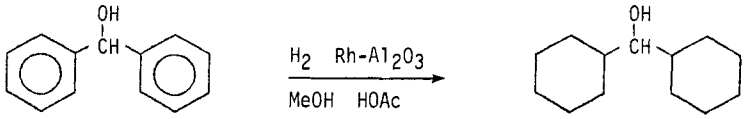
JACS (1952) 74 6246
JCS (1952) 100



JACS (1970) 92 1094



JACS (1936) 58 1594

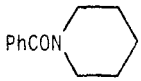


80%

JOC (1962) 27 2288

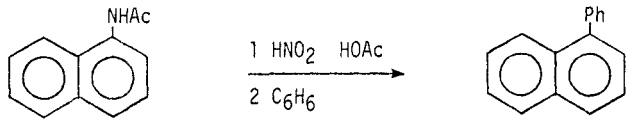
Section 66 Alkyls and Aryls from Amides

The conversions ArCONR'R" ⟶ ArMe and RCONHAr ⟶ ArAr' are included in this section. For the conversion RCONR'R" ⟶ RH see section 156 (Hydrides from Amides)



79%

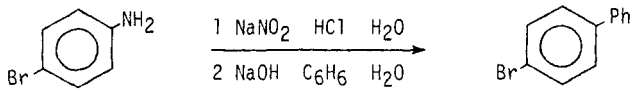
JACS (1934) 56 2419



JCS (1940) 361 369
Org React (1944) 2 224

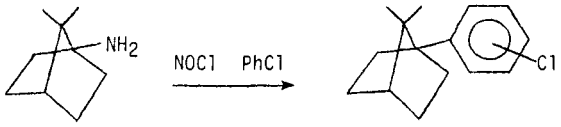
Section 67 Alkyls and Aryls from Amines

Reactions in which an amine group is replaced by alkyl or aryl are included in this section. For the conversion RNH_2 ⟶ RH see section 157 (Hydrides from Amines)



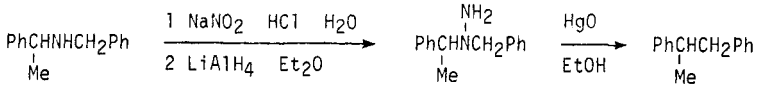
34%

Org Synth (1932) Coll Vol 1 113
Org React (1944) 2 224
JCS (1962) 4257



15%

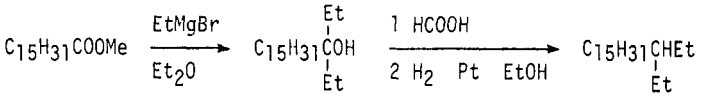
JACS (1969) 91 5073



Chem Pharm Bull (1970) 18 1137

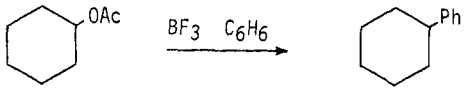
Section 68 Alkyls and Aryls from Esters

This section lists the conversion of the group COOR to alkyl or aryl. For the conversion RCOOR ⟶ RH see section 158 (Hydrides from Esters)



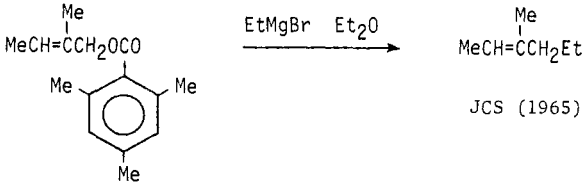
86%

JACS (1945) 67 2239

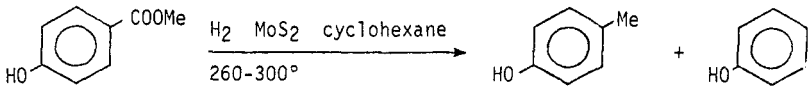


37%

JACS (1937) 59 1204
Org React (1946) 3 1



JCS (1965) 702



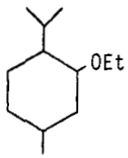
Coll Czech (1958) 23 1322

Section 69 Alkyls and Aryls from Ethers

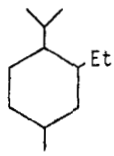
The conversion ROR ⟶ RR' (R'=alkyl or aryl) is included in this section. For the hydrogenolysis of ethers (ROR ⟶ RH) see section 159 (Hydrides from Ethers)

$Et_2O \xrightarrow{BF_3\ C_6H_6}$ EtPh (+ diethylbenzenes) 25%

JACS (1938) 60 125
Org React (1946) 3 1



EtNa cyclohexane ⟶

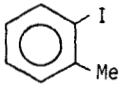


33%

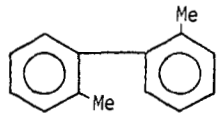
J Prakt Chem (1938) 151 61

Section 70 Alkyls and Aryls from Halides and Sulfonates

The replacement of halo and tosyloxy groups by alkyl or aryl groups is included in this section. For the conversion RX ⟶ RH (X=halo or OTs) see section 160 (Hydrides from Halides and Tosylates)



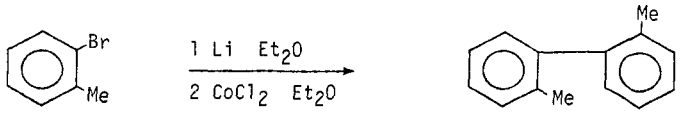
Cu 260° ⟶



JCS (1950) 711
Chem Rev (1946) 38 139

PhI $\xrightarrow{PhCu\ Pyr}$ PhPh 60%

Tetr Lett (1968) 3307
JCS (1950) 711

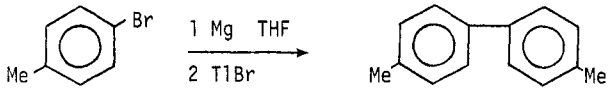


65%

Bull Soc Chim Fr (1964) 1331

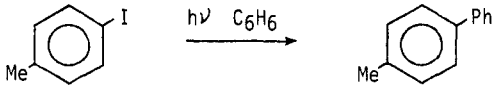
PhCl —PhLi piperidine Et_2O→ PhPh 61%

Angew (1957) 69 267



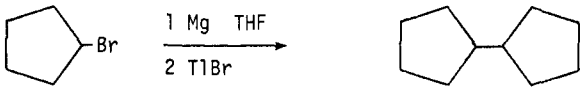
91%

JACS (1968) 90 2423
Tetrahedron (1970) 26 4041



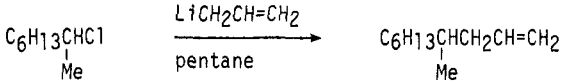
75%

JOC (1965) 30 2493



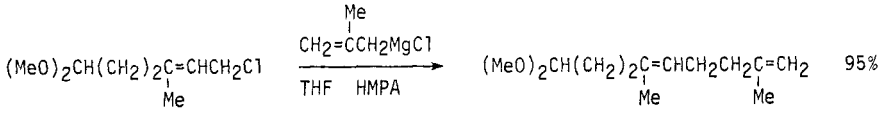
56%

JACS (1968) 90 2423



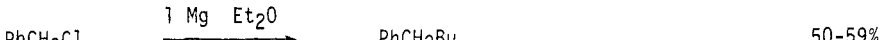
59%

JOC (1970) 35 22
(1954) 19 934



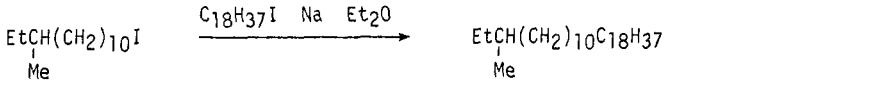
95%

Tetr Lett (1969) 1393

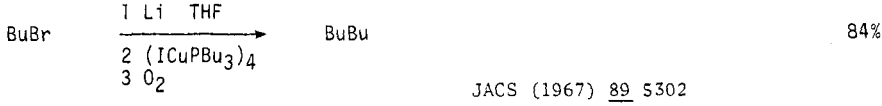


50-59%

Org Synth (1943) Coll Vol 2 47
(1932) Coll Vol 1 471



JACS (1965) 87 5452

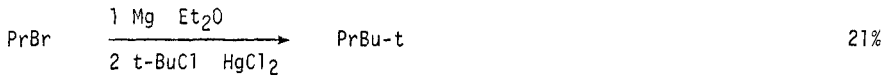


84%

JACS (1967) 89 5302

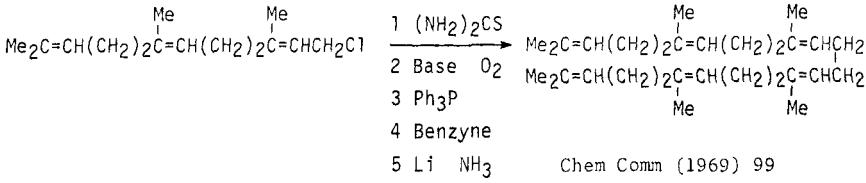
80%

Org React (1946) 3 1

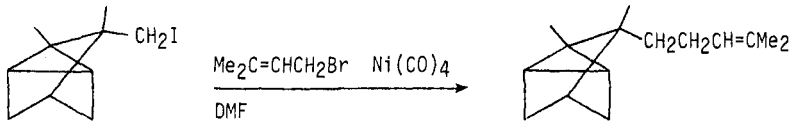


21%

JACS (1929) 51 1483
(1938) 60 2598

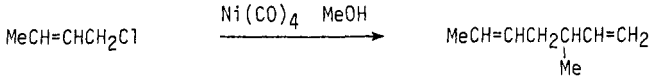


Chem Comm (1969) 99

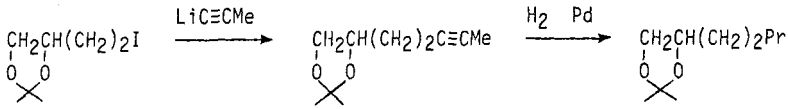


88%

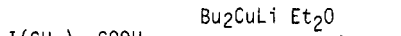
JACS (1967) 89 2755



JACS (1951) 73 2654

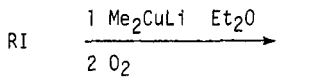


E. J. Corey, in press



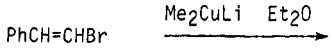
76%

JACS (1968) 90 5615



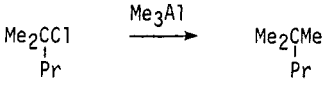
(R=C5H11 or Ph) 98-99%

JACS (1969) 91 4871



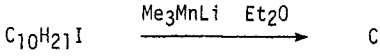
81%

JACS (1967) 89 3911 4245



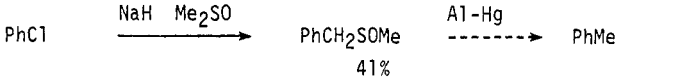
100%

JOC (1970) 35 532

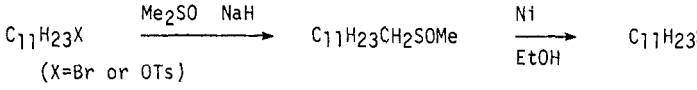


55%

Tetr Lett (1970) 315

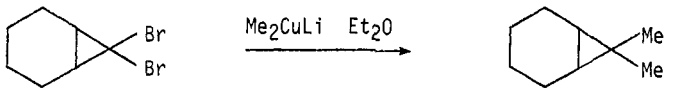


JACS (1965) 87 1345



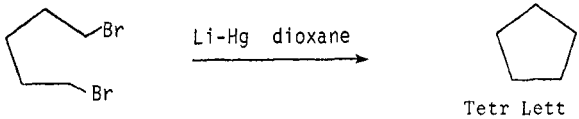
62%

Aust J Chem (1966) 19 521



65%

JACS (1967) 89 3911 4245

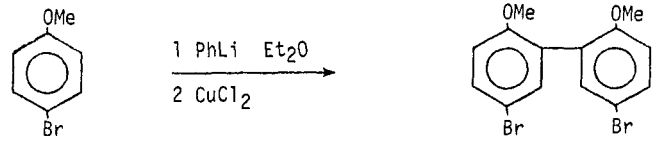


76%

Tetr Lett (1967) 4925

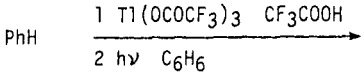
Section 71 Alkyls and Aryls from Hydrides (RH)

This section lists examples of the reaction RH → RR' (R,R'=alkyl or aryl)



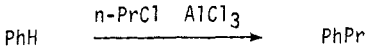
19%

JACS (1940) 62 1963

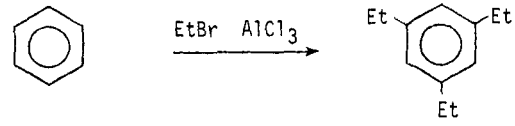


90%

JACS (1970) 92 6088

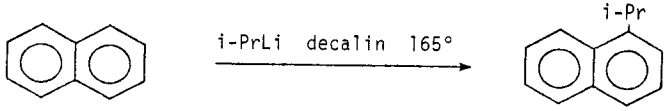


JOC (1940) 5 253
Org React (1946) 3 1



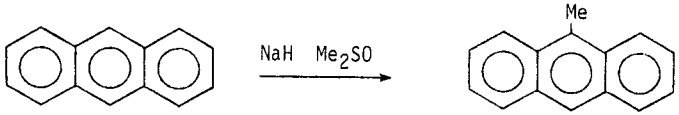
86%

Org React (1946) 3 1



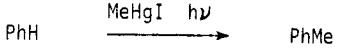
20%

JACS (1963) 85 1356

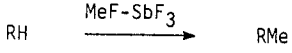


33%

JOC (1966) 31 248

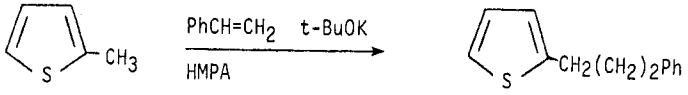


Proc Chem Soc (1961) 240

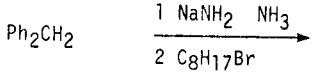


(R=alkyl or aryl)

JACS (1969) 91 2112



Tetr Lett (1968) 3723



99%

JACS (1957) 79 3142

$PhCH_3 \xrightarrow{PrCl \quad Na} PhCH_2Pr$ 43%

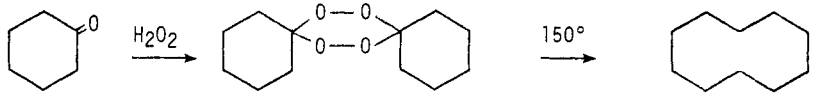
JACS (1941) 63 327

$Me_2CHMe \xrightarrow{CH_2{=}CH_2 \quad AlCl_3 \quad HCl} Me_2CHCHMe_2$

JACS (1945) 67 1778

Section 72 Alkyls, Methylenes and Aryls from Ketones

The conversions $R_2CO \longrightarrow RR$, R_2CH_2, R_2CHR, etc. (R=alkyl or aryl) are included in this section. For the conversion $R_2CO \longrightarrow RH$ see section 162 (Hydrides from Ketones)



44%

JACS (1968) 90 817

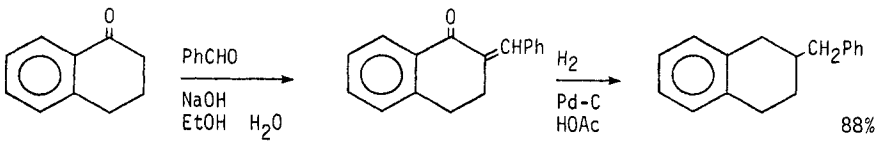
$EtCO(CH_2)_{14}COEt \xrightarrow[2\ HI \quad P_4 \quad 270°]{1\ C_{16}H_{33}C{\equiv}CMgBr} EtCH(C_{18}H_{37})(CH_2)_{14}CH(C_{18}H_{37})Et$ 26%

Helv (1937) 20 1179

$Me_2CO \xrightarrow[2\ I_2]{1\ BuMgBr \quad Et_2O} Me_2C{=}CHPr \xrightarrow[catalyst]{H_2} Me_2CHBu$

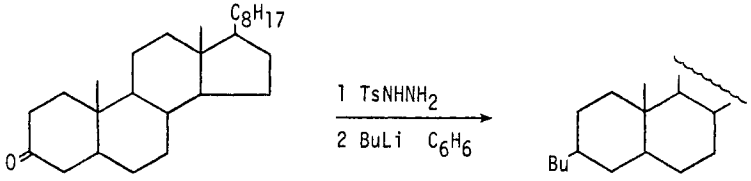
JACS (1929) 51 1483
(1949) 71 819
JOC (1948) 13 239

Further examples of the conversion of ketones into olefins and of the hydrogenation of olefins are included in section 207 (Olefins from Ketones) and section 74 (Alkyls and Methylenes from Olefins)

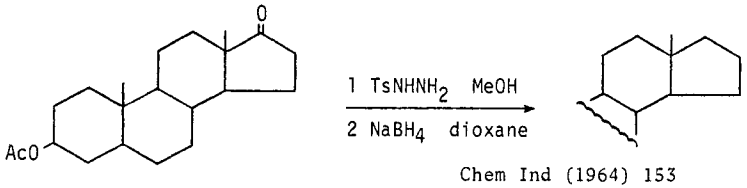


88%

Org Prep and Procedures (1970) 2 37

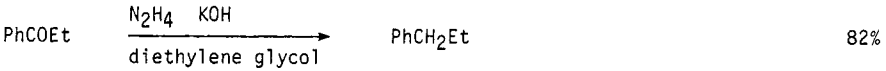


Chem Comm (1969) 1395



60-70%

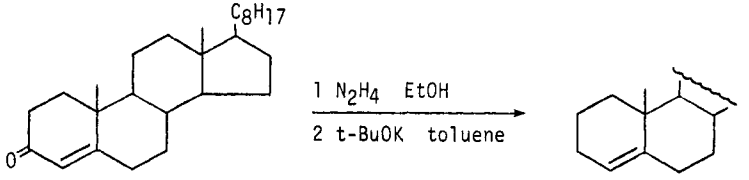
Chem Ind (1964) 153
Tetrahedron (1963) 19 1127



82%

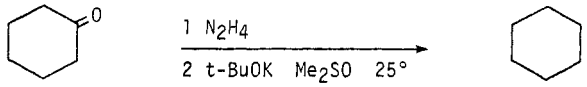
JACS (1946) 68 2487
Org React (1948) 4 378

For reduction of hindered ketones with $N_2H_4 \cdot HCl$ etc. see
Chem Ind (1964) 1194



~65%

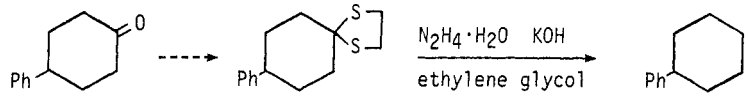
JCS (1963) 1855
Tetrahedron (1970) 26 649



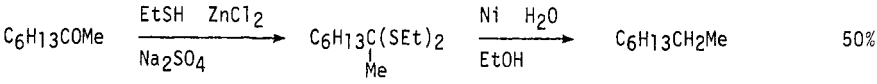
80%

JACS (1962) 84 1734

For reduction of hydrazones with BuLi see JACS (1968) 90 7287



JACS (1959) 81 5834
(1962) 84 2938
JCS (1960) 4413

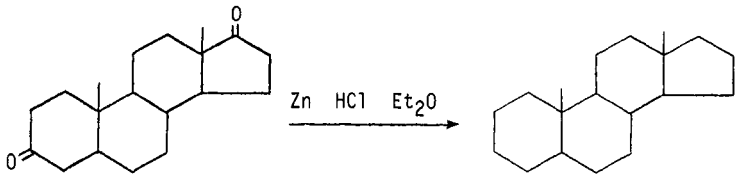


50%

JACS (1944) 66 909
Org React (1962) 12 356

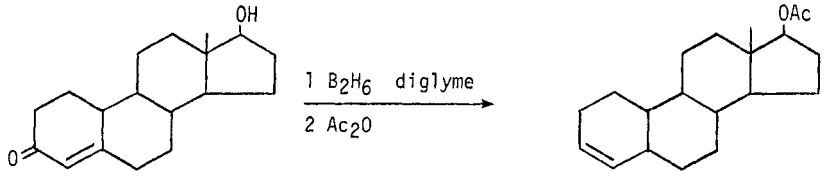
32%

Rec Trav Chim (1936) 55 903
Org React (1942) 1 155
JACS (1947) 69 2350



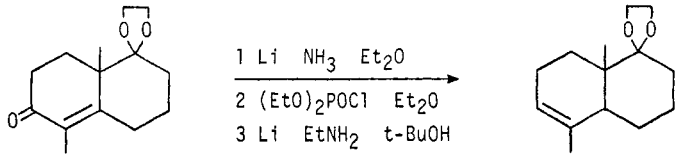
75%

Chem Comm (1969) 919



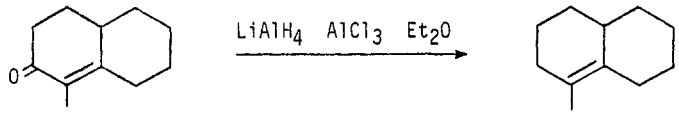
85%

Tetrahedron (1964) 20 957



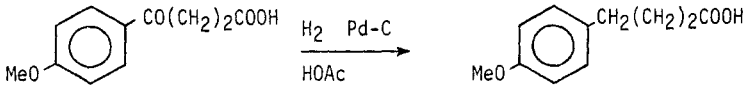
50%

Tetr Lett (1969) 2145



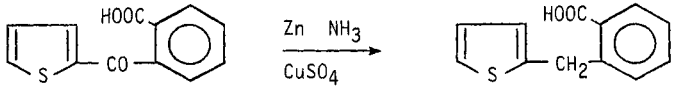
Tetrahedron (1965) 21 2641

For application to phenyl ketones see JCS (1957) 3755



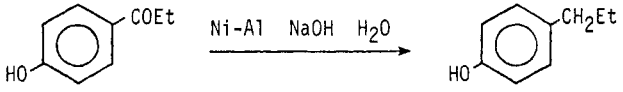
75%

JACS (1949) 71 1036
Org React (1953) 7 263



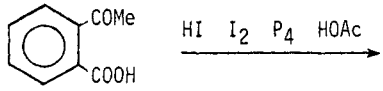
90%

JOC (1970) 35 711



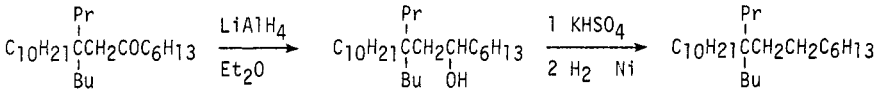
78%

Org React (1953) 7 263

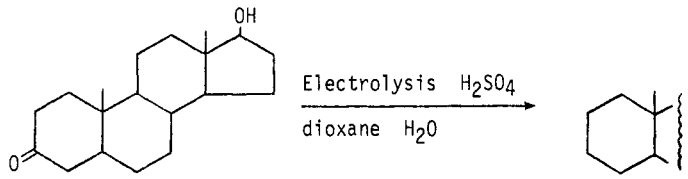


94%

Ber (1959) 92 1705

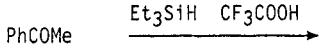


JOC (1959) 24 1964



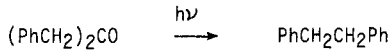
97%

JACS (1967) 89 4789

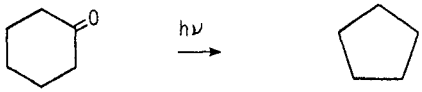


70%

Tetrahedron (1967) 23 2235



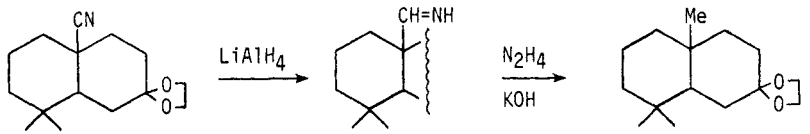
JACS (1970) 92 6076 6077



JACS (1942) 64 80
(1961) 83 4923

Section 73 Alkyls from Nitriles

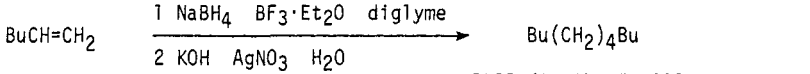
The conversion RCN ⟶ RMe is included in this section. For the replacement of CN by hydrogen, RCN ⟶ RH, see section 163 (Hydrides from Nitriles)



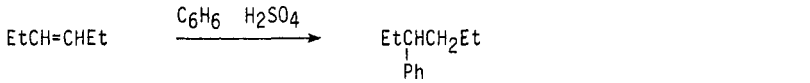
Tetr Lett (1966) 4255
Tetrahedron (1961) 13 287

Section 74 Alkyls, Methylenes and Aryls from Olefins

The hydrogenation, alkylation, arylation, dimerization etc. of olefins, forming alkanes or aryl-substituted alkanes, are included in this section. For the conversion $R_2C{=}CR_2$ ⟶ RH or R_2CH_2 see section 164 (Hydrides from Olefins)



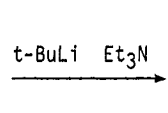
JACS (1961) 83 1002
Chem Comm (1968) 938



JACS (1939) 61 1002
Org React (1946) 3 1

$C_{10}H_{21}CH{=}CH_2 \xrightarrow[2\ H_2O]{1\ Pr_3Al} C_{10}H_{21}CHMe$ (Pr)

Angew (1952) 64 323



JOC (1965) 30 917

$C_5H_{11}CH{=}CH_2 \xrightarrow[\text{benzoyl peroxide}]{CHCl_2SO_2Cl} C_5H_{11}CHCH_2CHCl_2$ (Cl) $\xrightarrow[\text{dioxane}]{LiAlH_4} C_5H_{11}(CH_2)_2Me + C_5H_{11}CH(CH_2)_2$

Tetrahedron (1964) 20 1613

$PhCH{=}CH_2 \xrightarrow{Br_2} PhCHCH_2Br$ (Br) $\xrightarrow[Me_2SO]{NaBH_4} PhCH_2Me$ 64%

Tetr Lett (1969) 3495

$BuCH{=}CH_2 \xrightarrow[2\ EtCOOH]{1\ NaBH_4\ \ BF_3{\cdot}Et_2O\ \ diglyme} BuCH_2Me$ 91%

JACS (1959) 81 4108

$C_7H_{15}CH{=}CH_2 \xrightarrow[2\ Hg(OAc)_2\ 3\ NaBH_4]{1\ B_2H_6\ \ THF} C_7H_{15}CH_2Me$

JACS (1970) 92 3221

$C_6H_{13}CH=CH_2$ —(H_2 (2000 psi), $(i\text{-}Bu)_3B$, 225°)→ $C_6H_{13}CH_2Me$

JOC (1962) 27 4368
JACS (1961) 83 4672

$Ph_2C=CHMe$ —(1 Et_2AlCl, 2 H_2O)→ Ph_2CHCH_2Me

Tetr Lett (1970) 3471

$C_6H_{13}CH=CH_2$ —(H_2, Pt)→ $C_6H_{13}CH_2Me$

JACS (1962) 84 1495
Org Synth (1943) Coll Vol 2 191

For hydrogenation with Pd catalyst see JACS (1960) 82 6087
" " " Ru " " JOC (1959) 24 708
" " " Re_2S_7 " " JACS (1954) 76 1519
(1959) 81 3587
" " " Ni " " JOC (1970) 35 1900

$PhSCH_2CH=CH_2$ —(H_2, $(Ph_3P)_3RhCl$, C_6H_6)→ $PhS(CH_2)_2Me$ 93%

Tetr Lett (1967) 1935
JOC (1967) 32 2013 3074

For hydrogenation with $Rh(COOMe)_4$ catalyst see Chem Comm (1969) 825
" " " $RuClH(PPh_3)_3$ " " Chem Comm (1967) 305

$C_8H_{17}CH=CH(CH_2)_7COOH$ —(N_2H_4, air, EtOH)→ $C_8H_{17}(CH_2)_9COOH$ 90%

Chem Ind (1961) 433
JOC (1965) 30 3980
Chem Rev (1965) 65 51
For copper catalyzed diimide reduction see Tetr Lett (1961) 347
and JACS (1970) 92 6635

$HOCH_2CH=CH_2 \xrightarrow{TsNHNH_2 \ diglyme} HOCH_2CH_2Me$ 99%

JACS (1961) 83 3729

$\xrightarrow[NCOONa \ Pyr \ HOAc \ H_2O]{NCOONa}$

JACS (1963) 85 3297
(1961) 83 3725

$BuCH=CH_2 \xrightarrow{Na \ NH_3 \ MeOH} BuCH_2Me$ ~41%

JACS (1954) 76 1258
JOC (1970) 35 3565

$Me_2C=CH(CH_2)_2\underset{Me}{C}=CHCH_2CH=\underset{Me}{C}-CH=CH_2 \xrightarrow[EtOH]{Na} Me_2C=CH(CH_2)_2\underset{Me}{C}=CHCH_2CH_2\underset{Me}{C}=CHMe$

Tetr Lett (1967) 2201
Ber (1956) 89 1549

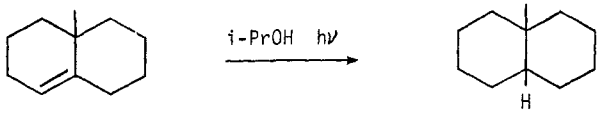
$BuCH=CHMe \xrightarrow{Li \ NH_2CH_2CH_2NH_2} Bu(CH_2)_2Me$ 82%

JOC (1957) 22 891
JACS (1959) 81 1745

$Me_2C=CHMe \xrightarrow{Et_3SiH \ CF_3COOH} Me_2CHCH_2Me$

($BuCH=CH_2$ is not reduced)

Tetrahedron (1967) 23 2235



50%

Chem Comm (1968) 296

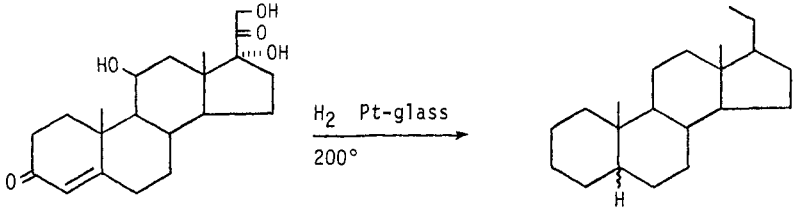
$Me_2CHCH{=}CHCHMe_2$ —(1 O_3, 2 hν)→ $Me_2CHCHMe_2$ 33%

Tetr Lett (1968) 3291

Section 75 Alkyls and Methylenes from Miscellaneous Compounds

$PrCOCH(CH_2)_{12}COOMe$ (EtCOO) —(1 $TsNHNH_2$, 2 $NaBH_4$)→ $PrCH_2CH_2(CH_2)_{12}COOMe$ 70%

Chem Ind (1967) 2150

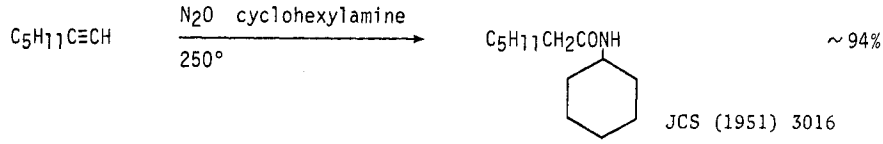


Biochem J (1967) 105 40P

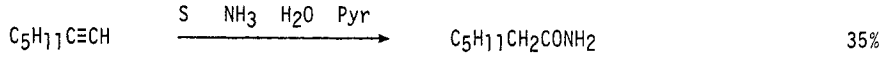
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 6 PREPARATION OF AMIDES

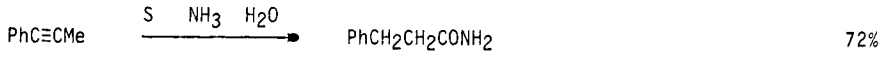
Section 76 Amides from Acetylenes



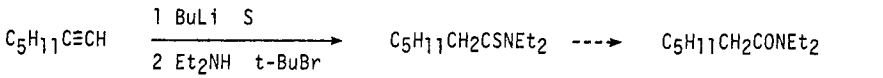
JCS (1951) 3016



JACS (1946) 68 2033

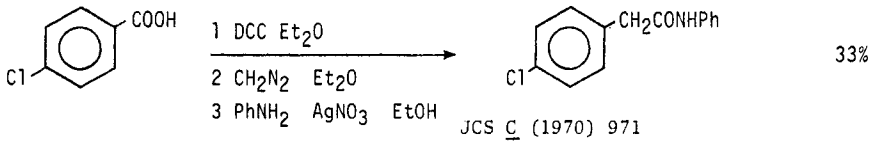


JACS (1946) 68 2029



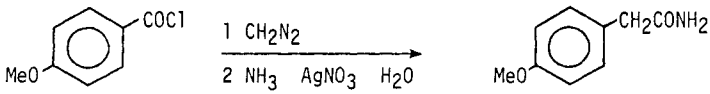
Rec Trav Chim (1968) 87 38

Section 77 Amides from Carboxylic Acids and Acid Halides



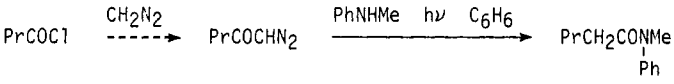
33%

JCS C (1970) 971



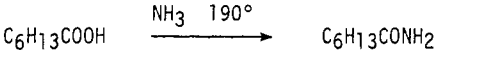
57%

Org React (1942) 1 38



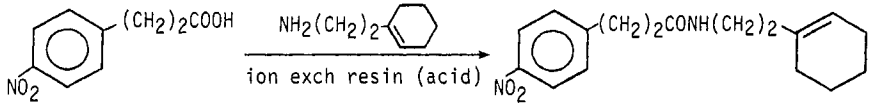
45%

Ber (1959) 92 528
JCS C (1970) 1208



75%

JACS (1931) 53 1879



Helv (1961) 44 1546
JCS C (1969) 874

$C_6H_{13}COOH \xrightarrow{NH_2CONH_2 \quad 170\text{-}180°} C_6H_{13}CONH_2$ 68-74%

Org Synth (1963) Coll Vol 4 513

$PhCOCl \xrightarrow{HCONMe_2 \quad 150°} PhCONMe_2$ 97%

JACS (1954) 76 1372
(1949) 71 2215

$i\text{-}PrCOCl \xrightarrow{NH_3 \quad H_2O} i\text{-}PrCONH_2$ 70%

Org Synth (1955) Coll Vol 3 490
JOC (1954) 19 623

$MeCH{=}CHCOCl \xrightarrow{NH_4OAc \quad Me_2CO} MeCH{=}CHCONH_2$ 63%

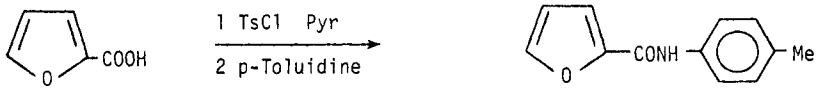
JCS (1962) 2824

$C_8H_{17}CH{=}CH(CH_2)_7COCl \xrightarrow[\text{pet ether}]{BuNH_2} C_8H_{17}CH{=}CH(CH_2)_7CONHBu$ 83%

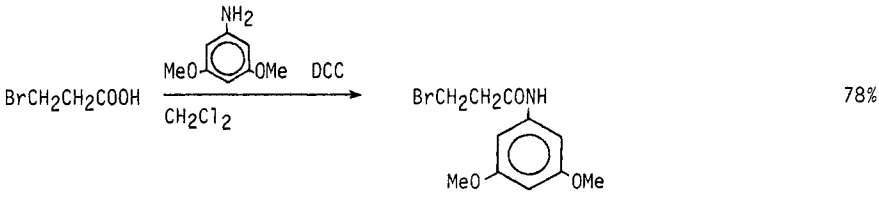
JACS (1949) 71 2215
Helv (1959) 42 2073

$PhCH{=}CHCH_2CH(CH_2Ph)COOH \xrightarrow[2\ NH_3]{1\ ClCOOEt \quad Et_3N \quad CHCl_3} PhCH{=}CHCH_2CH(CH_2Ph)CONH_2$ 94%

J Med Chem (1968) 11 534



JACS (1955) 77 6214 90%



78%

JACS (1968) 90 4706
Compt Rend (1965) 260 2249
JACS (1968) 90 2448

Amides by reaction of acids with amines and $HC{\equiv}COMe$

Rec Trav Chim (1955) 74 769

" " " " " " " " $HC{\equiv}CCH_2SMe_2Br$

JCS C (1969) 1904

" " " " " " " " $Me_2C(OMe)_2$

Chim Ther (1967) 2 195
(Chem Abs 67 108840)

" " " " " " " " $SiCl_4$

JOC (1969) 34 2766

" " " " " " " " $TiCl_4$

Can J Chem (1970) 48 983

" " " " " " " " $(PNCl_2)_3$

JOC (1968) 33 2979

" " " " " " " " 2-iodo-1-methylpyridinium iodide

JCS (1964) 4650

" " " " " " " " $SO_3 \cdot DMF$

JOC (1959) 24 368

Further examples of the reaction $RCOOH + R_2NH \longrightarrow RCONR_2$ are included in section 82 (Amides from Amines)

$C_{11}H_{23}COOH \xrightarrow{(Me_2N)_3PO\ 180\text{-}200^\circ} C_{11}H_{23}CONMe_2$ 95%

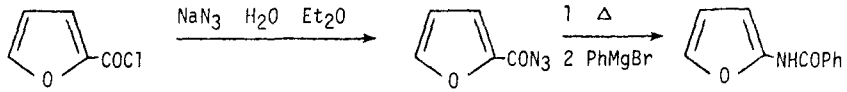
Chem Ind (1966) 1529

$C_{11}H_{23}COONa \xrightarrow{Bu_2NCOCl} C_{11}H_{23}CONBu_2$ 78%

JOC (1963) 28 232

$PhCH_2COOH \xrightarrow{(BuNH)_3B} PhCH_2CONHBu$ 90%

Tetrahedron (1970) 26 1539

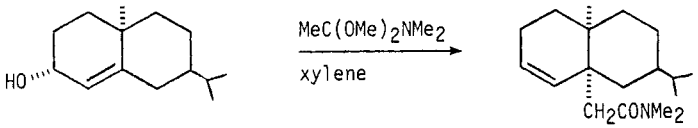


~50%

JACS (1938) 60 540

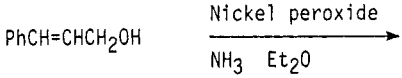
Amides may also be prepared from carboxylic acids via ester intermediates.
See section 83 (Amides from Esters)

Section 78 Amides from Alcohols and Phenols



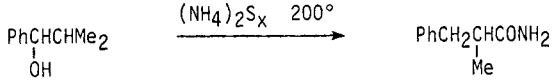
30%

Tetr Lett (1968) 1899
Angew (1968) 80 626
(Internat Ed 7 629)

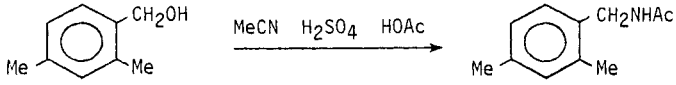


85%

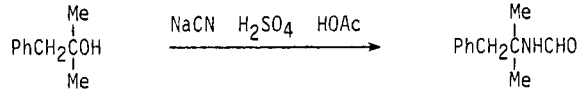
Chem Comm (1966) 17



JACS (1946) 68 632 2033

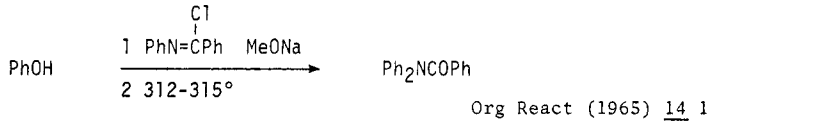


JOC (1960) 25 331
Org React (1969) 17 213



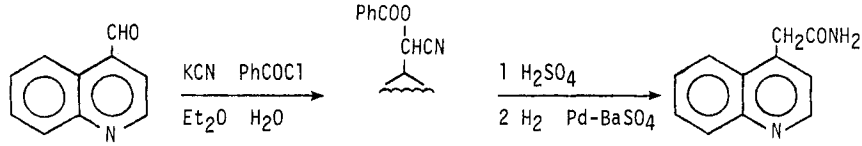
92%

JOC (1961) 26 3002

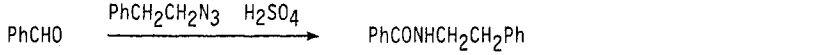


Org React (1965) 14 1

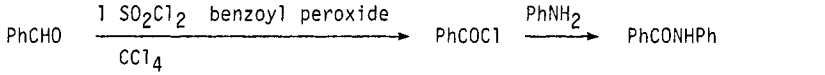
Section 79 Amides from Aldehydes



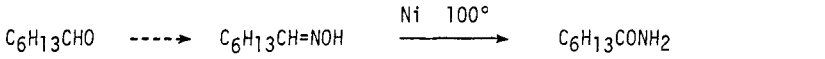
Arch Pharm (1957) 290 218



JACS (1955) 77 951



Nippon Kagaku Z (1960) 81 1450
(Chem Abs 56 2370)



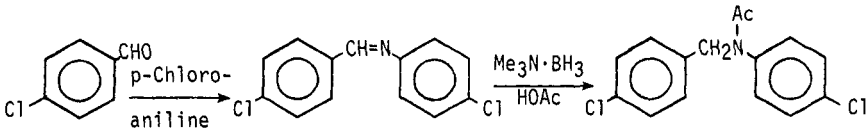
Org React (1960) 11 1
JCS (1946) 599
JACS (1961) 83 1983

$$PhCH{=}CHCHO \xrightarrow[Et_2O]{\text{Nickel peroxide } NH_3} PhCH{=}CHCONH_2 \qquad 85\%$$

Chem Comm (1966) 17

$$Ph(CH_2)_2CHO \xrightarrow{S \quad NH_3 \quad Pyr \quad H_2O} Ph(CH_2)_2CONH_2 \qquad 48\%$$

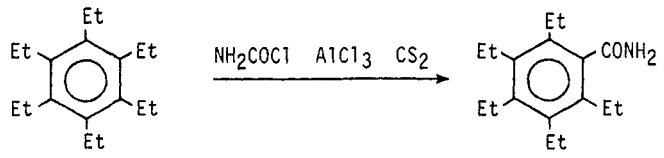
JACS (1946) 68 2029



JOC (1962) 27 2640

Section 80 Amides from Alkyls

This section lists the conversion of alkyl groups into amide. For the conversion RH ⟶ $RCONR_2$ see section 86 (Amides from Hydrides)



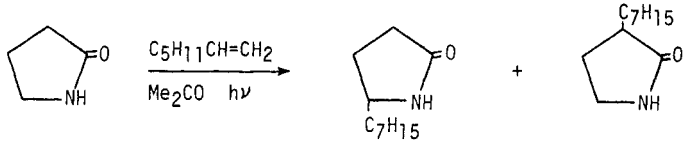
98%

Helv (1960) 43 1473

Section 81 Amides from Amides

$MeCH_2CONMe_2$ —(1 $NaNH_2$ NH_3; 2 EtBr)→ $MeCH(Et)CONMe_2$ 62%

JOC (1966) 31 982 989
Ber (1968) 101 3113
JACS (1967) 89 1647



Chem Ind (1965) 768

$MeCONH_2$ —(1 $MeCH=CH_2$ $PdCl_2$ Na_2HPO_4; 2 H_2)→ $MeCONHCHMe_2$

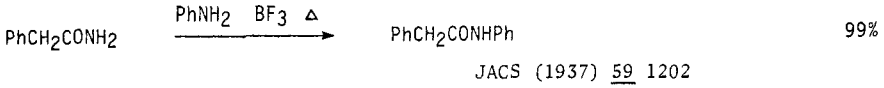
Proc Chem Soc (1961) 370

$MeCONH_2$ —($MeCH(OEt)_2$ H_2 Pd-C; H_2SO_4 HOAc)→ $MeCONHEt$ 45%

JOC (1962) 27 2205

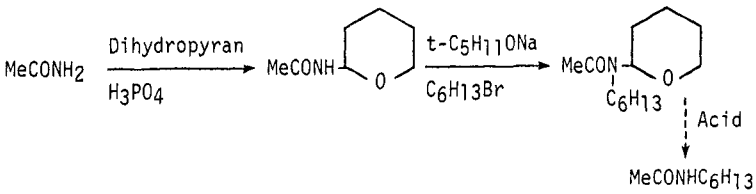
$MeCONH_2$ —($MeNH_2 \cdot HCl$ Δ)→ $MeCONHMe$ 75%

JACS (1943) 65 1566

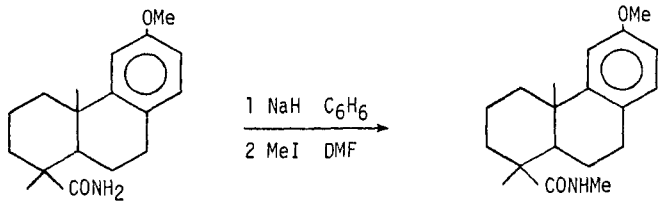


99%

JACS (1937) 59 1202



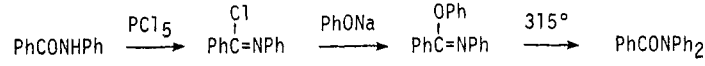
Bull Soc Chim Fr (1964) 292



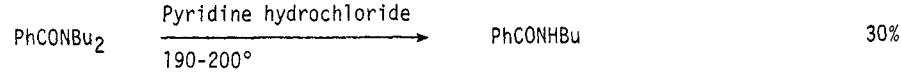
> 66%

JACS (1961) 83 1492
JOC (1949) 14 1099
(1967) 32 3679

Examples of the N-alkylation of acetyl- and trifluoroacetyl-amines are included in section 97 (Amines from Amines)

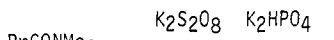


Org React (1965) 14 1



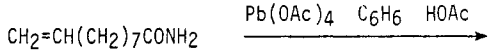
30%

Ber (1954) 87 1294



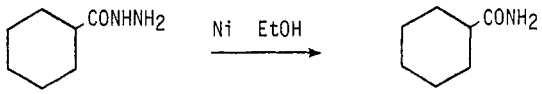
44%

JOC (1964) 29 3632



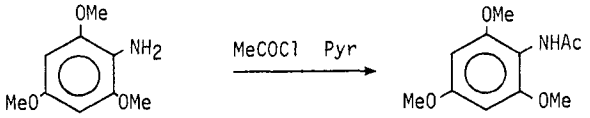
53%

Chem Comm (1965) 161
Aust J Chem (1968) 21 185



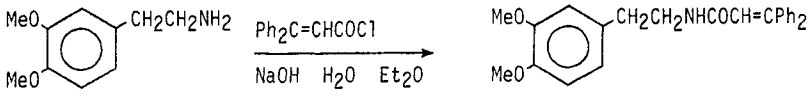
JACS (1954) 76 5774
JOC (1957) 22 148

Section 82 Amides from Amines



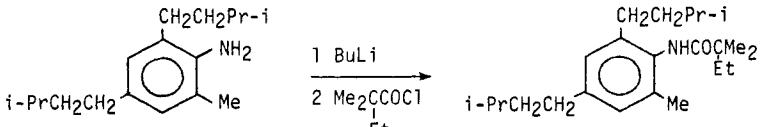
80%

JOC (1970) 35 1219

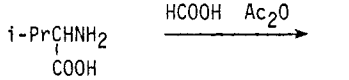


JOC (1970) 35 825
Ber (1954) 87 1760

For mild procedure see JCS (1962) 1445

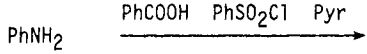


Tetr Lett (1964) 1597



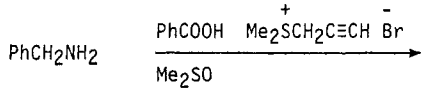
85-90%

JACS (1958) 80 1154
(1968) 90 3245



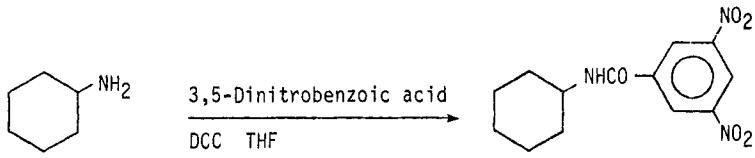
94%

JACS (1955) 77 6214



91%

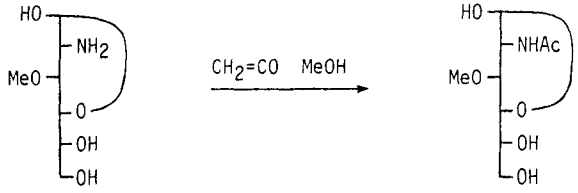
JCS C (1969) 1904



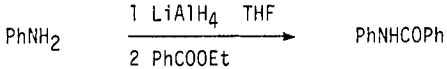
93%

Compt Rend (1965) 260 2249
JACS (1968) 90 4706

Further examples of the reaction $R_2NH + RCOOH \longrightarrow RCONR_2$ are included in section 77 (Amides from Carboxylic Acids and Acid Halides) and section 105A (Protection of Amines)

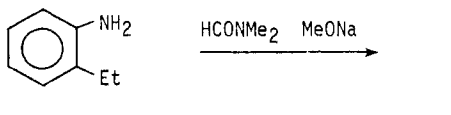


Ber (1954) 87 1138
Zh Org Khim (1967) 3 420
(Chem Abs 66 115529)



JOC (1962) 27 1042
JCS (1954) 1188

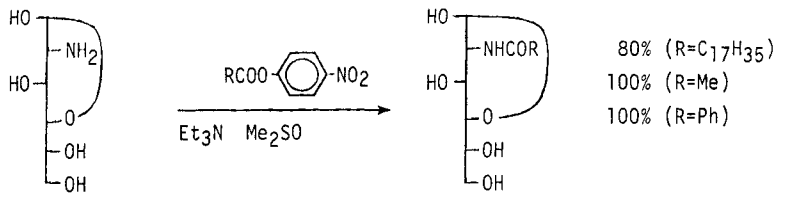
Further examples of the reaction $R_2NH + RCOOR \longrightarrow RCONR_2$ are included in section 83 (Amides from Esters)



97%

JOC (1961) 26 2563

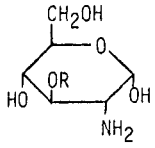
JACS (1943) 65 1566



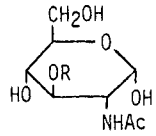
JOC (1970) 35 2042
Bull Chem Soc Jap (1963) 36 754

$HOCH_2CH_2NH_2$ —(CH_2=C(CN)OAc, $CHCl_3$)→ $HOCH_2CH_2NHAc$

Chem Zvesti (1964) 18 218
(Chem Abs 61 14773)

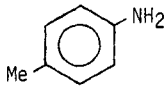


—(N-Acetoxyphthalimide; Et_3N MeOH)→

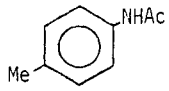


70%

JOC (1965) 30 448



—(3-Acetoxypyridine)→



88%

Bull Chem Soc Jap (1964) 37 864

$BuNH_2$ —(CCl_3CHO $CHCl_3$)→ BuNHCHO 83%

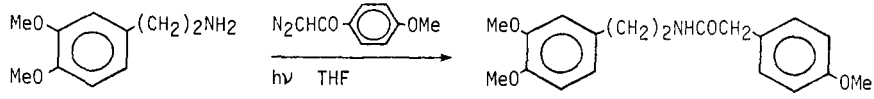
JACS (1952) 74 3933

$BuNH_2$ —(CO $RhCl_2(CO)_4$ Me_3P C_6H_6)→ BuNHCHO 96%

Tetr Lett (1969) 2329

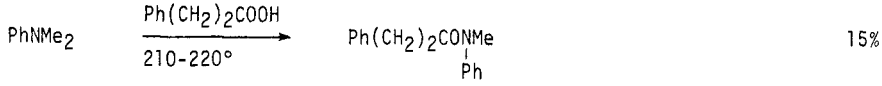
Me_2NH —(CO CuCl)→ Me_2NCHO 73%

Bull Chem Soc Jap (1969) 42 2610



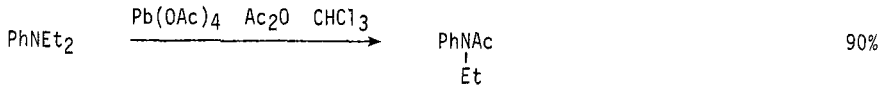
Chem Ind (1969) 493
JCS C (1970) 1208
Org React (1942) 1 38

72%



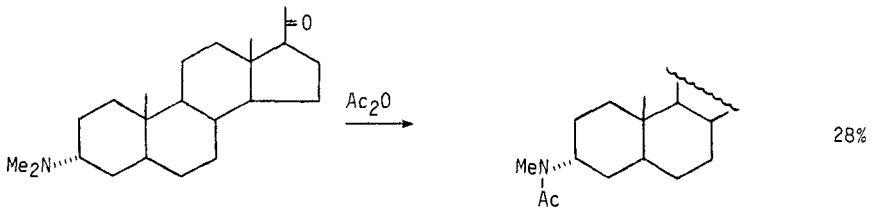
Ber (1930) 63B 489

15%



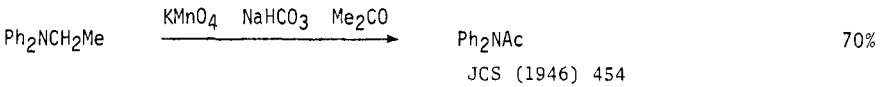
Ber (1959) 92 288

90%



Bull Soc Chim Fr (1964) 234

28%

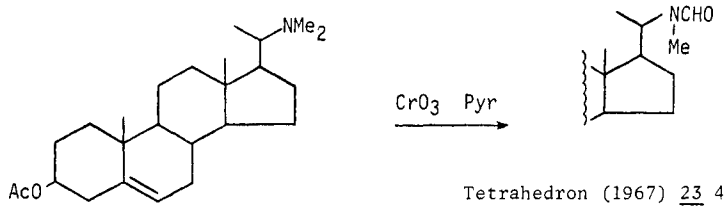


JCS (1946) 454
JACS (1968) 90 1648

70%

JCS (1957) 3032
(1966) 995

83% (R=H)
80% (R=Me)



Tetrahedron (1967) 23 4691

$PhCH_2NMe_2$ —(O_2 Pt C_6H_6)→ $PhCH_2N(Me)CHO$ 85%

Tetr Lett (1968) 4085
(1970) 5049
Chem Comm (1969) 639

$PrCH_2NBu_2$ —(O_3 pentane)→ $PrCONBu_2$ 44%

JCS (1964) 711

$PhCH_2CH_2NH_2$ —(S $(NH_4)_2S_x$ dioxane)→ $PhCH_2CONH_2$ 32%

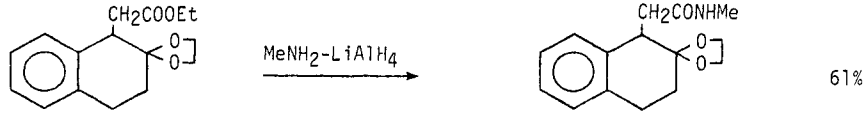
JACS (1953) 75 740 5392

Section 83 Amides from Esters

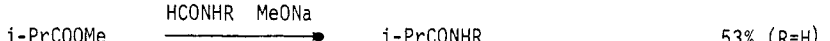
$C_8H_{17}CH{=}CH(CH_2)_7COOMe$ —($C_{12}H_{25}NH_2$, 230°)→ $C_8H_{17}CH{=}CH(CH_2)_7CONHC_{12}H_{25}$ 69%

JACS (1949) 71 2215

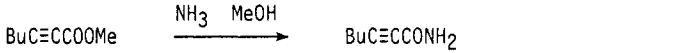
For catalysis by 2-hydroxypyridine see JCS C (1969) 89
" " " $NaNH_2$ " Chem Ind (1956) 277
" " " MeONa " JOC (1963) 28 2915



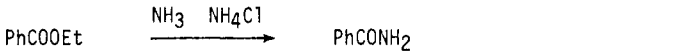
(Procedure for hindered esters)
Tetr Lett (1969) 1573
JCS (1954) 1188
Tetr Lett (1970) 1791



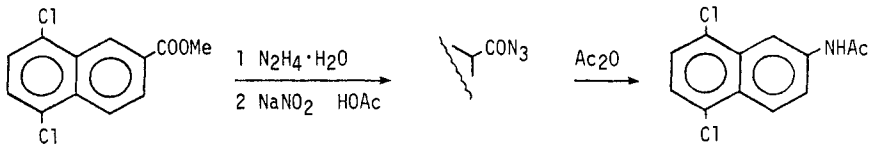
JOC (1965) 30 2376



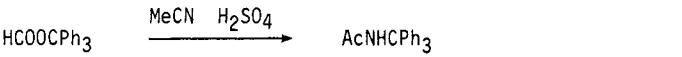
JACS (1941) 63 1151



JACS (1938) 60 579
For catalysis by $NaNH_2$ see JACS (1955) 77 469
" " " MeONa " JACS (1937) 59 1568
" " " BuLi " Tetr Lett (1970) 1791

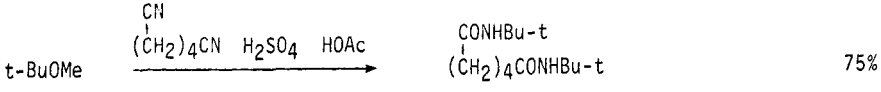


Helv (1944) 27 883
Org React (1946) 3 337



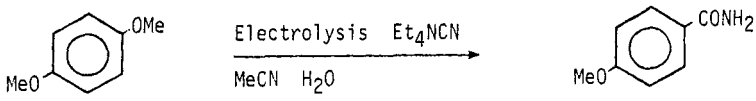
JCS (1964) 5609
Org React (1969) 17 213

Section 84 Amides from Ethers and Epoxides



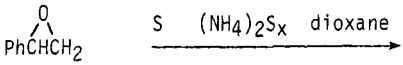
75%

Org React (1969) 17 213



9%

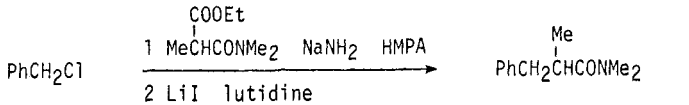
JACS (1969) 91 4181



87%

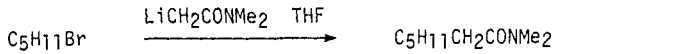
JACS (1953) 75 740

Section 85 Amides from Halides



46%

Ber (1968) 101 4230

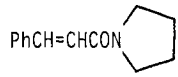


64%

Ber (1968) 101 3113
JOC (1966) 31 982 989

$PhCH_2Cl \xrightarrow{LiCH_2\overset{Li}{\underset{|}{C}}ONPh \quad Et_2O} PhCH_2CH_2CONHPh$ 69%

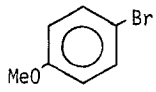
JACS (1967) 89 1647

$PhCH{=}CHBr \xrightarrow[MeOH]{Pyrrolidine \quad Ni(CO)_4}$  82%

JACS (1969) 91 1233

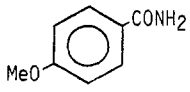
$C_7H_{15}Br \xrightarrow[2\ PhNCO]{1\ Mg} C_7H_{15}CONHPh$ 88%

JACS (1947) 69 2007
(1938) 60 540



1 Mg

2 Ethyl cyclohexylidene-carbamate



Bull Res Council Israel (1952) 2 72
(Chem Abs 48 8727)

$PhCH_2CH_2Br \xrightarrow{S \quad NH_3 \quad H_2O \quad 170°} PhCH_2CONH_2$ 80%

JACS (1953) 75 740 5395

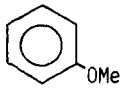
$C_8H_{17}Br \xrightarrow{HCONH_2 \quad NH_3} C_8H_{17}NHCHO$ 91%

JOC (1969) 34 3204

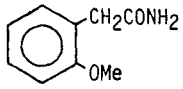
For examples of the reaction RCONHR' + R"Hal ⟶ RCONR'R" (R'=H or alkyl) see section 81 (Amides from Amides)

Section 86 Amides from Hydrides (RH)

The conversions RH $\longrightarrow$ RCH_2CONH_2, RCONR'R" or RNHAc are included in this section. For the reaction RR' $\longrightarrow$ $RCONH_2$ (R=Ar, R'=alkyl) see section 80 (Amides from Alkyls)

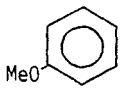


$ClCH_2CONH_2$ $h\nu$ H_2O

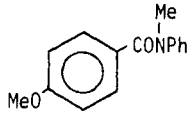


21%

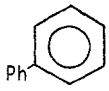
Tetr Lett (1969) 2387



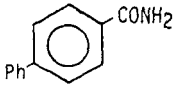
Me
PhNCOCl $AlCl_3$



Ber (1955) 88 301
JCS (1931) 2323

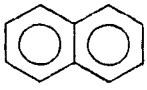


$(NH_2)_2CO$ $AlCl_3$

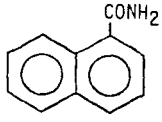


27%

JOC (1970) 35 2104



$HCONH_2$ $h\nu$ Me_2CO



20%

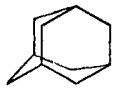
Tetr Lett (1963) 77

$PhCH_3$ $\xrightarrow[h\nu \quad Me_2CO]{HCONH_2}$ $PhCH_2CONH_2$ 23%

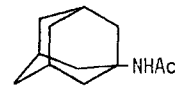
Tetr Lett (1963) 77

$PhCH_3$ —(Electrolysis MeCN; $LiClO_4$ H_2O)→ $PhCH_2NHAc$

Tetr Lett (1968) 2411



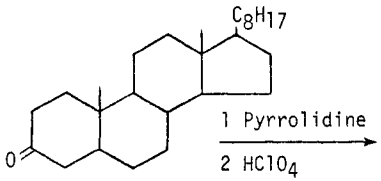
—(MeCN t-BuOH; H_2SO_4 hexane)→

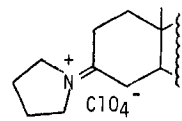


36%

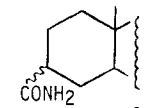
Ber (1964) 97 3234
Org React (1969) 17 213

Section 87 Amides from Ketones



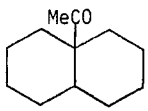


$HCONH_2$, $h\nu$ →

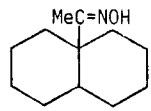


16%

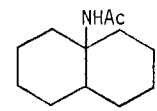
Helv (1967) 50 1759



----→



TsCl Pyr →

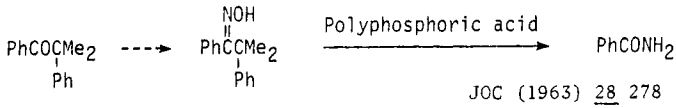


~92%

JACS (1962) 84 1064

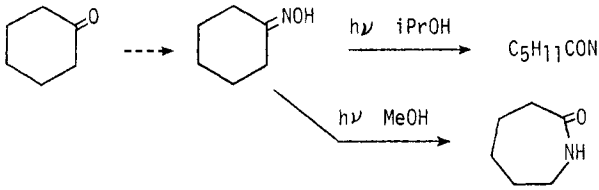
$PhCOMe$ ----→ $PhC(Me)=NOH$ —(CF_3COOH)→ $PhNHAc$ ~91%

Org React (1960) 11 1



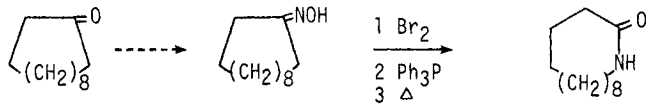
~63%

JOC (1963) 28 278



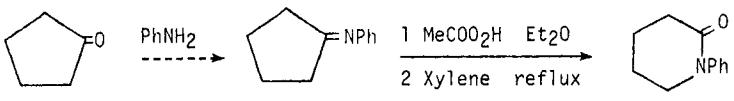
44%

Can J Chem (1968) 46 3381

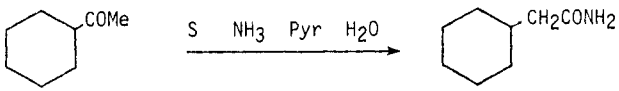


~81%

Tetr Lett (1965) 4541

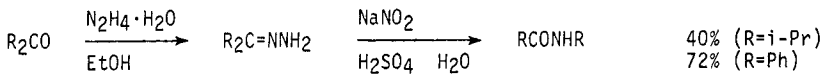


Ber (1958) 91 1057
Tetr Lett (1969) 2281



40%

Org React (1946) 3 83

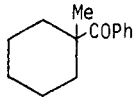


40% (R=i-Pr)
72% (R=Ph)

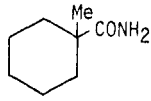
JACS (1953) 75 5905

$PhCH_2COMe \xrightarrow{NaN_3 \ \text{polyphosphoric acid}} PhCH_2NHAc$ 50%

JOC (1958) 23 1330
JCS (1942) 61
Org React (1946) 3 307



$\xrightarrow{NaNH_2 \ \text{toluene}}$



88%

JACS (1953) 75 369
Org React (1957) 9 1

Amides may also be prepared by conversion of ketones into amines followed by acylation. See section 102 (Amines from Ketones)

Section 88 Amides from Nitriles

$PhCH_2CN \xrightarrow{Me_2C{=}CHEt \ \ H_2SO_4 \ \ H_2O} PhCH_2CONHCMe_2(Pr)$ 69%

JACS (1948) 70 4045
Org React (1969) 17 213

$MeCN \xrightarrow{EtCH(Me)OH \ \ BF_3} MeCONHCH(Me)Et$ 65%

Acta Chem Scand (1968) 22 1787

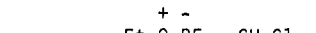
$PhCN \xrightarrow{(i\text{-}PrO)_2CH^+ \ BF_4^- \ \ CH_2Cl_2} PhCONHPr\text{-}i$

JOC (1969) 34 627

Org Synth (1963) Coll Vol 4 760
JACS (1948) 70 3091
Annalen (1968) 713 212

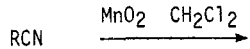
95%

JOC (1955) 20 1448



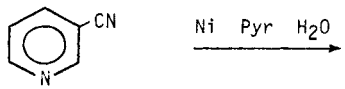
93%

JOC (1969) 34 627



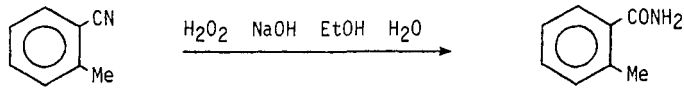
40% (R=Me)
72% (R=Ph)

Chem Comm (1966) 121



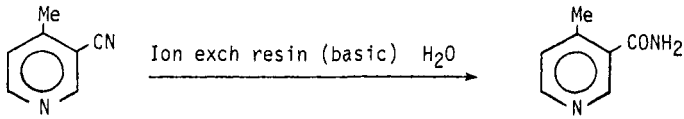
89%

Bull Chem Soc Jap (1966) 39 8
(1964) 37 1325



90-92%

Org Synth (1943) Coll Vol 2 586
JOC (1950) 15 800



89%

JOC (1960) 25 560

$PhCN \xrightarrow{NaOH\ \ Me_2SO} PhCONH_2$ 96%

JCS (1965) 1290

$PhCH_2CN \xrightarrow{H_2\ \ Ni\ \ NaOAc\ \ Ac_2O} PhCH_2CH_2NHAc$ 97%

JOC (1960) 25 1658

Amides may also be prepared by reduction of nitriles to amines followed by acylation. See section 103 (Amines from Nitriles)

Section 89 Amides from Olefins

$BuCH{=}CH_2 \xrightarrow[2\ Me_2SCHCONEt_2]{1\ B_2H_6\ \ THF} Bu(CH_2)_3CONEt_2$ ~50%

JACS (1967) 89 6804

$C_5H_{11}CH{=}CH_2 \xrightarrow[\text{di-t-butyl peroxide}]{CH_3COONHEt} C_5H_{11}(CH_2)_3CONHEt$

Dokl (1964) 158 1127
(Chem Abs 62 2703)
JCS (1965) 1918

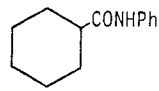
$C_6H_{13}CH{=}CH_2 \xrightarrow[\text{di-t-butyl peroxide}]{HCONMe_2} C_6H_{13}(CH_2)_2CONMe_2$ 56%

Tetr Lett (1961) 238

$BuCH{=}CH_2$ —($HCONH_2$, $h\nu$; Me_2CO, t-BuOH)→ $Bu(CH_2)_2CONH_2$ 50%

JOC (1964) 29 1855
(1965) 30 3361
Angew (1961) 73 621

—($PhNH_2$, CO, Co)→



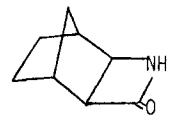
70%

JACS (1952) 74 4496

$PhCH_2CH{=}CH_2$ —($(NH_4)_2S_x$, H_2O)→ $Ph(CH_2)_2CONH_2$

JACS (1946) 68 632 2025 2029

—(1 $ClSO_2NCO$; 2 PhSH, Pyr, Me_2CO)→



66%

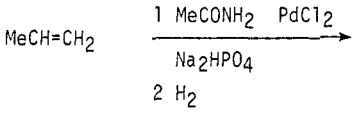
JOC (1968) 33 370
(1970) 35 2043
Annalen (1968) 718 94

$BuCH{=}CH_2$ —(1 $Hg(NO_3)_2$, MeCN; 2 $NaBH_4$, NaOH, H_2O)→ $BuCHMe(NHAc)$ 70%

JACS (1969) 91 5647

$C_{12}H_{25}CH{=}CH_2$ —(NaCN, H_2SO_4, MeCN)→ $C_{12}H_{25}CHMe(NHAc)$ 68%

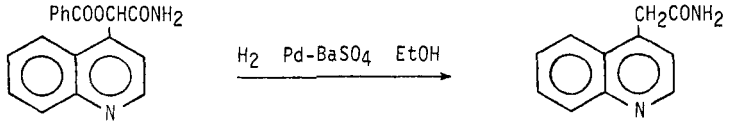
J Am Oil Chem Soc (1964) 41 78
(Chem Abs 60 6733)
JACS (1948) 70 4045
Org React (1969) 17 213



Proc Chem Soc (1961) 370

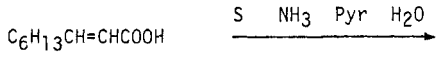
Amides may also be prepared by conversion of olefins into amines followed by acylation. See section 104 (Amines from Olefins)

Section 90 Amides from Miscellaneous Compounds



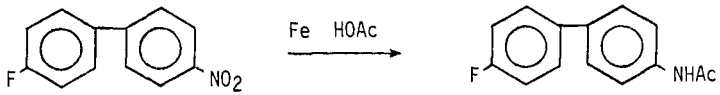
90%

Arch Pharm (1957) 290 218



41%

JOC (1947) 12 76



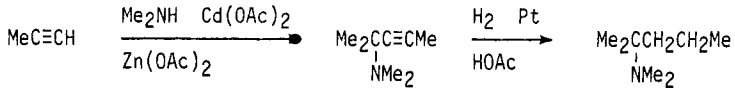
71%

JACS (1966) 88 3318

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

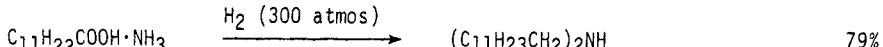
Chapter 7 PREPARATION OF AMINES

Section 91 Amines from Acetylenes

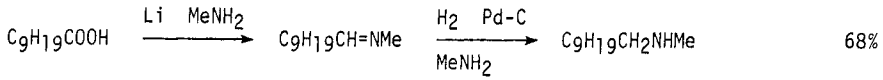


JACS (1961) 83 213 216

Section 92 Amines from Carboxylic Acids and Acid Halides



JACS (1934) 56 2419



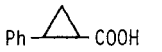
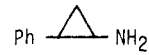
JACS (1970) 92 5774

$C_{17}H_{35}COOH$ —(HN_3 H_2SO_4 C_6H_6)→ $C_{17}H_{35}NH_2$ 96%

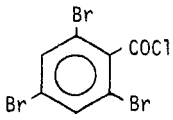
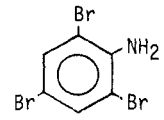
Org React (1946) 3 307

$PhCH_2COCl$ —(1 NaN_3 C_6H_6; 2 HCl H_2O)→ $PhCH_2NH_2$ 94%

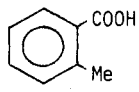
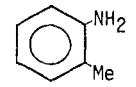
Org React (1946) 3 337
Nature (1963) 197 787

 —(1 ClCOOEt Et_3N Me_2CO; 2 NaN_3; 3 Toluene 100°; 4 HCl H_2O)→  77%

JOC (1961) 26 3511

 —(1 $N_2H_4 \cdot H_2O$; 2 $NaNO_2$ HOAc H_2O; 3 HCl H_2O)→ 

Rec Trav Chim (1921) 40 285

 —($NH_2OH \cdot HCl$; polyphosphoric acid)→  76%

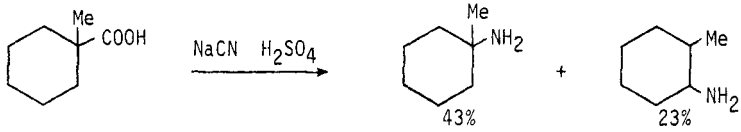
JACS (1953) 75 2014
Org React (1946) 3 337
Chem Rev (1943) 33 209

$C_5H_{11}COOH$ —(NH_2OSO_3H mineral oil; 170-180°)→ $C_5H_{11}NH_2$ 25%

JOC (1964) 29 2576

$PhCOOH \xrightarrow{MeNO_2 \text{ polyphosphoric acid}} PhNH_2$ 68%

JOC (1964) 29 2576

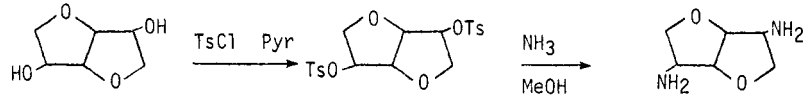


Ber (1963) 96 3359
Org React (1969) 17 213

Section 93 Amines from Alcohols and Phenols

$C_{12}H_{25}OH \xrightarrow[\text{Cu-Ba-Cr oxide}]{Et_3N \; H_2 \text{ (380 atmos)}} C_{12}H_{25}NEt_2$ 70%

JACS (1952) 74 4287

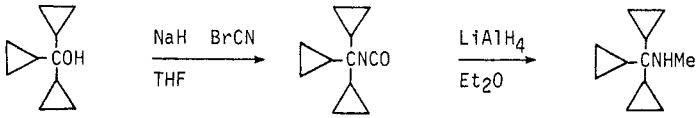


JCS (1946) 393
JACS (1933) 55 345

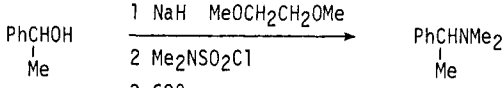
Further examples of the preparation of amines from tosylates are included in section 100 (Amines from Halides and Sulfonates)

$PhCHOH(Me) \xrightarrow{KCN \; H_2SO_4 \; Bu_2O} PhCHNCHO(Me) \xrightarrow{NaOH} PhCHNH_2(Me)$ 60%

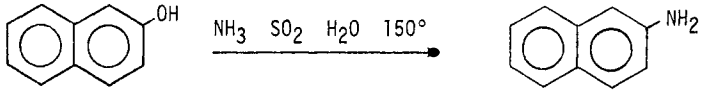
Org React (1969) 17 213
JOC (1961) 26 3002



JOC (1968) 33 4054
JACS (1964) 86 4732



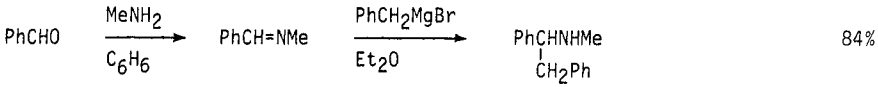
JACS (1965) 87 5261



94-96%

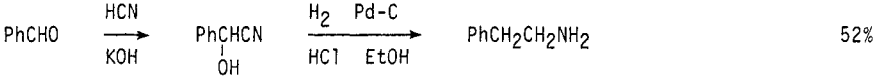
Org React (1942) 1 105

Section 94 Amines from Aldehydes



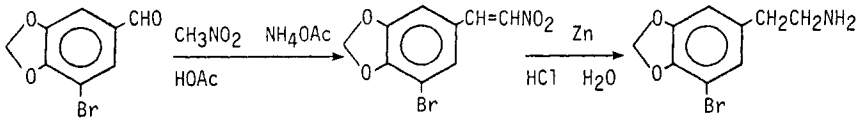
84%

Org Synth (1963) Coll Vol 4 605

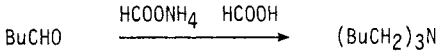


52%

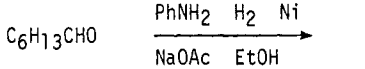
JACS (1928) 50 3370



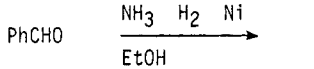
Tetr Lett (1967) 1201 50%



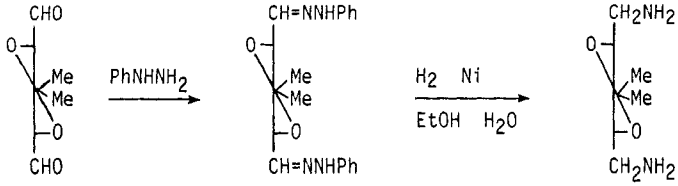
Org React (1949) 5 301



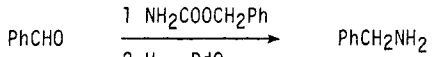
Org React (1948) 4 174 65%



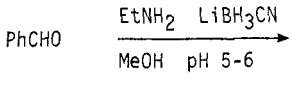
Org React (1948) 4 174 89%



JOC (1958) 23 571

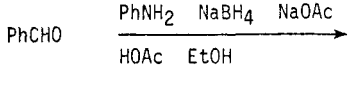


JOC (1941) 6 878 63%



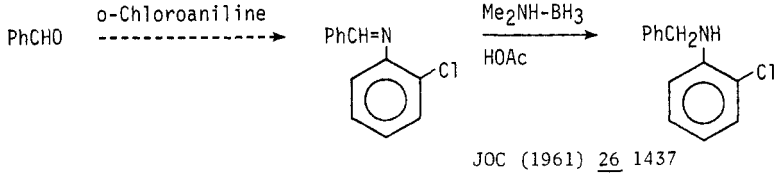
72%

JACS (1969) 91 3996



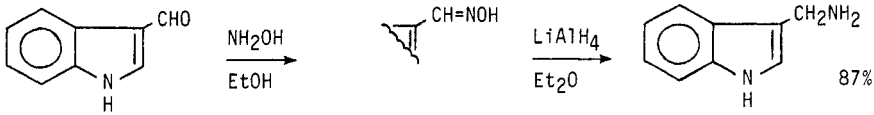
83%

JOC (1963) 28 3259



84%

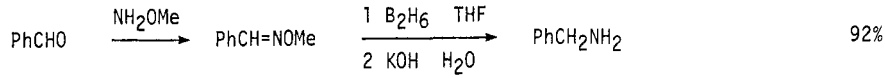
JOC (1961) 26 1437



87%

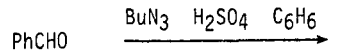
J Biol Chem (1954) 211 725

For reduction of oximes with H_2 and Pd-C see JACS (1928) 50 3370
" " " " " Ni " JCS C (1966) 531
" " " " " Na and EtOH " Org Synth (1943) Coll Vol 2 318
" " " " " Na-Hg " JACS (1949) 71 2257



92%

JOC (1969) 34 1817



22%

JOC (1959) 24 561

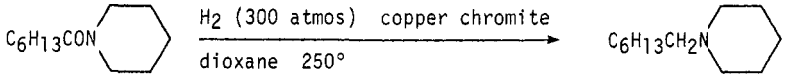
Section 95 Amines from Alkyls, Methylenes and Aryls

No examples of the reaction RR' $\longrightarrow$ RNR_2 (R,R'=alkyl, aryl etc.) occur in the literature. For the conversion RH $\longrightarrow$ RNR_2 see section 101 (Amines from Hydrides)

Section 96 Amines from Amides

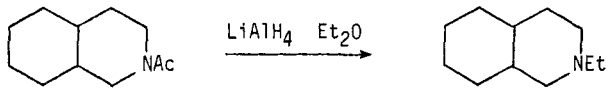
$(i\text{-}Pr)_2NCHO \xrightarrow{BuMgBr \quad Et_2O} (i\text{-}Pr)_2NCHBu_2$ 67%

Monatsh (1951) 82 330



92%

JACS (1934) 56 2419



84%

Helv (1948) 31 1397

$PhOCH_2CONH_2 \xrightarrow{LiAlH_4 \quad Et_2O} PhOCH_2CH_2NH_2$ 80%

Helv (1948) 31 1397
Org React (1951) 6 469
Org Synth (1963) Coll Vol 4 564

$i\text{-}Pr(CH_2)_2CONEt_2 \xrightarrow[Et_2O]{LiAlH_4\ AlCl_3} i\text{-}Pr(CH_2)_2CH_2NEt_2$

Z. Chem (1966) 6 224

$PhNHAc \xrightarrow[C_6H_6]{NaAlH_2(OCH_2CH_2OMe)_2} PhNHEt$ 84%

Tetr Lett (1968) 3303

$PrCONH_2 \xrightarrow{NaBH_4\ CoCl_2\ MeOH} PrCH_2NH_2$ 70%

Tetr Lett (1969) 4555

$C_7H_{15}CONMe_2 \xrightarrow{NaBH_4\ Pyr} C_7H_{15}CH_2NMe_2$ 41%

Chem Pharm Bull (1969) 17 98

$PhCONHEt \xrightarrow[2\ NaBH_4\ EtOH]{1\ Et_3O^+\ BF_4^-\ CH_2Cl_2} PhCH_2NHEt$ 92%

Tetr Lett (1968) 61
Tetrahedron (1970) 26 803

$C_6H_{13}CONMe_2 \xrightarrow{i\text{-}Bu_2AlH\ Et_2O} C_6H_{13}CH_2NMe_2$ 75-95%

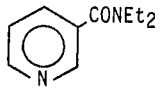
Izv (1959) 2146
(Chem Abs 54 10932)

$PrCONEt_2 \xrightarrow{Et_3SiH\ ZnCl_2} PrCH_2NEt_2$ 70%

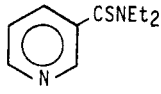
Compt Rend (1962) 254 2357

$C_5H_{11}CONHMe \xrightarrow{B_2H_6\ \ THF} C_5H_{11}CH_2NHMe$ 98%

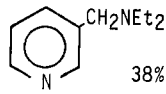
JACS (1964) 86 3566
JOC (1968) 33 3637



$\xrightarrow[2\ Na_2S]{1\ P_2S_5}$

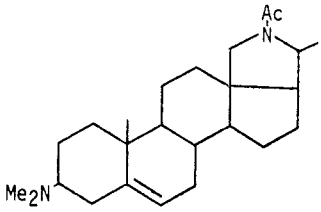


$\xrightarrow[H_2O]{Ni\ \ EtOH}$

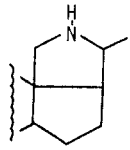


38%

JOC (1951) 16 131



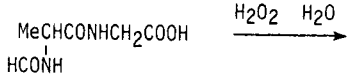
$\xrightarrow{Ca\ \ NH_3}$



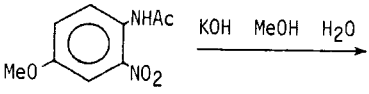
JACS (1962) 84 2018

$Et_2NCHO \xrightarrow{NaH\ \ diglyme} Et_2NH$ 40%

Tetr Lett (1965) 1713

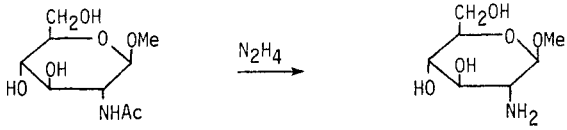


Annalen (1960) 636 140



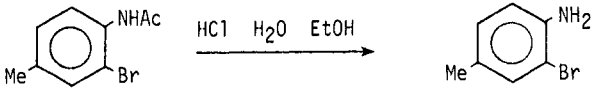
95-97%

Org Synth (1955) Coll Vol 3 661

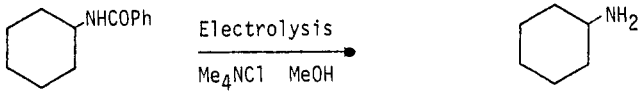


55%

Bull Chem Soc Jap (1966) 39 185

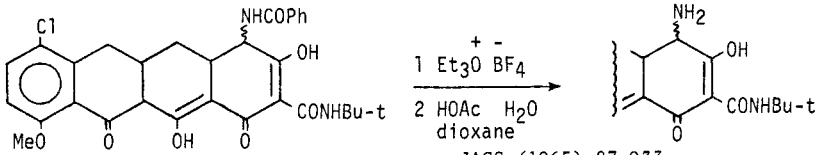


Org Synth (1932) Coll Vol 1 111

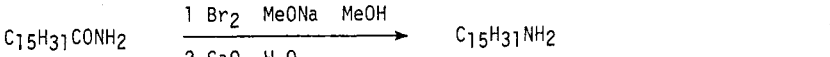


71%

Ber (1965) 98 3462

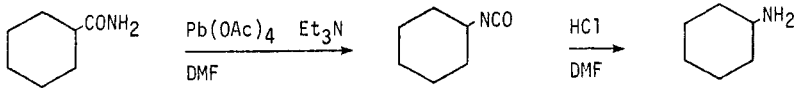


JACS (1965) 87 933
Helv (1968) 51 1108



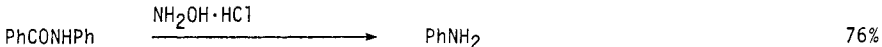
100%

Org React (1946) 3 267



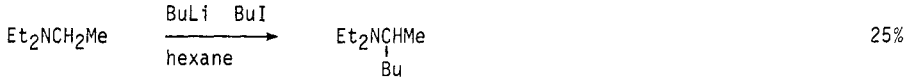
49%

JACS (1965) 87 1141
Tetr Lett (1965) 4039

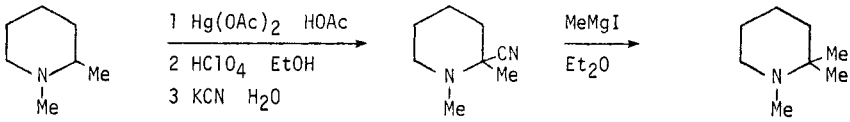


JACS (1953) 75 2014

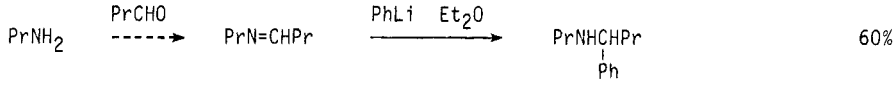
Section 97 Amines from Amines



JOC (1966) 31 2061



JACS (1957) 79 5279



Bull Soc Chim Fr (1964) 952

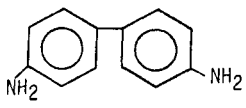
$(i\text{-}Pr)_2NH\cdot HCl \xrightarrow[KCN\ \ H_2O]{MeCHO} (i\text{-}Pr)_2NCHCN \xrightarrow[Et_2O]{MeMgCl} (i\text{-}Pr)_2NCHMe_2$

(Me)

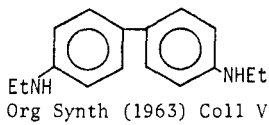
Monatsh (1962) 93 476

$(i\text{-}Pr)_2NH \xrightarrow{HCOOH} (i\text{-}Pr)_2NCHO \xrightarrow[Et_2O]{EtMgCl} (i\text{-}Pr)_2NCHEt_2$ 23%

Monatsh (1962) 93 476



$\xrightarrow{EtOH\ \ Ni}$



60-67%

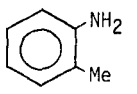
Org Synth (1963) Coll Vol 4 283
JACS (1954) 76 6174

$PhCH_2NH_2 \xrightarrow{HCOOH\ \ HCHO} PhCH_2NMe_2$ 80%

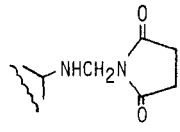
Org React (1949) 5 301

$MeNHCO(CH_2)_4NH_2 \xrightarrow[H_2O]{HCHO\ \ H_2\ \ Pd\text{-}C} MeNHCO(CH_2)_4NMe_2$ 60%

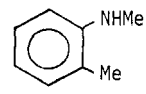
JCS C (1969) 1358



$\xrightarrow[H_2O\ \ EtOH]{HCHO\ \ succinimide}$



$\xrightarrow[EtOH]{H_2\ \ Ni}$



68%

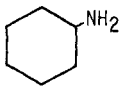
Chem Pharm Bull (1967) 15 1339

$PrNH_2 \xrightarrow{PrCHO\ \ KOH} PrN{=}CHPr \xrightarrow{H_2\ \ PtO_2\ \ EtOH} PrNHCH_2Pr$ 65%

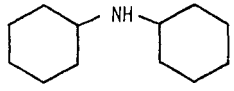
Org React (1948) 4 174
Tetr Lett (1968) 2639

$C_5H_{11}NH_2 \xrightarrow[2\ H_2\ \ PtO_2\ \ HOAc]{1\ PhCHO\ \ C_6H_6} C_5H_{11}NBu(CH_2Ph) \xrightarrow[HOAc]{H_2\ \ PtO_2} C_5H_{11}NHBu$

JACS (1941) 63 1964



Cyclohexanone
HCOOH HOAc



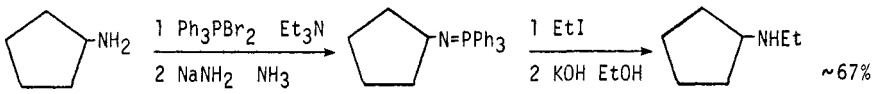
86%

Rev Chim (Bucharest) (1968) 19 360
(Chem Abs 69 105967)
Org React (1949) 5 301

$BuNH_2 \xrightarrow[NaOAc\ \ HOAc\ \ H_2O]{Me_2CO\ \ NaBH_4} BuNHCHMe_2$ 63%

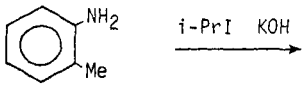
JOC (1963) 28 3259

For further examples of the reductive alkylation of amines with aldehydes and ketones see section 94 (Amines from Aldehydes) and section 102 (Amines from Ketones)



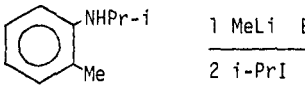
~67%

JOC (1970) 35 2826

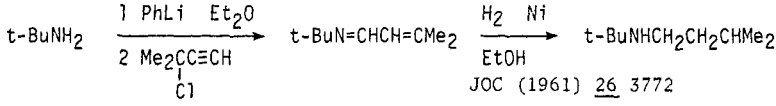


92%

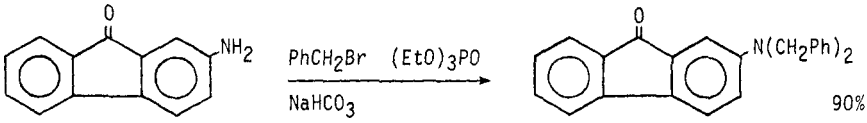
JACS (1960) 82 6163
Ber (1952) 85 1056



JACS (1960) 82 6163
(1964) 86 2813

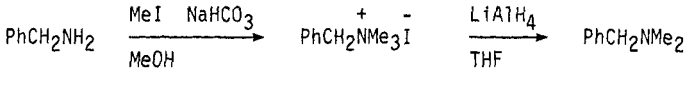


JOC (1961) 26 3772



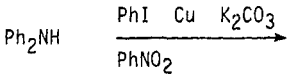
90%

JOC (1962) 27 3639



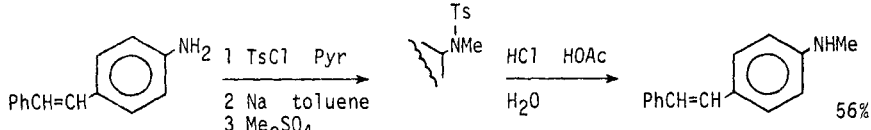
72%

JACS (1960) 82 4651
Ber (1957) 90 395

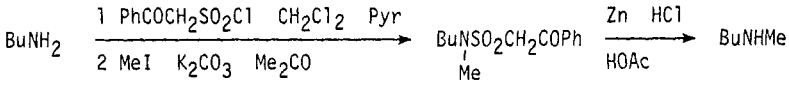


82%

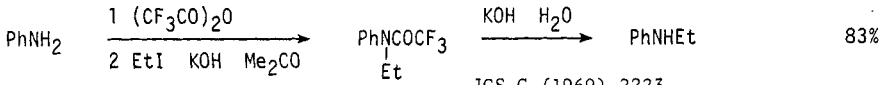
Org Synth (1941) Coll Vol 1 544
JCS (1946) 5



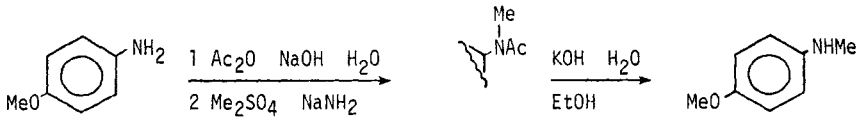
Annalen (1956) 598 174
JOC (1968) 33 1142
Ber (1953) 86 1246



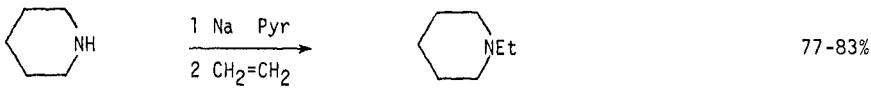
Tetr Lett (1970) 345



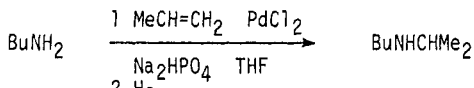
JCS C (1969) 2223



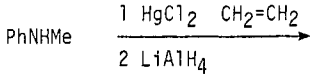
Ber (1954) 87 1760
JOC (1949) 14 1099



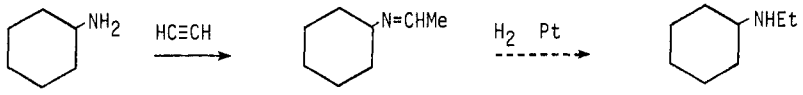
Org Synth (1963) 43 45
Bull Chem Soc Jap (1967) 40 2991



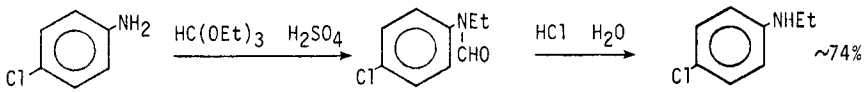
Proc Chem Soc (1961) 370



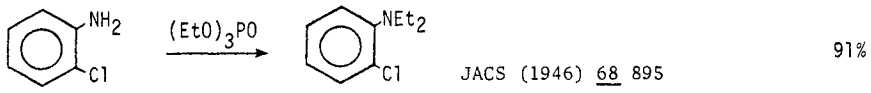
Compt Rend (1966) C 262 1591
Tetr Lett (1967) 5165
(1969) 2289



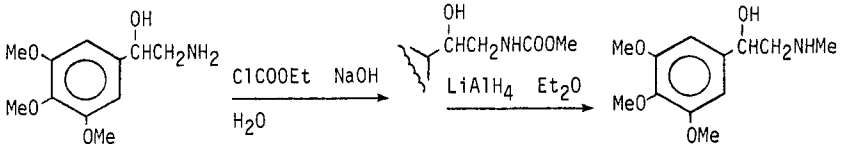
JACS (1961) 83 213



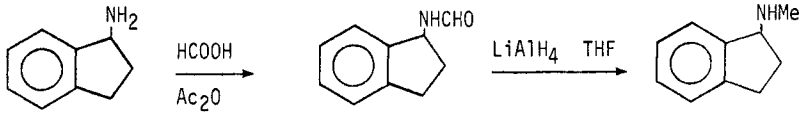
Org Synth (1963) Coll Vol 4 420
JACS (1956) 78 4778



JACS (1946) 68 895

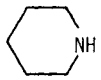


J Med Chem (1963) 6 227
JOC (1965) 30 2483

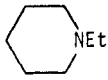


J Med Chem (1966) 9 830

Further examples of the preparation of N-alkyl amines by reduction of amides are included in section 96 (Amines from Amides)

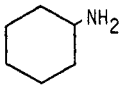


1 $LiAlH_4$ THF
2 MeCOOEt

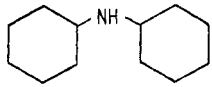


80%

JOC (1962) 27 1042



Ni toluene



82%

Annalen (1961) 644 23

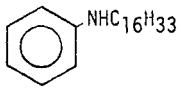
$PhNMe_2$ $\xrightarrow[150\text{-}160°]{C_5H_{11}Br}$ PhNMe(C_5H_{11})

Ber (1881) 14 622
Org React (1953) 7 198

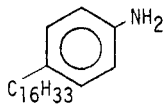
$BuNH(CH_2)_3CH_3$ $\xrightarrow[2\ H_2SO_4\ \ H_2O]{1\ Cl_2\ \ NaOH\ \ H_2O}$ 

70-80%

Org Synth (1955) Coll Vol 3 159
Chem Rev (1963) 63 55



$CoCl_2$ 212°

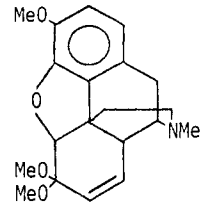


JCS (1937) 1119
Tetrahedron (1961) 14 208

$(C_6H_{13})_2NCH_2Ph$ $\xrightarrow{H_2\ \ PtO_2\ \ HOAc}$ $(C_6H_{13})_2NH$

100%

Org React (1953) 7 263
JACS (1950) 72 3410
(1941) 63 1964



$BrCN$ K_2CO_3 / $CHCl_3$ →  ($LiAlH_4$ THF →)  49%

JACS (1967) 89 1942
(1955) 77 4079
Org Synth (1955) Coll Vol 3 608
Org React (1953) 7 198

Bu_3N $\xrightarrow{ClCOOPh \quad CH_2Cl_2}$ $Bu_2NCOOPh$ (85%) $\xrightarrow{Acid}$ Bu_2NH

JCS C (1967) 2015

$(i\text{-}Pr)_2NEt$ $\xrightarrow[CuCl]{i\text{-}PrONO \quad O_2}$ $(i\text{-}Pr)_2NNO$ → $(i\text{-}Pr)_2NH$

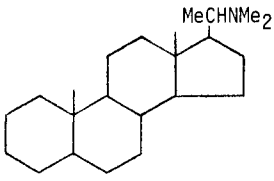
Angew (1970) 82 876
(Internat Ed 9 892)
JACS (1967) 89 1147

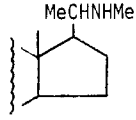
$PhNMe_2$ $\xrightarrow{HBr \quad 150°}$ $PhNHMe$

JOC (1963) 28 3144

Pr_3N $\xrightarrow{NBS \quad dioxane \quad H_2O}$ Pr_2NH 87%

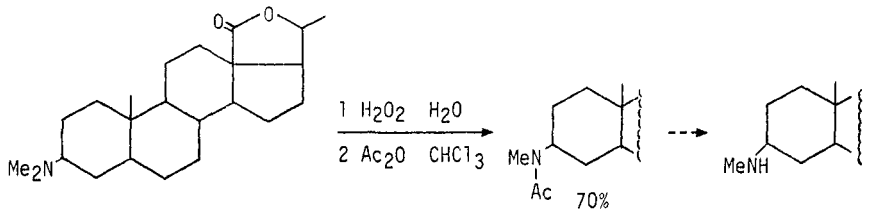
JCS (1957) 4905
JACS (1968) 90 3502
Chem Rev (1963) 63 21



$\xrightarrow[MeOH]{O_2 \quad h\nu \quad \text{methylene blue}}$ 

80%

Tetr Lett (1970) 3649



Tetrahedron (1967) 23 4681

$(i\text{-}Pr)_2NH \xrightarrow{t\text{-}BuOOH} i\text{-}PrNH_2$ 88%

JOC (1960) 25 2114

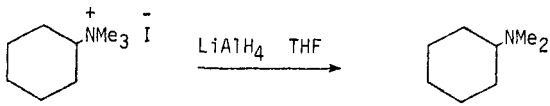
Further reactions which may be used for the dealkylation of amines are included in section 82 (Amides from Amines) and section 81 (Amides from Amides)

$Et_3NCH_2Ph\ Cl \xrightarrow{PhSH\ \ NaOH} Et_3N$ 22%

J Med Chem (1969) 12 694
Tetr Lett (1966) 1375

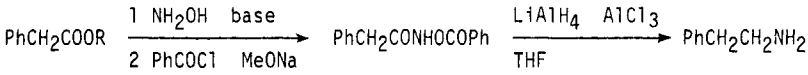
$BuNMe_3\ I \xrightarrow{HOCH_2CH_2NH_2} BuNMe_2$

Ber (1957) 90 395



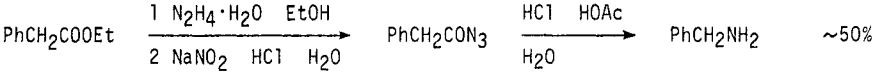
JACS (1960) 82 4651

Section 98 Amines from Esters

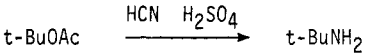


Bull Soc Chim Fr (1960) 509

Amines may also be prepared by conversion of esters into amides followed by reduction. See section 83 (Amides from Esters) and section 96 (Amines from Amides)

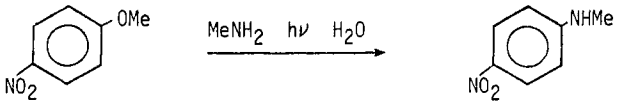


Org React (1946) 3 337



Org React (1969) 17 213

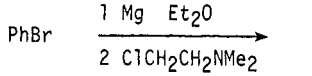
Section 99 Amines from Ethers



54%

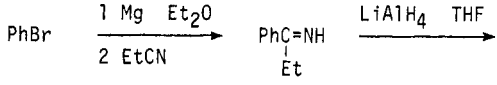
Rec Trav Chim (1966) 85 56

Section 100 Amines from Halides and Sulfonates



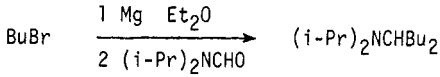
13%

J Med Chem (1966) 9 790



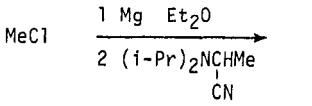
80%

JACS (1953) 75 5898



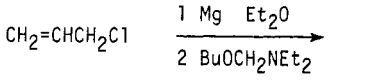
67%

Monatsh (1951) 82 330

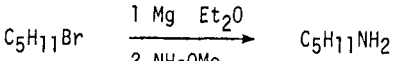


54%

Monatsh (1962) 93 476



JCS (1923) 123 532

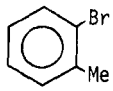


65%

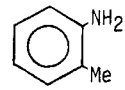
JCS (1946) 781

$BuBr \xrightarrow[2\ ClNH_2]{1\ Mg\ \ Et_2O\ \ dioxane} BuNH_2$ 97%

JACS (1941) 63 1692
(1936) 58 27



$\xrightarrow[2\ TsN_3\ \ 3\ Ni\text{-}Al\ \ NaOH\ \ H_2O]{1\ Mg\ \ THF}$



82%

JOC (1969) 34 3430

$C_7H_{15}Br \xrightarrow{NH_3\ \ MeOH} C_7H_{15}NH_2$ 47%

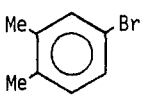
JACS (1932) 54 1499 3441

$i\text{-}PrBr \xrightarrow{Et_2NH\ \ HOCH_2CH_2OH} Et_2NPr\text{-}i$ 60%

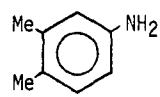
JACS (1932) 54 4457

$PrBr \xrightarrow{PhNH_2} PrNHPh$ 70%

JCS (1930) 992

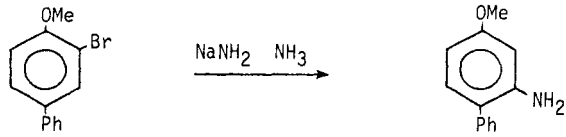


$\xrightarrow[H_2O\ \ 195°]{NH_3\ \ CuCl\ \ Cu}$



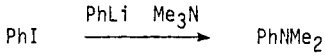
79%

Org Synth (1955) Coll Vol 3 307



60%

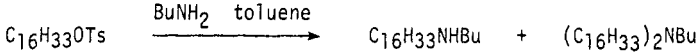
JOC (1957) 22 500
Ber (1964) 97 1994
Chem Rev (1962) 62 81



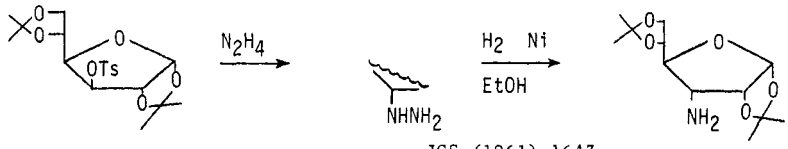
60%

Ber (1943) 76B 109

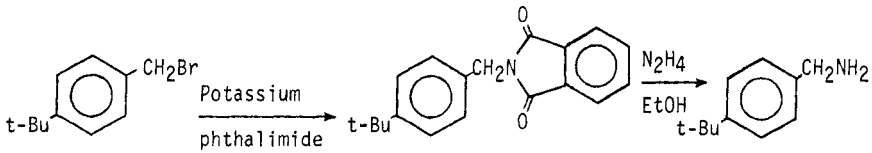
Further examples of the reaction RHal + R_2NH ⟶ RNR_2 (R=alkyl, aryl etc.) are included in section 97 (Amines from Amines)



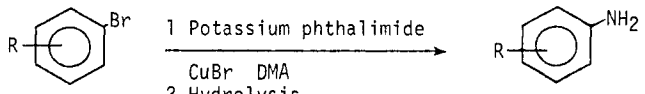
JACS (1933) 55 345
JCS (1955) 694



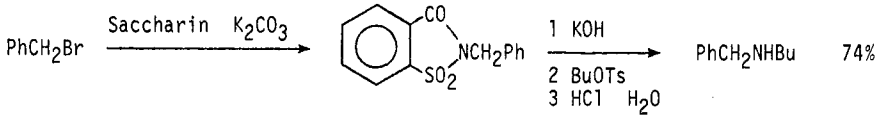
JCS (1961) 1643
Ber (1970) 103 475



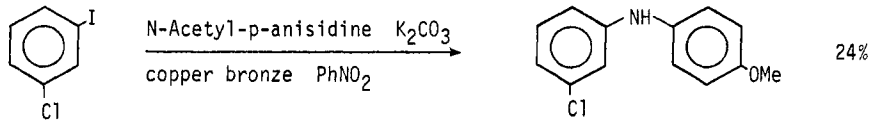
JCS (1935) 1847
JACS (1950) 72 2787
Angew (1968) 80 986
(Internat Ed 7 919)



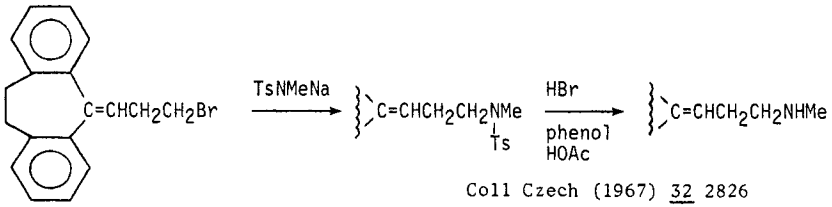
Chem Comm (1969) 578



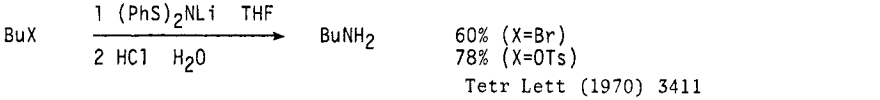
J Pharm Soc Jap (1953) 73 1319
(1955) 75 153 159



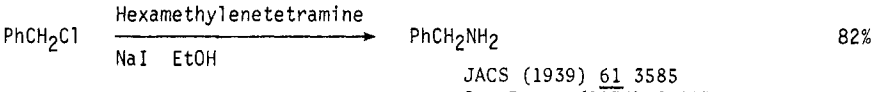
JCS (1946) 5



Coll Czech (1967) 32 2826



Tetr Lett (1970) 3411



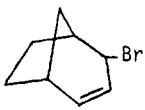
JACS (1939) 61 3585
Org React (1954) 8 197

$C_5H_{11}Br$ —(1 $(NH_2)_2C{=}NH$ EtOH H_2O; 2 NaOH)→ $C_5H_{11}NH_2$ 71%

Tetr Lett (1969) 13

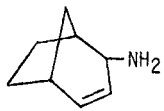
$Me_2C{=}CH(CH_2)_3Br$ —(1 NH_2CN $MeSOCH_2^-\ Na^+$ Me_2SO; 2 KCN MeOH; 3 HOAc H_2O)→ $[Me_2C{=}CH(CH_2)_3]_2NH$ 55%

Tetr Lett (1969) 3327
Tetrahedron (1970) 26 1275

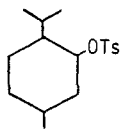


NaN3 H2O CCl4

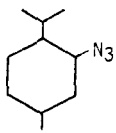
LiAlH4 Et2O



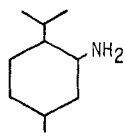
JACS (1970) 92 6302
(1951) 73 5865
Helv (1958) 41 181



NaN3 / DMF

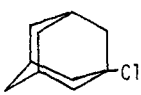


LiAlH4 / Et2O

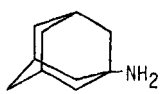


34%

JOC (1962) 27 2925
JACS (1969) 91 2961



1 MeCN H_2SO_4; 2 NaOH

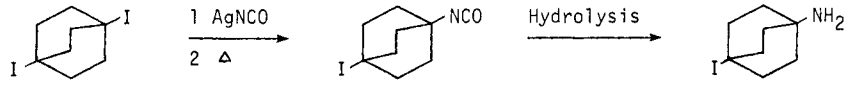


65%

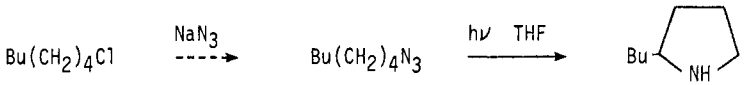
J Med Chem (1963) 6 760
Org React (1969) 17 213

t-BuCl —(NCl_3 $AlCl_3$)→ t-$BuNH_2$ 90%

JOC (1969) 34 911

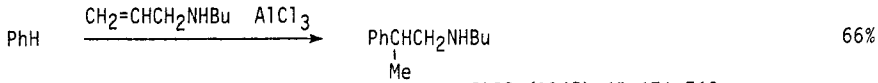


Chem Eng News (1970) March 9 39
JACS (1964) 86 4732



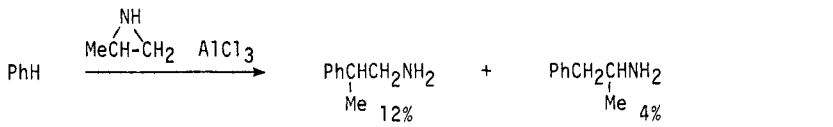
JCS (1962) 622

Section 101 Amines from Hydrides (RH)

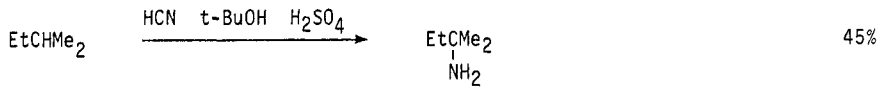


66%

JACS (1943) 65 674 762

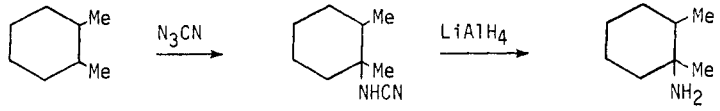


J Heterocyclic Chem (1968) 5 339

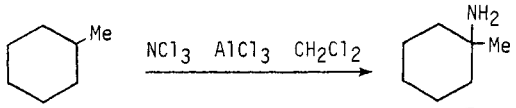


45%

Ber (1964) 97 3234
Org React (1969) 17 213

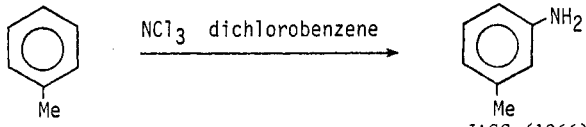


JACS (1967) 89 3177



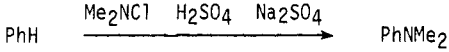
68%

Tetrahedron (1967) 23 3563



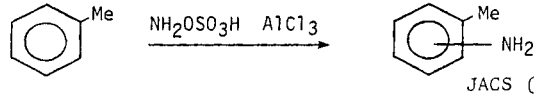
36%

JACS (1966) 88 100
(1964) 86 1650



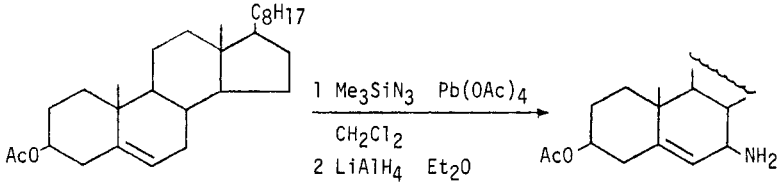
73%

Ber (1966) 99 1347 1361



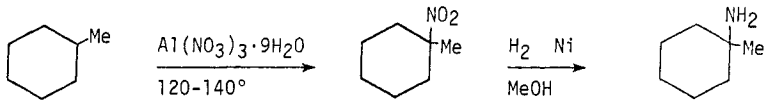
50%

JACS (1961) 83 221 743



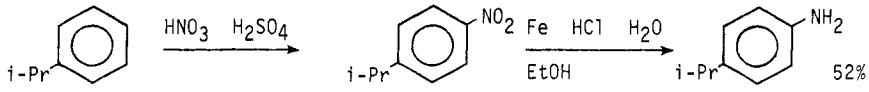
49%

Tetrahedron (1970) 26 1417



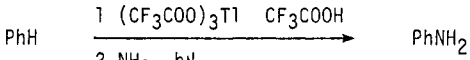
18%

JACS (1953) 75 369

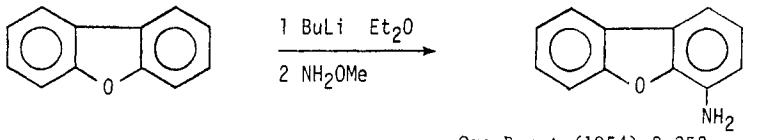


52%

JCS (1939) 1299

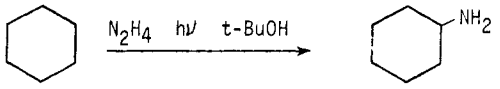


Acc Chem Res (1970) 3 338



54%

Org React (1954) 8 258

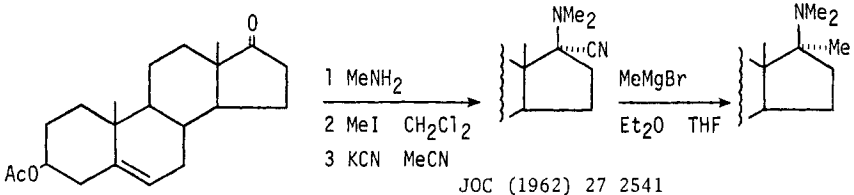


45%

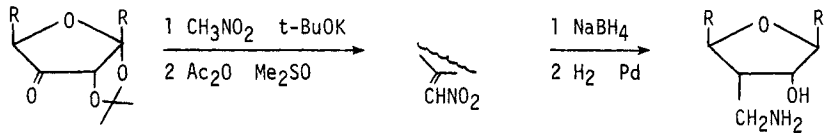
Tetrahedron (1966) 22 483

Amines may also be prepared by conversion of hydrides (RH) into amides (RNHCOR, $RCONR_2$ etc.) followed by hydrolysis or reduction. See section 86 (Amides from Hydrides) and section 96 (Amines from Amides)

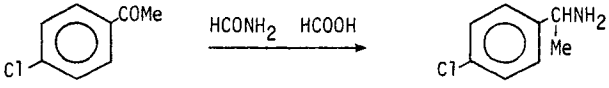
Section 102 Amines from Ketones



JOC (1962) 27 2541
(1965) 30 3203

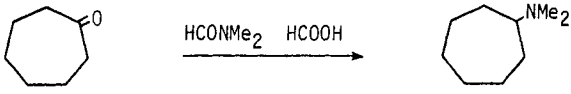


Tetr Lett (1970) 1063



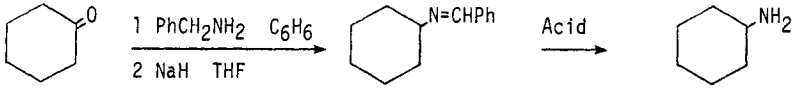
82%

Org React (1949) 5 301



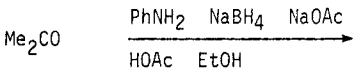
~71%

JOC (1968) 33 1647



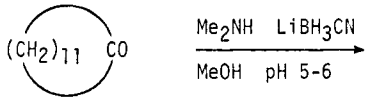
57%

Can J Chem (1970) 48 570



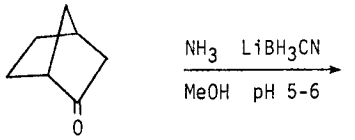
91%

JOC (1963) 28 3259



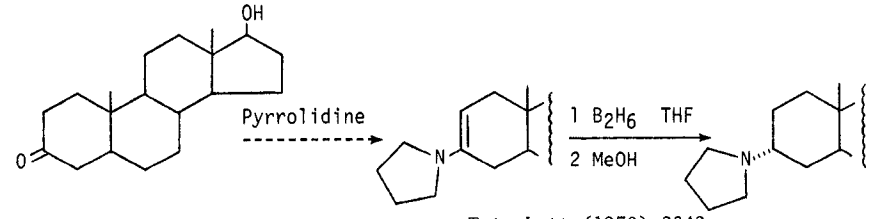
96%

JACS (1969) 91 3996

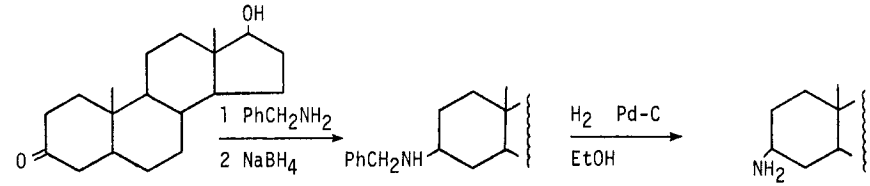


48%

JACS (1969) 91 3996



Tetr Lett (1970) 2849
JOC (1965) 30 3203



25%

Bull Soc Chim Fr (1963) 798

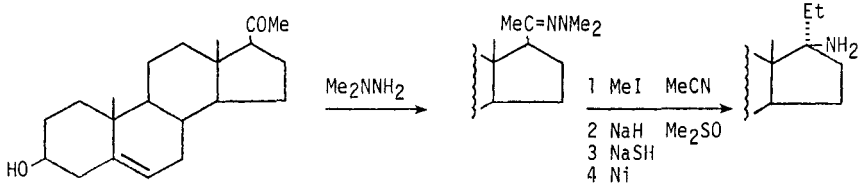
$Ph_2CO \xrightarrow{PhNH_2\ \ ZnCl_2} Ph_2C{=}NPh \xrightarrow{LiAlH_4\ \ Et_2O} Ph_2CHNHPh$ 62%

JOC (1958) 23 535

For reduction of imines with H_2 and Pt see Bull Soc Chim Fr (1964) 753
" " " " " H_2 " Pd " JCS C (1970) 1303
" " " " " H_2 " Ni " JOC (1962) 27 2209
" " " " by electrolysis " JOC (1970) 35 261
For review of reduction of Schiff's bases see Org React (1948) 4 174

$Ph_2CO \dashrightarrow Ph_2CN_2 \xrightarrow{Et_2NH\ \ h\nu} Ph_2CHNEt_2$ 23%

Annalen (1958) 614 19

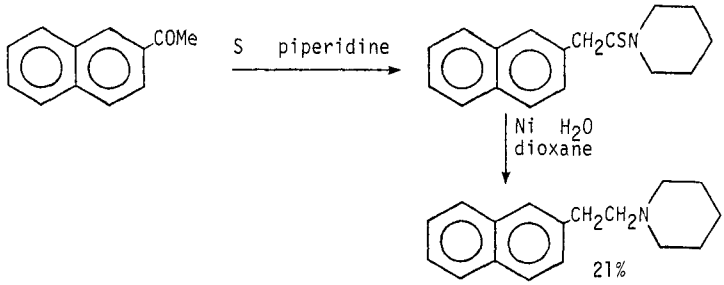


J Heterocyclic Chem (1964) 1 53

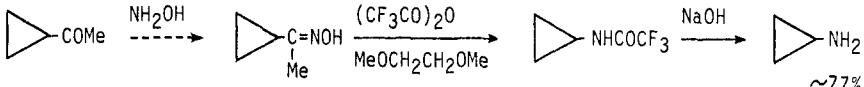
$PhCOEt \xrightarrow{NH_2OH} PhC(=NOH)Et \xrightarrow[EtOH\ \ H_2O]{Ni\ \ NaH_2PO_2} PhCHNH_2Et$ 78%

JCS C (1966) 531

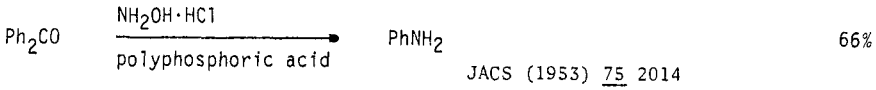
For reduction of oximes with Ni-Al and NaOH see JCS C (1966) 655
" " " " " Zn " NH_3 " Monatsh (1963) 94 677
" " " " " Na and NH_3 see Zh Obshch Khim (1965) 35 125 (Chem Abs 62 13068)
" " " " " $LiAlH_4$ see JOC (1952) 17 294
" " " " " B_2H_6 " JOC (1969) 34 1817
" " " " " H_2 and Rh " JOC (1962) 27 2209
" " " " by electrolysis " JACS (1967) 89 6374



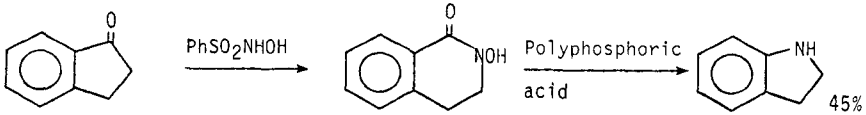
JOC (1951) 16 131



JACS (1957) 79 6522



JACS (1953) 75 2014

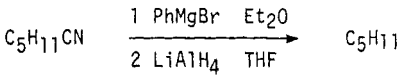


Proc Chem Soc (1963) 224

Amines may also be prepared by conversion of ketones into amides followed by hydrolysis or reduction. See section 87 (Amides from Ketones) and section 96 (Amines from Amides)

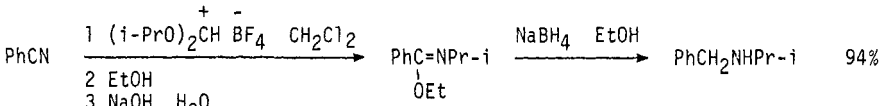
Some of the reactions listed in section 94 (Amines from Aldehydes) may also be applied to the preparation of amines from ketones

Section 103 Amines from Nitriles



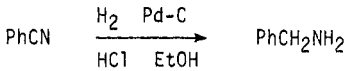
54%

JACS (1953) 75 5898

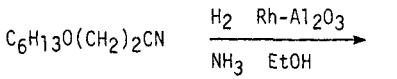


94%

JOC (1969) 34 627

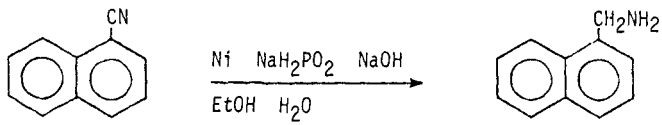


JACS (1928) 50 3370
JCS (1942) 426



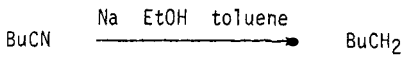
90%

JACS (1960) 82 2386



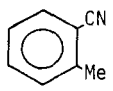
82%

JCS C (1966) 531
Bull Chem Soc Jap (1967) 40 1548

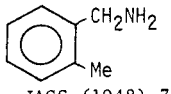


76%

JACS (1934) 56 1614
Ber (1942) 75B 991



$LiAlH_4$ Et_2O



88%

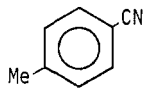
JACS (1948) 70 3738
Org React (1951) 6 469

$PhCH_2CN$ $LiAlH_4$ $AlCl_3$ Et_2O $PhCH_2CH_2NH_2$ 83%

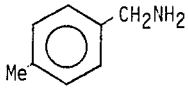
JACS (1955) 77 2544

PhCN $(i\text{-}Bu)_2AlH$ C_6H_6 PhCH=NH H_2 Pd $PhCH_2NH_2$ 57%

JOC (1959) 24 627



$NaBH_4$ $AlCl_3$
diglyme



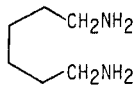
85%

JACS (1956) 78 2582

$C_7H_{15}CN$ $NaBH_4$ $CoCl_2$ MeOH $C_7H_{15}CH_2NH_2$ 80%

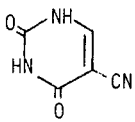
Tetr Lett (1969) 4555

B_2H_6 THF

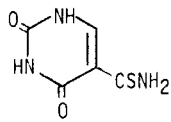


85%

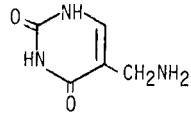
JACS (1960) 82 681



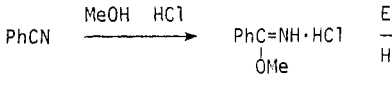
H_2S NaOH
H_2O



H_2 Pd-C

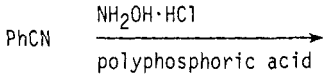


Chem Pharm Bull (1961) 9 119
JOC (1951) 16 131



76%

JACS (1935) 57 772

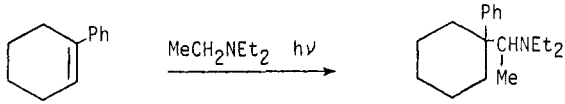


20%

JACS (1953) 75 2014

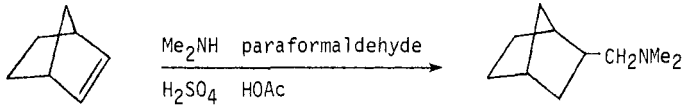
Amines may also be prepared by conversion of nitriles into amides followed by hydrolysis or reduction. See section 88 (Amides from Nitriles) and section 96 (Amines from Amides)

Section 104 Amines from Olefins



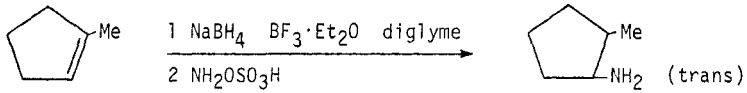
11%

Chem Comm (1969) 753



19%

Tetr Lett (1966) 6483



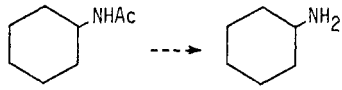
45%

JACS (1966) 88 2870
JOC (1967) 32 3199

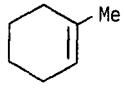
$MeCH{=}CH_2$ —(1 $Hg(OAc)_2$ $PhNH_2$; 2 $NaBH_4$)→ $Me_2CHNHPh$ 70%

Tetr Lett (1967) 5165
(1969) 2289
Compt Rend (1966) C 262 1591

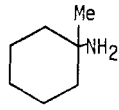
(1 $Hg(NO_3)_2$ MeCN; 2 $NaBH_4$ NaOH H_2O)



JACS (1969) 91 5647



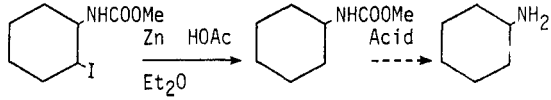
(1 NaCN H_2SO_4 HOAc; 2 H_2O)



58%

Tetrahedron (1967) 23 3563
Org React (1969) 17 213

(1 AgCNO I_2 Et_2O; 2 MeOH)



(Zn HOAc, Et_2O; Acid)

JACS (1970) 92 1326

$MeCH{=}CH_2$ —(1 $BuNH_2$ $PdCl_2$ Na_2HPO_4 THF; 2 H_2)→ $Me_2CHNHBu$

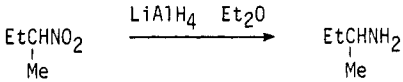
Proc Chem Soc (1961) 370

$C_8H_{17}CH{=}CH_2$ —(1 O_3 MeOH; 2 H_2 Ni NH_3)→ $C_8H_{17}CH_2NH_2$ 60%

JOC (1962) 27 2392

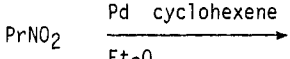
Amines may also be prepared by conversion of olefins into amides followed by hydrolysis or reduction. See section 89 (Amides from Olefins) and section 96 (Amines from Amides)

Section 105 Amines from Miscellaneous Compounds



85%

JACS (1948) 70 3738
(1951) 73 1293



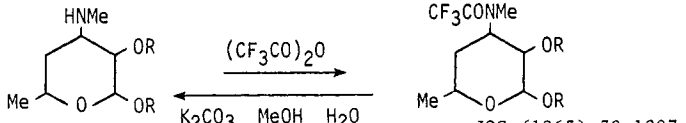
55%

JCS (1954) 3586

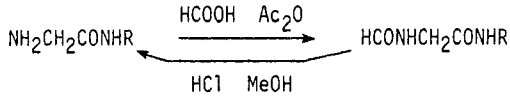
For reduction of nitro compounds with H_2 and Pd-C see Ber (1953) 86 939
" " " " " " H_2 and Ni see Org Synth (1955) Coll Vol 3 59
" " " " " " Fe and HCl see Org Synth (1943) Coll Vol 2 160
" " " " " " Al-Hg see JACS (1968) 90 3245

Section 105A Protection of Amines

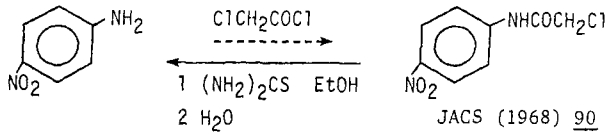
Amine protecting groups which are generally applicable are included in this section. For a review of the protection of amino acids and peptides see Advances in Org Chem (1963) 3 159



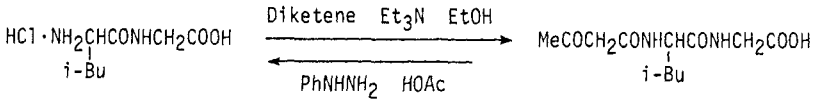
JOC (1965) 30 1287
JACS (1953) 75 3473



Chem Ind (1953) 107
Helv (1960) 43 1751

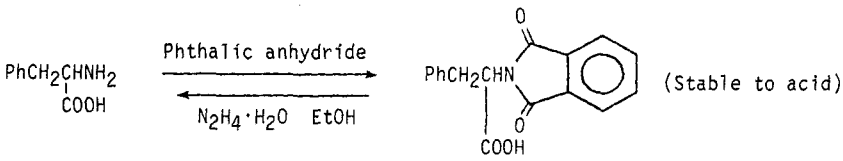


JACS (1968) 90 4508



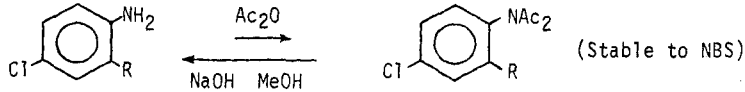
Tetr Lett (1965) 605

Further examples of the preparation and cleavage of acyl derivatives of amines are included in section 82 (Amides from Amines) and section 96 (Amines from Amides)



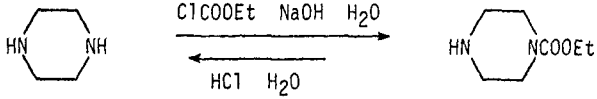
(Stable to acid)

JACS (1952) 74 3822
Rec Trav Chim (1960) 79 688



(Stable to NBS)

Can J Chem (1955) 33 1819



JCS (1929) 39
JACS (1954) 76 1164

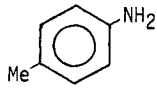
$PhNH_2$ $\xrightarrow[HBr]{ClCOOCH_2Ph}$ $PhNHCOOCH_2Ph$

JOC (1952) 17 1564

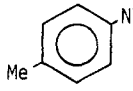
For the hydrogenolysis of benzyloxycarbonyl groups see
JACS (1957) 79 1636
and Org React (1953) 7 263
For the photolytic cleavage of benzyloxycarbonyl groups see
Tetr Lett (1962) 697

$HCl \cdot NH_2CH_2COOMe$ $\xrightarrow[HBr \quad HOAc]{N_3COOBu\text{-}t \quad Et_3N \quad EtOAc}$ $t\text{-}BuOCONHCH_2COOMe$

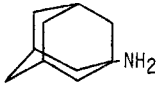
Helv (1959) 42 2622
JACS (1957) 79 4686



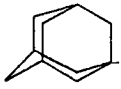
$\xrightarrow[Zn \quad MeOH]{ClCOOCH_2CH_2I}$



JCS (1965) 7136



$\xrightarrow[Zn \quad MeOH]{ClCOOCH_2CCl_3}$

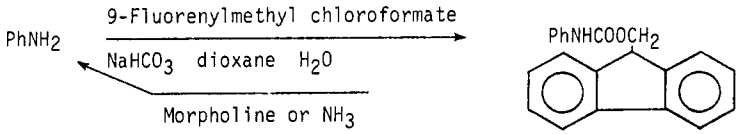


(Stable to acid, base and CrO_3)

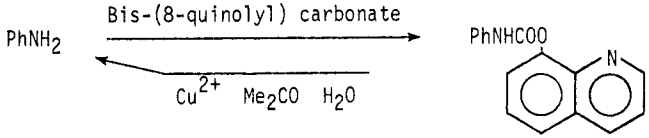
Tetr Lett (1967) 2555

$PhNH_2$ $\xrightarrow[KOH \quad EtOH]{ClCOOCH_2CH_2Ts}$ $PhNHCOOCH_2CH_2Ts$

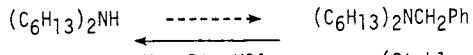
Proc Chem Soc (1962) 363



JACS (1970) 92 5748

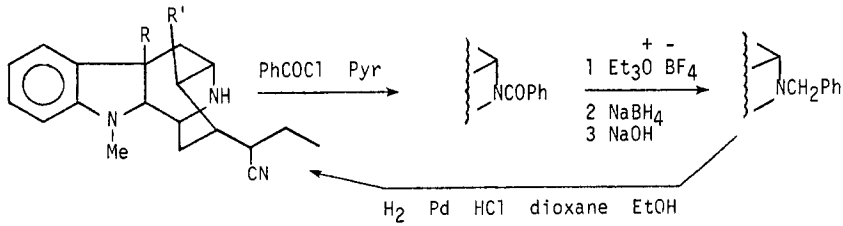


JACS (1962) 84 4899

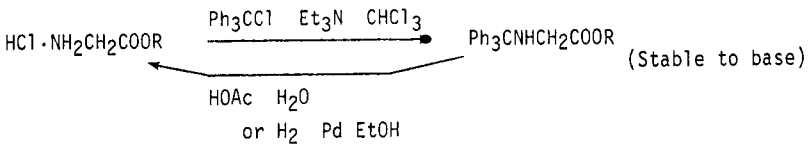


(Stable to acid, base and RMgX)

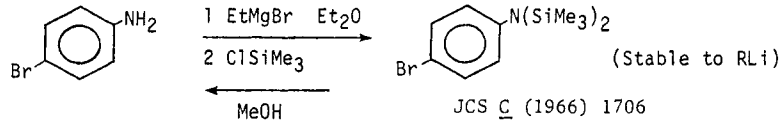
JCS (1940) 1307
Org React (1953) 7 263
JACS (1950) 72 3410



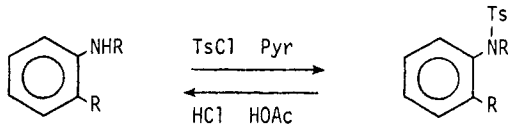
Tetrahedron (1970) 26 803



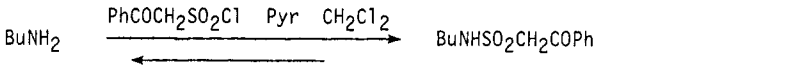
JACS (1956) 78 1359



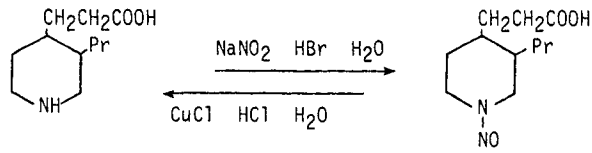
JCS C (1966) 1706



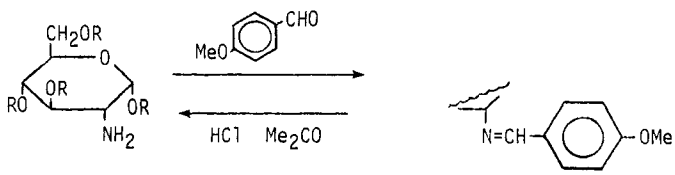
JACS (1949) 71 1901
(1952) 74 2006



(Stable to acid, base and CrO_3)
Tetr Lett (1970) 345



JACS (1946) 68 146
(1957) 79 2215

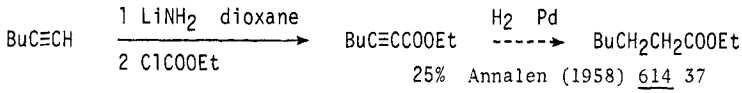


JACS (1956) 78 1393

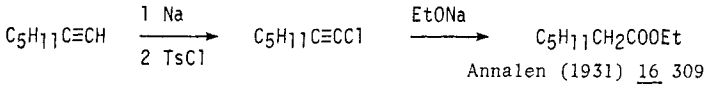
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 8 PREPARATION OF ESTERS

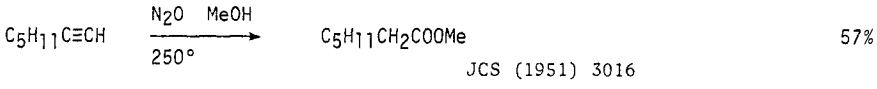
Section 106 Esters from Acetylenes



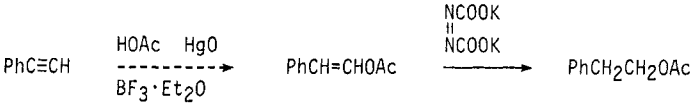
25% Annalen (1958) 614 37



Annalen (1931) 16 309

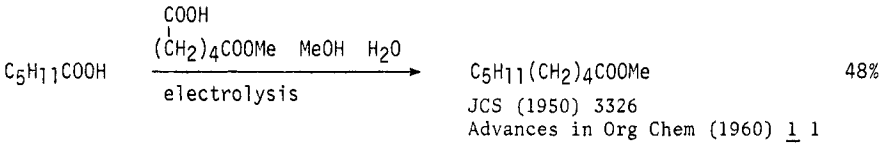


JCS (1951) 3016

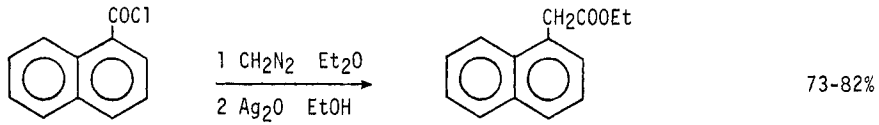


JOC (1965) 30 3985
JACS (1934) 56 1802

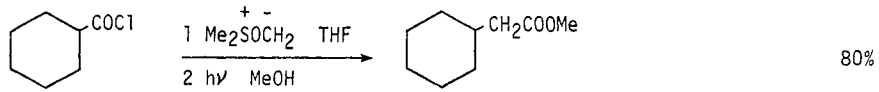
Section 107 Esters from Carboxylic Acids, Acid Halides and Anhydrides



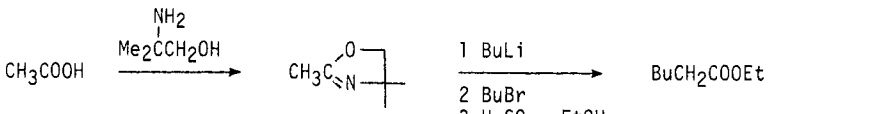
JCS (1950) 3326
Advances in Org Chem (1960) 1 1



Org React (1942) 1 38

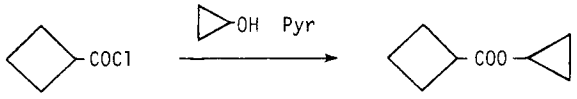


JACS (1964) 86 1640



JACS (1970) 92 6644

Further methods for the alkylation and homologation of carboxylic acids and esters are included in section 17 (Carboxylic Acids, Acid Halides and Anhydrides from Carboxylic Acids and Acid Halides) and section 113 (Esters from Esters)



55%

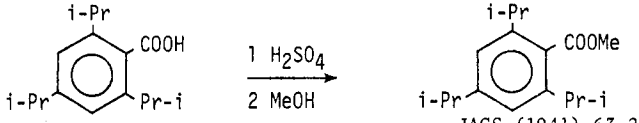
JACS (1951) 73 5487

$t\text{-BuCH}_2\text{COOH}$ $\xrightarrow{\text{EtOH}\quad H_2SO_4}$ $t\text{-BuCH}_2\text{COOEt}$ 77%

JACS (1938) 60 2790

$C_8H_{17}COOH$ $\xrightarrow[\text{molecular sieves}]{\text{MeOH}\quad H_2SO_4}$ $C_8H_{17}COOMe$

Chem Ind (1968) 1568
(1967) 825

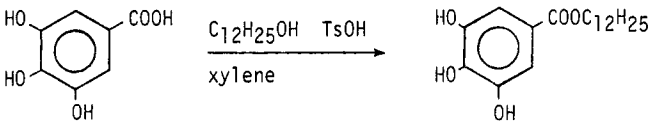


81%

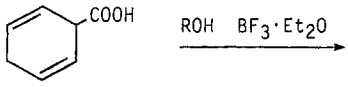
JACS (1941) 63 2431

$C_{12}H_{25}COOH$ $\xrightarrow{\text{EtOH}\quad HCl}$ $C_{12}H_{25}COOEt$

Org Synth (1943) Coll Vol 2 292
(1932) Coll Vol 1 246

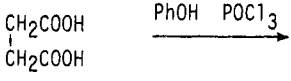


Rec Trav Chim (1951) 70 277
JACS (1945) 67 902
Acta Chem Scand (1959) 13 1407



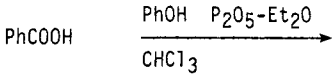
(R=Me, Et, i-Pr) 75-81%

Tetr Lett (1970) 4011
JCS (1965) 5770



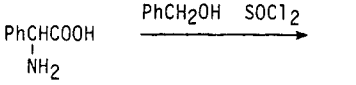
62-67%

Org Synth (1963) Coll Vol 4 390 178



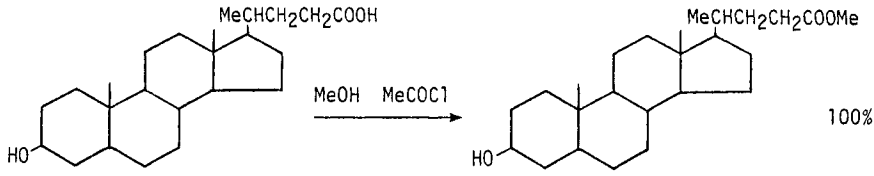
90%

Chem Ind (1964) 2102



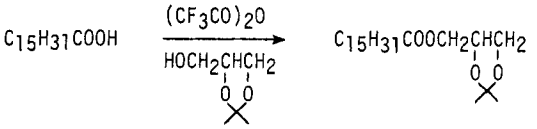
90%

JOC (1965) 30 3575
Annalen (1961) 640 136



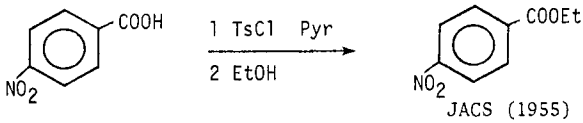
100%

Org Synth (1955) Coll Vol 3 237



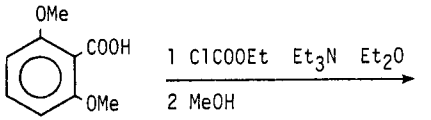
Applicable to hindered acids

JCS (1965) 4594
JOC (1965) 30 927

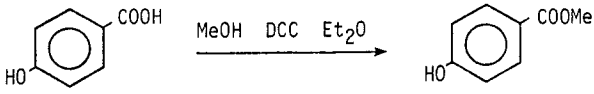


90%

JACS (1955) 77 6214

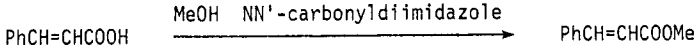


Rev Roumaine Chim (1966) 11 1237
(Chem Abs 66 65249)
JACS (1958) 80 5714
(1969) 91 3931



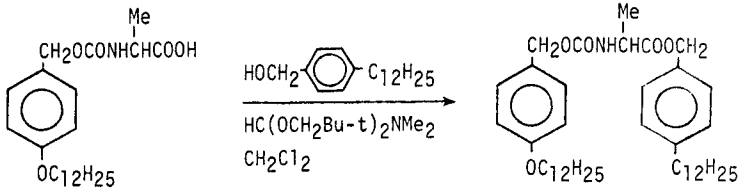
45%

Tetrahedron (1965) 21 3531
Compt Rend (1963) 256 1804
(1962) 255 945



83%

Ber (1962) 95 1284
JCS C (1969) 1610



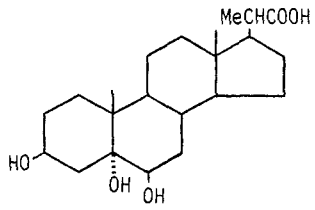
83%

Helv (1965) 48 1746
JACS (1969) 91 5674

$(PhO)_2CHCOOH \xrightarrow{EtOH \quad Me_2C(OMe)_2} (PhO)_2CHCOOEt$

Bull Soc Chim Fr (1964) 381
JOC (1959) 24 261

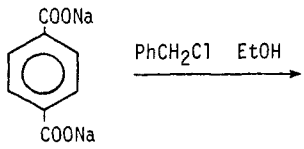
Further examples of the reaction RCOOH + ROH ⟶ RCOOR are included in section 108 (Esters from Alcohols and Phenols) and section 30A (Protection of Carboxylic Acids)



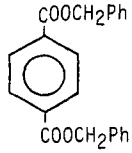
MeI NaHCO$_3$ DMA ⟶ MeCHCOOMe

91%

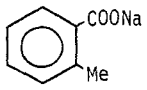
JOC (1968) 33 2143



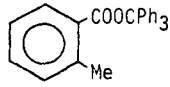
$PhCH_2Cl$ EtOH ⟶



J Med Chem (1967) 10 706

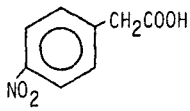


$Ph_3CBr \quad C_6H_6$ ⟶

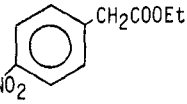


84%

JOC (1962) 27 3595
JCS C (1966) 1191



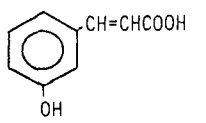
$Et_2SO_4 \quad Na_2CO_3 \quad DMF$ ⟶



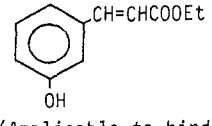
88%

(Applicable to hindered acids)

Monatsh (1968) 99 103
Helv (1943) 26 2283



Et_2SO_4 N-ethyldicyclohexylamine Me_2CO



92%

(Applicable to hindered acids)

JOC (1964) 29 2490
JACS (1969) 91 3544

$PhCOOH \xrightarrow[\text{xylene}]{C_6H_{13}Cl \quad Et_3N} PhCOOC_6H_{13}$ 47%

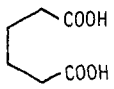
JOC (1961) 26 5180

$CH_2{=}\underset{\underset{Me}{|}}{C}CH_2COOH \xrightarrow[2\ AgNO_3]{1\ NaOH \quad H_2O} CH_2{=}\underset{\underset{Me}{|}}{C}CH_2COOAg \xrightarrow{MeI \quad Et_2O} CH_2{=}\underset{\underset{Me}{|}}{C}CH_2COOMe$ 47%

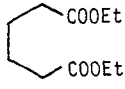
JACS (1949) 71 3214
(1951) 73 5487
(1952) 74 3944

$Bu_3CCOONa \xrightarrow{BuOSOCl \quad C_6H_6} Bu_3CCOOBu$ 82%

JACS (1947) 69 1046



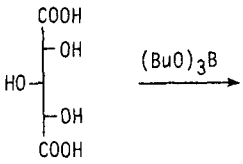
$HC(OEt)_3$



89%

(Applicable to hindered acids)

Chem Ind (1965) 349

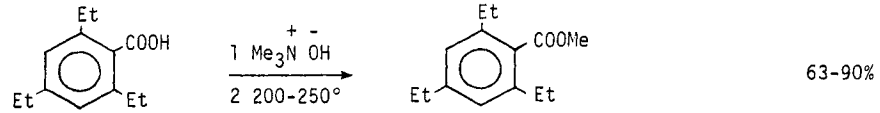


98%

Zh Obshch Khim (1967) 37 1481
(Chem Abs 68 22157)

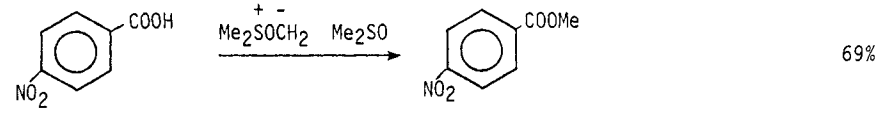
$PhCOOH \xrightarrow{Me_2NCH(OR)_2 \quad C_6H_6} PhCOOR$ (R=Me, Et, CH_2Ph) 80-95%

Helv (1965) 48 1746



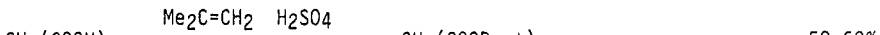
63-90%

JACS (1939) 61 1290
Z Physiol Chem (1936) 244 56



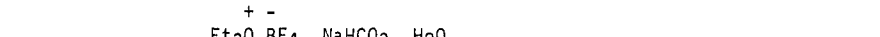
69%

Tetr Lett (1964) 867



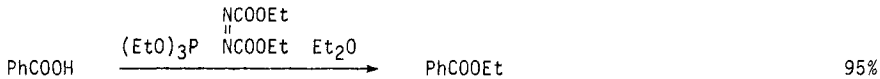
58-60%

Org Synth (1963) Coll Vol 4 261
JOC (1963) 28 1251



82%

Tetr Lett (1969) 1819
Ber (1956) 89 209 2060



95%

Bull Chem Soc Jap (1967) 40 2380

JACS (1954) 76 4481

$PhCOOH \xrightarrow{Ph_2CN_2\ \ Et_2O} PhCOOCHPh_2$ 100%

Org Synth (1955) Coll Vol 3 351

For preparation of CH_2N_2 see Org Synth (1943) Coll Vol 2 165 and Org React (1942) 1 50

" " " Me_2CN_2 and Pr_2CN_2 see JCS C (1966) 467

" " " $PhCHN_2$ " JACS (1964) 86 658

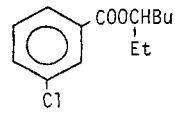
" " " anthryldiazomethane " Bull Chem Soc Jap (1967) 40 691

$C_{15}H_{31}COOH \xrightarrow[2\ I_2]{1\ Pb(OAc)_4\ \ tetrachloroethane} C_{15}H_{31}COOC_{15}H_{31}$ 54%

JOC (1963) 28 65

$(PrCH_2CO)_2O \xrightarrow{HgO\ \ I_2\ \ BrCH_2CH_2Br} PrCH_2COOCH_2Pr$ 50%

JOC (1970) 35 3167

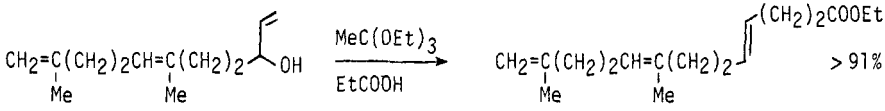
$BuCHCOCl$ (Et) $\xrightarrow[Pyr\ \ hexane]{m\text{-Chloroperbenzoic acid}}$  ~73%

JOC (1965) 30 3760
JACS (1950) 72 67

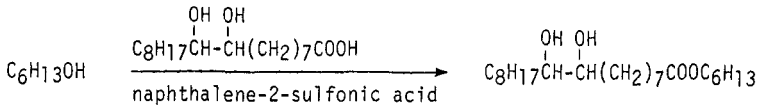
$Ph_2CHCOOH \xrightarrow{Electrolysis\ \ HOAc} Ph_2CHOAc$ 37%

JCS (1952) 3624

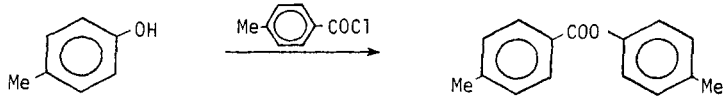
Section 108 Esters from Alcohols and Phenols



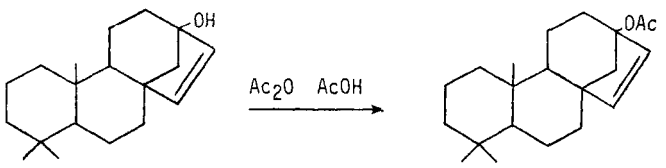
JACS (1970) 92 741
Chem Comm (1970) 1512 1513



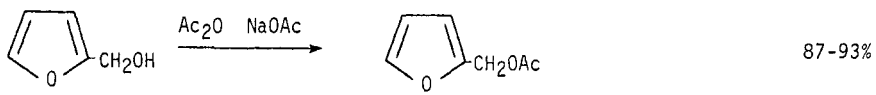
JACS (1945) 67 902
Rec Trav Chim (1951) 70 277



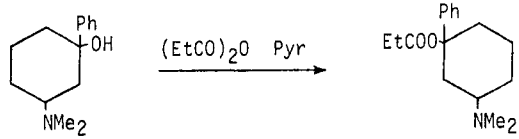
Annalen (1969) 726 216



JCS C (1969) 2115

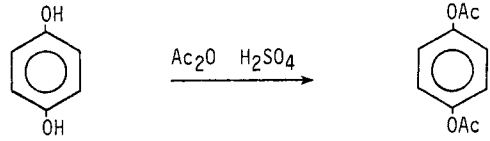


Org Synth (1941) Coll Vol 1 285
JOC (1965) 30 3480



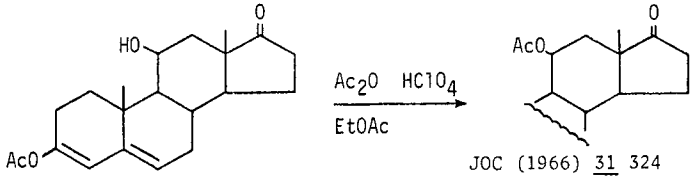
60%

J Med Chem (1970) 13 125

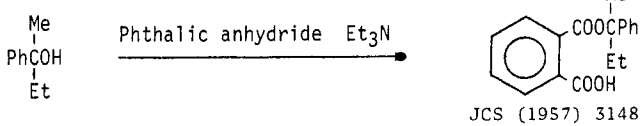


96-98%

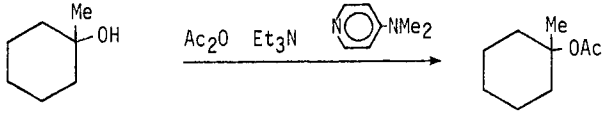
Org Synth (1955) Coll Vol 3 452



JOC (1966) 31 324

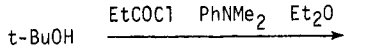


JCS (1957) 3148



86%

Angew (1969) 81 1001
(Internat Ed 8 981)



JACS (1943) 65 986
Helv (1944) 27 513
JCS (1952) 4883

$t\text{-BuOH} \xrightarrow[Et_2O]{MeCOCl \quad tetramethylurea} t\text{-BuOAc}$ 50-60%

Tetr Lett (1967) 3267

$Et_3COH \xrightarrow[2\ PhCOCl]{1\ BuLi \quad THF} PhCOOCEt_3$ 94%

JOC (1970) 35 1198

Esters from alcohols, Ph_3CNa and $(RCO)_2O$ JOC (1963) 28 582

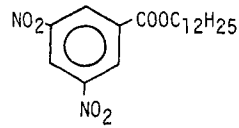
" " " EtMgBr " " JACS (1936) 58 1384
JCS (1963) 3578

" " " K " " JACS (1961) 83 423

" " " CaC_2 " " Monatsh (1966) 97 62

" " " Mg and RCOCl Org Synth (1955) Coll Vol 3 144

" " " NaH " " Chem Comm (1967) 259

$C_{12}H_{25}OH \xrightarrow[TsCl \quad Pyr]{3,5\text{-Dinitrobenzoic acid}}$  82%

(Applicable to hindered alcohols)

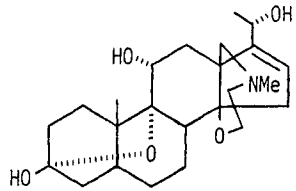
JACS (1955) 77 6214
(1963) 85 2446

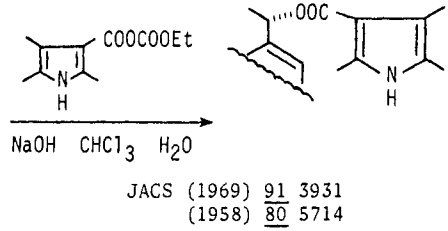
$PhOH \xrightarrow{PhCOOH \quad (CF_3CO)_2O} PhCOOPh$ 70%

(Applicable to hindered alcohols and phenols)

Tetrahedron (1965) 21 3531
Tetr Lett (1964) 1285
JCS (1965) 4594

For selective esterification of 2ry-OH in the presence of 1ry-OH
see JOC (1961) 26 177





JACS (1969) 91 3931
(1958) 80 5714

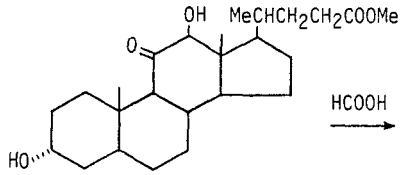
$PhOH \xrightarrow{PhCOOH \quad DCC \quad Et_2O} PhCOOPh$

Tetrahedron (1965) 21 3531
Compt Rend (1963) 256 1804
(1962) 255 945

$PhCH_2OH \xrightarrow{PhCOOH \quad N,N'\text{-carbonyl diimidazole}} PhCOOCH_2Ph$ 89%

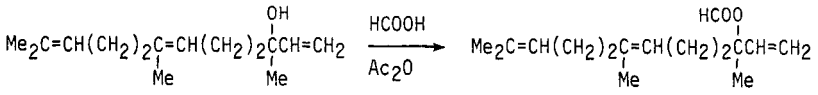
Ber (1962) 95 1284
JCS C (1969) 1610

Further examples of the reaction ROH + RCOOH ⟶ RCOOR are included in section 107 (Esters from Carboxylic Acids, Acid Halides and Anhydrides) and section 45A (Protection of Alcohols and Phenols)

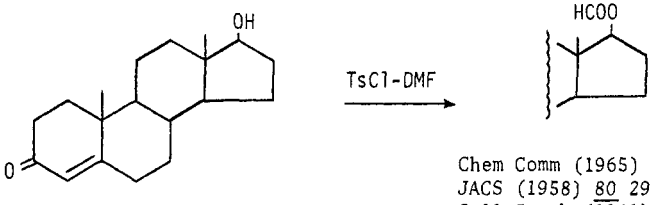


91%

JACS (1954) 76 4915
(1945) 67 740



Bull Soc Chim Fr (1965) 484
Rec Trav Chim (1964) 83 1287 1294

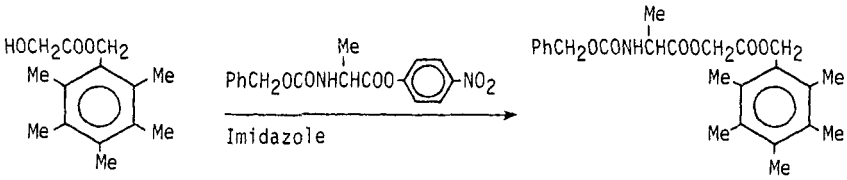


79%

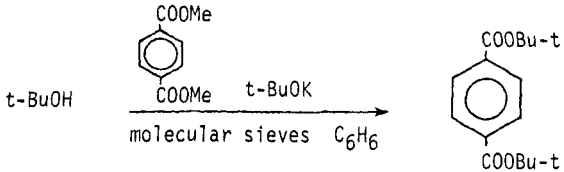
Chem Comm (1965) 413
JACS (1958) 80 2906
Coll Czech (1961) 26 1723

$C_8H_{17}OH$ —(HCOF, Et_3N, Et_2O)→ $HCOOC_8H_{17}$ 73%

JACS (1960) 82 2380



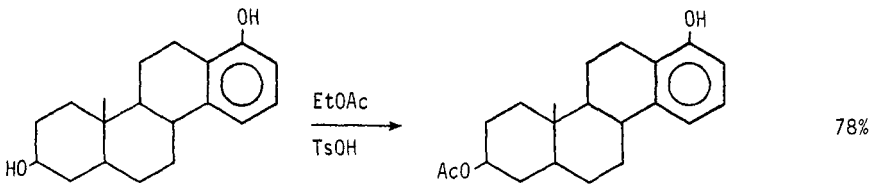
Chem Ind (1967) 1960



Chem Ind (1966) 1622

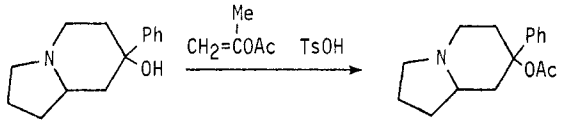
$Me(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$ —(EtOAc, MeONa)→ $Me(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc$

Lipids (1967) 2 437
JACS (1956) 78 6347



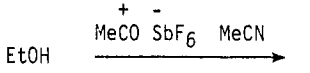
78%

JACS (1956) 78 6322



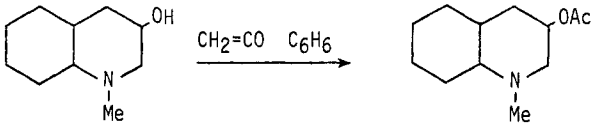
59%

J Med Chem (1969) 12 563



(Applicable to hindered alcohols)

JACS (1962) 84 2733
Gazz (1967) 97 442
(Chem Abs 67 117049)

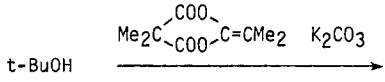


95%

(Applicable to hindered alcohols)

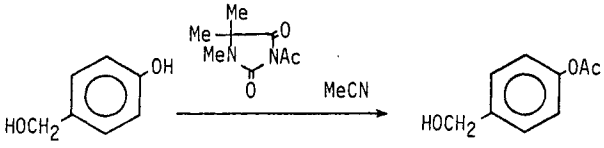
J Med Chem (1969) 12 432
JOC (1968) 33 3695
Org React (1946) 3 108

For preparation of $CH_2=CO$ see



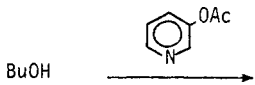
95%

Angew (1963) 75 841
(Internat Ed 2 608)



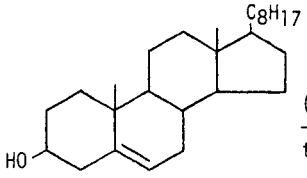
~91%

JACS (1969) 91 2162

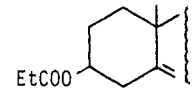


BuOH → BuOAc 93%

Bull Chem Soc Jap (1964) 37 864
Chem Ind (1965) 1498

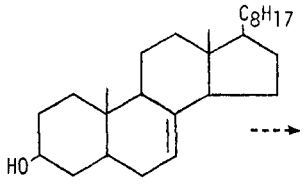


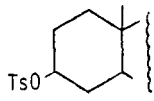
$(EtCO)_2NH$ HBr, toluene



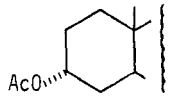
85%

Roczniki Chem (1952) 26 692
(Chem Abs 49 2464)





Bu_4NOAc, Me_2CO



JCS (1969) 1605

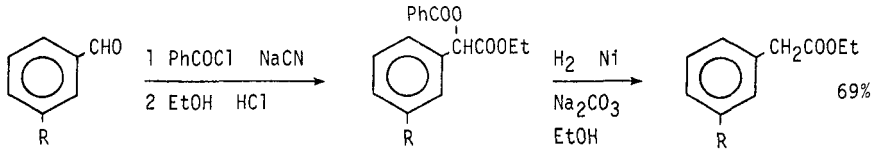
i-$PrCH_2CH_2OH$ → (t-Butylhypochlorite, CCl_4) → i-$PrCH_2COOCH_2CH_2Pr$-i 89%

Helv (1953) 36 1763

$PrCH_2OH$ → ($Na_2Cr_2O_7$, H_2SO_4, H_2O) → $PrCOOCH_2Pr$ 41-47%

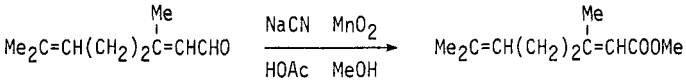
Org Synth (1941) Coll Vol 1 138

Section 109 Esters from Aldehydes



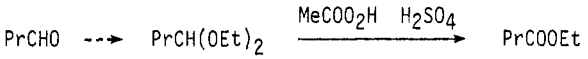
69%

JOC (1949) 14 1013

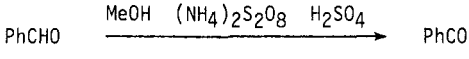


(Applicable to unsaturated and aromatic aldehydes only)

JACS (1968) 90 5616
Ber (1970) 103 3774

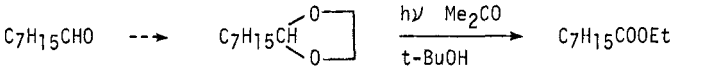


JOC (1960) 25 1699

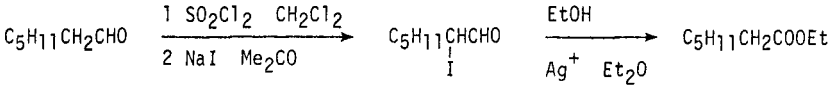


100%

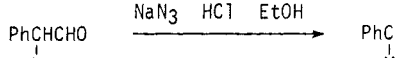
JOC (1968) 33 2525



Tetr Lett (1963) 2189

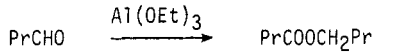


Tetr Lett (1968) 4415
JACS (1954) 76 2695



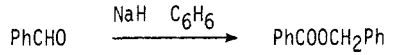
51%

JACS (1954) 76 4564



81%

JACS (1947) 69 2605



92%

JACS (1946) 68 2647

For examples of the reaction RCHO ⟶ HCOOR see page 84 (Section 34, Alcohols and Phenols from Aldehydes)

Esters may also be prepared by oxidation of aldehydes to carboxylic acids followed by esterification. See section 19 (Carboxylic Acids and Acid Halides from Aldehydes)

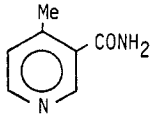
Section 110 Esters from Alkyls, Methylenes and Aryls

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

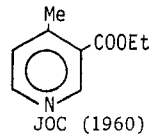
Section 111 Esters from Amides

$PhCONH_2 \xrightarrow[105°]{MeOH\ \ BF_3} PhCOOMe$ 100%

Chem Comm (1969) 414



$\xrightarrow{EtOH\ \ HCl}$



85%

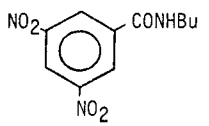
JOC (1960) 25 560
Arch Pharm (1957) 290 218
JOC (1970) 35 125

$PhCONH_2 \xrightarrow[170°]{C_8H_{17}Br\ \ H_2O} PhCOOC_8H_{17}$ 79%

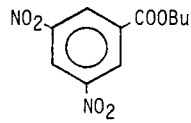
JOC (1969) 34 3204

$MeCONHBu \xrightarrow[2\ CCl_4\ \ 77°]{1\ HNO_3\ \ Ac_2O} MeCOOBu$ 75%

JACS (1955) 77 6011
JOC (1969) 34 3834



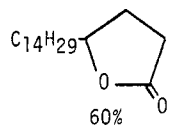
$\xrightarrow[2\ Hexane\ reflux]{1\ NaNO_2\ \ Ac_2O}$



83%

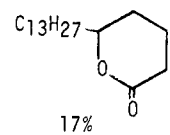
JACS (1955) 77 6008 6011
(1954) 76 4497
Tetr Lett (1965) 2627

$C_{17}H_{35}CONH_2 \xrightarrow[2\ NaHSO_3\ \ H_2O]{1\ Pb(OAc)_4\ \ I_2 \atop h\nu\ \ C_6H_6}$



60%

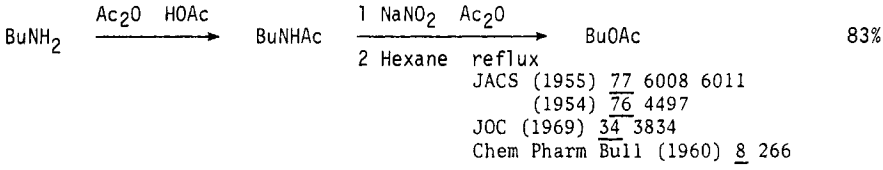
+



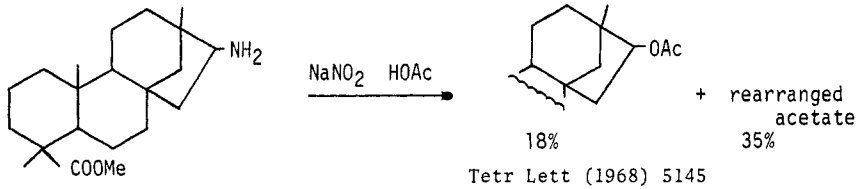
17%

JCS (1965) 181

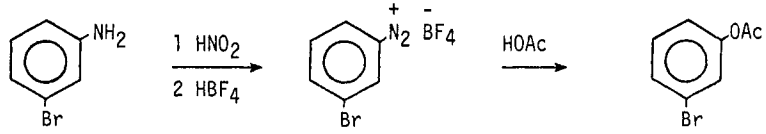
Section 112 Esters from Amines



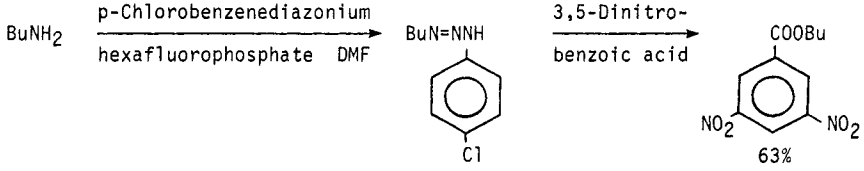
JACS (1955) 77 6008 6011
(1954) 76 4497
JOC (1969) 34 3834
Chem Pharm Bull (1960) 8 266



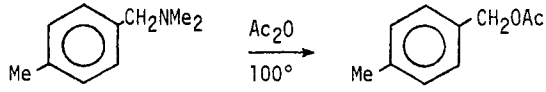
Tetr Lett (1968) 5145
Tetrahedron (1970) 26 147



JACS (1939) 61 143
(1933) 55 4954

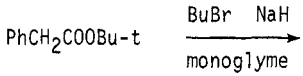


Tetr Lett (1961) 758



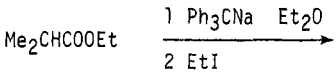
Bull Soc Chim Fr (1914) 15 162

Section 113 Esters from Esters



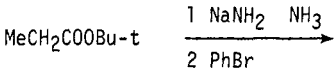
66%

JOC (1965) 30 2937
(1964) 29 2990



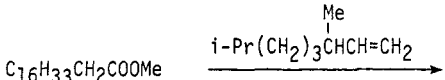
58%

JACS (1940) 62 2457



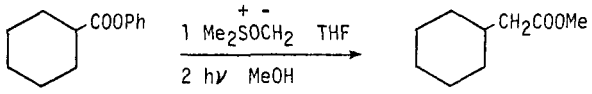
38%

JACS (1959) 81 1627



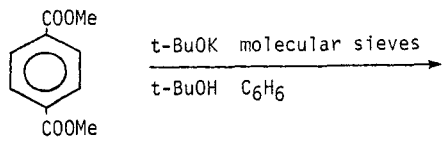
42%

J Amer Oil Chem Soc (1968) 45 453
(Chem Abs 70 3210)



JACS (1964) 86 1640

Further examples of the alkylation and homologation of carboxylic acids and esters are included in section 17 (Carboxylic Acids, Acid Halides and Anhydrides from Carboxylic Acids and Acid Halides) and section 107 (Esters from Carboxylic Acids, Acid Halides and Anhydrides)



> 90%

Chem Ind (1966) 1622

$C_{17}H_{35}COOEt$ —(Ion exch resin (basic), MeOH)→ $C_{17}H_{35}COOMe$ 80-90%

JOC (1969) 34 2032

CH_2=CHCOOMe —($C_{10}H_{21}OH$ H_2SO_4)→ CH_2=CHCOO$C_{10}H_{21}$ 83%

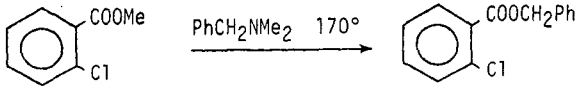
JACS (1944) 66 1203
Org Synth (1955) Coll Vol 3 146 605

RCOOBu —(HBr Et_2O)→ RCOOEt

J Pharm Sci (1969) 58 949

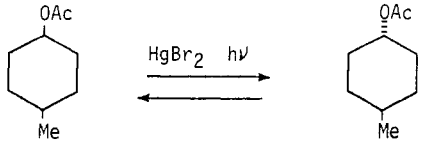
PhCOOBu-t —(MeOH, reflux)→ PhCOOMe 62%

JACS (1941) 63 3382



65%

JACS (1952) 74 547



JACS (1970) 92 1094

$PhCH(COOEt)_2 \xrightarrow{470°} PhCH_2COOEt$ 36%

JOC (1964) 29 1249

$EtCH(COOEt)_2 \xrightarrow{NaCN\ \ Me_2SO} EtCH_2COOEt$ 80%

Tetr Lett (1967) 215

Section 114 Esters from Ethers

$PhCH_2OBu\text{-}t \xrightarrow{O_3\ \ Freon\ 11} PhCOOBu\text{-}t$ 62%

JACS (1968) 90 6777
Annalen (1929) 476 233

$PrCH_2OBu \xrightarrow{Trichloroisocyanuric\ acid\ \ H_2O} PrCOOBu$ 100%

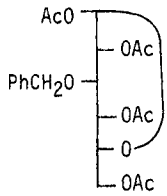
Tetr Lett (1968) 5819

$PrCH_2OBu \xrightarrow{RuO_4\ \ CCl_4} PrCOOBu$ 100%

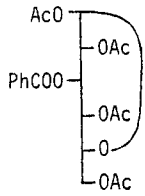
JACS (1958) 80 6682

$RCH_2OC_{15}H_{31} \xrightarrow{CrO_3\ \ HOAc\ \ CH_2Cl_2} RCOOC_{15}H_{31}$ 48% (R=H), 9% (R=Me)

Chem Comm (1966) 752



$\xrightarrow{CrO_3\ \ HOAc}$

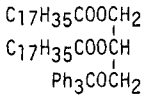


50%

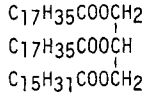
Carbohydrate Res (1970) 12 147

$CH_2=CH(CH_2)_3CH=CHCH_2OPh \xrightarrow[HOAc]{PdCl_2(Ph_3P)_2} CH_2=CH(CH_2)_3CH=CHCH_2OAc$

Chem Comm (1970) 1392



$\xrightarrow{C_{15}H_{31}COCl\ \ AgClO_4\ \ MeCN}$

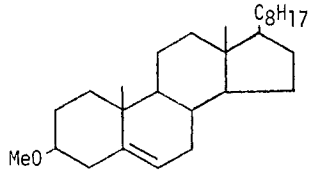


70%

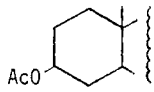
Ber (1961) 94 812
JCS (1950) 1992

$Bu_2O \xrightarrow[MeCN]{TsOAc} BuOAc$ 50%

JACS (1968) 90 3878



$\xrightarrow[Ac_2O]{BF_3\cdot Et_2O}$



93%

JOC (1965) 30 1734
Chem Rev (1954) 54 615

$$BuOBu\text{-}t \xrightarrow{HOAc\ \ TsOH} BuOAc$$

Tetr Lett (1970) 4269 94%

Section 115 Esters from Halides and Sulfonates

$$PrBr \xrightarrow[2\ MeCOCH_2CH_2COOEt\ C_6H_6]{1\ Mg\ \ Et_2O} PrC(Me)=CHCH_2COOEt \xrightarrow[EtOH]{H_2\ \ PtO_2} PrCH(Me)CH_2CH_2COOEt$$

3 $SOCl_2$
4 185-195°

JACS (1944) 66 1764

$$BuBr \xrightarrow[2\ MeCH=CHCOOBu\text{-}s]{1\ Mg\ \ Et_2O} BuCH(Me)CH_2COOBu\text{-}s$$

~60%

Org Synth (1961) 41 60

$$PhBr \xrightarrow[2\ CdCl_2\ 3\ BrCH_2COOEt]{1\ Mg\ \ THF} PhCH_2COOEt$$

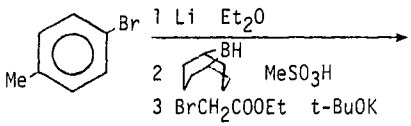
53%

JOC (1968) 33 1675

$$PhBr \xrightarrow[2\ CuBr\ 3\ N_2CHCOOEt]{1\ Li\ \ Et_2O} PhCH_2COOEt$$

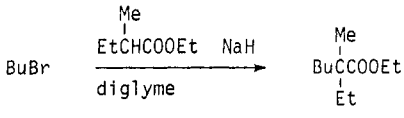
51%

Chem Comm (1969) 515



73%

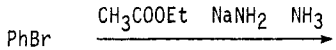
JACS (1969) 91 4304



38%

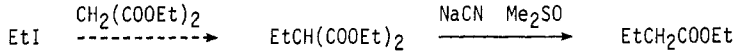
JOC (1964) 29 2990

Further examples of the alkylation of esters with halides are included in section 113 (Esters from Esters)

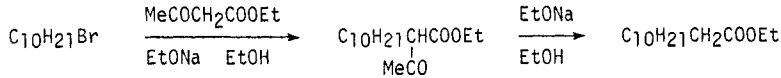


42%

JACS (1959) 81 1627

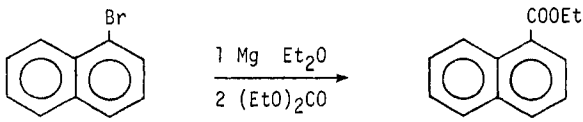


Tetr Lett (1967) 215



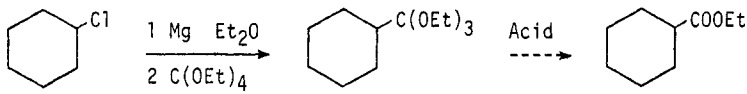
84%

JOC (1962) 27 622



68-73%

Org Synth (1943) Coll Vol 2 282



Ber (1905) 38 561

$$PhBr \xrightarrow[2\ ClCOOEt]{1\ Mg\ \ Et_2O} PhCOOEt \qquad 75\%$$

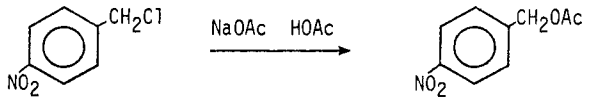
Ber (1903) 36 3087

$$C_7H_{15}I \xrightarrow[t\text{-}BuOH]{Ni(CO)_4\ \ t\text{-}BuOK} C_7H_{15}COOBu\text{-}t \qquad 66\%$$

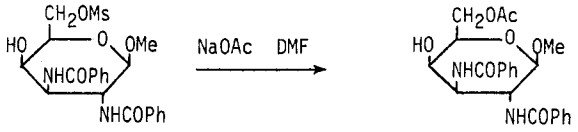
JACS (1969) 91 1233
(1963) 85 2779

$$RBr \xrightarrow[MeOH]{Ni(CO)_4\ \ MeONa} RCOOMe \qquad \begin{matrix} 88\%\ (R=Ph) \\ 95\%\ (R=\ PhCH{=}CH) \end{matrix}$$

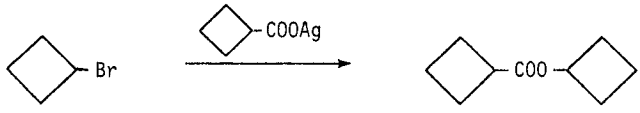
JACS (1969) 91 1233



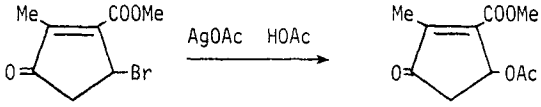
Org Synth (1955) Coll Vol 3 650
Ber (1956) 89 1732



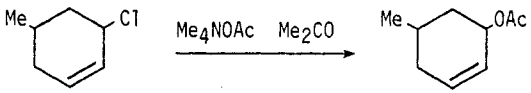
Ber (1970) 103 37



JACS (1951) 73 5487
(1949) 71 3214

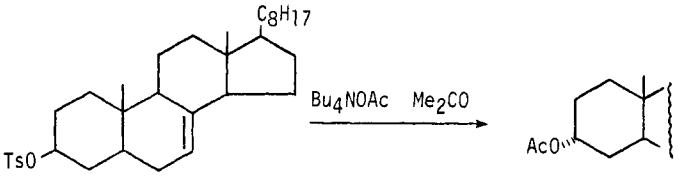


Tetrahedron (1968) 24 5421
Ber (1964) 97 443

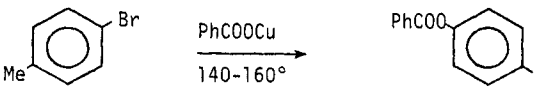


76%

JACS (1955) 77 4042
(1967) 89 2758

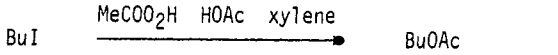


JCS C (1969) 1605



79%

JACS (1966) 88 4521

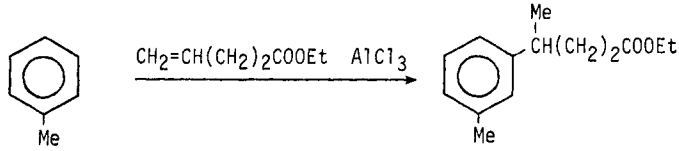


78%

JOC (1969) 34 3974

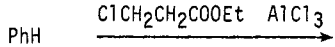
Section 116 Esters from Hydrides (RH)

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



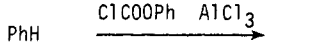
81%

JOC (1953) 18 1499
Tetrahedron (1967) 23 2481



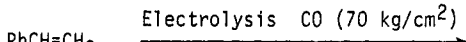
68%

Dokl (1945) 50 257
(Chem Abs 43 4638)

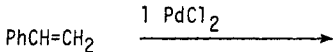


64%

JOC (1957) 22 325

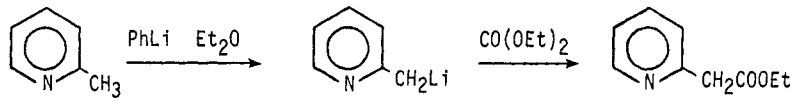


Bull Chem Soc Jap (1965) 38 2122
JACS (1965) 87 3525



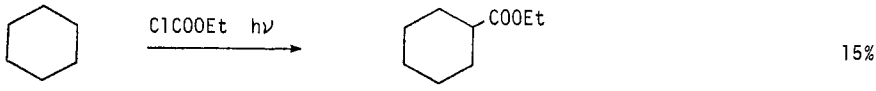
41%

JOC (1969) 34 738



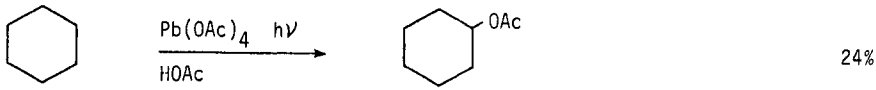
44%

JACS (1953) 75 3843



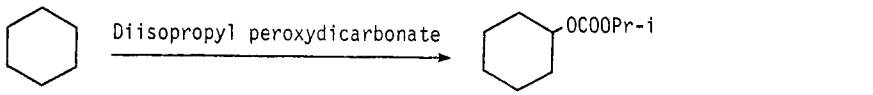
15%

Bull Chem Soc Jap (1966) 39 2463

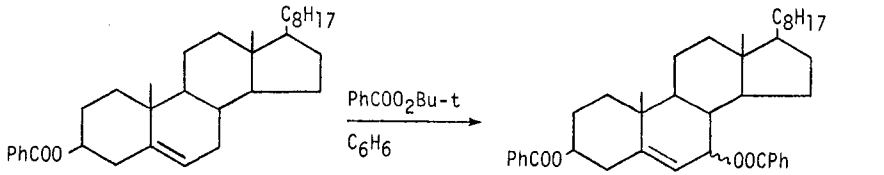


24%

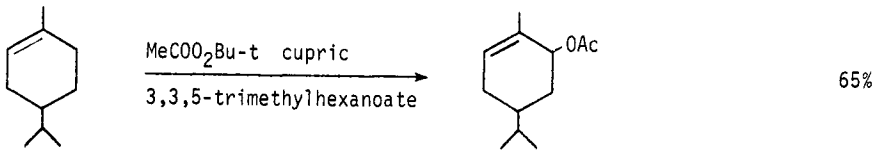
Nature (1966) 209 395



JCS (1965) 1932



Proc Chem Soc (1962) 63
JACS (1958) 80 756



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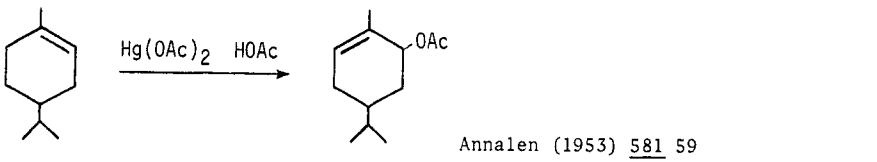
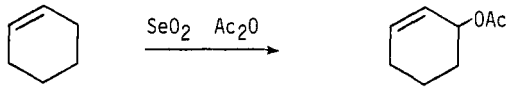
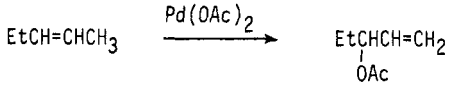
JACS (1962) 84 4969 774



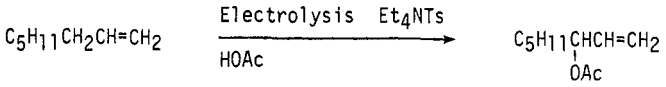
Annalen (1953) 581 59



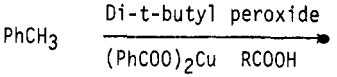
Tetrahedron (1964) 20 1017
Org React (1949) 5 331



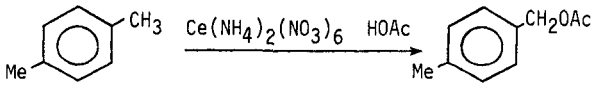
JACS (1966) 88 2054



Tetr Lett (1968) 6207



Proc Chem Soc (1962) 63



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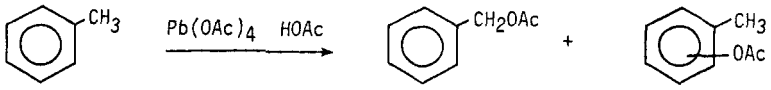
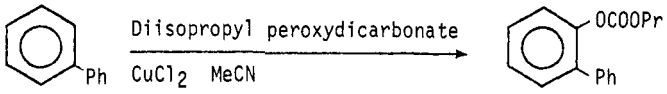
JOC (1966) 31 2033



JACS (1968) 90 1082



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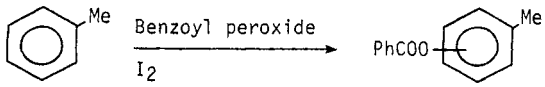
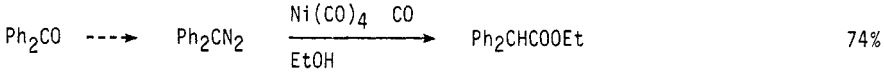
JOC (1969) 34 3302

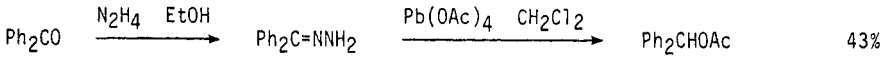


Bull Chem Soc Jap (1969) 42 2733
Rec Trav Chim (1927) 46 54

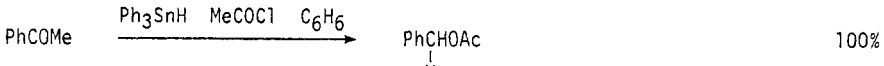
Section 117 Esters from Ketones



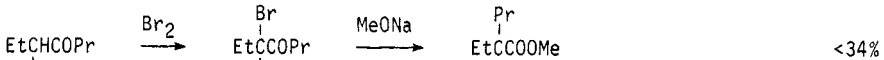
Ber (1960) 93 1840



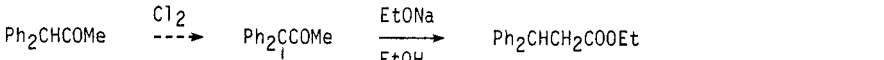
JCS C (1970) 1033



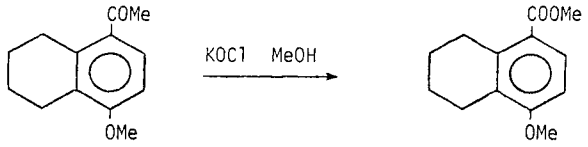
JACS (1966) 88 1833 4970



JACS (1942) 64 300
Org React (1960) 11 261

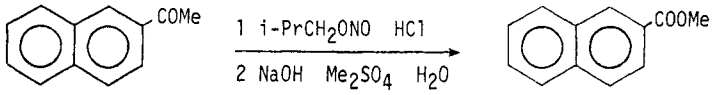


Org React (1960) 11 261

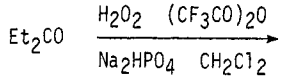


80%

JACS (1944) 66 208

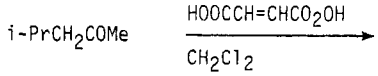


Compt Rend (1942) 214 113



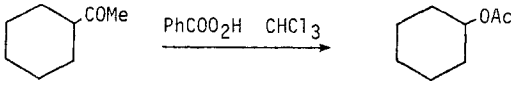
78%

JACS (1955) 77 2287



72%

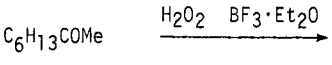
Tetrahedron (1962) 17 31



67%

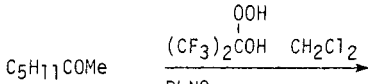
JACS (1949) 71 14
Org React (1957) 9 73

For use of m-chloroperbenzoic acid see JACS (1967) 89 4530
and JOC (1964) 29 2914



62%

JOC (1962) 27 24

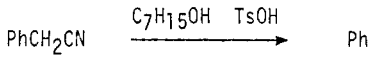


81%

Tetr Lett (1970) 2741

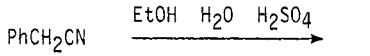
Esters may also be prepared by conversion of ketones into carboxylic acids followed by esterification. See section 27 (Carboxylic Acids from Ketones)

Section 118 Esters from Nitriles



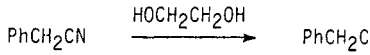
70%

JOC (1958) 23 1225
(1960) 25 560

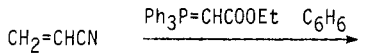


83-87%

Org Synth (1941) Coll Vol 1 270



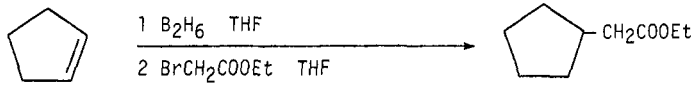
JCS (1963) 2417



Tetr Lett (1967) 2407

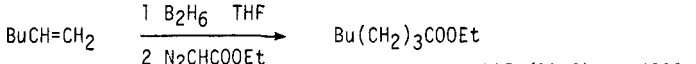
Esters may also be prepared by hydrolysis of nitriles to carboxylic acids followed by esterification. See section 28 (Carboxylic Acids from Nitriles)

Section 119 Esters from Olefins



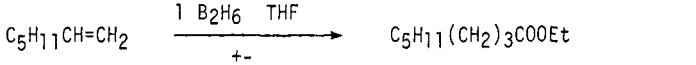
75%

JACS (1969) 91 6855 2146
(1968) 90 818 1911



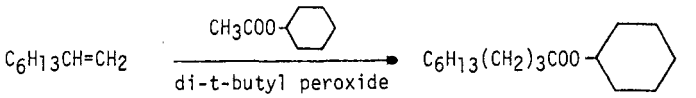
83%

JACS (1968) 90 6891



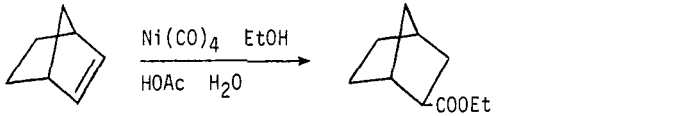
45%

JACS (1967) 89 6804



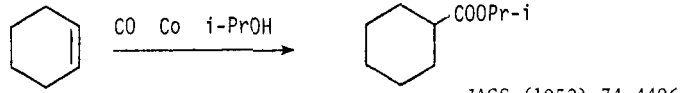
59%

JCS (1965) 1918



72%

JCS (1963) 410

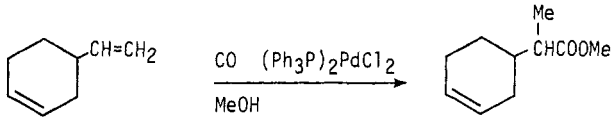


12%

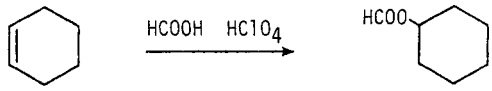
JACS (1952) 74 4496

$C_{12}H_{25}CH{=}CH_2 \xrightarrow[MeOH]{CO\ \ H_2PtCl_6\text{-}SnCl_2} C_{12}H_{25}(CH_2)_2COOMe$ 65%

JOC (1970) 35 2846

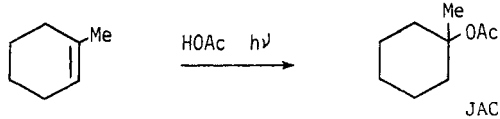


Angew (1968) 80 352
(Internat Ed 7 329)



69%

JACS (1953) 75 6212
Org Synth (1965) 45 74



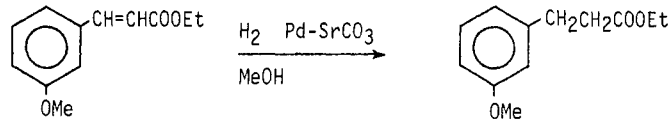
JACS (1967) 89 5199

$\underset{(CH_2)_8CH{=}CH_2}{\overset{COOEt}{|}} \xrightarrow[2\ EtOH\ \ 150\text{-}155°]{1\ O_3\ \ EtOH} \underset{(CH_2)_8COOEt}{\overset{COOEt}{|}}$ 50%

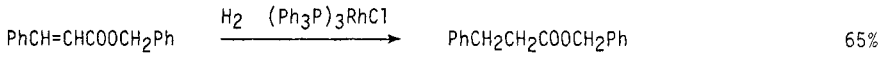
Can J Chem (1965) 43 319

Esters may also be prepared by conversion of olefins into carboxylic acids or alcohols followed by esterification. See section 29 (Carboxylic Acids from Olefins) and section 44 (Alcohols from Olefins)

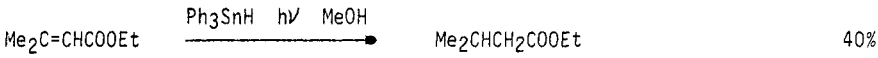
Section 120 Esters from Miscellaneous Compounds



JCS (1936) 192
JACS (1962) 84 4951



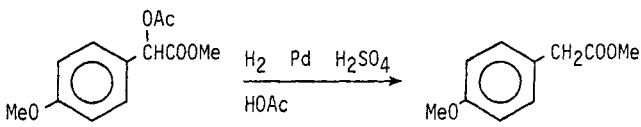
Compt Rend (1966) 263 251



Tetr Lett (1967) 4805

JOC (1965) 30 3985

JOC (1965) 30 3985



Ber (1941) 74B 315
Org React (1953) 7 263

$ClCH_2COOPr\text{-}i \xrightarrow{Mg \quad i\text{-}PrOH} MeCOOPr\text{-}i$ 63%

Proc Chem Soc (1963) 219

$PhCH{=}CHCHO \xrightarrow[2\ NaOH \quad MeOH]{1\ PhNH_2 \quad NaCN} PhCH_2CH_2\overset{\overset{OMe}{|}}{C}{=}NPh \dashrightarrow PhCH_2CH_2COOMe$

Chem Comm (1967) 1290
Chem Ind (1967) 583

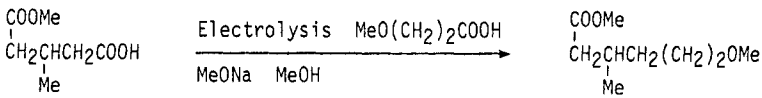
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 9 PREPARATION OF ETHERS AND EPOXIDES

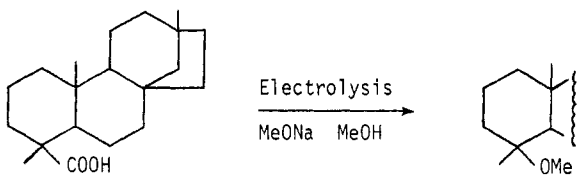
Section 121 Ethers and Epoxides from Acetylenes

No examples

Section 122 Ethers from Carboxylic Acids



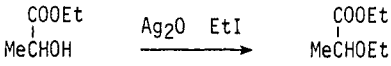
JCS (1956) 1620
Advances in Org Chem (1960) 1 1



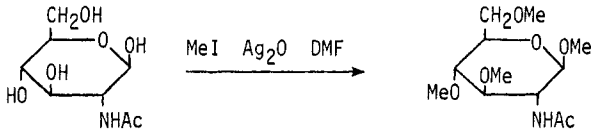
JOC (1962) 27 4689
(1960) 25 136
JACS (1960) 82 2645

Section 123 Ethers from Alcohols and Phenols

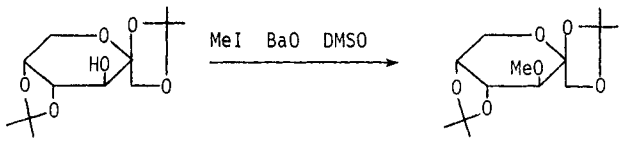
For the preparation of allyl, t-butyl, methoxymethyl, tetrahydropyranyl and triphenylmethyl ethers see section 45A (Protection of Alcohols and Phenols)



JACS (1932) 54 3732
JCS (1959) 2594

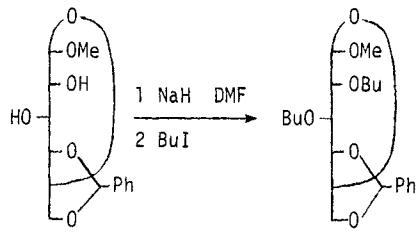


Angew (1955) 67 32
JCS C (1969) 2372
Can J Chem (1963) 41 1801



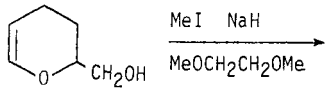
59%

JCS (1967) 2681



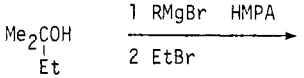
97%

Carbohydrate Res (1966) 2 167
Can J Chem (1966) 44 1591



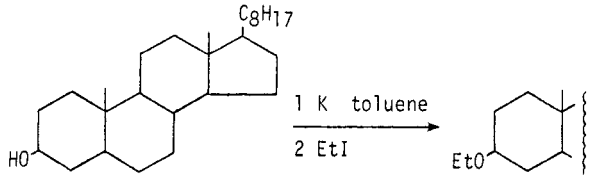
91%

Can J Chem (1966) 44 1591



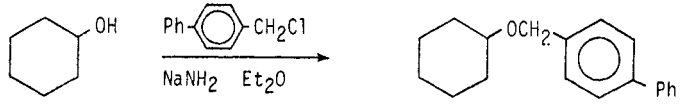
40%

Compt Rend (1968) C 266 1178



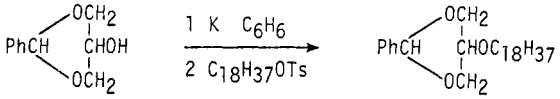
~41%

JOC (1961) 26 4553



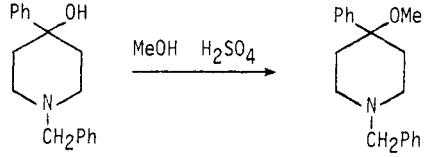
41%

JOC (1958) 23 1700

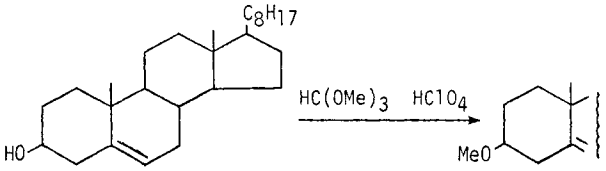


99%

JOC (1959) 24 409
(1966) 31 498



Tetrahedron (1961) 16 85
J Med Chem (1965) 8 57

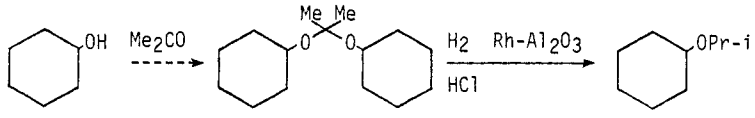


52%

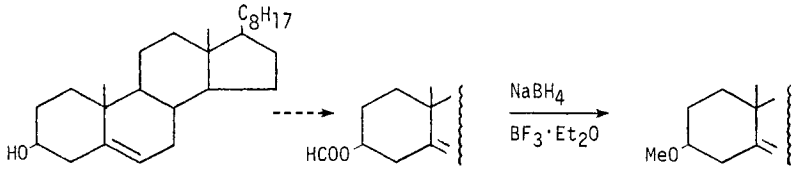
Steroids (1966) 8 495

$C_8H_{17}OH$ $\xrightarrow{CH_2N_2\ HBF_4\ Et_2O}$ $C_8H_{17}OMe$ 84%

Tetrahedron (1959) 6 36
Annalen (1963) 662 38
(1964) 677 55



JOC (1961) 26 1026



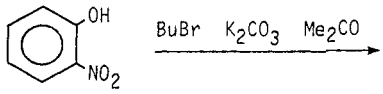
JOC (1961) 26 1685
(1962) 27 2127

PhOH $\xrightarrow[2\ C_5H_{11}Br]{1\ NaNH_2\ \ NH_3}$ $PhOC_5H_{11}$ 45%

JACS (1935) 57 510

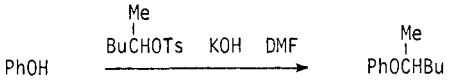
PhOH $\xrightarrow[150\text{-}190°]{PhCH_2Cl\ \ Et_3N}$ $PhOCH_2Ph$ 46%

JOC (1961) 26 5180



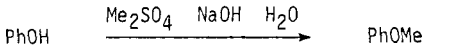
75-80%

Org Synth (1955) Coll Vol 3 140 418
Tetr Lett (1964) 1431
JACS (1950) 72 3396



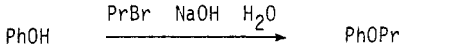
38%

JACS (1969) 91 1376



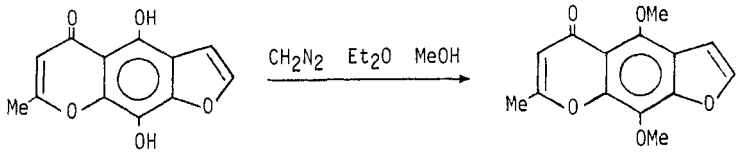
72-75%

Org Synth (1941) Coll Vol 1 58

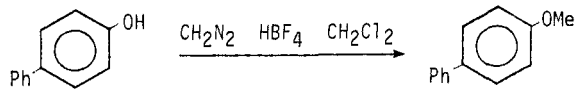


63%

JACS (1947) 69 2451

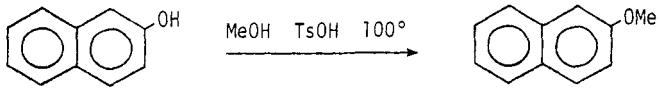


JACS (1950) 72 3396
(1962) 84 2972



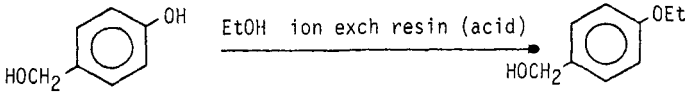
41%

Tetrahedron (1959) 6 36
Annalen (1963) 662 38



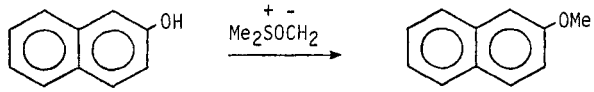
70%

JOC (1960) 25 832



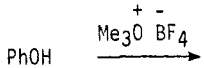
37%

JOC (1962) 27 2662



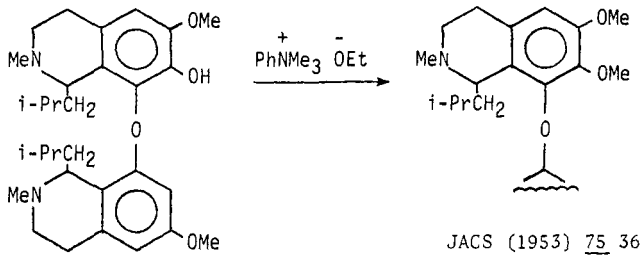
77%

Tetr Lett (1964) 867



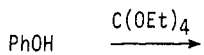
73%

J Prakt Chem (1937) 147 257



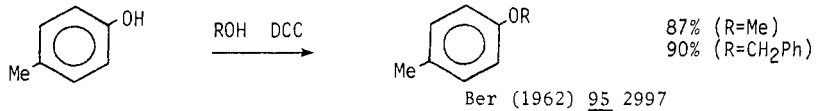
53%

JACS (1953) 75 3632



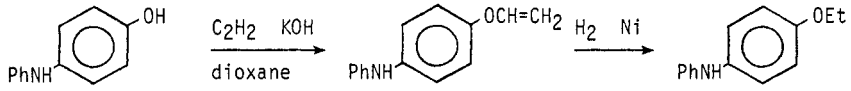
85%

Acta Chem Scand (1956) 10 1006

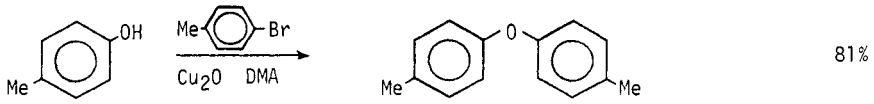


Ber (1962) 95 2997
Angew (1963) 75 377
(Internat Ed 2 218)

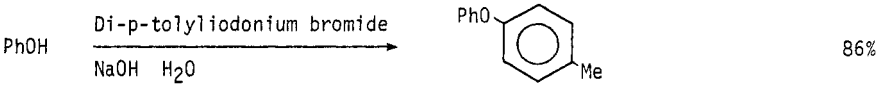
Angew (1963) 75 296
(Internat Ed 2 211)



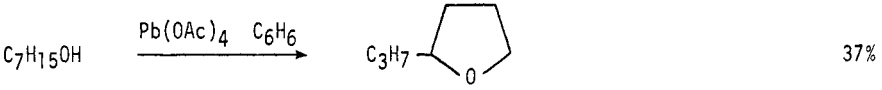
Zh Obshch Khim (1964) 34 3424
(Chem Abs 62 2727)



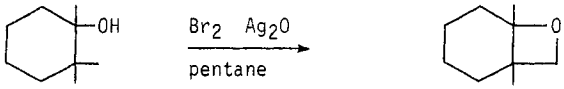
JCS (1965) 4953
Chem Rev (1946) 38 405



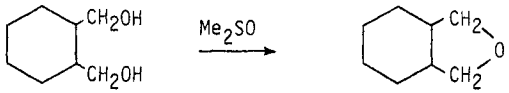
JCS (1963) 4578



Tetr Lett (1963) 2091
Synthesis (1970) 209



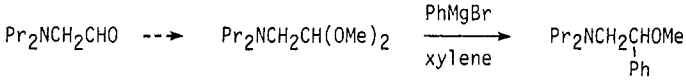
JACS (1964) 86 3905 1528



66%

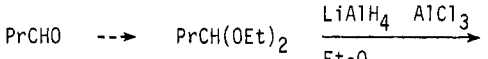
JOC (1963) 28 1388

Section 124 Ethers and Epoxides from Aldehydes



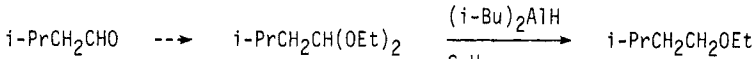
65%

JACS (1951) 73 4893



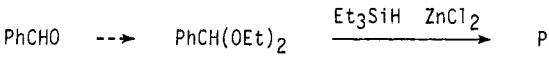
49%

JACS (1962) 84 2371
JOC (1958) 23 1088

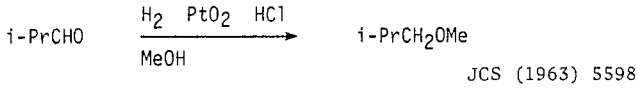


83%

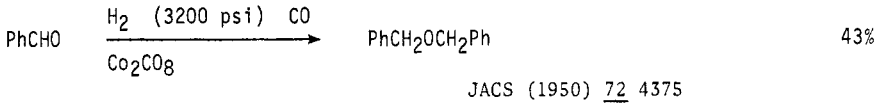
Izv (1959) 2255
(Chem Abs 54 10837)



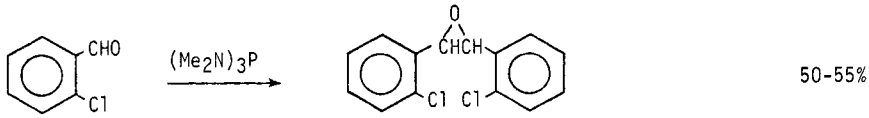
Compt Rend (1962) 254 1814



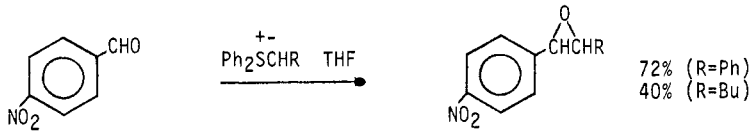
JCS (1963) 5598



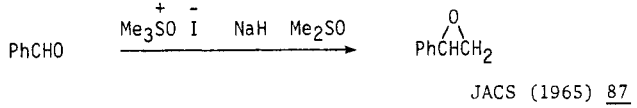
JACS (1950) 72 4375



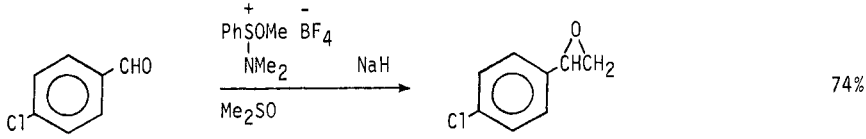
Org Synth (1966) 46 31
JACS (1963) 85 1884



JACS (1964) 86 918



JACS (1965) 87 1353



JACS (1970) 92 6594

$C_{11}H_{23}CHO \xrightarrow{CH_2Br_2\ \ Li\ \ THF} C_{11}H_{23}\underset{\diagdown\,\diagup}{\overset{O}{CH}}CH_2$ 35%

Chem Comm (1969) 1047

Some of the methods listed in section 132 (Ethers and Epoxides from Ketones) may also be applied to the preparation of ethers and epoxides from aldehydes

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=alkyl, aryl etc.) see section 131 (Ethers from Hydrides)

Section 126 Ethers and Epoxides from Amides

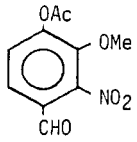
No examples

Section 127 Ethers from Amines

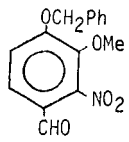
$PhNH_2 \dashrightarrow PhN_2^+\,Cl^- \xrightarrow{MeOH} PhOMe$ 93%

JACS (1955) 77 1745
(1958) 80 6072
Org React (1944) 2 262

Section 128 Ethers from Esters

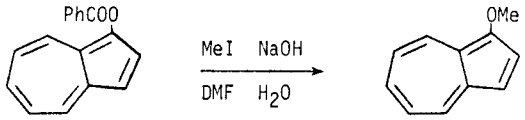


$\xrightarrow[MeOH]{PhCH_2Cl\ \ NaHCO_3}$



48%

JCS (1948) 376
Ber (1943) 76 466

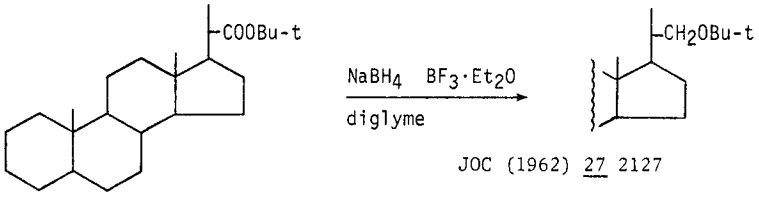


81%

JOC (1964) 29 2805

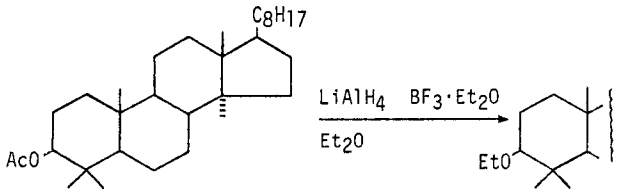
HCOOBu $\xrightarrow[MeOCH_2CH_2OMe]{PhCH_2Br\ \ NaH}$ $BuOCH_2Ph$ 43%

Tetr Lett (1965) 1713



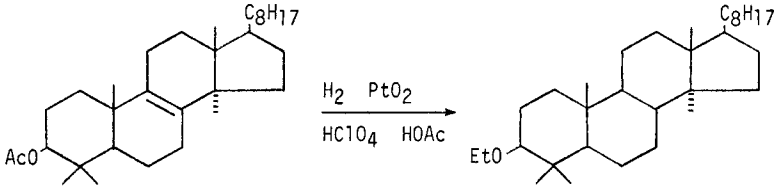
76%

JOC (1962) 27 2127



38%

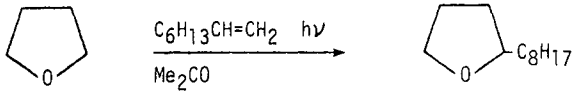
JOC (1961) 26 4553 1685



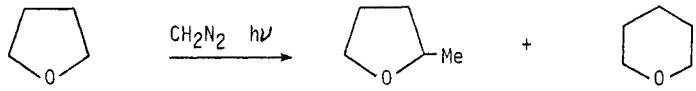
24%

JOC (1964) 29 228
Chem Ind (1964) 975

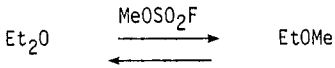
Section 129 Ethers and Epoxides from Ethers and Epoxides



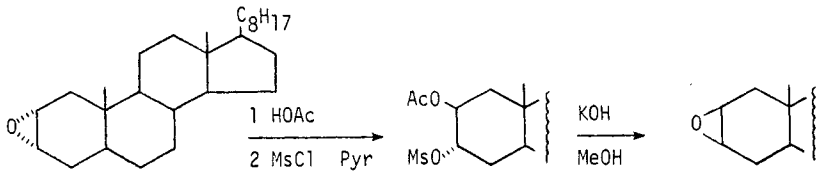
JOC (1964) 29 2031
Tetrahedron (1967) 23 3193



Chem Comm (1966) 454

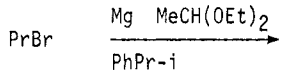


Chem Comm (1968) 1533



Helv (1949) 32 275

Section 130 Ethers and Epoxides from Halides and Sulfonates

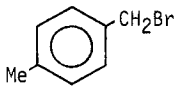


73%

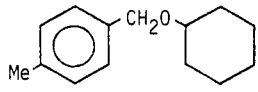
Rec Trav Chim (1962) 81 238
JACS (1951) 73 4893

$BuBr \dashrightarrow BuLi \xrightarrow{ClCH_2OBu} BuCH_2OBu$ 70%

Ber (1964) 97 636



$\xrightarrow[Et_2O]{\text{Cyclohexanol } NaNH_2}$



44%

JOC (1958) 23 1700

$C_{18}H_{37}OTs \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} C_{18}H_{37}OBu\text{-}t$ 99%

JACS (1964) 86 3072

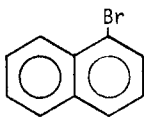
$PhBr \xrightarrow[Me_2SO]{t\text{-BuOK } t\text{-BuOH}} PhOBu\text{-}t$ 42-46%

Org Synth (1965) 45 89
JOC (1968) 33 259

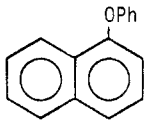
$RBr \xrightarrow[2\ PhCOO_2Bu\text{-}t]{1\ Mg\ \ Et_2O} ROBu\text{-}t$

74% (R=C_8H_{17})
65% (R=Ph)

JACS (1959) 81 4230
Org Synth (1963) 43 55

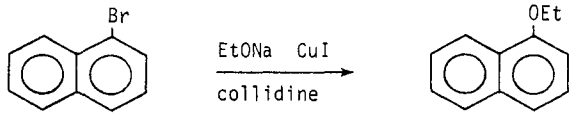


$\xrightarrow[collidine]{PhOH\ \ Cu_2O}$



67%

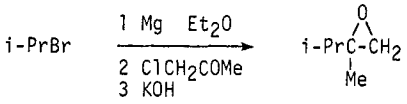
JCS (1965) 4953
Chem Rev (1946) 38 405



100%

JCS C (1969) 312

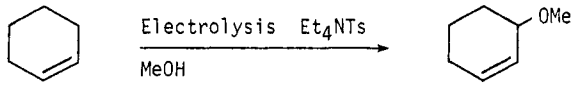
Further examples of the preparation of ethers by the reaction ROH + RHal ⟶ ROR are included in section 123 (Ethers from Alcohols and Phenols)



JACS (1946) 68 2339

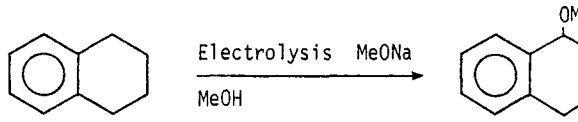
Section 131 Ethers from Hydrides (RH)

This section lists examples of the reaction RH ⟶ ROR



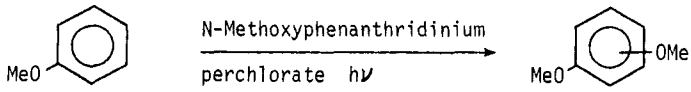
21%

Tetr Lett (1968) 6207



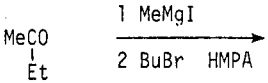
24%

Bull Chem Soc Jap (1964) 37 1597
Tetr Lett (1968) 2415



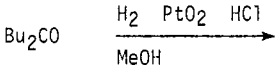
JACS (1970) 92 5814

Section 132 Ethers and Epoxides from Ketones



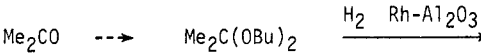
40%

Compt Rend (1968) C 266 1178



54%

JCS (1963) 5598
Chem Comm (1967) 422



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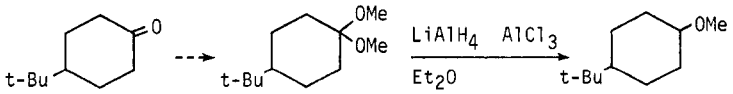
JOC (1961) 26 1026



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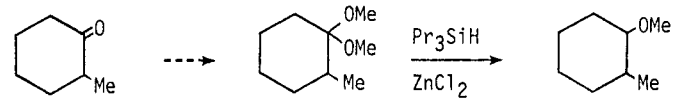
JACS (1962) 84 2371
JOC (1958) 23 1088



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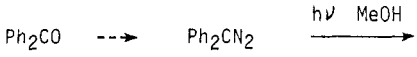
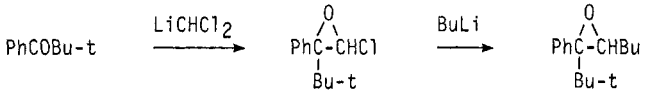
Compt Rend (1962) C 254 1814

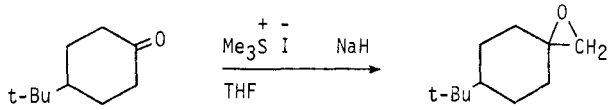


Annalen (1958) 614 19

Some of the methods listed in section 124 (Ethers and Epoxides from Aldehydes) may also be applied to the preparation of ethers from ketones

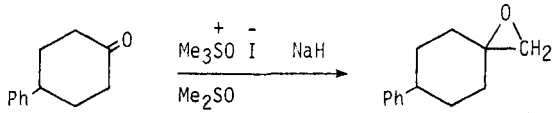


Tetr Lett (1969) 2181



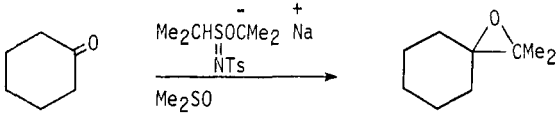
77%

JACS (1965) 87 1353



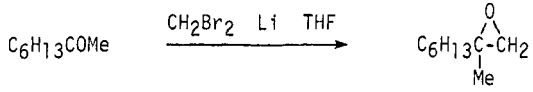
72%

JACS (1965) 87 1353
(1970) 92 6594



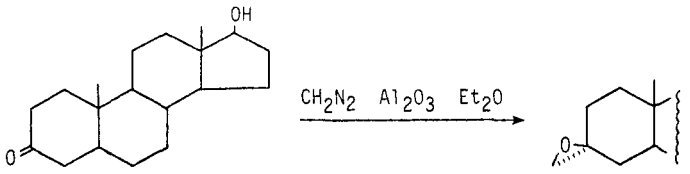
63%

JACS (1970) 92 5753



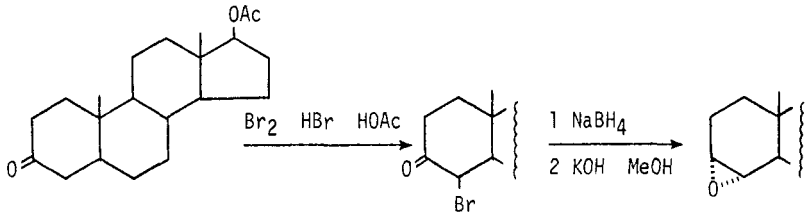
52%

Chem Comm (1969) 1047



50%

Tetr Lett (1969) 305
Org React (1954) 8 364



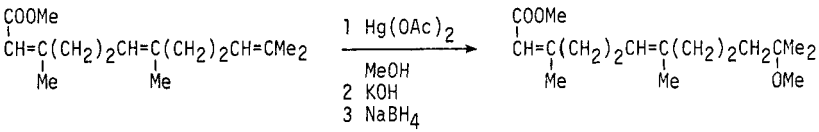
20%

JACS (1953) 75 1704

Section 133 Ethers and Epoxides from Nitriles

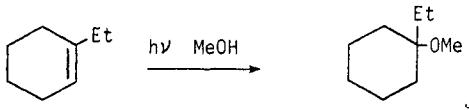
No examples

Section 134 Ethers and Epoxides from Olefins



74%

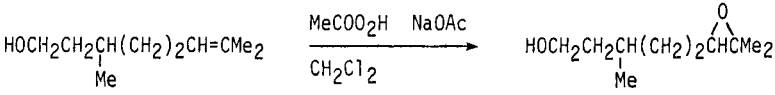
J Med Chem (1969) 12 191
JACS (1969) 91 5646



60%

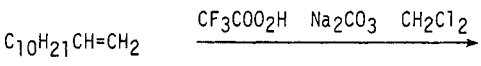
JACS (1967) 89 5199
Acc of Chem Res (1969) 2 33

Review: Epoxidation and Hydroxylation of Ethylenic Compounds with Organic Peracids
Org React (1953) 7 378



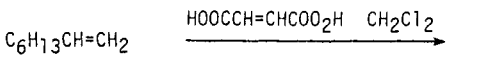
87%

Helv (1965) 48 182
JACS (1960) 82 4328
Org Synth (1963) Coll Vol 4 860



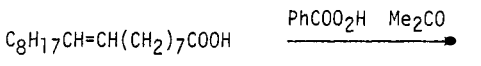
90%

JACS (1955) 77 89



80%

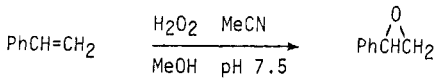
Tetrahedron (1962) 17 31



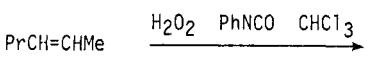
62-67%

Org React (1953) 7 378

For use of m-chloroperbenzoic acid see JOC (1970) 35 251
and Tetr Lett (1965) 849
For preparation and use of monoperphthalic acid see Org React (1953) 7 378
and JACS (1960) 82 6373
For preparation of various aliphatic and aromatic peracids see
JOC (1962) 27 1336

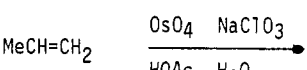


JOC (1961) 26 659
JCS C (1970) 731

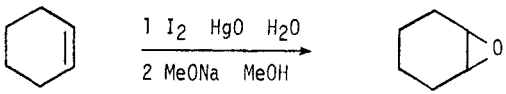


39%

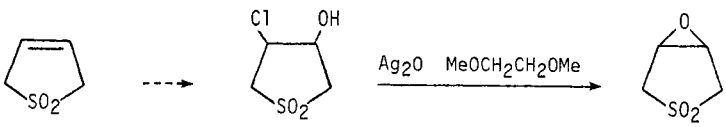
Tetr Lett (1970) 2029



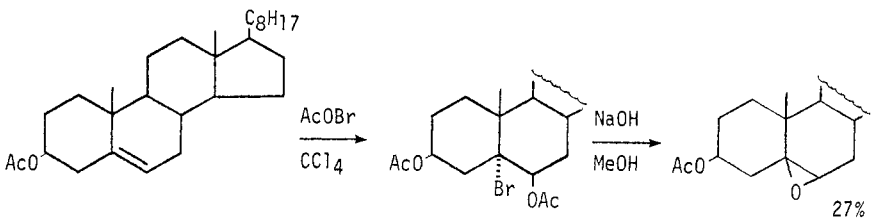
Chem Comm (1968) 1610



Tetrahedron (1964) 20 1017

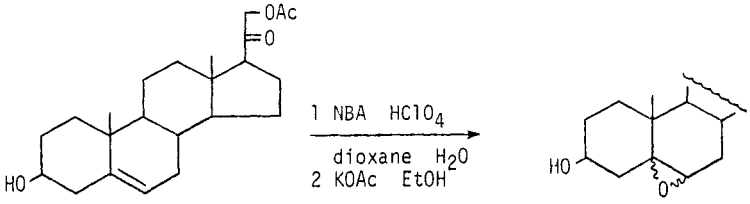


JOC (1967) 32 3888



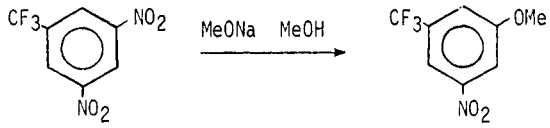
27%

JACS (1959) 81 2826



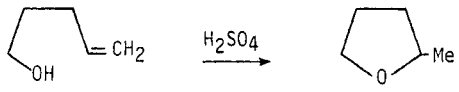
JCS (1956) 4417
JACS (1959) 81 2195

Section 135 Ethers and Epoxides from Miscellaneous Compounds

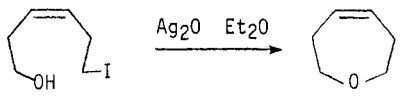


91%

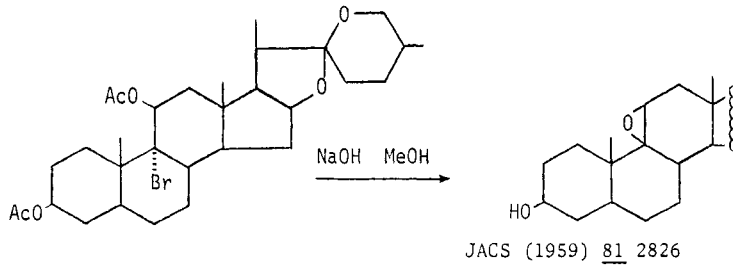
JCS (1951) 2013



Bull Soc Chim Fr (1944) 11 365



JACS (1958) 80 3132



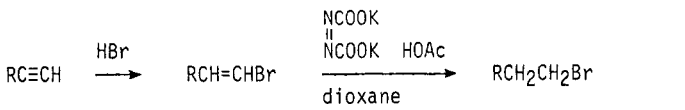
62%

JACS (1959) 81 2826

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

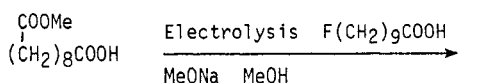
Chapter 10 PREPARATION OF HALIDES AND SULFONATES

Section 136 Halides from Acetylenes

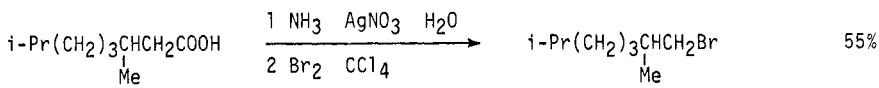


JOC (1965) 30 3985
JACS (1936) 58 1806

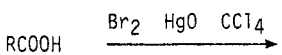
Section 137 Halides from Carboxylic Acids



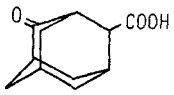
JACS (1956) 78 2255
Advances in Org Chem (1960) 1 1



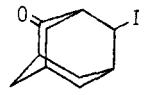
JCS (1953) 132
Chem Rev (1956) 56 219



46% (R=$C_{11}H_{23}$)
<83% (R=Ph)
JOC (1965) 30 415



I_2 HgO
PhCl



38%

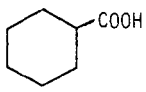
Ber (1968) 101 2010

$C_8H_{17}COONa \xrightarrow[H_2O]{F_2} C_8H_{17}F$ ~50%

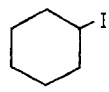
JOC (1969) 34 2446

$C_{17}H_{35}COOH \xrightarrow{I_2 \text{ benzoyl peroxide}} C_{17}H_{35}I$

J Amer Oil Chem Soc (1969) 46 615



t-BuOI hν
C_6H_6



70%

JCS (1965) 2438

$RCOOH \xrightarrow[CCl_4]{I_2\ Pb(OAc)_4\ h\nu} RI$ 100% (R=C_5H_{11})
61% (R=Ph)

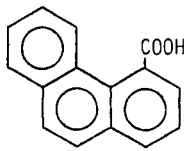
JCS (1965) 2438
JOC (1963) 28 65

$C_{15}H_{31}COOH \xrightarrow[HOAc]{Pb_3O_4\ Ac_2O} (C_{15}H_{31}COO)_4Pb \xrightarrow[C_2H_2Cl_4]{I_2} C_{15}H_{31}I$ 72%

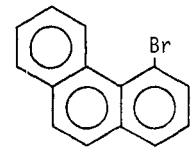
JOC (1963) 28 65
Annalen (1970) 735 47

$$BuCOOH \xrightarrow{Pb(OAc)_4\ \ LiCl\ \ C_6H_6} BuCl \qquad 96\%$$

JOC (1965) 30 3265



$$\xrightarrow[2\ Pyr\cdot Br_2]{1\ Hg(OAc)_2\ \ N\text{-methylpyrrolidone}}$$



JOC (1969) 34 1904

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow[CH_2Cl_2]{RhCl(Ph_3P)_3} RCl \qquad \begin{matrix} 86\%\ (R=PhCH_2) \\ 61\%\ (R=Ph) \end{matrix}$$

JACS (1968) 90 99 94
(1966) 88 3452

Section 138 Halides and Sulfonates from Alcohols and Phenols

$$C_{12}H_{25}OH \xrightarrow{HBr\ \ H_2SO_4} C_{12}H_{25}Br \qquad 91\%$$

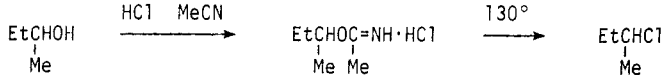
Org Synth (1941) Coll Vol 1 29
JCS (1953) 132

$$HO(CH_2)_6OH \xrightarrow{KI\ \ polyphosphoric\ acid} I(CH_2)_6I \qquad 83\text{-}85\%$$

Org Synth (1963) Coll Vol 4 323

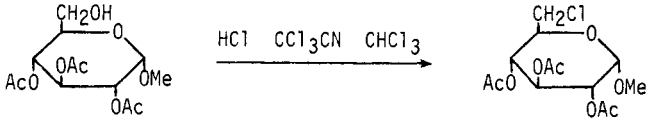
$$Et_3COH \xrightarrow{HCl} Et_3CCl \qquad 94\%$$

JOC (1966) 31 1090



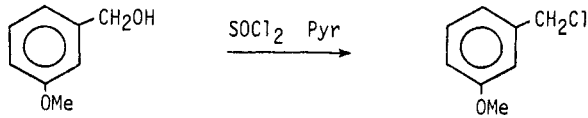
56%

JACS (1955) 77 2341



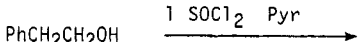
85-90%

Tetr Lett (1970) 2517



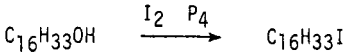
91%

JCS (1942) 684
(1943) 99
(1950) 3650
Tetr Lett (1970) 2931
(1971) 87



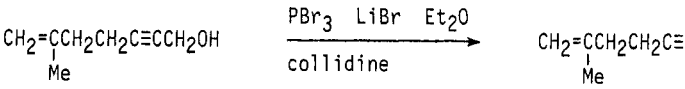
91%

Chem Ind (1954) 931
JOC (1961) 26 3645



85%

Org Synth (1943) Coll Vol 2 322

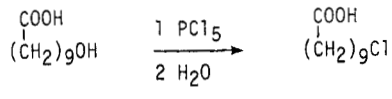


87%

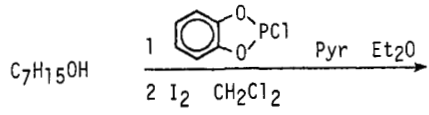
Chem Comm (1969) 611
JCS (1950) 3650

$Et_2CHOH \xrightarrow[Et_2O]{PBr_3 \text{ or } PBr_5} Et_2CHBr$ 22-47%

JOC (1961) 26 3645
(1959) 24 143
J Lipid Res (1966) 7 453

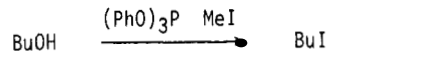


JCS (1936) 1605
(1970) 1124



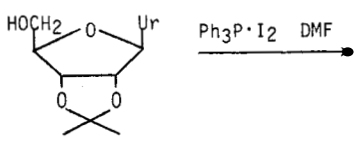
77%

JOC (1967) 32 4160
(1968) 33 300



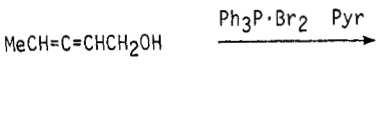
90%

JCS (1953) 2224
(1954) 2281

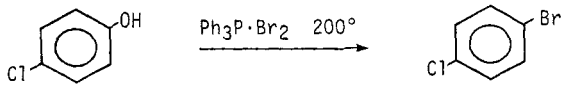


59%

JACS (1964) 86 2093

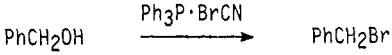


JCS (1967) 2260
JACS (1969) 91 7405
JOC (1965) 30 3469

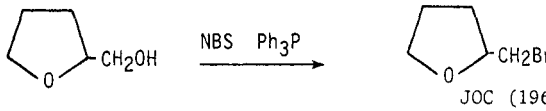


90%

JACS (1964) 86 964

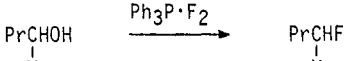


Annalen (1959) 626 26



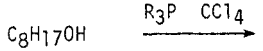
92%

JOC (1969) 34 212



52%

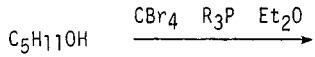
Chem Pharm Bull (1968) 16 1009 1784



(R=Ph or C_8H_{17})

94%

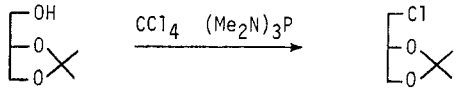
Can J Chem (1968) 46 86
Chem Comm (1968) 1358
Chem Ind (1966) 900



(R=Ph or C_8H_{17})

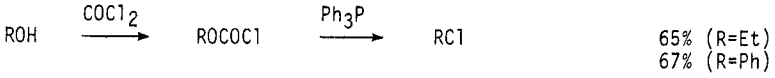
97%

Can J Chem (1968) 46 86



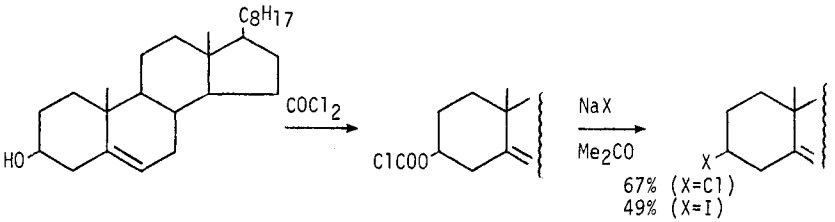
70%

Chem Comm (1968) 1350



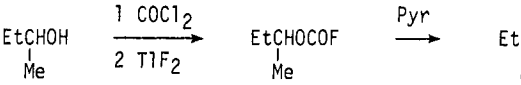
65% (R=Et)
67% (R=Ph)

Annalen (1966) 698 106



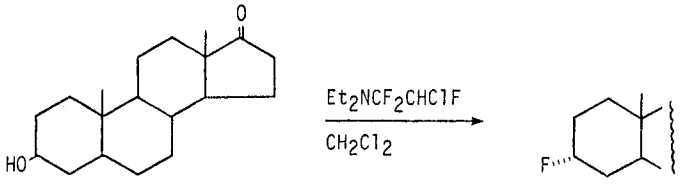
67% (X=Cl)
49% (X=I)

JOC (1967) 32 2633



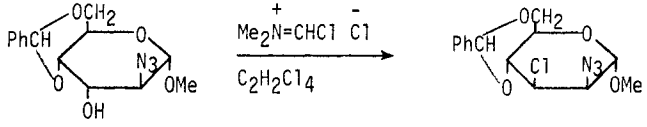
64%

JACS (1955) 77 3099



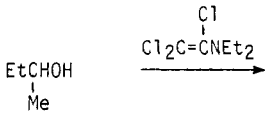
35%

Tetr Lett (1962) 1065



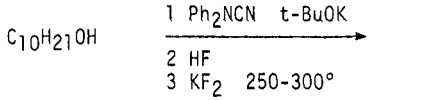
~70%

Chem Comm (1967) 1152



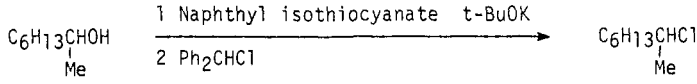
69%

JACS (1960) 82 909



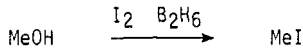
68%

Can J Chem (1965) 43 3173



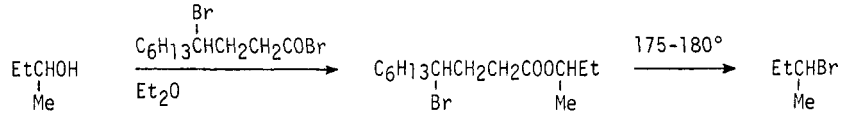
47%

JCS (1953) 3572



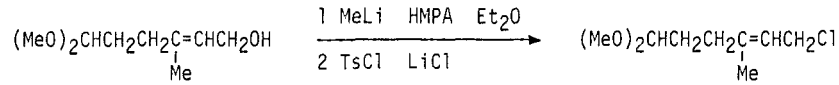
70%

Chem Ind (1964) 1582
(1965) 223

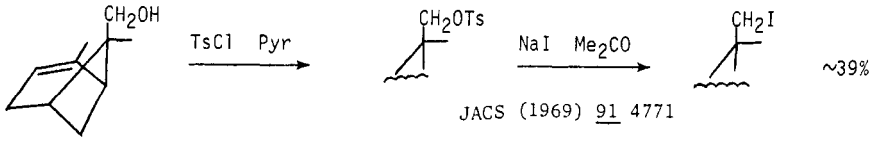


40%

JACS (1956) 78 4967



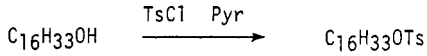
Tetr Lett (1969) 1393



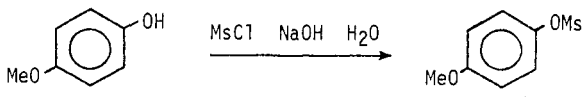
~39%

JACS (1969) 91 4771

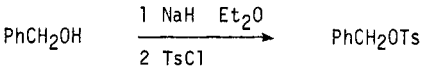
Further examples of the preparation of halides from sulfonates are included in section 145 (Halides and Sulfonates from Halides and Sulfonates)



JACS (1933) 55 345
(1970) 92 553

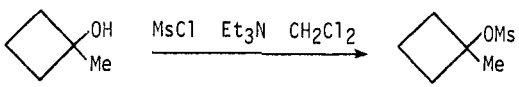


JCS (1955) 522

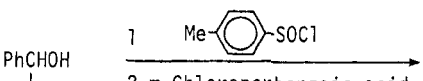


80%

JACS (1953) 75 3443
(1960) 82 3982



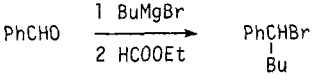
JOC (1970) 35 3195



53%

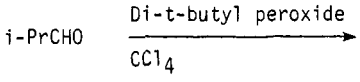
Tetr Lett (1969) 2705

Section 139 Halides from Aldehydes



Zh Obshch Khim (1955) 25 505
(Chem Abs 50 3356)

56%

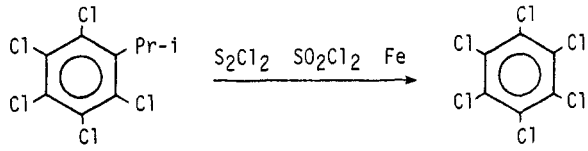


JACS (1965) 87 2194

45%

Section 140 Halides from Alkyls

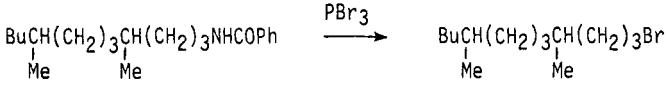
The conversion RR' ⟶ RHal (R,R'=alkyl or aryl) is included here. For the reaction RH ⟶ RHal see section 146 (Halides from Hydrides)



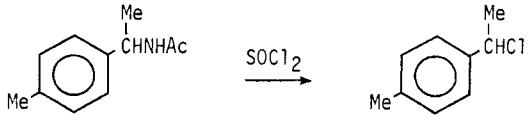
JACS (1947) 69 3146

45%

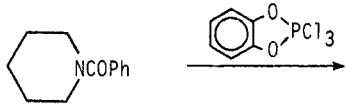
Section 141 Halides from Amides



Z Physiol Chem (1942) 273 225
Org Synth (1941) Coll Vol 1 428



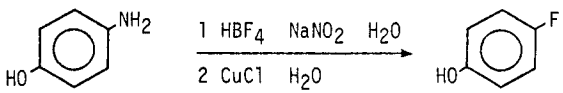
JACS (1962) 84 769



$Cl(CH_2)_5Cl$ 55%

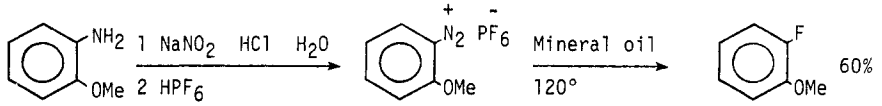
Ber (1963) 96 1387
Org Synth (1941) Coll Vol 1 428

Section 142 Halides from Amines



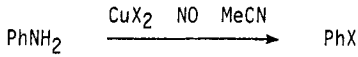
71%

JACS (1956) 78 6037
Chem Ind (1961) 179
Org Synth (1944) Coll Vol 2 295
Org React (1949) 5 193



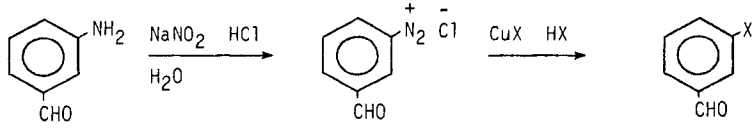
60%

JOC (1961) 26 5149
(1963) 28 568

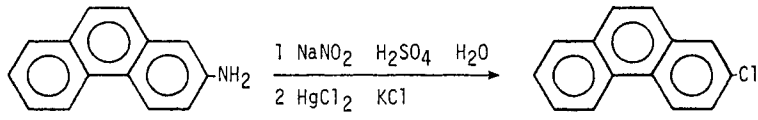


73% (X=Cl)
65% (X=Br)

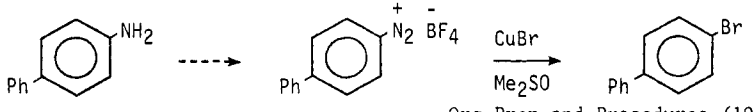
Rec Trav Chim (1966) 85 857
JACS (1947) 69 1221



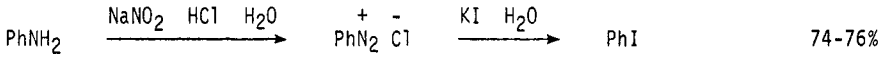
~75% (X=Cl)
~65% (X=Br)
Org Synth (1944) Coll Vol 2 130



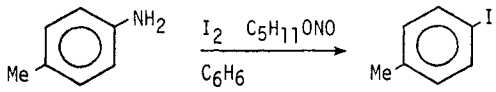
JACS (1936) 58 2194



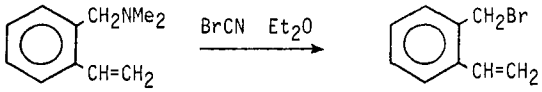
~97%
Org Prep and Procedures (1969) 1 221



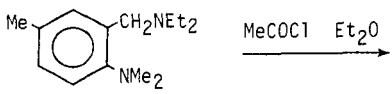
74-76%
Org Synth (1944) Coll Vol 2 351
Chem Ind (1962) 1760



40%
JOC (1968) 33 1636

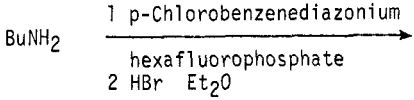


50%
Org React (1953) 7 198
Ber (1910) 43 3209

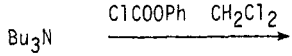


56%

Ber (1960) 93 1310 1305

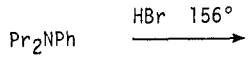


Tetr Lett (1961) 758

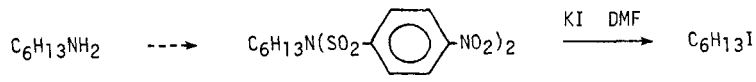


(Not isolated)

JCS (1967) 2015

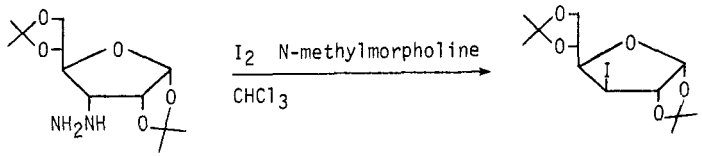


JOC (1963) 28 3144



79%

JACS (1969) 91 2384



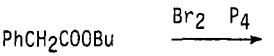
72%

JCS C (1967) 252

Halides may also be prepared from amines via amide intermediates. See section 141 (Halides from Amides)

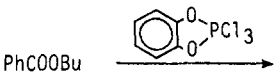
Section 143 Halides from Esters

For the conversion of sulfonic acid esters to halides see section 145 (Halides and Sulfonates from Halides and Sulfonates)



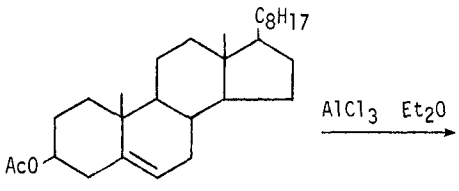
Arch Pharm (1953) 286 108
JCS B (1967) 1067

80%



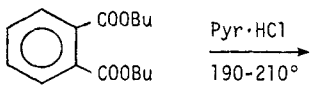
Ber (1963) 96 1387

73%



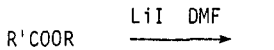
JCS (1957) 2071
Zesz Nauk Pol Slask (1964) 24 193
(Chem Abs 63 11338)
JACS (1940) 62 1432

97%

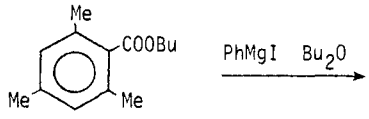


Monatsh (1952) 83 1398

66%



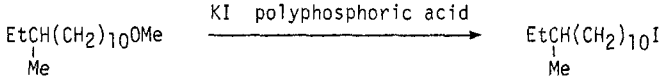
JCS (1965) 6655



JACS (1942) 64 1450

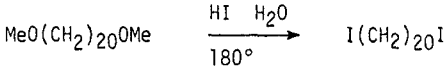
54%

Section 144 Halides from Ethers

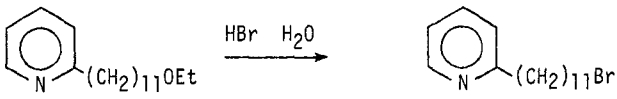


~97%

JACS (1965) 87 5452

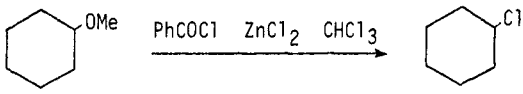


Ber (1942) 75B 1715
JCS (1957) 463
Chem Rev (1954) 54 615



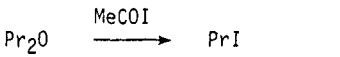
81%

Helv (1946) 29 1204



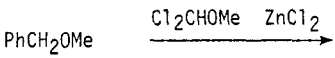
84%

J Prakt Chem (1938) 151 61
JCS (1954) 2819



45%

JACS (1933) 55 378



88%

Ber (1959) 92 83

$Et_2O \xrightarrow{SOCl_2\ SnCl_4} EtCl$

Ber (1936) 69B 1036

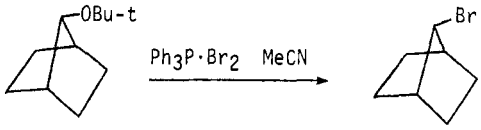
$ROBu \xrightarrow{BBr_3} BuBr$

77% (R=Bu)
76% (R=Ph)

JACS (1942) 64 1128
Tetrahedron (1968) 24 2289

$(C_5H_{11})_2O \xrightarrow{Ph_3P\cdot Br_2\ PhCN} C_5H_{11}Br$ 78%

JACS (1964) 86 5037



83%

Chem Ind (1969) 200

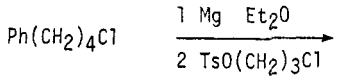
$(n\text{-}Bu)_2O \xrightarrow{ICl\ LiBH_4} s\text{-}BuI$

Chem Ind (1965) 223
(1964) 1582
Tetr Lett (1967) 4131

$Et_2O \xrightarrow{Pyr\cdot BH_2I\ C_6H_6} EtI$

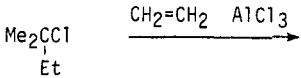
JACS (1968) 90 6260

Section 145 Halides and Sulfonates from Halides and Sulfonates



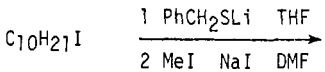
$Ph(CH_2)_4Cl \rightarrow Ph(CH_2)_7Cl$ 24%

JACS (1928) 50 1491
(1946) 68 1101



$Me_2CCl(Et) \rightarrow Me_2CCH_2CH_2Cl(Et)$ 25%

JACS (1945) 67 1152

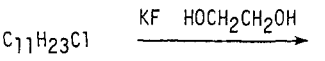


$C_{10}H_{21}I \rightarrow C_{10}H_{21}CH_2I$

Tetr Lett (1968) 5787

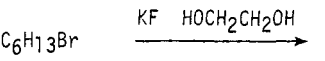
$CH_2=CHCH_2Cl \rightarrow CH_2=CHCH_2CH_2Cl + CH_2(-CH_2)CH_2CH_2Cl$

Ber (1966) 99 2855



$C_{11}H_{23}Cl \rightarrow C_{11}H_{23}F$ 48%

JACS (1957) 79 2311

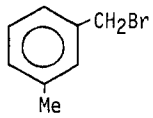


$C_6H_{13}Br \rightarrow C_6H_{13}F$ 40-45%

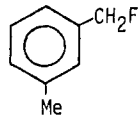
Org Synth (1963) Coll Vol 4 525

$C_{12}H_{25}Br$ —(1 Li THF pet ether; 2 $FClO_3$)→ $C_{12}H_{25}F$ 39%

Ber (1969) 102 1944



—(HgF_2 $CHCl_3$)→

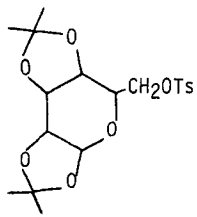


50%

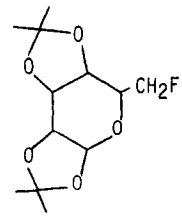
JACS (1948) 70 2310
Org React (1944) 2 49

$C_6H_{13}OTs$ —(KF diethylene glycol)→ $C_6H_{13}F$ 90%

Chem Ind (1958) 157
Can J Chem (1956) 34 757
JACS (1955) 77 4899



—(Bu_4NF MeCN)→



69%

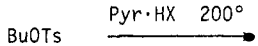
Carbohydrate Res (1967) 5 292

$C_8H_{17}Br$ —($ClF_2CCOOAg$)→ $C_8H_{17}Cl$ 89%

Tetr Lett (1970) 3447

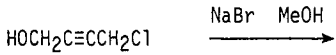
$HC{\equiv}CCH_2CH_2OTs$ —(LiCl $EtOCH_2CH_2OH$)→ $HC{\equiv}CCH_2CH_2Cl$ 90%

JCS (1950) 3650



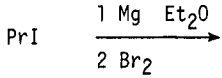
89% (X=Cl)
66% (X=Br)

Monatsh (1952) 83 1398
JOC (1961) 26 2883



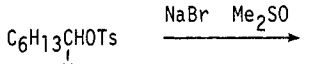
62%

JACS (1955) 77 165



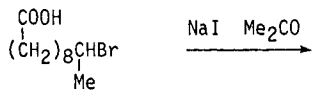
JACS (1919) 41 287

30-40%



52%

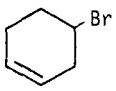
JOC (1961) 26 3645
(1962) 27 624
(1970) 35 2803



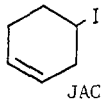
JCS (1936) 1605
JACS (1968) 90 6225

82%

JOC (1969) 34 3519



1 Mg Et_2O
2 $HgBr_2$
3 I_2 Pyr



13%

JACS (1969) 91 5774
(1939) 61 1585

$HC{\equiv}CCH_2CH_2OTs$ —NaI Me_2CO→ $HC{\equiv}CCH_2CH_2I$ 64%

JCS (1950) 3650

$C_7H_{15}I$ —AgOTs MeCN→ $C_7H_{15}OTs$

JACS (1959) 81 4113
JOC (1962) 27 2365

PhBr —1 Li Et_2O; 2 $FClO_3$→ PhF 42%

Ber (1969) 102 1944

PhI —hν CCl_4→ PhCl 76%

JOC (1970) 35 528

PhBr --> PhMgBr —Ph_3PCl_2 Et_2O→ PhCl

JOC (1967) 32 3710

PhI —1 Mg Et_2O; 2 Br_2→ PhBr 30-40%

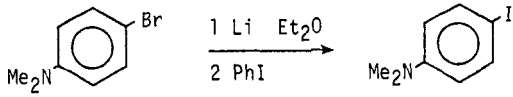
JACS (1919) 41 287

PhBr $\xrightarrow[2\ I_2]{1\ Mg\ \ Et_2O}$ PhI 90%

JACS (1919) 41 287
(1945) 67 1479
JOC (1938) 3 55

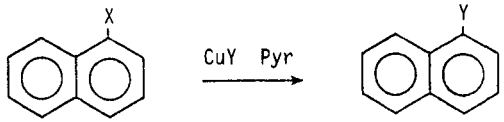
PhBr $\xrightarrow[2\ ICN]{1\ Mg\ \ Et_2O}$ PhI 64%

Annales de Chimie (1915) 4 28



51%

JACS (1950) 72 2767



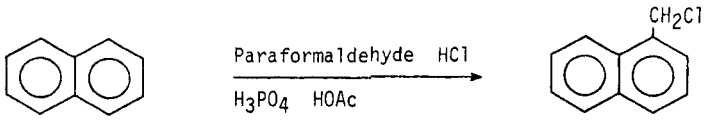
X=Br	Y=Cl	84%
I	Cl	100%
I	Br	100%
Br	I	30%

JCS (1964) 1097 1108
Proc Chem Soc (1962) 113

Section 146 Halides from Hydrides (RH)

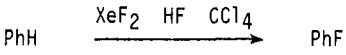
PhH $\xrightarrow[BF_3 \text{ or } BBr_3]{FCH_2CH_2X}$ $PhCH_2CH_2X$ (X=Cl, Br or I) 50-94%

JOC (1964) 29 2317



74-77%

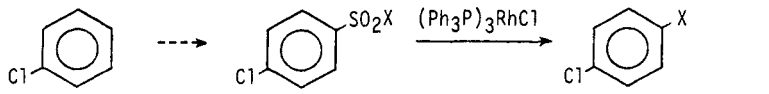
Org Synth (1955) Coll Vol 3 195
Org React (1942) 1 63



68%

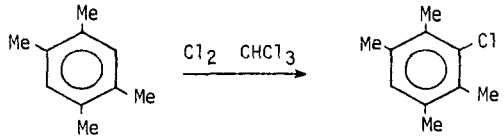
JACS (1969) 91 1563
JOC (1970) 35 723 4020

For aromatic fluorination with CF_3OF see JACS (1970) 92 7494



(X=F, Cl or Br)

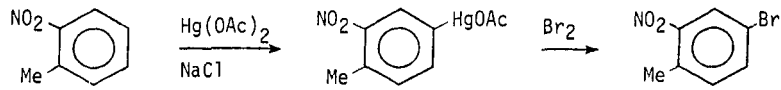
JOC (1970) 35 1895
Monatsh (1915) 36 719



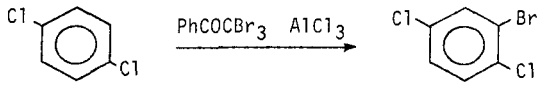
61%

JACS (1936) 58 1

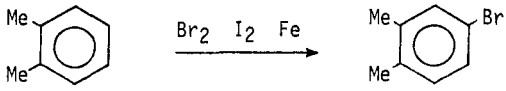
For aromatic chlorination with $TiCl_4$ and CF_3CO_2H see Tetr Lett (1970) 2611
" " " " trichlorocyanuric acid see JOC (1970) 35 719



JCS (1926) 637

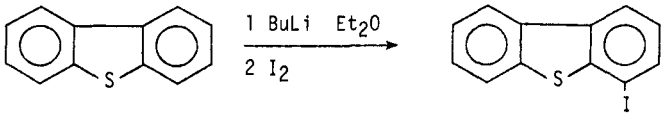


Zh Org Khim (1969) 5 387
(Chem Abs 70 105613)



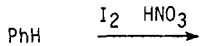
Org Synth (1955) Coll Vol 3 138

For aromatic bromination with $Tl(OAc)_3$ and Br_2 see Tetr Lett (1969) 1623
" " " " NBS " JOC (1965) 30 304
and JACS (1958) 80 4327
" " " " CBr_4 see JACS (1932) 54 2025
" " " " $CuBr_2$ " JACS (1964) 86 427
" " " " 1,3-dibromo-5,5-dimethylhydantoin see
An Argentina (1950) 38 181 188
(Chem Abs 45 2873)



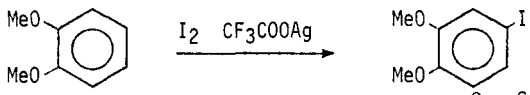
22%

Org React (1954) 8 258
JACS (1950) 72 2767



86-87%

Org Synth (1932) Coll Vol 1 323



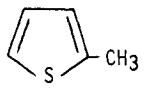
85-91%

Org Synth (1963) Coll Vol 4 547

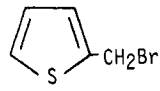
For aromatic iodination with I_2 and oleum see JCS C (1970) 1480
" " " " I_2 " KIO_3 " JACS (1943) 65 1273
" " " " I_2 " Ag_2SO_4 " JCS (1952) 150
" " " " I_2 " electrolysis see Tetr Lett (1968) 1831
" " " " AlI_3 " $CuCl_2$ see JOC (1970) 35 3436
" " " " $(CF_3COO)_3Tl$ and KI see Tetr Lett (1969) 2427

$PrCH_2CH{=}CHMe \xrightarrow[CCl_4]{NBS\ \ dibenzoyl\ peroxide} PrCH(Br)CH{=}CHMe$ 58-64%

Org Synth (1963) Coll Vol 4 108

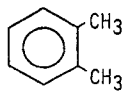


NBS dibenzoyl peroxide, C_6H_6

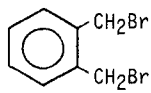


71-79%

Org Synth (1963) Coll Vol 4 921



Br_2 $h\nu$



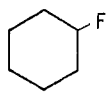
Org Synth (1963) Coll Vol 4 984

For reviews of allylic and benzylic halogenation see Chem Rev (1948) 43 271 and Angew (1959) 71 349

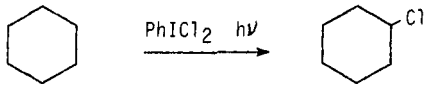
The following reagents may also be used for allylic/benzylic halogenation:

N-Chloro-N-cyclohexylbenzenesulfonamide	Annalen (1967) 703 34
SO_2Cl_2	JACS (1939) 61 2142 and JCS (1951) 1851
PCl_5	JOC (1969) 34 3655
$PhICl_2$	JOC (1964) 29 3692
1,2-Dibromotetrachloroethane	Chem Ind (1963) 1954
$BrCCl_3$	JACS (1960) 82 391
CBr_4	JACS (1932) 54 2025
$Ph_2C{=}NBr$	JOC (1967) 32 223
CCl_3SO_2Br	JOC (1965) 30 38
1,3-Dibromo-5,5-dimethylhydantoin	Helv (1958) 41 70
t-BuOI	JACS (1968) 90 808

CF_3OF $h\nu$

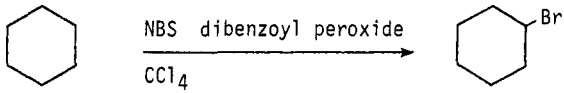


JACS (1970) 92 7494



JOC (1964) 29 3692

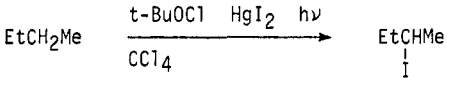
For chlorination of saturated compounds with SO_2Cl_2 see JCS (1951) 1851
" " " " " " CCl_3SO_2Cl " JACS (1960) 82 5246
" " " " " " NCS " JOC (1953) 18 649



30%

JOC (1953) 18 649
JCS (1952) 2240

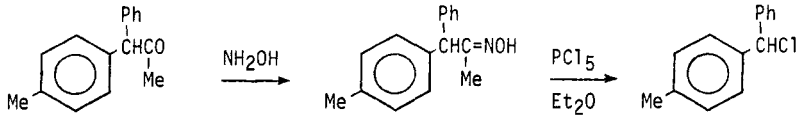
For bromination of saturated compounds with Br_2 see
Rec Trav Chim (1964) 83 67
" " " " " " CCl_3SO_2Br see
JOC (1965) 30 38
" " " " " " $Ph_2C{=}NBr$ see
JOC (1967) 32 223



35%

JACS (1968) 90 808

Section 147 Halides from Ketones



64%

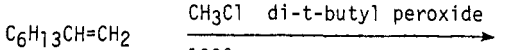
Tetr Lett (1965) 525

Section 148 Halides from Nitriles

No examples

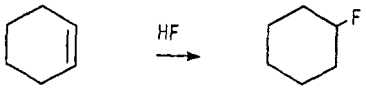
Section 149 Halides from Olefins

The conversion of olefins into saturated halides is considered in this section. For allylic halogenation see section 146 (Halides from Hydrides)



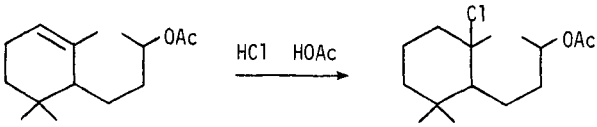
23%

Chem Comm (1966) 258



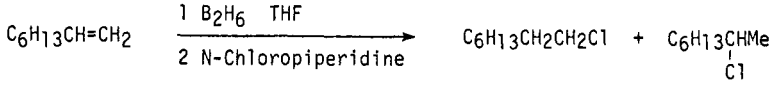
60%

Org React (1944) 2 49
JOC (1970) 35 4020

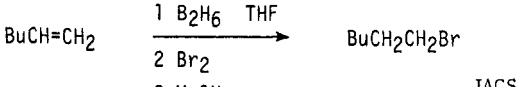


97%

Helv (1955) 38 1587
JOC (1966) 31 1090
JACS (1957) 79 456

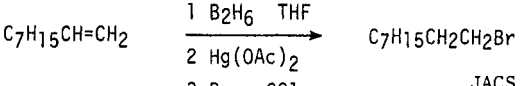


JOC (1965) 30 4313



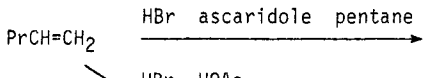
93%

JACS (1970) 92 6660 7212



69%

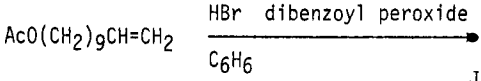
JACS (1970) 92 3221
Chem Comm (1970) 372



$PrCH_2CH_2Br$ 81%

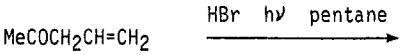
PrCHMe
Br
> 84%

JACS (1934) 56 1642
Org React (1963) 13 150



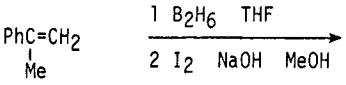
$AcO(CH_2)_9CH_2CH_2Br$ 82%

JOC (1946) 11 281
JACS (1946) 68 1101



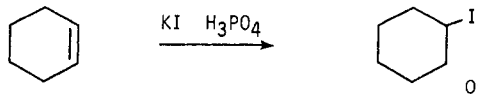
$MeCOCH_2CH_2CH_2Br$

Tetrahedron (1969) 25 5149



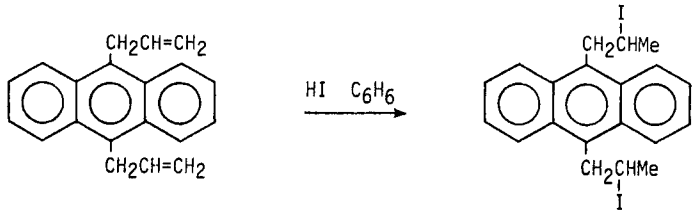
PhCHCH2I
Me
63%

JACS (1968) 90 5038



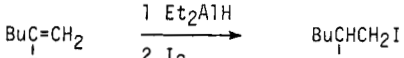
88-90%

Org Synth (1963) Coll Vol 4 543



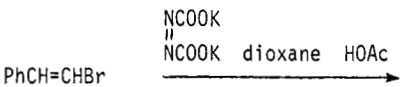
83%

JCS (1957) 463



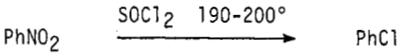
Annalen (1954) 589 91

Section 150 Halides from Miscellaneous Compounds



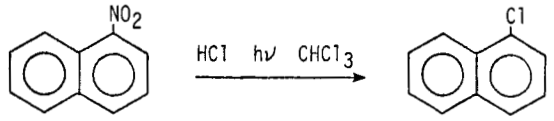
22%

JOC (1965) 30 3985



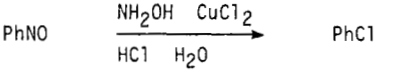
100%

Monatsh (1915) 36 723



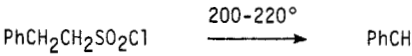
~90%

Tetr Lett (1969) 4603



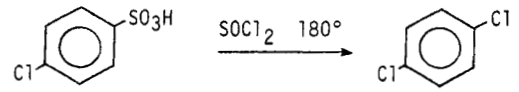
15-20%

JCS (1949) S181



59%

Zh Obshch Khim (1953) 23 204
(Chem Abs 48 2568)



Monatsh (1915) 36 719
JOC (1970) 35 1895

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

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

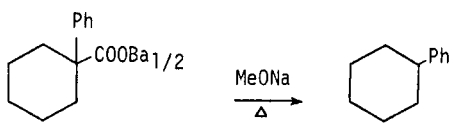
No examples of the reaction $RC{\equiv}CR \longrightarrow RH$ occur in the literature. For the hydrogenation of acetylenes see section 61 (Alkyls and Methylenes from Acetylenes)

Section 152 Hydrides from Carboxylic Acids

This section lists examples of the decarboxylation of acids, $RCOOH \longrightarrow RH$ (R=alkyl, aryl, vinyl etc). For the conversion $RCOOH \longrightarrow RCH_3$ see section 62 (Alkyls from Carboxylic Acids)

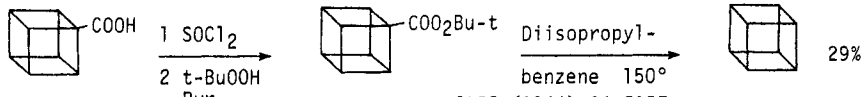
$$C_{17}H_{35}COOH \xrightarrow{Ni\ \ 350^\circ} C_{17}H_{36}$$

JOC (1944) 9 319



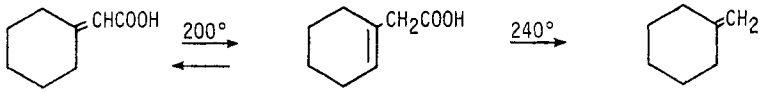
64%

JACS (1934) 56 715



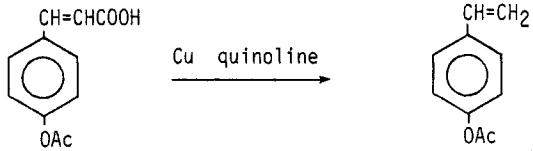
29%

JACS (1964) 86 3157
(1961) 83 3998
J Med Chem (1969) 12 192



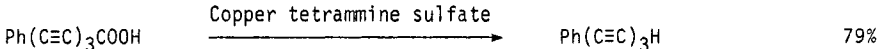
~60%

JCS (1930) 1603
JACS (1950) 72 4359



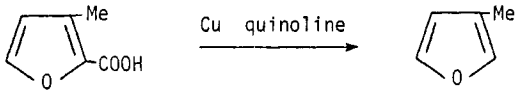
37%

JACS (1950) 72 1200
Org Synth (1963) Coll Vol 4 857
Chem Comm (1967) 96



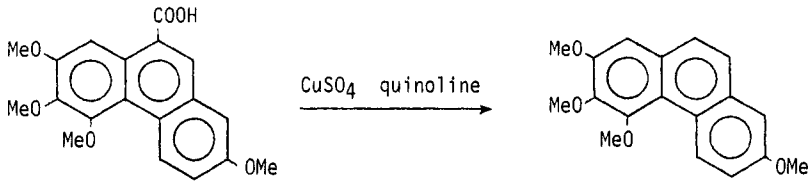
79%

Ber (1964) 97 2586



83-89%

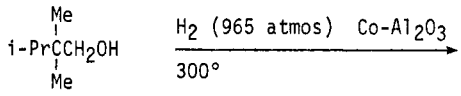
Org Synth (1963) Coll Vol 4 628



JACS (1951) 73 1414

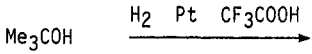
Section 153 Hydrides from Alcohols and Phenols

This section lists examples of the hydrogenolysis of alcohols and phenols, ROH ⟶ RH and RR'CHOH ⟶ RH (R=alkyl or aryl, R'=H or aryl). For the conversion ROH ⟶ RR' (R'=alkyl or aryl) see section 63 (Alkyls and Aryls from Alcohols)

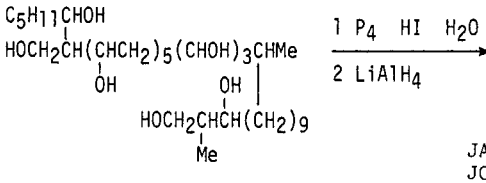


20%

JACS (1948) 70 3793
(1951) 73 553
(1933) 55 1293

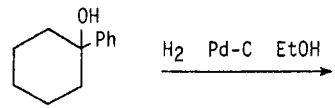


JOC (1964) 29 2325

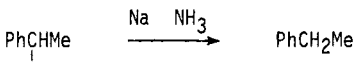


13%

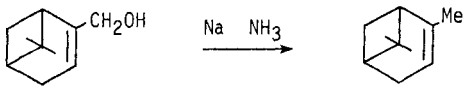
JACS (1962) 84 2170
JCS (1959) 1044
Tetrahedron (1970) 26 2199



JCS C (1967) 136
Chem Ind (1963) 1354
Org React (1953) 7 263

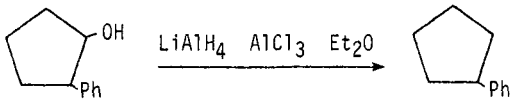


JCS (1945) 809
(1949) 2531



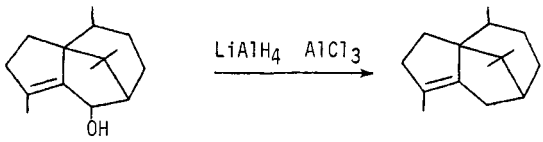
85%

Ber (1956) 89 1549
JCS (1957) 1969
(1945) 809



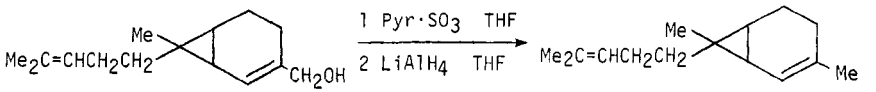
78%

JOC (1964) 29 121



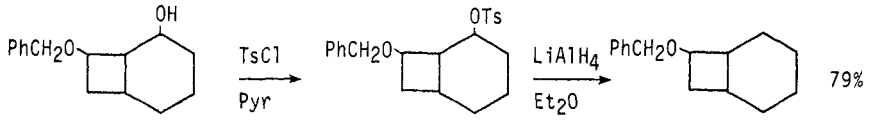
Tetr Lett (1967) 2447

For reduction of benzylic alcohols see JCS (1957) 3755



Tetr Lett (1969) 1837
JOC (1969) 34 3667

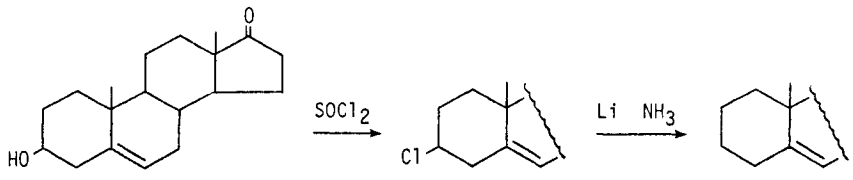
86%



79%

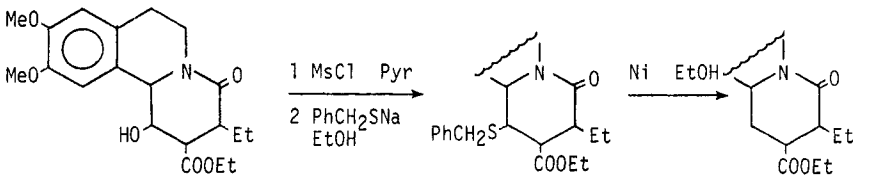
JACS (1970) 92 553
(1955) 77 1820

Further examples of the reduction of sulfonates are included in section 160 (Hydrides from Halides and Sulfonates)



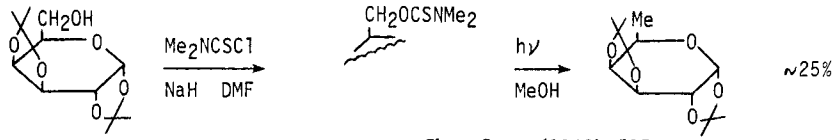
JOC (1968) 33 1196

For further examples of the reaction ROH ⟶ RHal and RHal ⟶ RH see section 138 (Halides and Sulfonates from Alcohols and Phenols) and section 160 (Hydrides from Halides and Sulfonates)



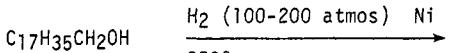
Helv (1959) 42 2431
JACS (1953) 75 384
(1963) 85 173

77%

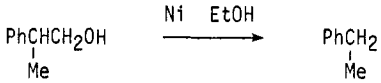


~25%

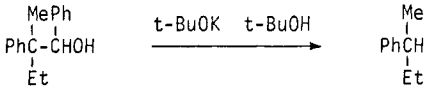
Chem Comm (1968) 323
Carbohydrate Res (1967) 4 115



JACS (1933) 55 1293

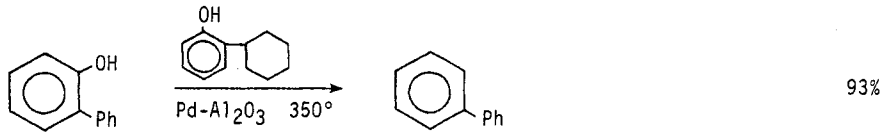


JACS (1957) 79 1696



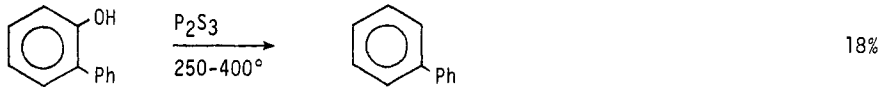
JACS (1969) 91 1009

Alcohols (ROH) may also be converted into hydrides (RH) via ester or ether intermediates. See section 158 (Hydrides from Esters) and section 159 (Hydrides from Ethers)



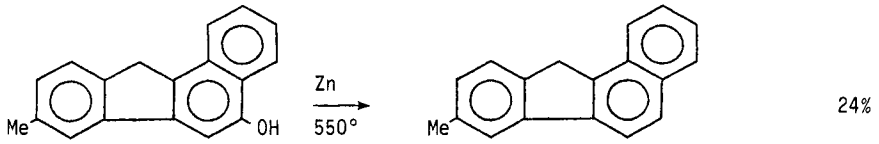
93%

Tetr Lett (1969) 1577



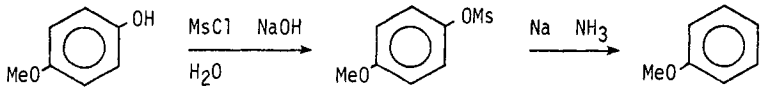
18%

JOC (1961) 26 2528



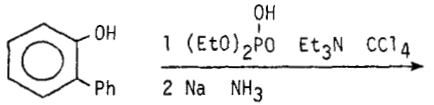
24%

JACS (1951) 73 3439



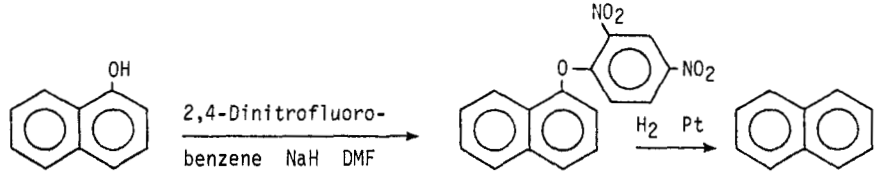
JCS (1955) 522

Further examples of the reduction of sulfonates are included in section 160 (Hydrides from Halides and Sulfonates)



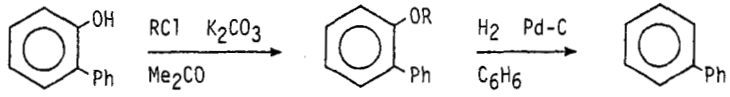
48%

JOC (1958) 23 131
J Med Chem (1965) 8 409
JCS (1955) 522

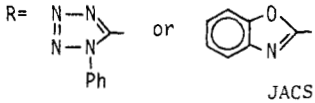


JOC (1964) 29 3124

40%



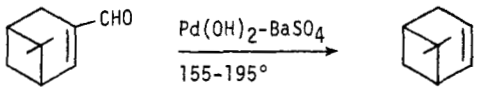
70-76%



JACS (1966) 88 4271

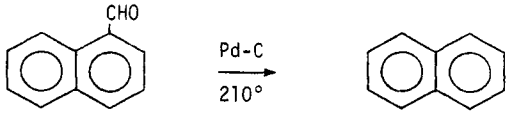
Section 154 Hydrides from Aldehydes

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



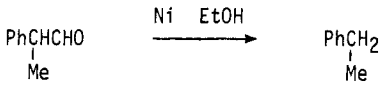
76%

JOC (1959) 24 1369

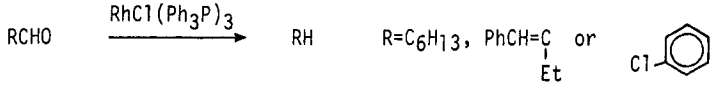


80%

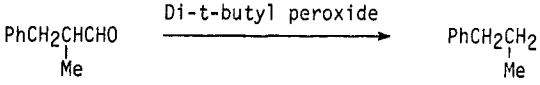
JOC (1960) 25 2215



JACS (1957) 79 1696

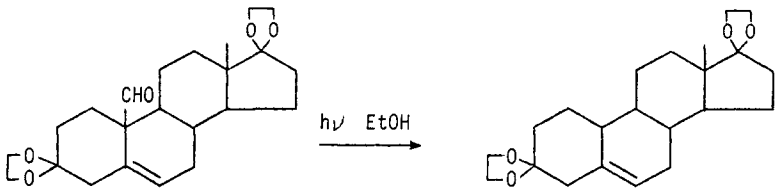


JACS (1968) 90 99
Tetr Lett (1970) 823
(1968) 1899



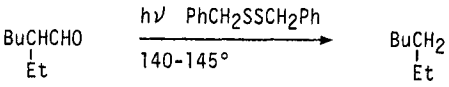
69%

JOC (1964) 29 1663
JACS (1941) 63 226



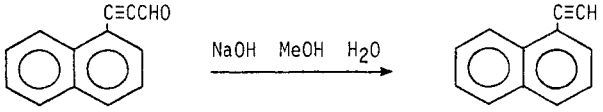
90%

Proc Chem Soc (1963) 114



68%

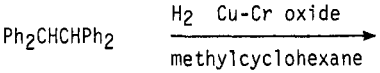
Tetr Lett (1962) 43



JCS C (1969) 2173

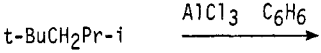
Section 155 Hydrides from Alkyls

This section lists examples of the conversion RR' ⟶ RH (R,R'=alkyl, aryl etc.)

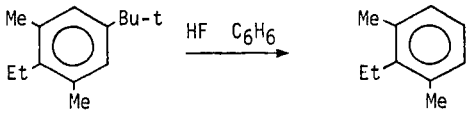


90%

JACS (1932) 54 1668

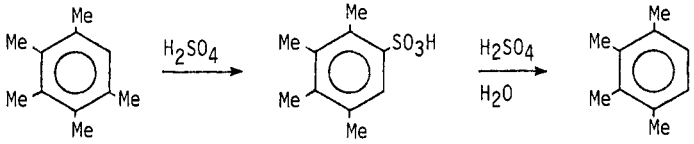


JACS (1935) 57 2415



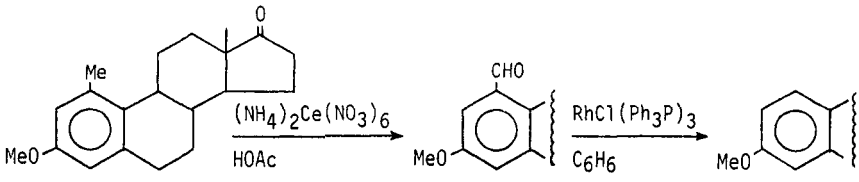
60%

JACS (1954) 76 4952
(1937) 59 1417



88%

Org React (1942) 1 370

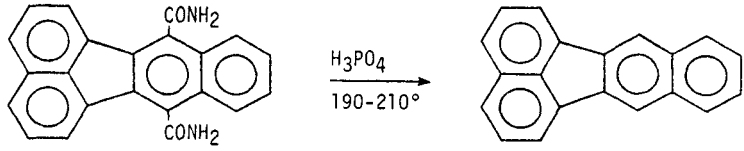


JCS C (1968) 2915

The conversion Ar-Alkyl ⟶ ArH may also be achieved via intermediate carboxylic acids ArCOOH. See section 20 (Carboxylic Acids from Alkyls and Aryls) and section 152 (Hydrides from Carboxylic Acids)

Section 156 Hydrides from Amides

This section lists examples of the conversions $RCONH_2$ ⟶ RH and RNHCOR' ⟶ RH. For the conversions $RCONR'_2$ ⟶ RR" and RNHCOR' ⟶ RR" (R"=alkyl or aryl) see section 66 (Alkyls and Aryls from Amides)



95%

JACS (1951) 73 436

$Ph_2CHCONH_2$ —BuLi THF hexane→ Ph_2CH_2 86%

JACS (1969) 91 7774

$PhC{\equiv}CCONH_2$ —$NaNH_2$ NH_3 Et_2O→ $PhC{\equiv}CH$ 90%

JCS (1963) 4402

PhNHAc ⇢ PhNAc (NO) —Et_2O, 25°→ PhH

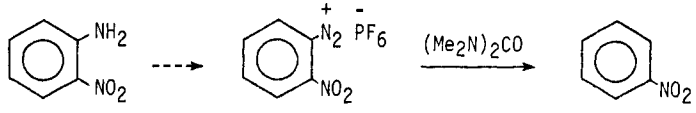
JACS (1964) 86 3180

Amides may also be converted into hydrides via intermediate amines or carboxylic acids. See section 157 (Hydrides from Amines) and section 152 (Hydrides from Carboxylic Acids)

Section 157 Hydrides from Amines

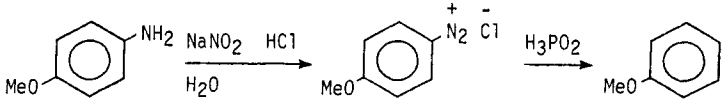
This section lists examples of the conversions $RNH_2 \longrightarrow RH$, $RCH_2NH_2 \longrightarrow RH$ and $R'NR_3^+ X^- \longrightarrow R'H$. For the conversion $RNH_2 \longrightarrow RR'$ (R'=alkyl or aryl) see section 67 (Alkyls and Aryls from Amines)

Review: Replacement of the Aromatic Primary Amino Group by Hydrogen
Org React (1944) 2 262



~75%

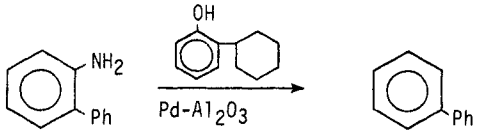
JOC (1963) 28 568



80%

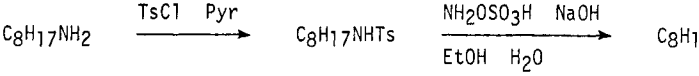
JACS (1952) 74 3074
Org Synth (1963) Coll Vol 4 947
(1955) Coll Vol 3 295

For reduction of diazonium salt with $NaBH_4$ see JACS (1961) 83 1251
" " " " " " HCHO derivatives see
Angew (1958) 70 211
" " " " " " H_3PO_2, HCHO, EtOH, Zn or N_2H_4 see
Org React (1944) 2 262
For selective diazotization of $ArNH_2$ in the presence of $AliphNH_2$ see
JACS (1949) 71 2137



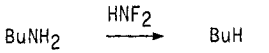
Tetr Lett (1969) 1577

Aromatic amines (RNH_2) may also be converted into hydrides (RH) via N-acetyl derivatives. See section 156 (Hydrides from Amides)



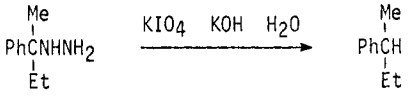
25-30%

JACS (1964) 86 1152



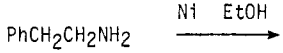
61%

JACS (1963) 85 97
(1964) 86 2233

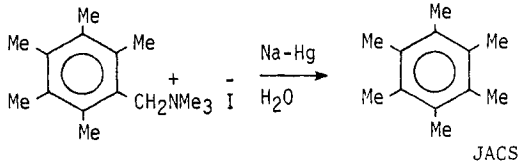


68%

JACS (1963) 85 1108



JACS (1957) 79 1696

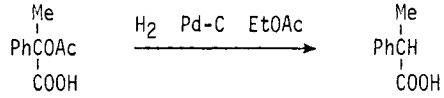


99%

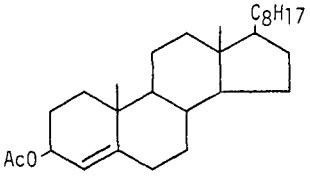
JACS (1951) 73 4122
Org React (1953) 7 263

Section 158 Hydrides from Esters

This section lists examples of the hydrogenolysis of esters, R'COOR ⟶ RH. For the conversion R'COOR ⟶ R'R" or RR" (R"=alkyl) see section 68 (Alkyls and Aryls from Esters). The reduction of esters of sulfonic acids (e.g. ROTs ⟶ RH) is included in section 160 (Hydrides from Halides and Sulfonates)



JCS C (1967) 136
Org React (1953) 7 263

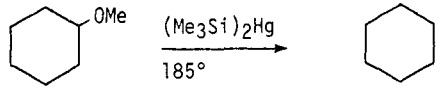


94%

JCS (1957) 1969
JOC (1968) 33 435

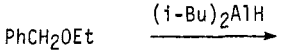
Section 159 Hydrides from Ethers

This section lists examples of the hydrogenolysis of ethers, ROR' ⟶ RH. For the conversion ROR' ⟶ RR" (R"=alkyl or aryl) see section 69 (Alkyls and Aryls from Ethers)



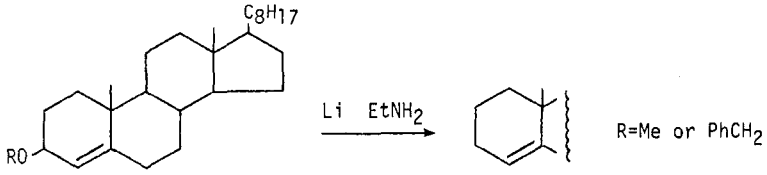
58-76%

JCS C (1967) 2188

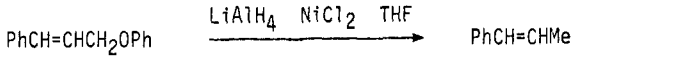


92%

Izv (1959) 2255
(Chem Abs 54 10837)



JCS (1957) 1969



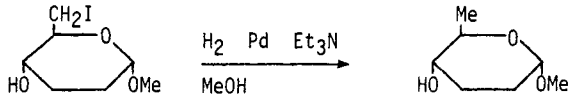
JACS (1957) 79 5463

$PhCH_2OBu \xrightarrow{H_2\ Ni} PhMe$ ~93%

Org React (1953) 7 263
Chem Ind (1963) 1354

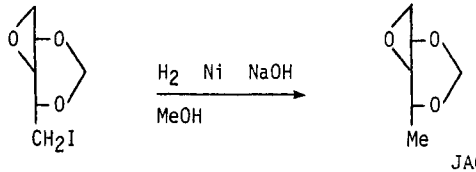
Further examples of the hydrogenolysis of allyl and benzyl ethers are included in section 39 (Alcohols and Phenols from Ethers and Epoxides) and section 45A (Protection of Alcohols and Phenols)

Section 160 Hydrides from Halides and Sulfonates



81%

JOC (1969) 34 3519

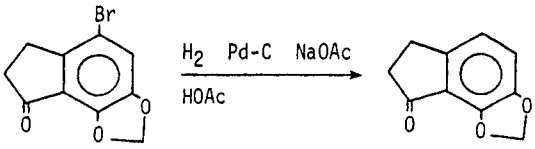


37%

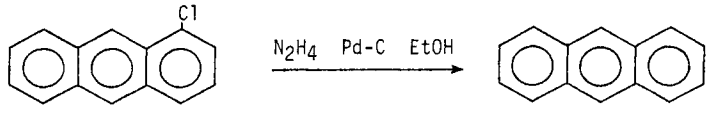
JACS (1950) 72 561
Helv (1946) 29 378 360

$PrF \xrightarrow[190°]{H_2\ Pd\text{-}C} PrH$ 100%

J Phys Chem (1956) 60 1454

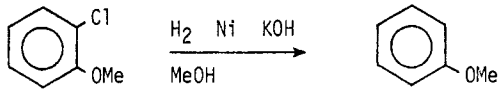


JCS C (1969) 2600



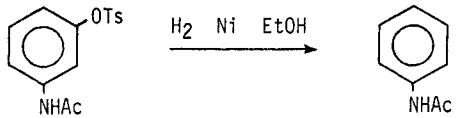
88%

Chem Ind (1959) 1348



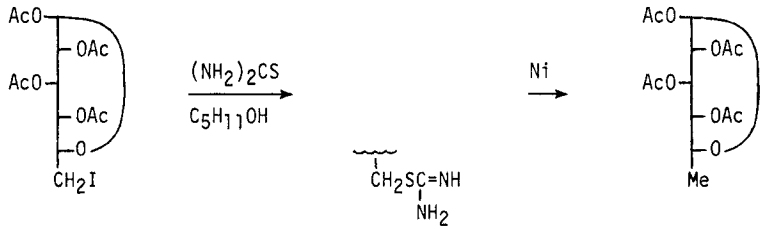
90%

Ber (1958) 91 1376



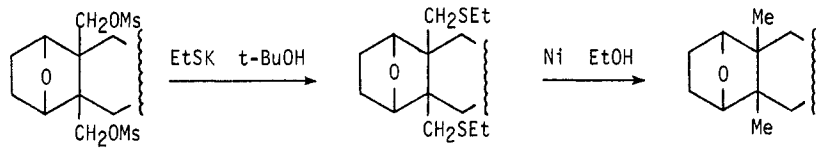
90%

JCS (1949) S178
Aust J Chem (1963) 16 647

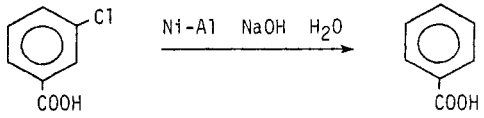


55%

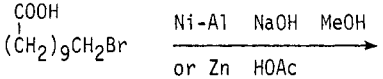
Helv (1946) 29 1199
JACS (1969) 91 7342
(1950) 72 561



JACS (1953) 75 384

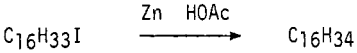


JOC (1944) 9 1



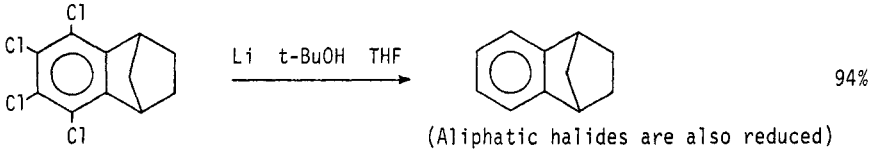
100%

Bull Soc Chim Fr (1967) 2018



85%

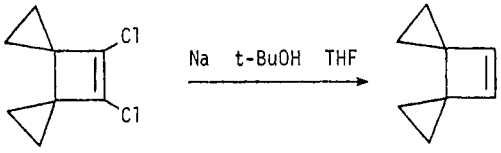
Org Synth (1943) Coll Vol 2 320



94%

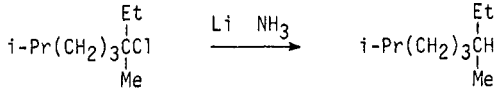
(Aliphatic halides are also reduced)

Tetr Lett (1962) 449
(1968) 1575
JOC (1964) 29 160

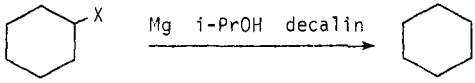


80%

JACS (1968) 90 3594



Rec Trav Chim (1964) 83 367
JACS (1951) 73 3329
Chem Comm (1969) 138



33% (X=F)
83% (X=Cl)

Proc Chem Soc (1963) 219

PhX —(Mg, i-PrOH, decalin)→ PhH

89% (X=Cl or Br)
95% (X=I)

Proc Chem Soc (1963) 219

$PrCHBrMe$ —(1 Mg, Bu_2O; 2 H_2SO_4, H_2O)→ $PrCH_2Me$ 50-53%

Org Synth (1943) Coll Vol 2 478

$C_8H_{17}Br$ —(BuLi, hexane)→ C_8H_{18} + $C_8H_{17}Bu$

JOC (1963) 28 280

$C_8H_{17}Cl$ —($NaBH_4$, Me_2SO)→ C_8H_{18} 42%

JOC (1969) 34 3923
Tetr Lett (1969) 3495

PrOTs —($NaBH_4$, Me_2SO)→ PrH 90%

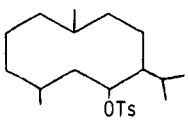
JOC (1969) 34 3923

$C_8H_{17}Br$ and $C_6H_{13}CHBrCH_2Br$ —($LiAlH_4$)→ C_8H_{18} ~70%

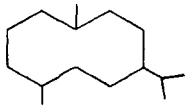
JACS (1948) 70 3664 3738
Org React (1951) 6 469

PhBr —($LiAlH_4$, THF)→ PhH 95%

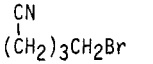
JOC (1969) 34 3918



1 $LiAlH_4$ Et_2O
2 H_2 Pt HOAc



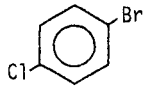
Tetrahedron (1964) 20 2903
Helv (1949) 32 1371
JACS (1970) 92 553



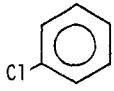
Bu_3SnH

JOC (1969) 34 2014
Synthesis (1970) 499

60%



Ph_3SnH
150°



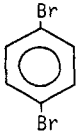
JOC (1960) 25 2203
(1969) 34 2014
(1959) 24 294

75%

BuBr $\xrightarrow[Me_2SO \quad H_2O]{Cr^{2+} \quad NH_2CH_2CH_2NH_2}$ BuH

JACS (1966) 88 4094
Angew (1968) 80 271
(Internat Ed 7 247)

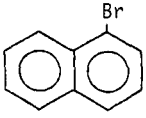
100%



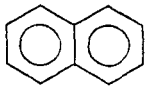
$Cr(ClO_4)_2$ $NH_2CH_2CH_2NH_2$
DMF H_2O

(Vinyl halides are also reduced)
Tetrahedron (1968) 24 3503

100%

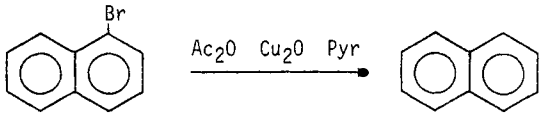


$PhCH_2ONa$ Cu_2O
collidine



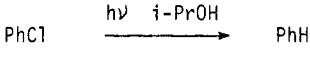
JCS C (1969) 308

95%



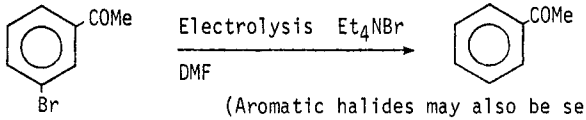
64%

JCS (1964) 1112
Proc Chem Soc (1962) 113



72%

Tetr Lett (1969) 1267

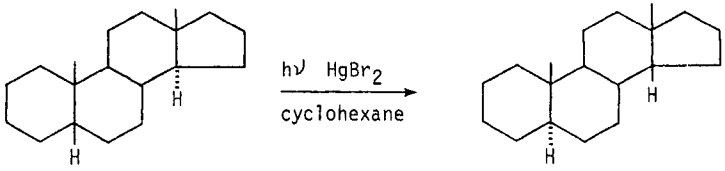


94%

(Aromatic halides may also be selectively reduced in the presence of aliphatic halides)
JOC (1970) 35 1232
Ber (1968) 101 4179

Section 161 Hydrides from Hydrides

This section lists examples of hydrocarbon epimerization. Many related reactions are included in section 65 (Alkyls and Aryls from Alkyls and Aryls)

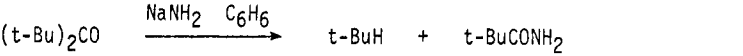


70%

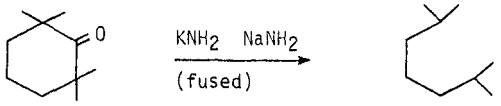
JACS (1970) 92 1094

Section 162 Hydrides from Ketones

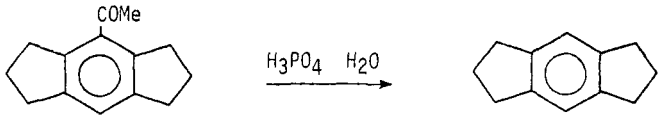
This section lists examples of the conversion $R_2CO \longrightarrow RH$. For the conversion $R_2CO \longrightarrow R_2CH_2$ or R_2CHR' see section 72 (Alkyls, Methylenes and Aryls from Ketones)



Compt Rend (1910) 150 661
Org React (1957) 9 1



Bull Acad Sci URSS (1941) 167
(Chem Abs 37 3749)



JACS (1946) 68 2176

$$PhC{\equiv}CCOPh \xrightarrow{NaNH_2\ NH_3\ THF} PhC{\equiv}CH \qquad 25\%$$

Bull Chem Soc Jap (1962) 35 1488

Section 163 Hydrides from Nitriles

This section lists examples of the conversion RCN ⟶ RH. For the conversion RCN ⟶ RMe see section 73 (Alkyls from Nitriles)

$$PhO(CH_2)_3\underset{\displaystyle CN}{\underset{|}{C}}HPh \xrightarrow[\text{toluene}]{Na\ \ EtOH} PhO(CH_2)_3CH_2Ph \qquad 89\%$$

JACS (1934) 56 1614
Gazz (1963) 93 525
(Chem Abs 59 8825)

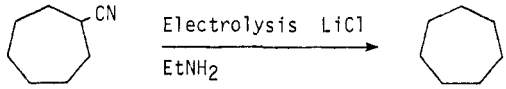
$$RCN \xrightarrow{Na\ \ NH_3} RH$$

35% (R=$C_{12}H_{25}$)
90% (R=$PhCH_2$)

JACS (1969) 91 2059

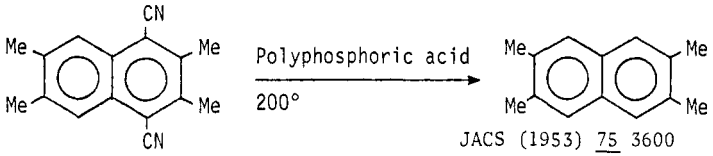
$$\begin{matrix} Ph_2CCN \\ | \\ Me_2NCHCH_2 \\ | \\ CH_2NMe_2 \end{matrix} \xrightarrow[Et_2O\ \ xylene]{EtMgBr} \begin{matrix} Ph_2CH \\ | \\ Me_2NCHCH_2 \\ | \\ CH_2NMe_2 \end{matrix}$$

JACS (1952) 74 5793
Chem Comm (1970) 350



60-80%

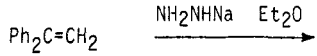
Tetr Lett (1968) 1975



JACS (1953) 75 3600

Section 164 Hydrides from Olefins

This section lists examples of the conversion $R_2C{=}CR_2 \longrightarrow R_2CH_2$. For the hydrogenation, dimerization and alkylation of olefins see section 74 (Alkyls, Methylenes and Aryls from Olefins)

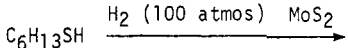


97%

Angew (1962) 74 650
(Internat Ed 1 456)

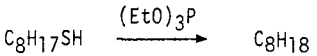
Section 165 Hydrides from Miscellaneous Compounds

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



90%

Coll Czech (1966) 31 2202



88%

JACS (1956) 78 6414

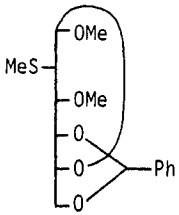
$$Ph\text{-}X\text{-}Ph \xrightarrow{Ni\ \ EtOH} PhH$$

68% (X=S)
75% (X=SO)
65% ($X=SO_2$)

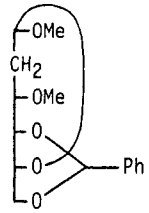
JACS (1943) 65 1013
For use of Ni_2B see JOC (1965) 30 1316

$$C_{10}H_{21}\text{-}X\text{-}C_{10}H_{21} \xrightarrow{Li\ \ MeNH_2} C_{10}H_{22} \qquad (X=S \text{ or } SO_2)$$

JACS (1960) 82 2872

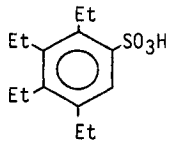


Ni EtOH

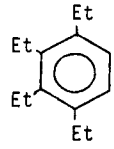


95%

Helv (1946) 29 371
JACS (1953) 75 384
(1963) 85 173



H_2SO_4 H_2O



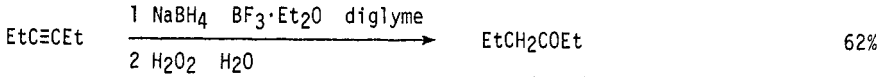
91%

Org React (1942) 1 370

Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

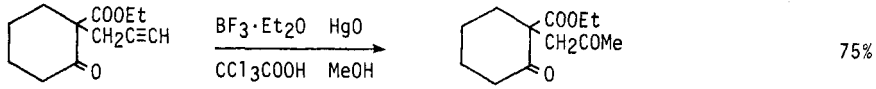
Chapter 12 PREPARATION OF KETONES

Section 166 Ketones from Acetylenes



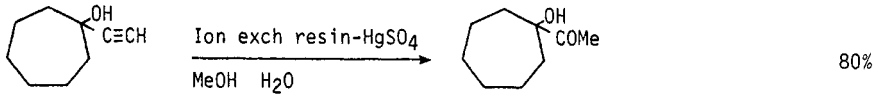
62%

JACS (1961) 83 3834
(1967) 89 5086
Org React (1963) 13 1



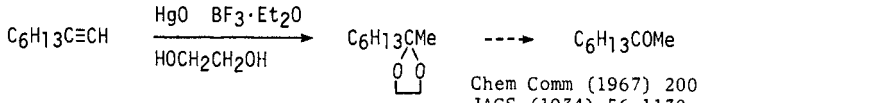
75%

JCS (1952) 4086
Helv (1945) 28 1355
(1943) 26 680



80%

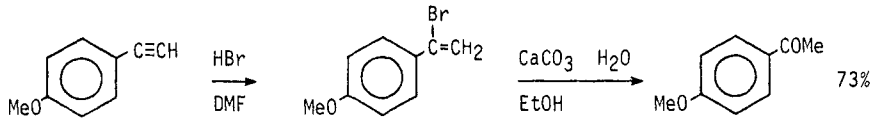
JCS (1954) 3257



Chem Comm (1967) 200
JACS (1934) 56 1130
(1936) 58 80

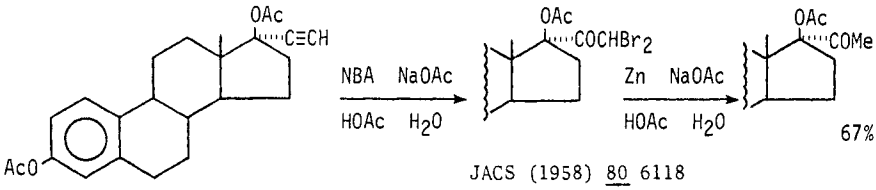
$EtC{\equiv}CEt \xrightarrow[2\ H_2O]{1\ ClSO_2CNO\ \ CH_2Cl_2} EtCOCH_2Et$ 67%

Tetr Lett (1970) 27



73%

Helv (1964) 47 194



67%

JACS (1958) 80 6118

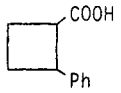
Section 167 Ketones from Carboxylic Acids, Acid Halides and Anhydrides

$C_{17}H_{34}COOH \xrightarrow[\text{electrolysis}]{HOOCCH_2\overset{Me}{\overset{|}{C}}HCH_2\overset{Me}{\overset{|}{C}}HCH_2COMe} C_{17}H_{34}CH_2\overset{Me}{\overset{|}{C}}HCH_2\overset{Me}{\overset{|}{C}}HCH_2COMe$

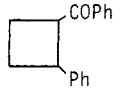
Acta Chem Scand (1956) 10 478
Advances in Org Chem (1960) 1 1

$PhCH_2COOH \xrightarrow[]{MeLi\ \ Et_2O} PhCH_2COMe$ 76%

Acta Chem Scand (1952) 6 782
Org React (1970) 18 1



$\xrightarrow{PhLi \quad Et_2O}$



JACS (1969) 91 456
(1970) 92 2590

$EtCOONa \xrightarrow{EtMgBr \quad Et_2O} Et_2CO$

Ber (1909) 42 4500
JACS (1933) 55 1258
JCS (1950) 2012

Review: The Synthesis of Ketones from Acid Halides and Organometallic Compounds of Magnesium, Zinc and Cadmium

Org React (1954) 8 28

$C_{17}H_{35}COCl \xrightarrow[Et_2O \quad C_6H_6]{PhCH_2CH_2MgBr\text{-}CdCl_2} C_{17}H_{35}COCH_2CH_2Ph$ 65%

Org React (1954) 8 28
JACS (1950) 72 5333

For use of aryl cadmium reagents see JACS (1945) 67 740

$(CH_2)_{10}(COOEt)COCl \xrightarrow[Et_2O \quad C_6H_6]{C_{18}H_{37}MgBr\text{-}ZnCl_2} (CH_2)_{10}(COOEt)COC_{18}H_{37}$ ~79%

Org React (1954) 8 28

$(CH_2)_8(COOEt)COCl \xrightarrow{i\text{-}PrCH_2MgBr \quad Et_2O} (CH_2)_8(COOEt)COCH_2Pr\text{-}i$

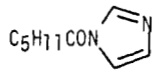
Org React (1954) 8 28
JOC (1961) 26 1768
Tetr Lett (1970) 2523

$C_5H_{11}COCl \xrightarrow{Bu_2CuLi} C_5H_{11}COBu$ 79%

Tetr Lett (1970) 4647

$(PhCO)_2O$ —(t-BuMgCl-$CdCl_2$ Et_2O)→ $PhCOBu\text{-}t$ 40%

JOC (1941) 6 462
(1948) 13 592
Ber (1964) 97 1649

$C_5H_{11}COOH$ ---→  —(EtMgBr, Et_2O)→ $C_5H_{11}COEt$ ~64%

Annalen (1962) 655 90

$PhCOCl$ —(Me_3SiCH_2Ph BuLi, HMPA)→ $PhCOCH_2Ph$

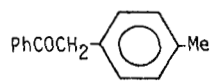
Tetr Lett (1970) 1137

$PhCOCl$ —(Bu_2Hg $AlBr_3$ CH_2Cl_2)→ $PhCOBu$ 73%

J Organometallic Chem (1969) 17 P21

$PrCOCl$ —($(C_6H_{13})_3Al$ CH_2Cl_2)→ $PrCOC_6H_{13}$ 78%

Tenside (1967) 4 167
(Chem Abs 67 116507)

$PhCOCl$ —(CH_2N_2)→ $PhCOCHN_2$ —(p-Tolylcopper)→  ~31%

Chem Comm (1969) 515

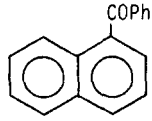
$C_{10}H_{21}COCl$ —(R, $MgC(COOEt)_2$, C_6H_6 EtOH)→ $C_{10}H_{21}COC(R)(COOEt)_2$ —(H_2SO_4, EtCOOH, H_2O)→ $C_{10}H_{21}COCH_2R$

JCS (1950) 322
Org Synth (1963) Coll Vol 4 285

For use of malonic tetrahydropyranyl esters see JCS (1952) 3945
" " " " t-butyl " " JACS (1952) 74 831
" " " " benzyl " " JCS (1950) 325
and JACS (1963) 85 1409

$PhCOCl \xrightarrow[Ph_3CNa \quad Et_2O]{Et_2CHCOOEt} PhCOCEt_2(COOEt) \xrightarrow[\text{or HI} \quad H_2O]{H_2SO_4 \quad HOAc} PhCOCHEt_2$ 44%

JACS (1941) 63 3163

$PhCOCl \xrightarrow{Naphthalene \quad AlCl_3 \quad PhNO_2}$ 

JCS (1949) S99
Chem Rev (1955) 55 229

For further examples of the acylation of aromatic compounds see section 176 (Ketones from Hydrides)

$PhCOOH \xrightarrow[250°]{C_8H_{17}COOH \quad Fe} PhCOC_8H_{17}$ 70%

JOC (1963) 28 879
Org Synth (1963) Coll Vol 4 854

$(C_5H_{11}CO)_2O \xrightarrow{BF_3} (C_5H_{11})_2CO$ 64%

JACS (1950) 72 3294

$(PrCO)_2O \xrightarrow{(Me_3Si)_2 \quad AlCl_3} PrCOMe$ 75%

Compt Rend (1965) 261 1329

$PhCOCl \xrightarrow{Et_3SiH \quad RhCl_3(PBu_2Ph)_3} Ph_2CO$

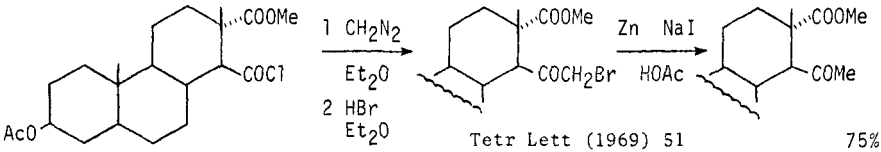
Chem Comm (1970) 1703

$PhCOCl \xrightarrow[2\ H_2O]{1\ MeCH{=}PPh_3 \quad C_6H_6} PhCOCH_2Me$ < 85%

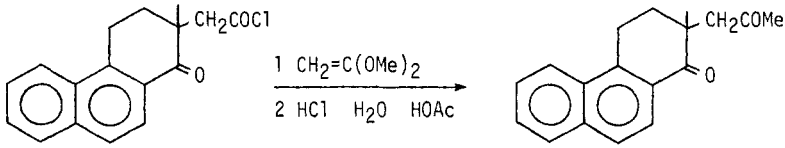
Tetr Lett (1960) (4) 7
Annalen (1964) 674 11
Ber (1962) 95 1513

$PrCOOAg \xrightarrow[2\ 300°]{1\ Bu_4P^+\ Br^-\ \ MeOH} PrCOBu$ 39%

JOC (1963) 28 1133



Tetr Lett (1969) 51
JACS (1943) 65 1516 75%



JACS (1956) 78 6086

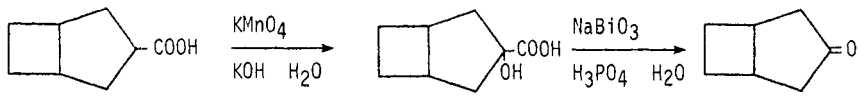
$C_7H_{15}COCl \xrightarrow[2\ H_2O]{1\ Me_3N\ \ Et_2O} (C_7H_{15})_2CO$ 95%

JACS (1947) 69 2444
Org Synth (1963) Coll Vol 4 555
Aust J Chem (1955) 8 506

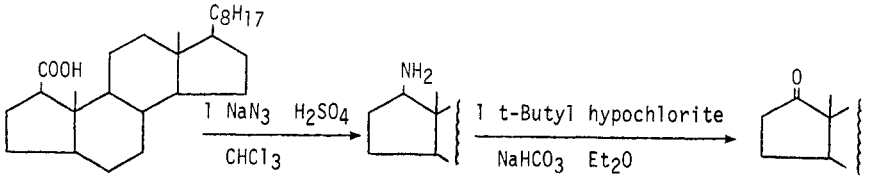
For preparation of cyclic ketones from dicarboxylic acids see
JACS (1948) 70 34

$(Me_2CHCO)_2O \xrightarrow[PhCl]{Pyridine\ N\text{-}oxide} Me_2CO$

Tetr Lett (1965) 233

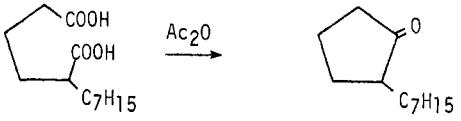


JOC (1964) 29 2914
JCS (1953) 2129 3580



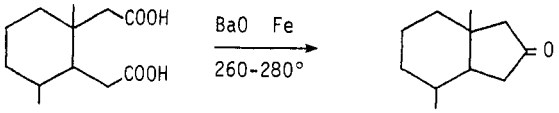
65%

JOC (1965) 30 3775

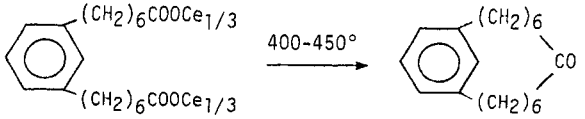


~80%

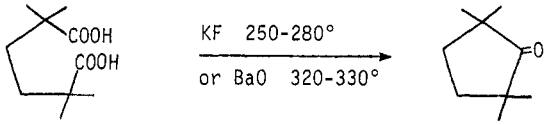
Compt Rend (1955) 240 317
Helv (1945) 28 1651



Helv (1947) 30 2158
Org Synth (1941) Coll Vol 1 192

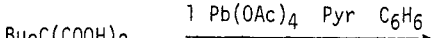


Helv (1932) 15 1220 1459
(1928) 11 1174



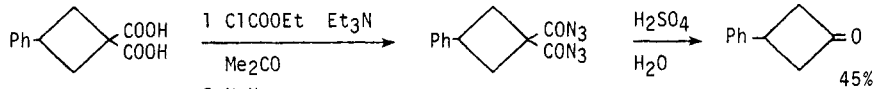
52-72%

JOC (1962) 27 1034



70%

Tetr Lett (1966) 6145
JOC (1964) 29 2914



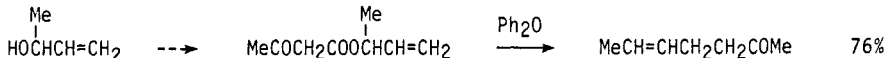
45%

JOC (1962) 27 1647
(1964) 29 2914

Section 168 Ketones from Alcohols and Phenols

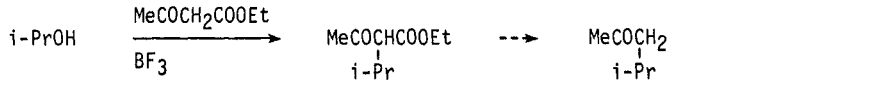
41%

Helv (1967) 50 2091



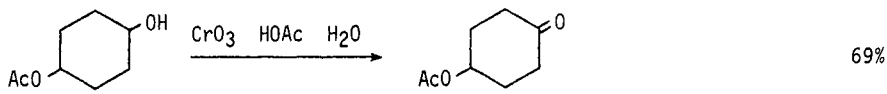
76%

Tetr Lett (1969) 3253



60-67%

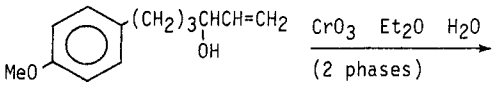
Org Synth (1955) Coll Vol 3 405



69%

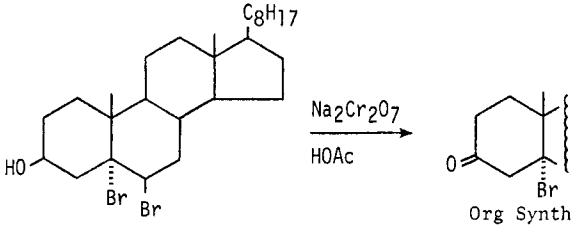
JCS (1949) 615
(1940) 10

For use of CrO_3-$Mn(NO_3)_2$ see JOC (1967) 32 1098



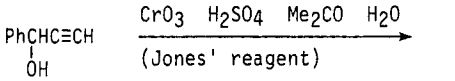
63%

JCS C (1966) 1972
Chem Pharm Bull (1964) 12 1184
JOC (1971) 36 387



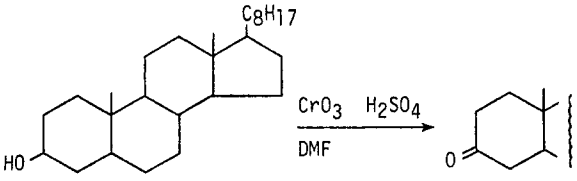
96%

Org Synth (1963) Coll Vol 4 195
Annalen (1967) 707 203



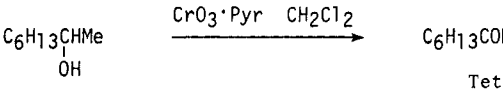
77%

JCS (1946) 39
(1970) 2631
JOC (1960) 25 1434



79%

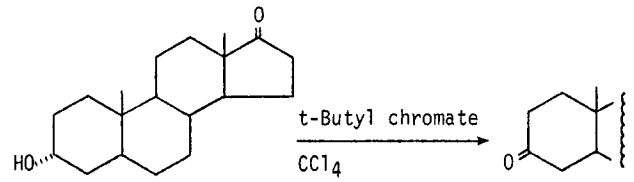
Ber (1961) 94 729



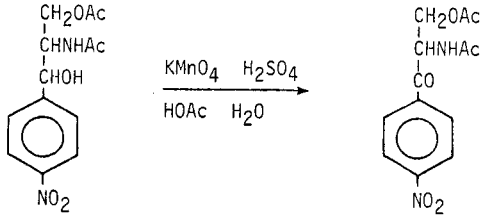
97%

Tetr Lett (1968) 3363

For use of CrO_3 in Pyr-H_2O see Tetrahedron (1962) 18 1351
For in situ preparation of CrO_3-Pyr see JOC (1970) 35 4000

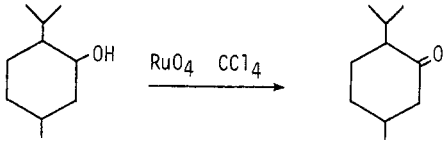


Biochem J (1962) 84 195
Helv (1957) 40 487



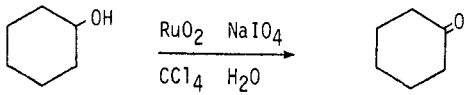
86%

Ber (1960) 93 387
(1961) 94 169



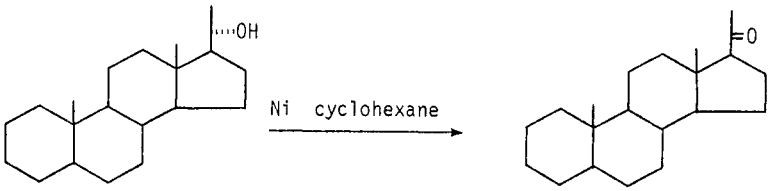
96%

JACS (1958) 80 6682

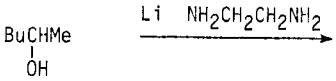


79%

Tetr Lett (1967) 4729
(1970) 4233
Tetrahedron (1963) 19 1959

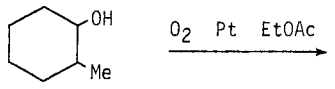


JCS C (1969) 968
JOC (1968) 33 175 2814
(1958) 23 899



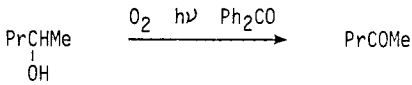
45%

JOC (1962) 27 2662

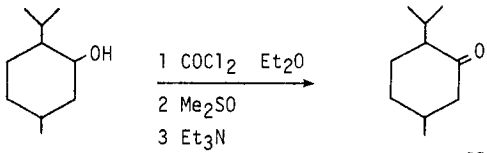


50%

JACS (1955) 77 190
Tetrahedron (1968) 24 6583
Angew (1957) 69 600
Advances in Carbohydrate Chem (1962) 17 169

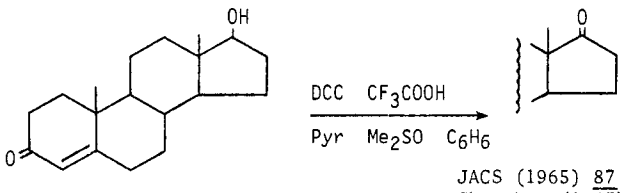


Ber (1963) 96 509



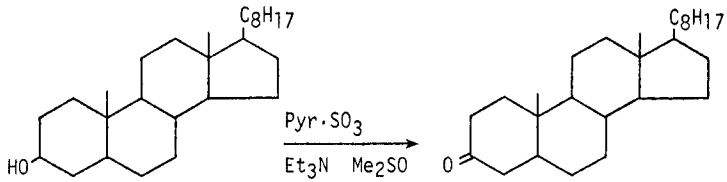
20%

JCS (1964) 1855



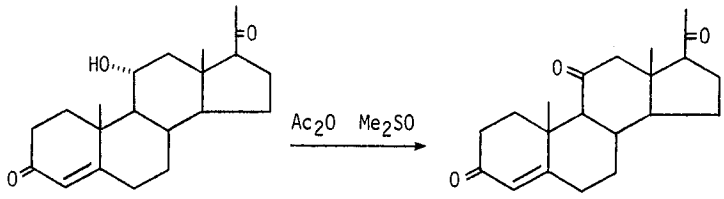
92%

JACS (1965) 87 5670
Chem Rev (1967) 67 247
Can J Chem (1966) 44 2517



83%

JACS (1967) 89 5505



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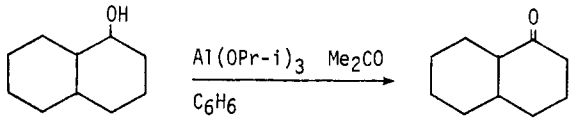
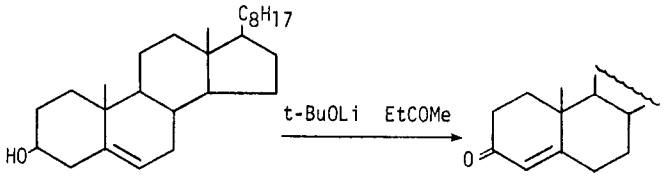
JACS (1967) 89 2416
Carbohydrate Res (1966) 2 251



80%

Org React (1951) 6 207



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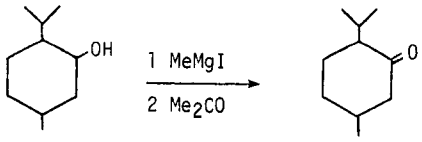
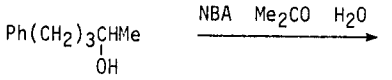
JCS C (1969) 804



Tetr Lett (1964) 3481



59%

Chem Comm (1965) 5
JACS (1954) 76 3682
Chem Rev (1963) 63 21

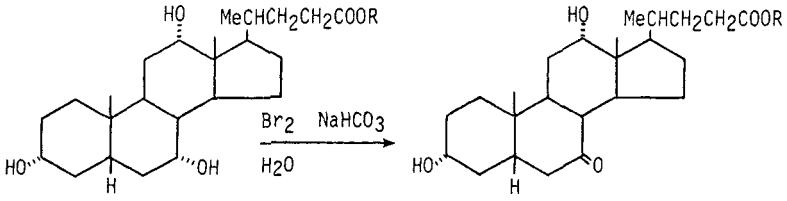
For oxidation with NBS see JCS (1959) 2594 and JOC (1957) 22 1678

" " " N-bromocaprolactam see JOC (1960) 25 263

" " " NCS " Helv (1953) 36 1763

" " " Tribromoisocyanuric acid see Bull Chem Soc Jap (1958) 31 450

" " " 1-chlorobenzotriazole see JCS C (1969) 1474



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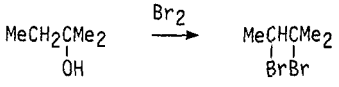
JACS (1945) 67 312



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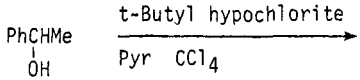
JACS (1933) 55 1136



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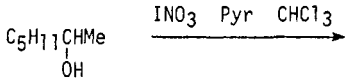
Helv (1953) 36 1763
JACS (1955) 77 172



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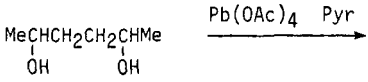
JCS C (1970) 676



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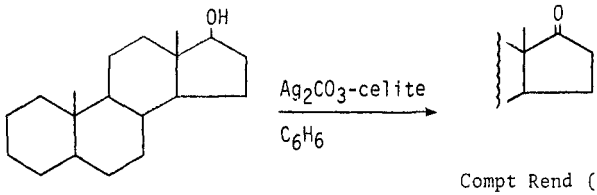
Tetr Lett (1964) 3071
JACS (1960) 82 4956



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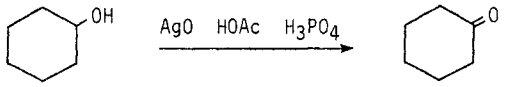
Compt Rend (1968) C 267 900
JACS (1955) 77 490



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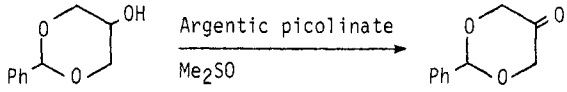
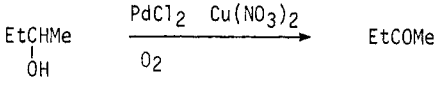
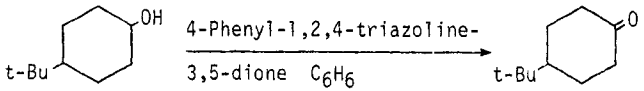
Tetr Lett (1967) 4193
(1968) 5685



Tetr Lett (1967) 415
Can J Chem (1969) 47 1649



JOC (1967) 32 2816



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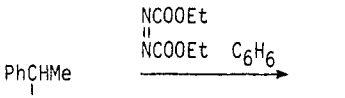
Chem Comm (1966) 744



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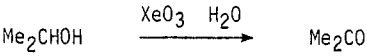
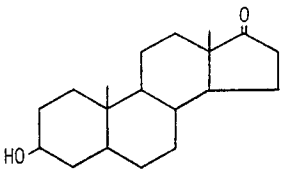
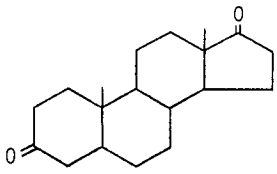
JOC (1967) 32 727
Bull Chem Soc Jap (1968) 41 1491



JACS (1964) 86 2078



MnO_2, MeCN



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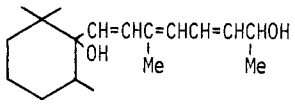
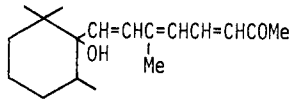
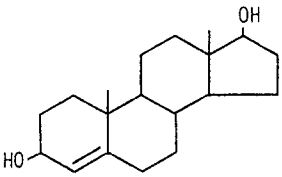
Proc Chem Soc (1964) 110
Chem Comm (1966) 121



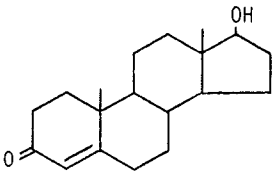
MnO_2, Pet ether



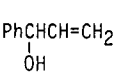
(Applicable to allylic and benzylic alcohols only)
JCS (1952) 1094
JACS (1955) 77 4330
JOC (1959) 24 1051



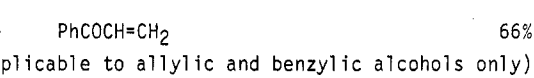
CrO_3, HMPA



(Applicable to allylic and benzylic alcohols only)
Bull Soc Chim Fr (1969) 335



Chloranil CCl_4



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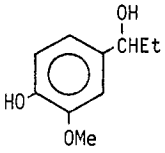
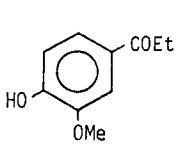
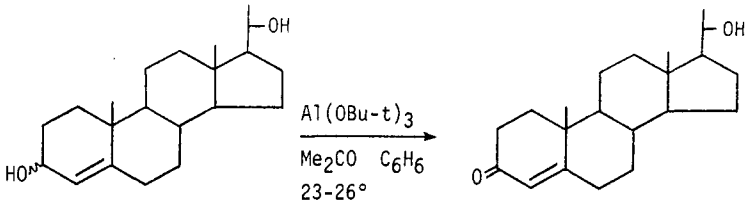
(Applicable to allylic and benzylic alcohols only)
JCS (1956) 3070



DDQ dioxane



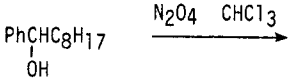
(Applicable to allylic and benzylic alcohols only)
Acta Chem Scand (1961) 15 218
Tetr Lett (1960) (9) 14
Chem Pharm Bull (1970) 18 2343
Chem Rev (1967) 67 153



> 65%

(Method for selective oxidation of allylic alcohols)

Helv (1961) 44 179



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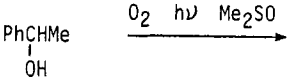
(Applicable to benzylic alcohols only)

JCS (1957) 5087



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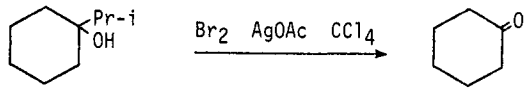
(Applicable to benzylic alcohols only)

Bull Chem Soc Jap (1965) 38 1225



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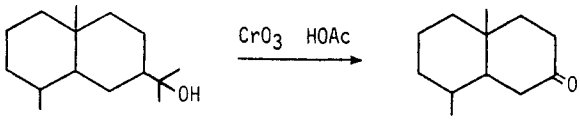
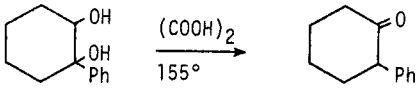
JACS (1965) 87 1807



Helv (1942) 25 1364



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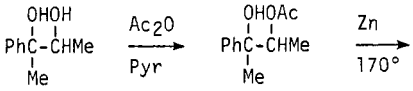
Rec Trav Chim (1948) 67 489
JACS (1957) 79 147
Helv (1948) 31 1077



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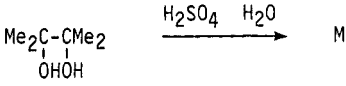
JOC (1970) 35 660



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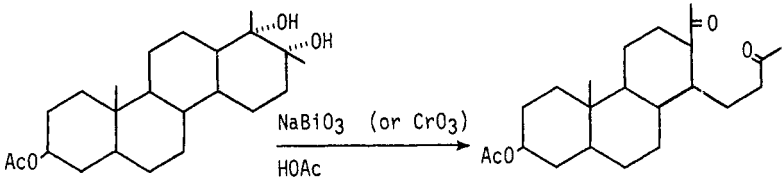
Org Synth (1941) Coll Vol 1 462
JACS (1960) 82 4965



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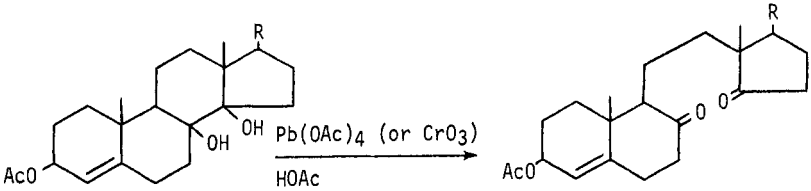
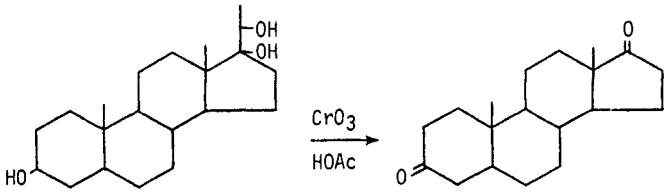
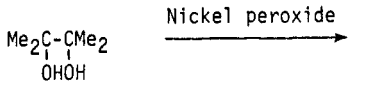
JACS (1960) 82 4965



Helv (1959) 42 1620



Helv (1938) 21 546
JACS (1962) 84 2241



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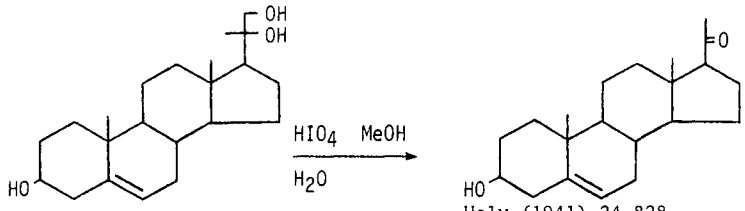
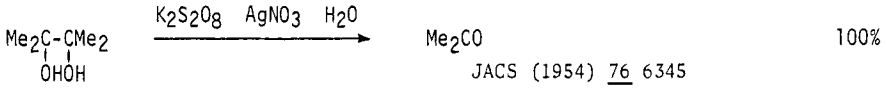
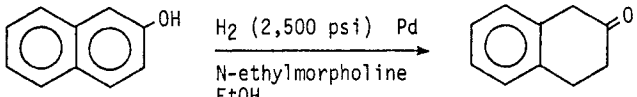
Chem Pharm Bull (1964) 12 403



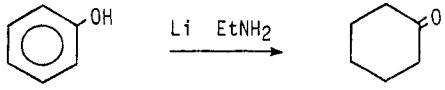
Helv (1941) 24 828
JACS (1956) 78 3087
Org React (1944) 2 341



JACS (1954) 76 6345 100%

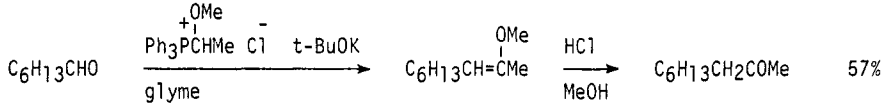


JACS (1946) 68 2172 40%

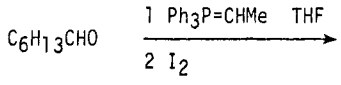


JACS (1955) 77 6042 96%

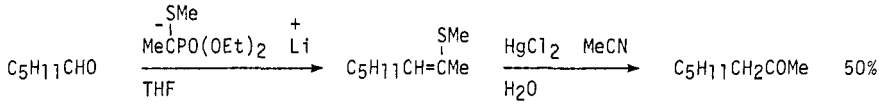
Section 169 Ketones from Aldehydes



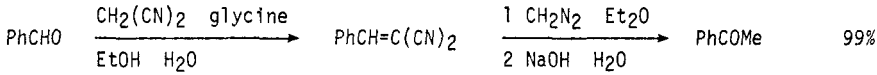
Tetr Lett (1964) 3323 57%



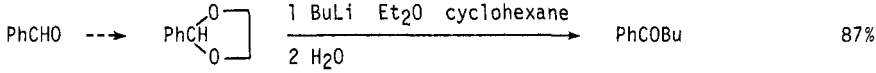
Tetr Lett (1970) 447



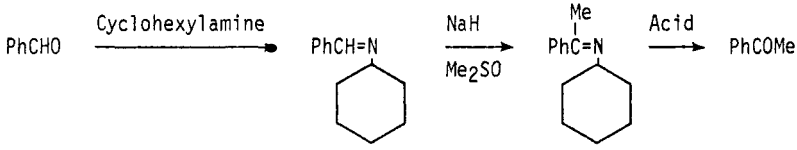
JOC (1970) 35 777



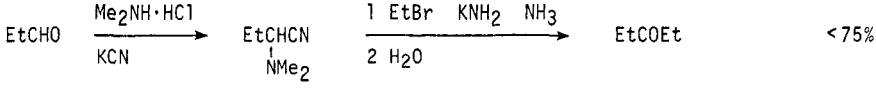
Tetr Lett (1963) 955



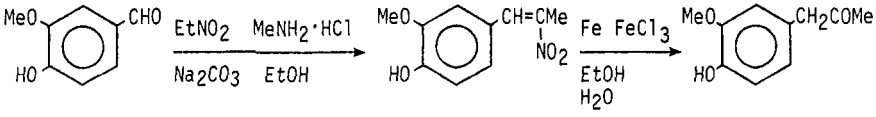
JOC (1965) 30 226



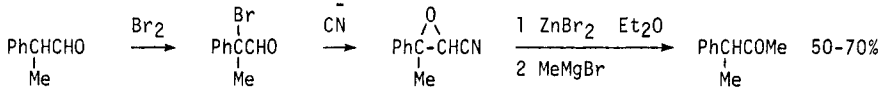
Can J Chem (1970) 48 570



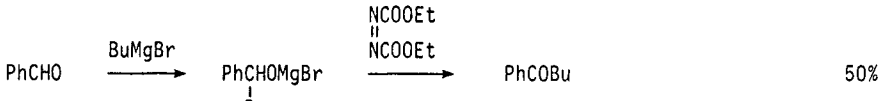
Bull Soc Chim Fr (1961) 1653
JACS (1960) 82 1960
JOC (1961) 26 4740



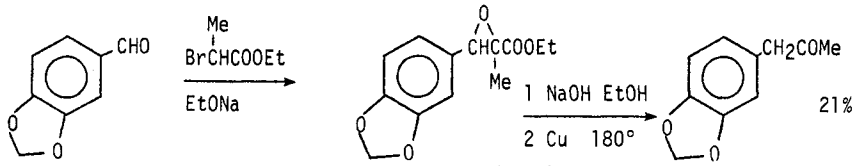
JOC (1951) 16 221
Chem Comm (1967) 1258



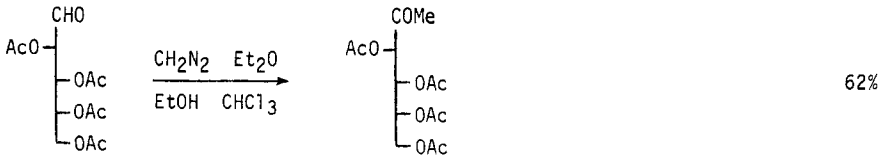
Tetr Lett (1970) 2947



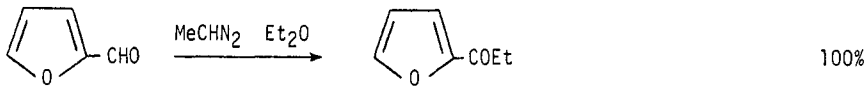
Bull Chem Soc Jap (1968) 41 1491
JCS C (1966) 313



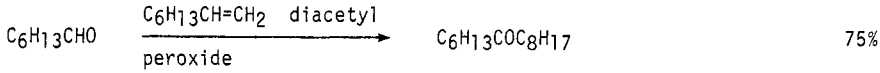
JCS (1943) 15
JACS (1963) 85 955
Org React (1949) 5 413
Chem Rev (1955) 55 283



Org React (1954) 8 364



JACS (1950) 72 2737



JOC (1949) 14 248
Aust J Chem (1967) 20 2033

$PhCHO \xrightarrow[MeOH\ \ H_2O]{HOAc\ \ KOH\ \ electrolysis} PhCOMe$ 18%

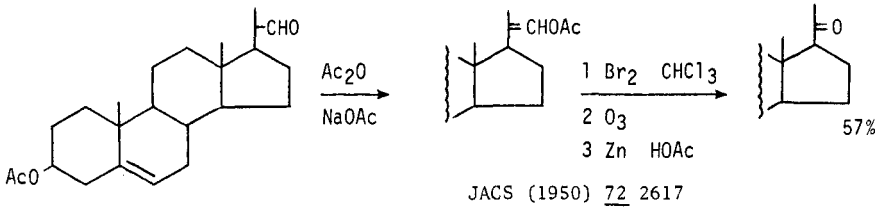
Tetr Lett (1968) 1781

$Me_3CCHO \xrightarrow{AlCl_3} Me_2CHCOMe$ 100%

Ber (1936) 69B 2244

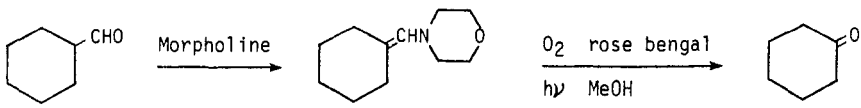
$PhCH(Me)CHO \xrightarrow[2\ H_2SO_4\ \ H_2O]{1\ NH_2CONHNH_2} PhCH_2COMe$ 65%

Zh Obshch Khim (1948) 18 2000
(Chem Abs 43 4632)



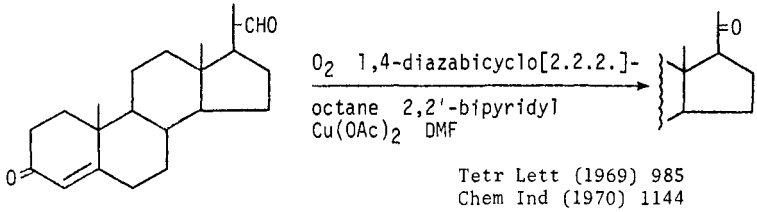
57%

JACS (1950) 72 2617



Tetr Lett (1968) 3271 3267
Chem Comm (1969) 314

For oxidation of enamines with $Na_2Cr_2O_7$ see JACS (1955) 77 1212 1216
" " " " " O_3 " JACS (1952) 74 3627

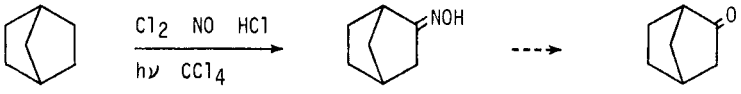


90%

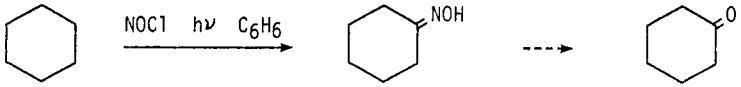
Tetr Lett (1969) 985
Chem Ind (1970) 1144
Ber (1967) 100 259

Section 170 Ketones from Alkyls and Methylenes

This section lists examples of the oxidation of methylenes ($RCH_2R' \longrightarrow RCOR'$), the replacement of alkyl groups by ketonic groups and the degradation of alkyl groups to ketones ($R_2CHR' \longrightarrow R_2CO$). For the acylation of hydrocarbons ($RH \longrightarrow RCOR'$) see section 176 (Ketones from Hydrides)

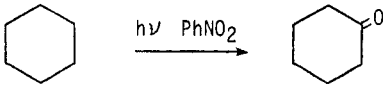


Ber (1965) 98 3493 3501

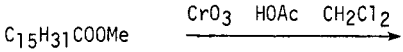


71%

JOC (1953) 18 115
Compt Rend (1965) 260 4514

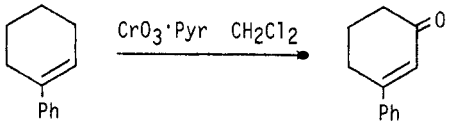


Chem Comm (1970) 1390



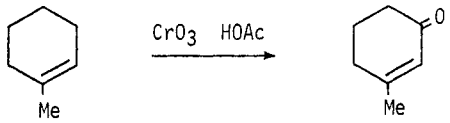
n=7 to 11

Chem Ind (1966) 2168
JACS (1952) 74 3910



71%

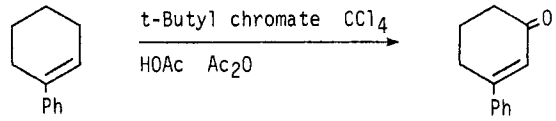
JOC (1969) 34 3587



< 20%

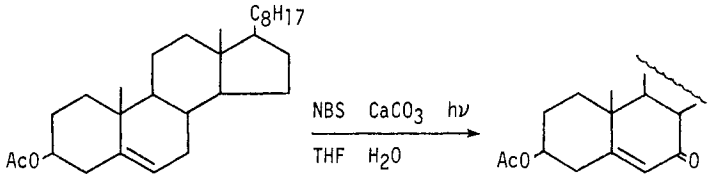
JACS (1941) 63 758
(1949) 71 2226

For oxidation with Na_2CrO_4 in HOAc see JOC (1970) 35 192



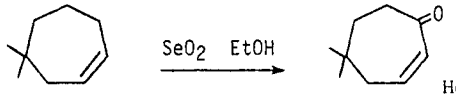
22%

JCS (1951) 516
Helv (1952) 35 284

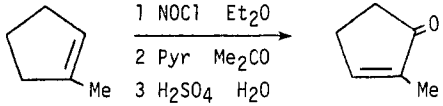


81%

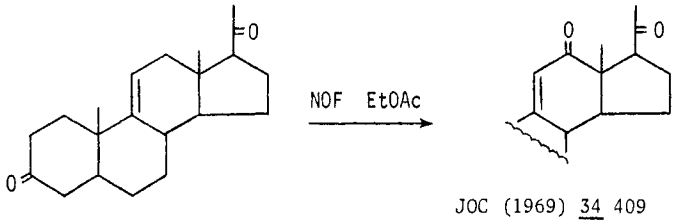
Chem Comm (1969) 1220



Helv (1940) 23 524 1477
Org React (1949) 5 331



Zh Org Khim (1965) 1 865
(Chem Abs 63 6873)
JCS (1951) 516



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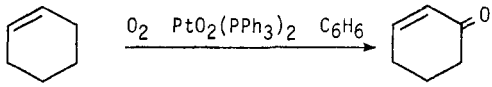
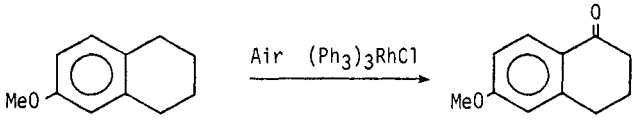
JOC (1969) 34 409



JACS (1967) 89 4809



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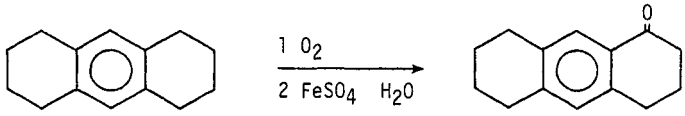
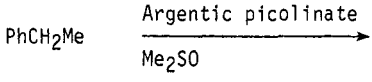
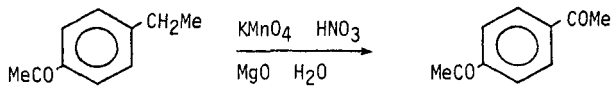
Tetr Lett (1968) 2917
(1967) 3665



Ber (1943) 76B 1130

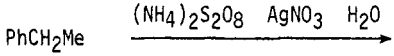


Tetr Lett (1967) 415



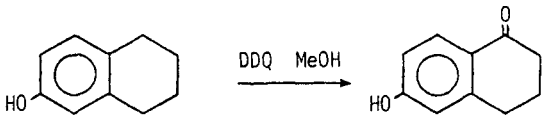
82%

JOC (1961) 26 4151



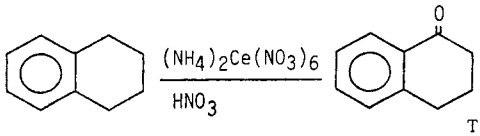
<73%

Org Prep and Procedures (1970) 2 207



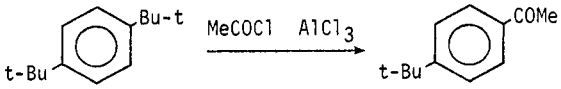
78%

Chem Ind (1970) 158



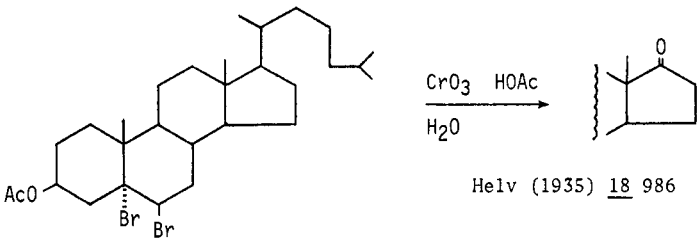
76%

Tetr Lett (1966) 4493



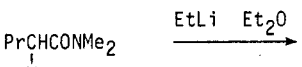
72%

JACS (1942) 64 2421
Helv (1960) 43 1473



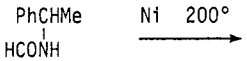
Helv (1935) 18 986

Section 171 Ketones from Amides

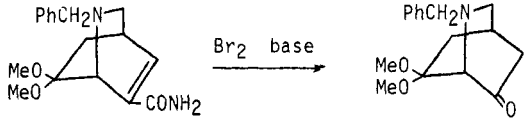


80%

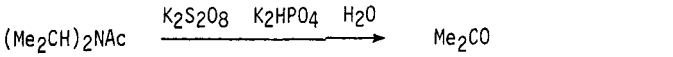
JOC (1959) 24 701
JACS (1939) 61 232
Ber (1959) 92 2555



Compt Rend (1947) 225 457



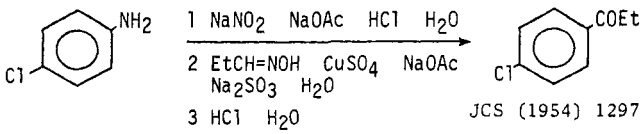
JACS (1968) 90 2448
Org React (1946) 3 267



JOC (1964) 29 3632

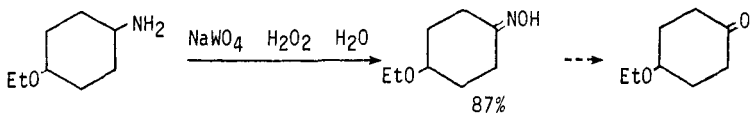
Amides may also be converted into ketones via intermediate amines. See section 96 (Amines from Amides) and section 172 (Ketones from Amines)

Section 172 Ketones from Amines

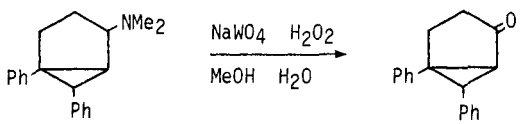


30%

JCS (1954) 1297

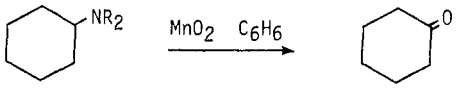


Ber (1960) 93 132



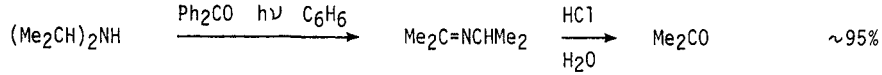
54%

JACS (1968) 90 4892



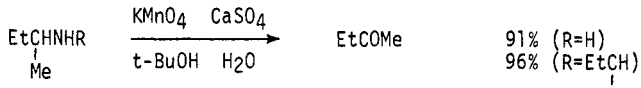
(R=H or Me)

JCS (1960) 3559
JCS C (1966) 995



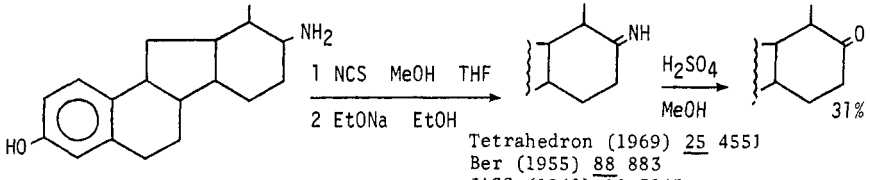
~95%

JACS (1965) 87 2996



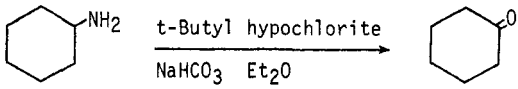
91% (R=H)
96% (R=EtCH(Me))

JOC (1967) 32 3129



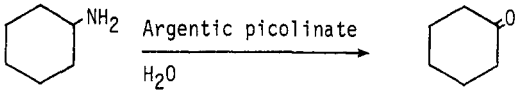
31%

Tetrahedron (1969) 25 4551
Ber (1955) 88 883
JACS (1968) 90 3245



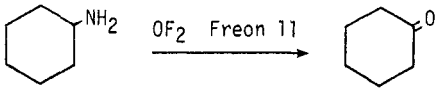
73%

JACS (1954) 76 5554



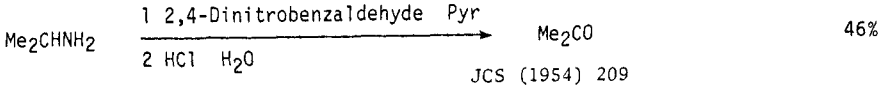
41%

JCS (1965) 4962

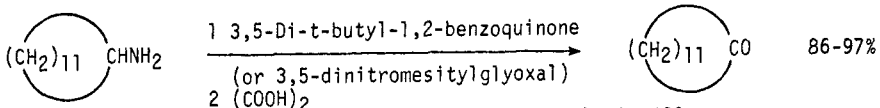


66%

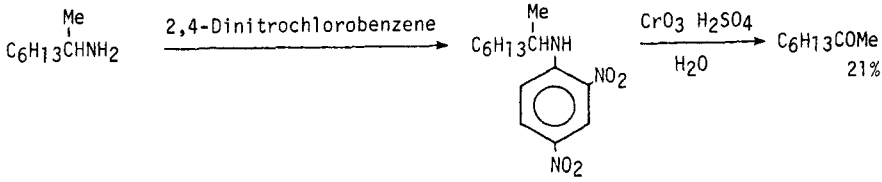
JACS (1964) 86 1392



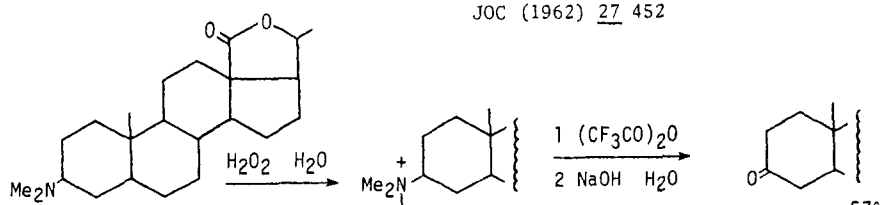
JCS (1954) 209



JACS (1969) 91 1429

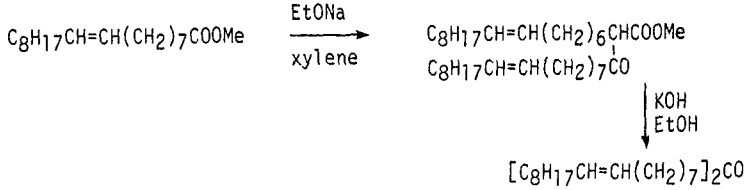


JOC (1962) 27 452

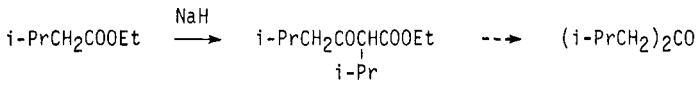


Tetrahedron (1967) 23 4681
JACS (1968) 90 5622

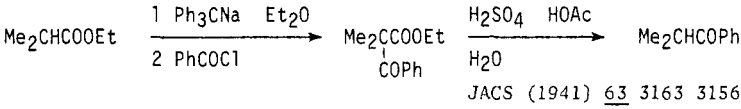
Section 173 Ketones from Esters



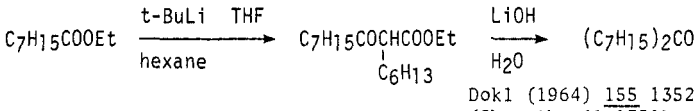
Aust J Chem (1955) 8 506



JACS (1946) 68 2647

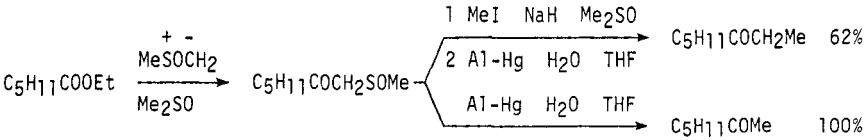


JACS (1941) 63 3163 3156

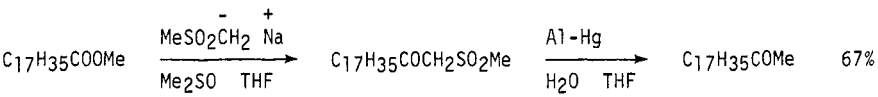


Dokl (1964) 155 1352
(Chem Abs 61 1750)

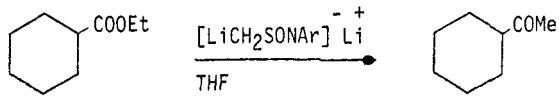
For the preparation of ketones by alkylation of β-ketoesters with halides followed by hydrolysis see section 175 (Ketones from Halides and Sulfonates)



JOC (1966) 31 2355
JACS (1965) 87 1345



JOC (1968) 33 61



JACS (1968) 90 5548

$PhCH_2COOEt \xrightarrow[2\ HCl\quad H_2O]{1\ CH_2{=}C(OEt)NMe_2} PhCH_2COMe$ 54%

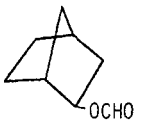
Chem Pharm Bull (1969) 17 2314

$PhCOOEt \xrightarrow[2\ NaOH\quad MeOH]{1\ Ph_3P{=}CH_2\quad Et_2O} PhCOMe$ 41%

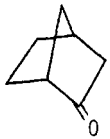
Ber (1962) 95 1513

$Me_2CHOAc \xrightarrow{Br_2\quad H_2O\quad pH\ 4.6} Me_2CO$

JACS (1967) 89 3555



$\xrightarrow[Me_2CO]{CrO_3\quad H_2SO_4}$



83-87%

Org Synth (1962) 42 79

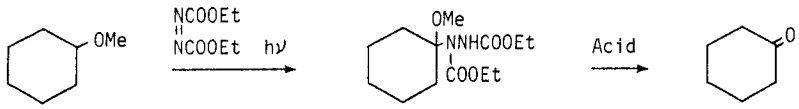
$PhCH_2CH_2C(COOEt)_2(Me) \xrightarrow[2\ NaNO_2\quad HOAc]{1\ N_2H_4} PhCH_2CH_2C(CON_3)_2(Me) \xrightarrow[2\ Acid]{1\ ROH} PhCH_2CH_2COMe$ 28%

Org React (1946) 3 337
JOC (1962) 27 1647

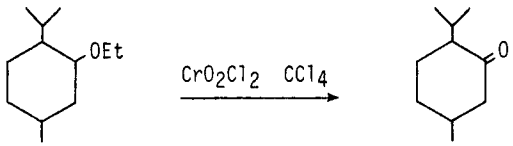
Section 174 Ketones from Ethers and Epoxides

$(Me_2CH)_2O \xrightarrow[BuOH\quad CuCl]{t\text{-Butyl perbenzoate}} Me_2C(OBu)_2 \xrightarrow{Acid} Me_2CO$

Angew (1961) 73 65
Tetrahedron (1961) 13 241

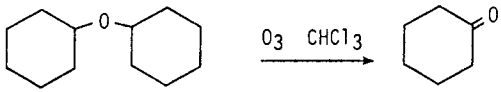


Chem Comm (1965) 259



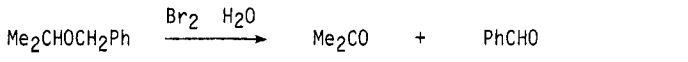
87%

J Prakt Chem (1938) 151 61

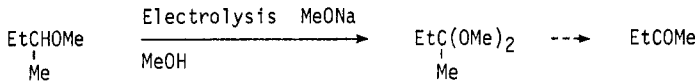


25%

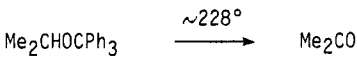
JOC (1962) 27 2392



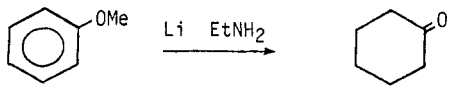
JACS (1967) 89 3550



JACS (1969) 91 2803



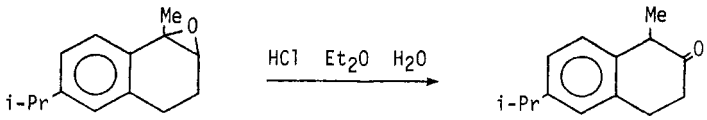
JACS (1930) 52 753
(1924) 46 2580



40%

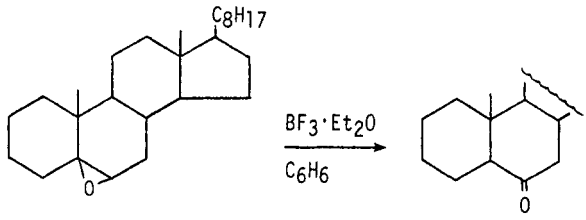
JACS (1955) 77 6042
JCS (1942) 689
Org Synth (1963) Coll Vol 4 903

Some of the methods listed in section 54 (Aldehydes from Ethers and Epoxides) may also be applied to the preparation of ketones from ethers

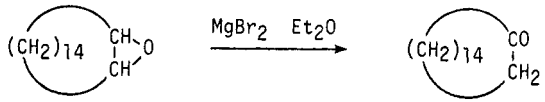


79%

JACS (1962) 84 284

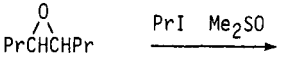


JCS (1957) 4596 4765
Helv (1953) 36 398



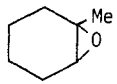
75%

Helv (1948) 31 1077
Chem Rev (1959) 59 737

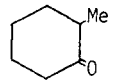


100%

Chem Comm (1968) 227



Bu_3PO $LiClO_4$ C_6H_6



80%

JACS (1968) 90 4193
(1965) 87 1405

$Co_2(CO)_8$ MeOH

$MeCH_2COMe$ 77%

JOC (1962) 27 2706

H_2O_2 KOH
MeOH H_2O

PhCOMe 85-90%

JACS (1957) 79 503

Section 175 Ketones from Halides and Sulfonates

BuBr $\xrightarrow[EtOH]{MeCOCH_2COOEt\ \ EtONa}$ $MeCOCH(Bu)COOEt$ $\xrightarrow{NaOH\ \ H_2O}$ $MeCOCH_2Bu$ ~40%

Org Synth (1941) Coll Vol 1 248 351

For cleavage of β-ketoesters with CaI_2 see JOC (1966) 31 3267
" " " " " LiI " Org Synth (1965) 45 7
" " " " by pyrolysis see JOC (1957) 22 1189

BuBr $\xrightarrow[THF]{CH_2COCHCOOMe\ \ 2Na}$ $BuCH_2COCH_2COOMe$

$BuCH_2COCH_2COOMe$ $\xrightarrow{1\ NaH}$ $\xrightarrow[3\ PhCH_2Cl]{2\ BuLi}$ $BuCHCOCH_2COOMe$ (CH_2Ph)

$BuCH_2COCH_2COOMe$ $\xrightarrow{Hydrolysis}$ $BuCH_2COMe$

$BuCHCOCH_2COOMe$ (CH_2Ph) $\xrightarrow{Hydrolysis}$ $BuCHCOMe$ (CH_2Ph)

JACS (1970) 92 6702

$C_8H_{17}Br \xrightarrow[NaH\ \ t\text{-}BuOH]{CH_2(COOBu\text{-}t)_2} C_8H_{17}CH(COOBu\text{-}t)_2 \xrightarrow[2\ C_7H_{15}COCl]{1\ NaH\ \ C_6H_6} C_8H_{17}C(COOBu\text{-}t)_2(COC_7H_{15}) \xrightarrow{TsOH\ \ HOAc} C_8H_{17}CH_2COC_7H_{15}$

JACS (1952) 74 831
JCS (1952) 3945
(1950) 325

46%

$BuI \xrightarrow[EtOH]{MeCOCH_2COMe\ \ K_2CO_3} BuCH_2COMe$

JOC (1965) 30 3321

60%

$BuBr \xrightarrow[2\ \text{2-chloropyran}]{1\ Mg\ \ Et_2O}$  $\xrightarrow[340\text{-}350°]{Pt\text{-}C} BuCO(CH_2)_3Me$

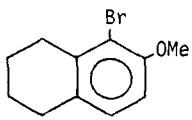
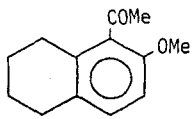
Izv (1964) 747
(Chem Abs 61 3057)

71%

$BuBr \xrightarrow[2\ PhCN]{1\ Mg\ \ Et_2O} PhCOBu$

JACS (1957) 79 881

Further examples of the reaction RMgX + R'CN ⟶ RCOR' are included in section 178 (Ketones from Nitriles)

 $\xrightarrow[2\ CdCl_2\ \ 3\ MeCOCl\ \ C_6H_6]{1\ Mg\ \ EtBr\ \ Et_2O}$ 

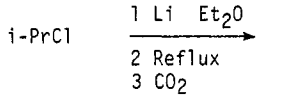
JCS (1955) 3986
Org React (1954) 8 28

$BuBr \xrightarrow[2\ Ac_2O]{1\ Mg\ \ Et_2O} BuCOMe$

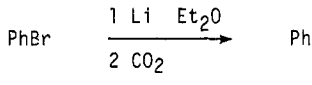
JACS (1945) 67 154
JOC (1948) 13 592

79%

Further examples of the preparation of ketones by reaction of organometallic derivatives of Li, Mg, Cd and Zn with carboxylic acids, acid halides and anhydrides are included in section 167 (Ketones from Carboxylic Acids, Acid Halides and Anhydrides)

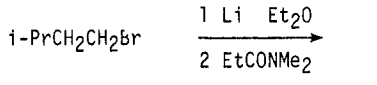


JACS (1953) 75 1771



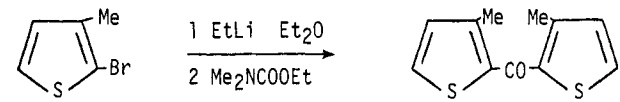
70%

JACS (1933) 55 1258
(1955) 77 2806



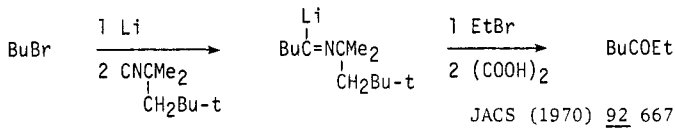
75%

JOC (1959) 24 701



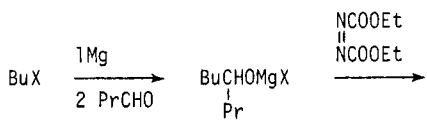
75%

Tetr Lett (1970) 5219



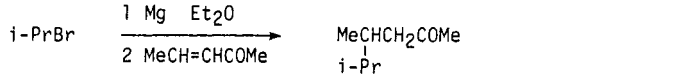
87%

JACS (1970) 92 6675



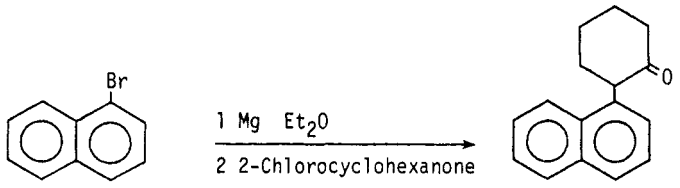
66%

Bull Chem Soc Jap (1968) 41 1491



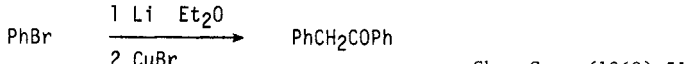
JACS (1951) 73 2721

For promotion of 1:4 addition of Grignard reagents by CuX_2 see JACS (1941) 63 2308
and JACS (1965) 87 82
and JOC (1966) 31 3128



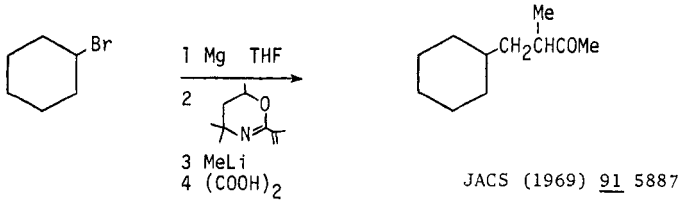
48%

JOC (1959) 24 843
(1947) 12 737



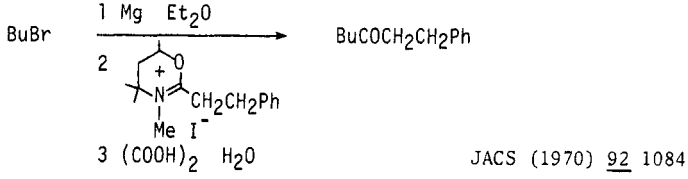
35%

Chem Comm (1969) 515



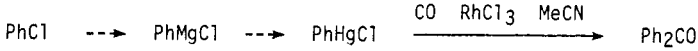
82%

JACS (1969) 91 5887



71%

JACS (1970) 92 1084

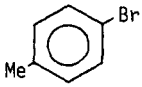


<48%

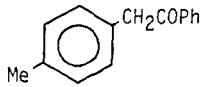
JACS (1968) 90 5546

$$BuBr \dashrightarrow BuHgBr \xrightarrow[2\ Ph_3P\ \ C_6H_6]{1\ Co_2(CO)_8\ \ THF} Bu_2CO \qquad <42\%$$

JACS (1969) 91 3037



$$\xrightarrow[2\ 9\text{-Borabicyclo[3.3.1]-nonane}\ 3\ MeSO_3H\ 4\ PhCOCH_2Br\ \ t\text{-BuOK}\ \ THF]{1\ Li\ \ Et_2O}$$



95%

JACS (1969) 91 4304 6852

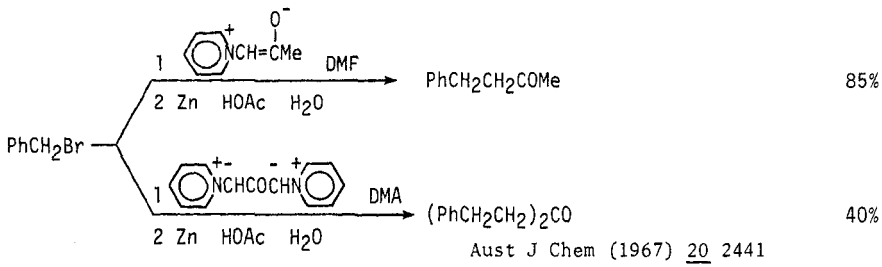
$$PhCH_2Br \xrightarrow{Li[PhCOFe(CO)_4]\ \ C_6H_6} PhCH_2COPh \qquad 67\%$$

JOC (1970) 35 4183
Trans New York Acad Sci (1965) 27 724

$$C_6H_{13}Br \xrightarrow[2\ Ph_3\overset{+}{P}CMe_2\ \overset{-}{Cl}\ \ THF]{1\ Mg} C_6H_{13}COPr\text{-}i \qquad 45\%$$

$$\text{(COOEt)}$$

Tetr Lett (1969) 23



$$PhCH_2Br \xrightarrow[2\ Zn\ \ HOAc\ \ H_2O]{1\ \overset{+}{\text{N}}CH{=}C(O^-)Me\ \ DMF} PhCH_2CH_2COMe \qquad 85\%$$

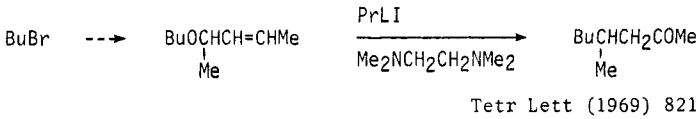
$$PhCH_2Br \xrightarrow[2\ Zn\ \ HOAc\ \ H_2O]{1\ \overset{+-}{\text{N}}CHCOCH\overset{-\ +}{N}\ \ DMA} (PhCH_2CH_2)_2CO \qquad 40\%$$

Aust J Chem (1967) 20 2441

$$BuBr \dashrightarrow BuC(COOH)_2 \xrightarrow[Pyr\ \ C_6H_6]{Pb(OAc)_4} BuCOEt$$

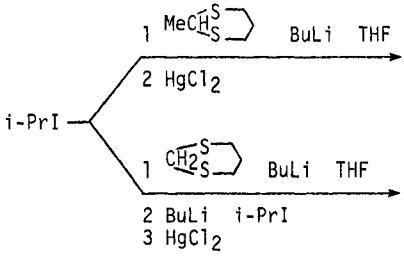
$$\text{(Et)}$$

Tetr Lett (1966) 6145



~30%

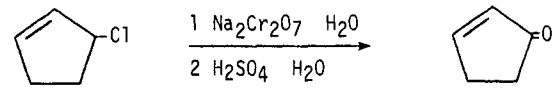
Tetr Lett (1969) 821



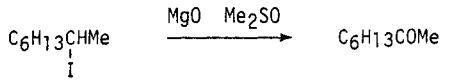
84%

70%

Angew (1965) 77 1134
(Internat Ed 4 1075)
Tetr Lett (1969) 173
JOC (1968) 33 298
Synthesis (1969) 17

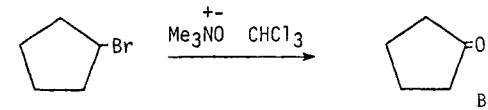


Ber (1956) 89 1732



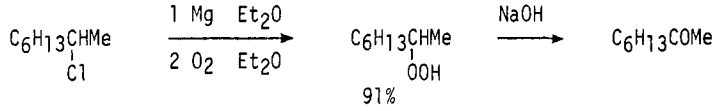
JCS (1964) 520
JOC (1959) 24 1792
(1960) 25 670
Chem Rev (1967) 67 247

32%

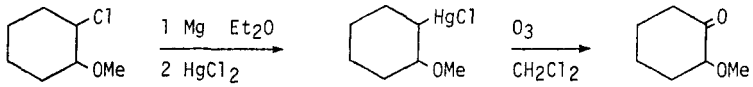


50%

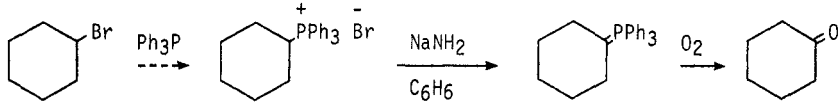
Ber (1961) 94 1360



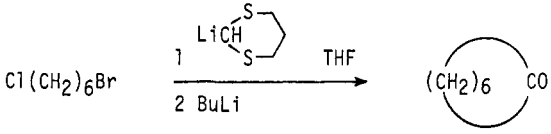
JACS (1955) 77 6032
Ber (1960) 93 2151



Tetr Lett (1970) 2679

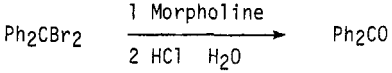


Ber (1963) 96 1899
(1961) 94 1987



68%

JOC (1968) 33 300

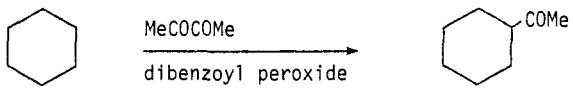


63%

Bull Soc Chim Fr (1965) 3544
Org Synth (1941) Coll Vol 1 95
JACS (1966) 88 3515

Section 176 Ketones from Hydrides (RH)

This section lists examples of the replacement of hydrogen by ketonic groups e.g. RH ⟶ RCOMe (R=alkyl, aryl, vinyl etc.). For the oxidation of methylenes R_2CH_2 ⟶ R_2CO, and the degradation of alkyls R_2CHR' ⟶ R_2CO, see section 170 (Ketones from Alkyls and Methylenes)



JACS (1968) 90 3588

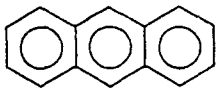
$Me_2CHCH_3 \xrightarrow{MeCOCl\ \ AlCl_3} Me_2CHCH_2COMe$

Ber (1936) 69B 2244

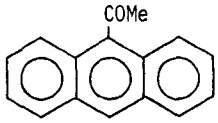
$BuCH{=}CH_2 \xrightarrow{MeCOOH\ \ (CF_3CO)_2O} BuCH{=}CHCOMe$ 22%

JCS (1953) 3628

Review: The Friedel-Crafts Acylation Reaction and its Application to Polycyclic Aromatic Hydrocarbons Chem Rev (1955) 55 229

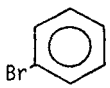


$\xrightarrow[C_6H_6]{MeCOCl\ \ AlCl_3}$

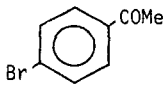


57-60%

Org Synth (1963) Coll Vol 4 8
(1955) Coll Vol 3 23

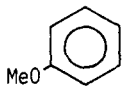


$\xrightarrow{Ac_2O\ \ AlCl_3\ \ CS_2}$

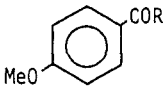


69-79%

Org Synth (1941) Coll Vol 1 109



$\xrightarrow{RCOOH\ \ (CF_3CO)_2O}$



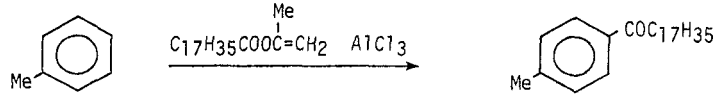
78% (R=Me)
56% (R=Ph)

JCS (1951) 718

$PhH \xrightarrow{RCO^+\ SbF_6^-} PhCOR$

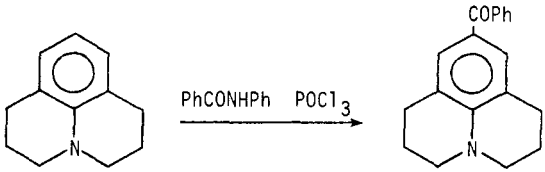
81-93% (R=Et)
86-93% (R=Ph)

JACS (1962) 84 2733



83%

JOC (1970) 35 2351

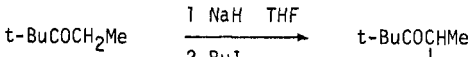


70%

JOC (1952) 17 1281
JCS (1932) 642

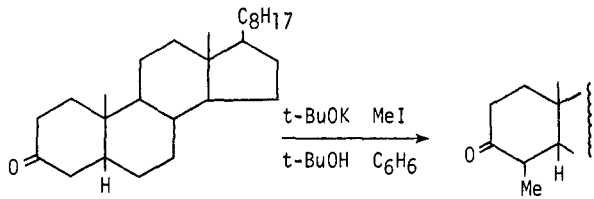
Section 177 Ketones from Ketones

All reactions of enones forming saturated ketones (e.g. RCH=CHCOR → RCH_2-CHCOR) are listed in section 180 (Ketones from Miscellaneous Compounds)
R'



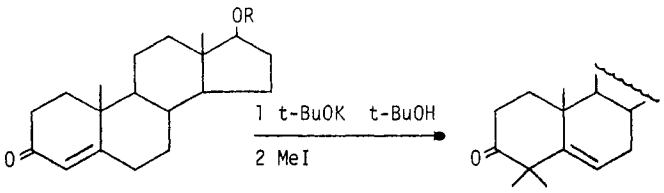
57%

Bull Soc Chim Fr (1968) 4990
Tetrahedron (1968) 24 6583

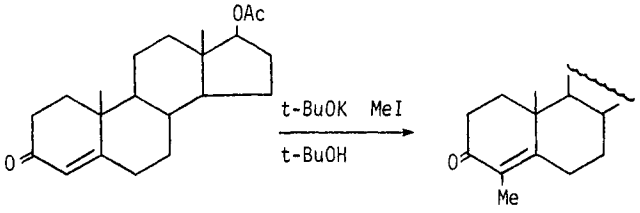


40%

JACS (1958) 80 5220

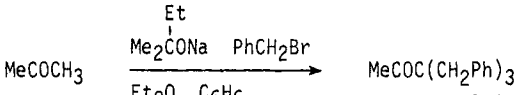


JCS (1956) 4490
(1960) 67

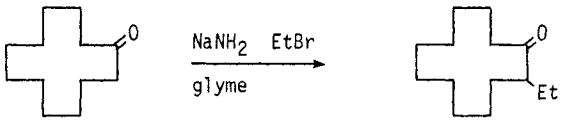


44%

JACS (1960) 82 2847
(1962) 84 3402

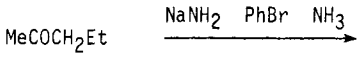


Bull Soc Chim Fr (1961) 836
(1956) 1392



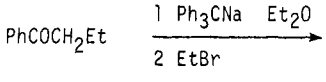
45%

JACS (1969) 91 1264
(1953) 75 369
Org Synth (1955) Coll Vol 3 44



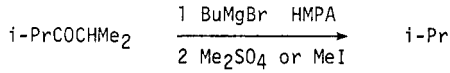
65%

JACS (1959) 81 1169

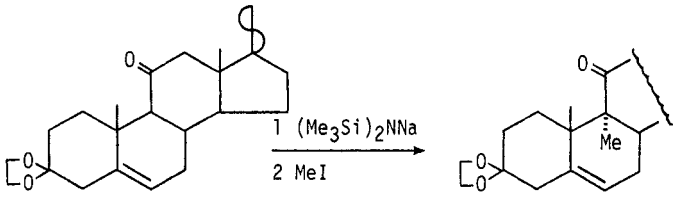


62%

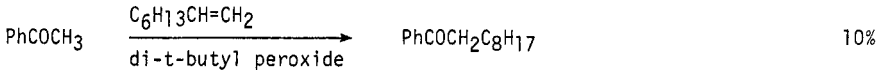
JACS (1957) 79 881
(1959) 81 1745



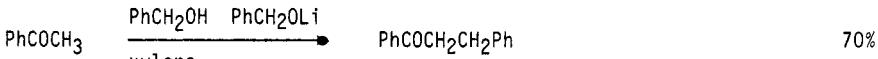
Compt Rend (1966) C 263 488



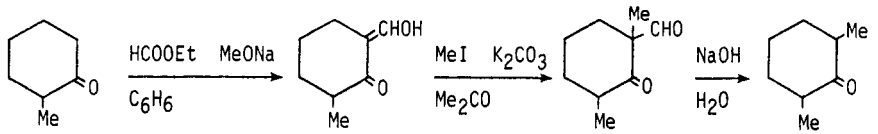
Chem Comm (1969) 1498



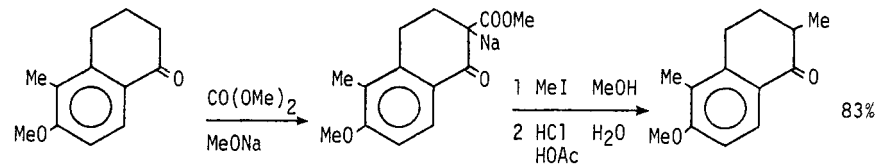
JCS (1965) 1918



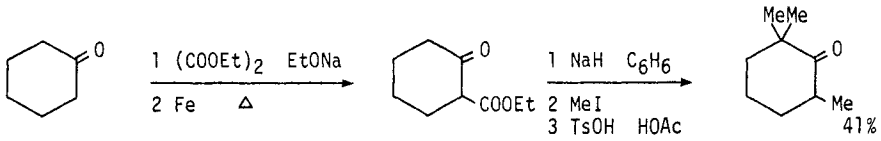
JACS (1956) 78 4950



JCS (1954) 1373
JACS (1947) 69 1361
(1957) 79 6313

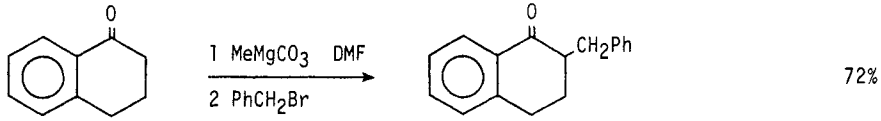


Tetrahedron (1957) 1 49

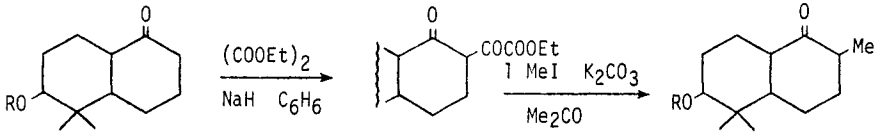


JACS (1958) 80 4072
Org Synth (1943) Coll Vol 2 531

For the preparation of β-ketoesters from ketones via enamines see
JACS (1963) 85 207



JACS (1959) 81 2598



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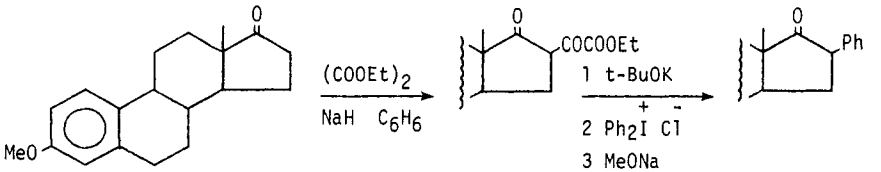
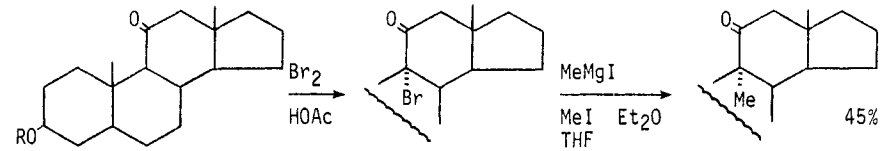
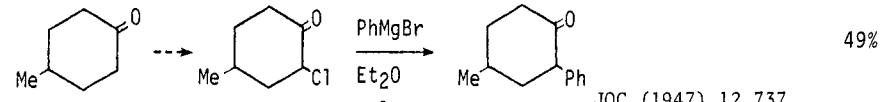


J Med Chem (1967) 10 106



JCS (1964) 1161
JOC (1961) 26 2426
Tetr Lett (1969) 2269



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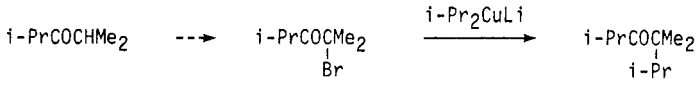
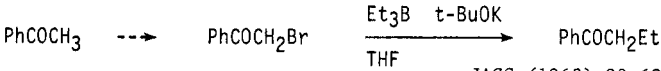
(1959) 24 843
JCS (1957) 4089



Tetr Lett (1971) 177



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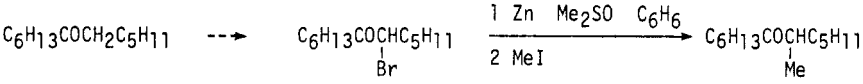
(1969) 91 4304 6852



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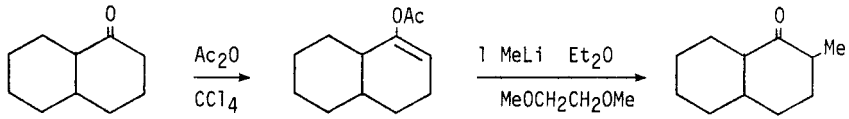

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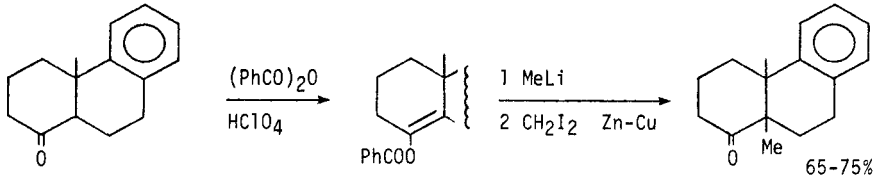
Tetr Lett (1971) 105



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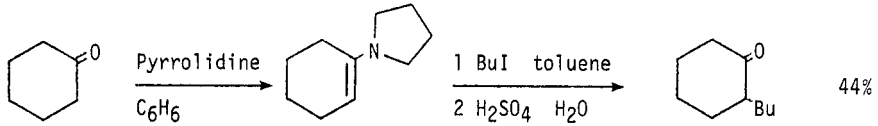
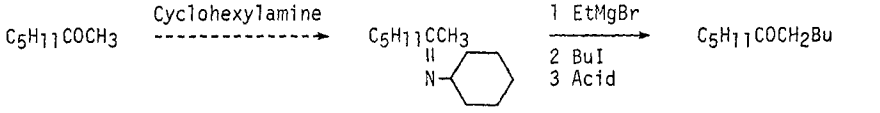


JACS (1963) 85 207
Advances in Org Chem (1963) 4 1

For preparation of enamines from unreactive ketones
see JCS (1965) 5142
and JOC (1967) 32 213



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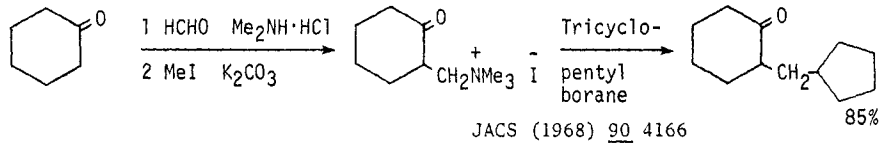

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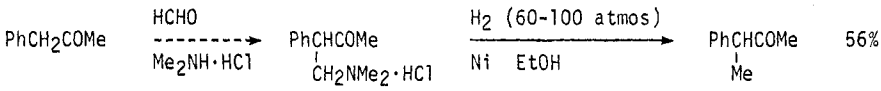
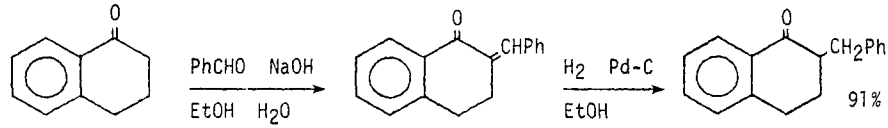
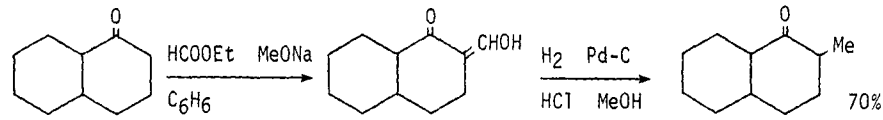


JACS (1953) 75 1128



Org Prep and Procedures (1970) 2 37



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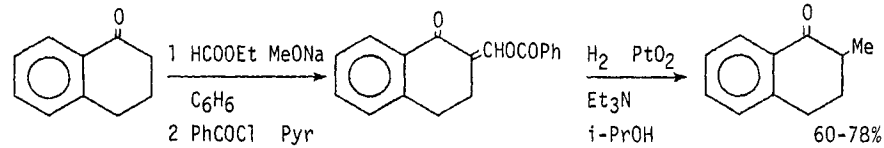
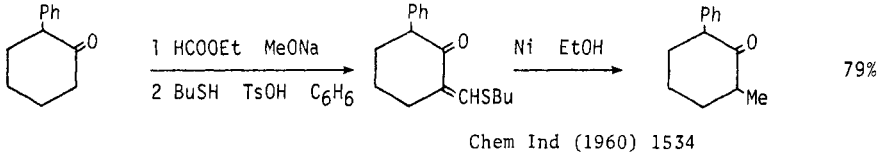


Synthesis (1970) 476
Org React (1954) 8 119



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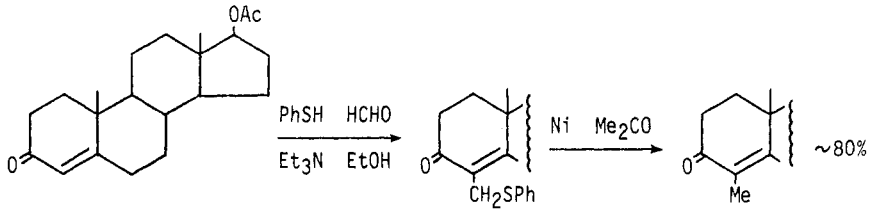
Chem Ind (1960) 1534



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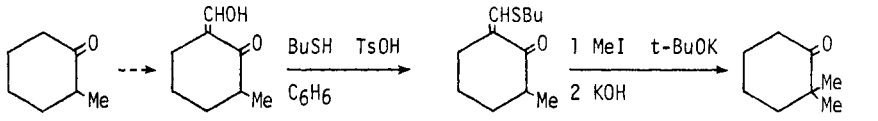
JCS (1962) 1091



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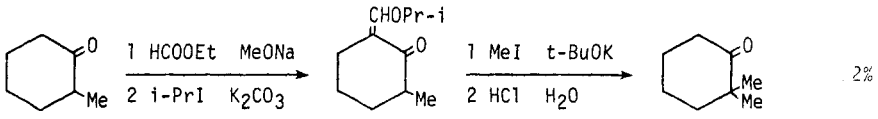
JOC (1962) 27 1615 1620
Tetrahedron (1968) 24 3095



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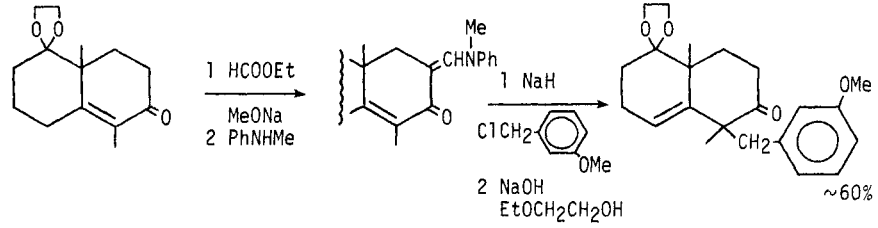

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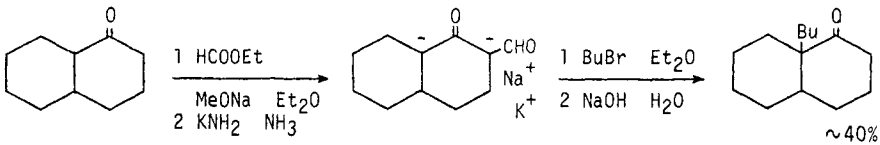
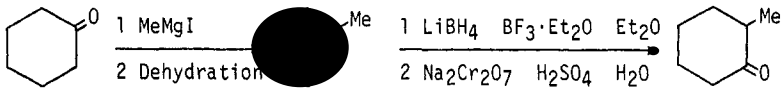
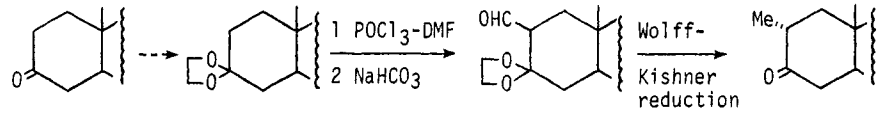
JOC (1970) 35 468



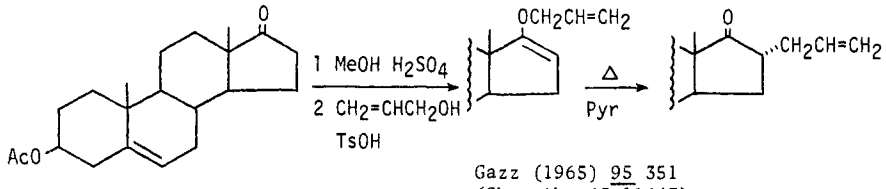
JACS (1965) 87 82



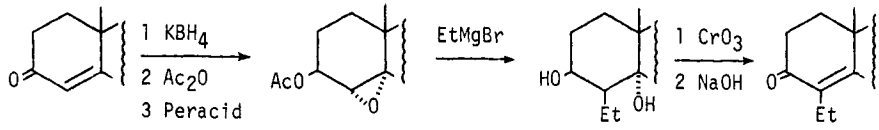
JACS (1961) 83 2951



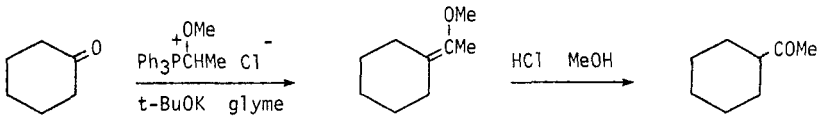
Tetr Lett (1964) 2161



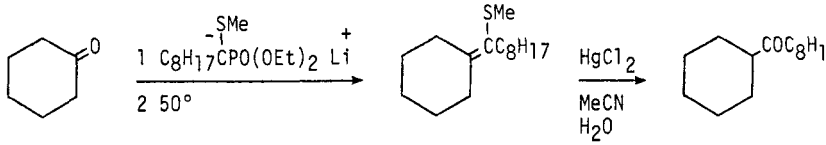
Gazz (1965) 95 351
(Chem Abs 63 11647)



Bull Soc Chim Fr (1964) 321



Tetr Lett (1964) 3323



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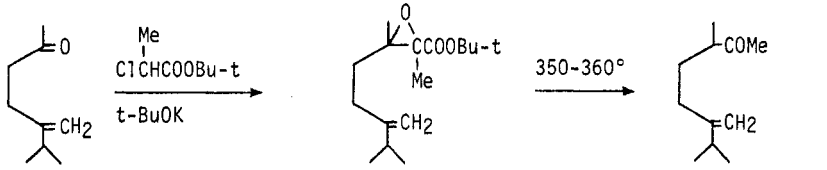
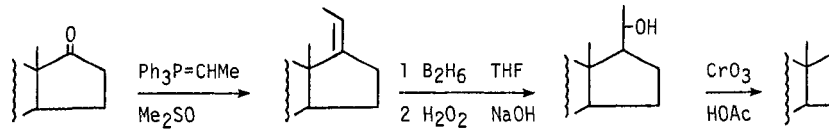
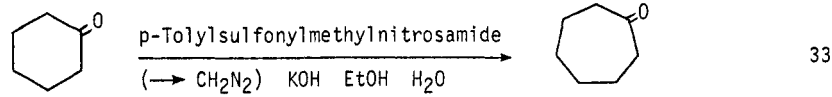


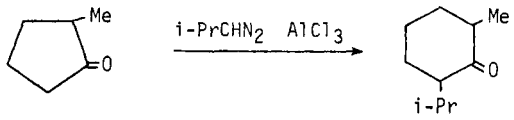
JACS (1963) 85 955
Org React (1949) 5 413
Chem Rev (1955) 55 283



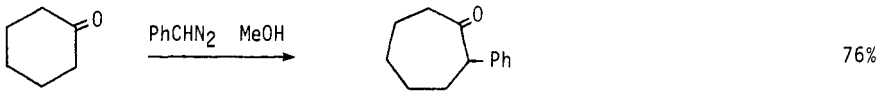
JOC (1966) 31 24



Org Synth (1963) Coll Vol 4 225
Org React (1954) 8 364
JACS (1966) 88 3515



Tetr Lett (1962) 775



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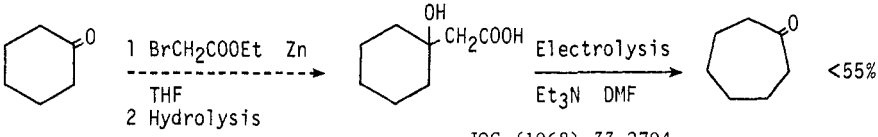

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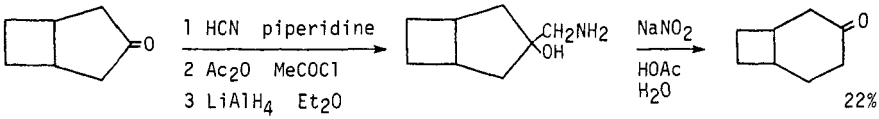

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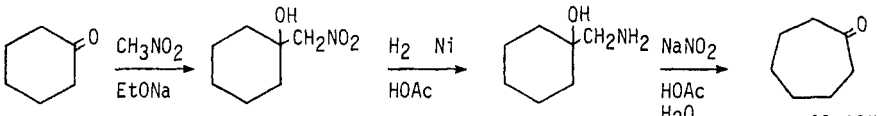
JACS (1952) 74 2278
JCS C (1970) 1454



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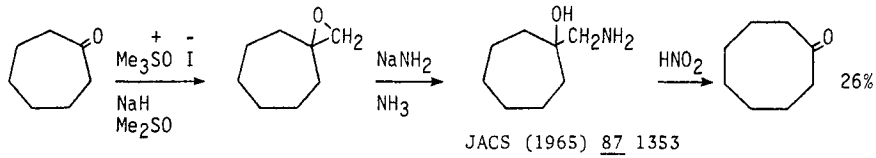

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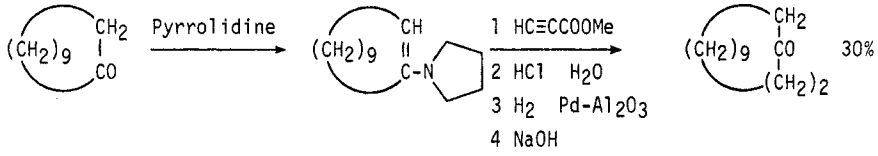

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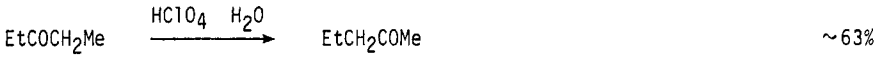
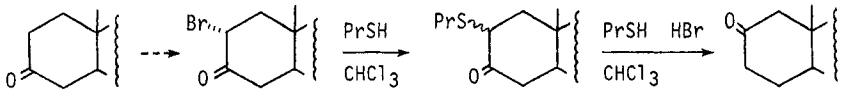


JOC (1960) 25 1252
(1969) 34 806



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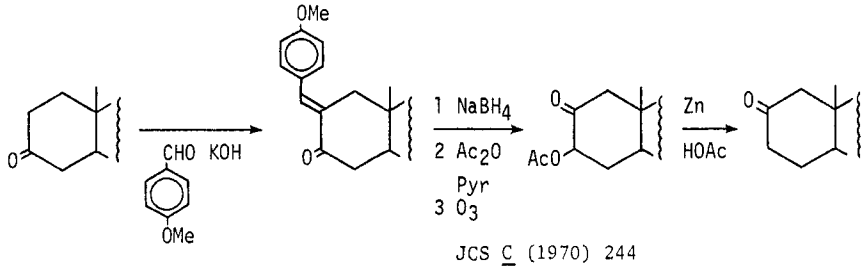
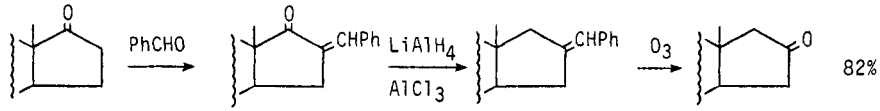
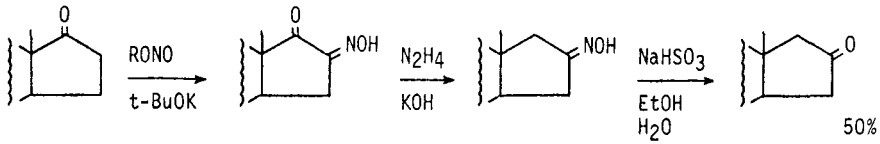


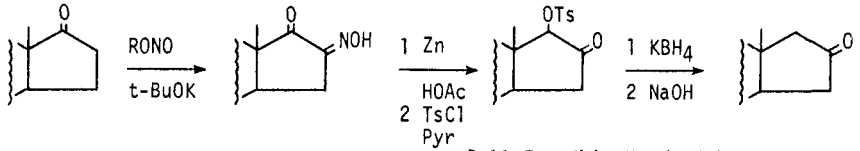
JCS C (1970) 244



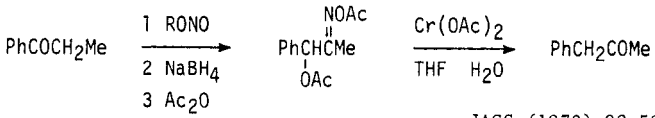
Chem Comm (1967) 898
Compt Rend (1967) C 265 929



Chem Comm (1968) 1350



Bull Soc Chim Fr (1965) 67



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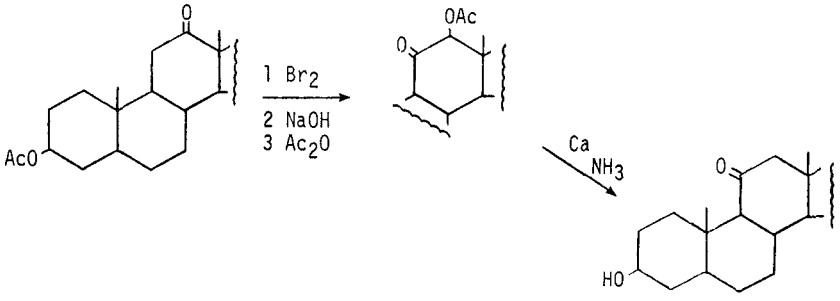
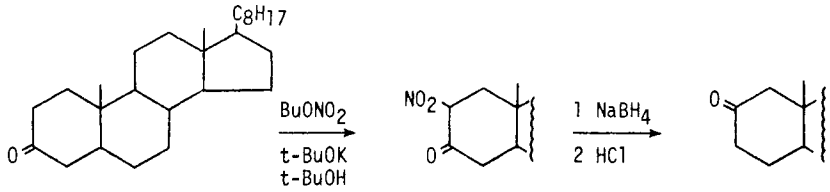
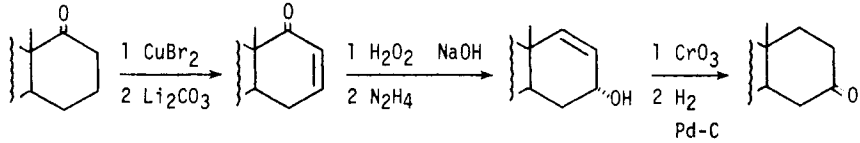


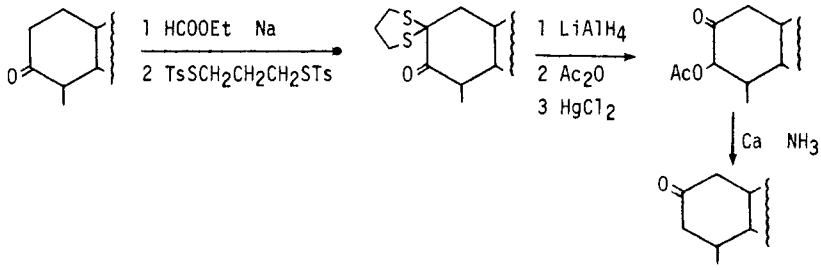
JCS (1956) 4330 4344



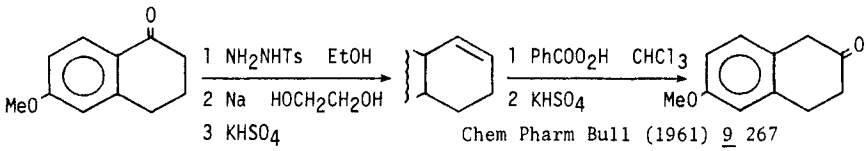
JOC (1968) 33 1733



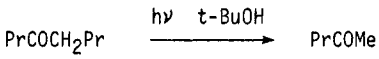
JCS C (1970) 1454



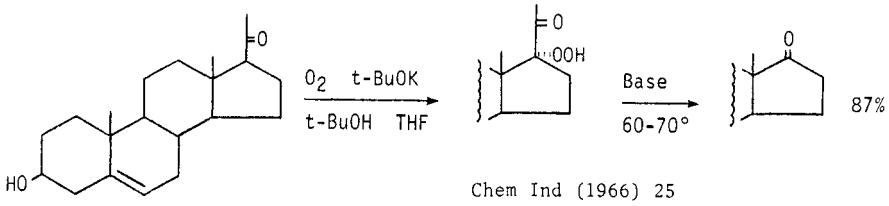
JOC (1969) 34 4188



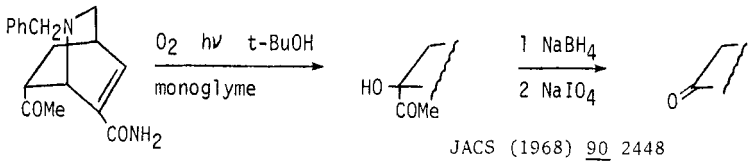
Chem Pharm Bull (1961) 9 267



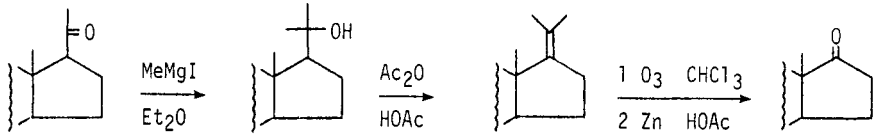
Tetr Lett (1968) 5385
Chem Comm (1969) 204



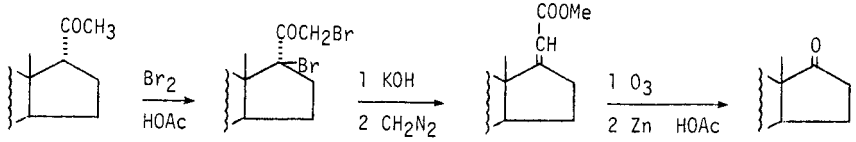
Chem Ind (1966) 25



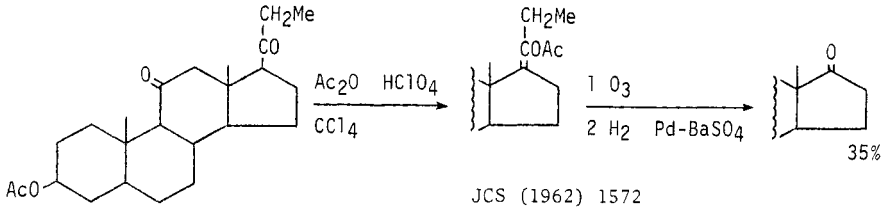
JACS (1968) 90 2448



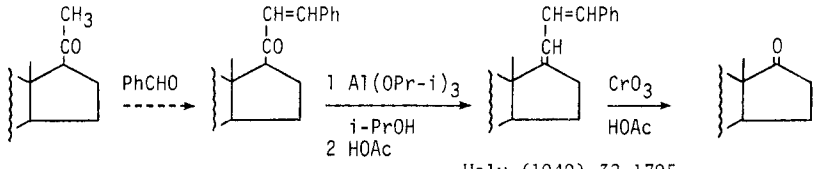
JACS (1942) 64 1276



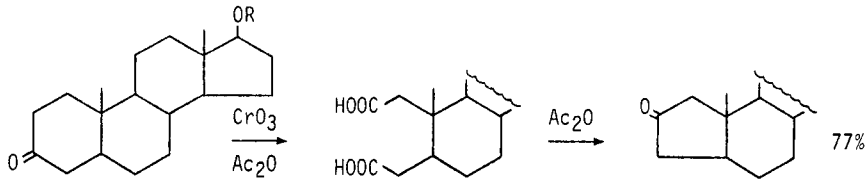
Helv (1944) 27 549



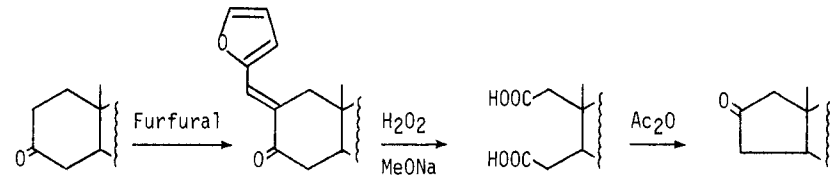
JCS (1962) 1572



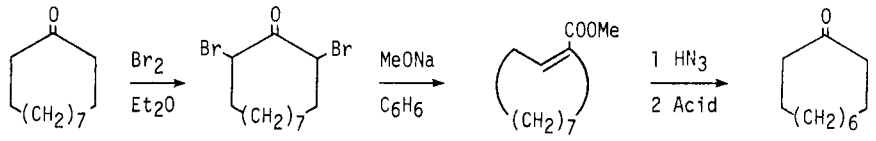
Helv (1949) 32 1795



Bull Soc Chim Fr (1958) 1573

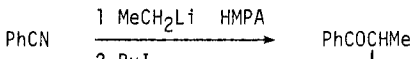


Bull Soc Chim Fr (1958) 1573



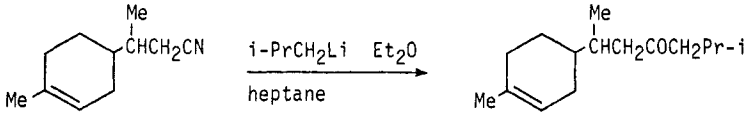
JOC (1968) 33 2157

Section 178 Ketones from Nitriles



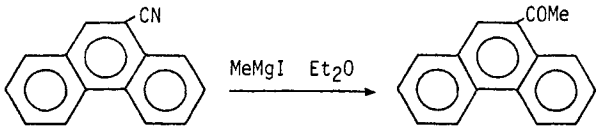
70%

Compt Rend (1967) C 265 245
Bull Soc Chim Fr (1968) 4990



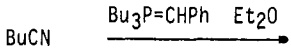
76%

JACS (1970) 92 336



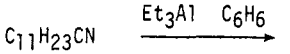
52-59%

Org Synth (1955) Coll Vol 3 26



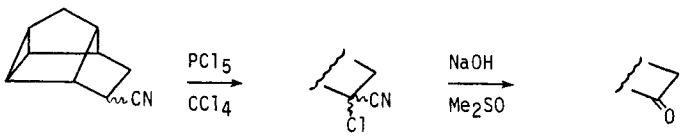
73%

JACS (1967) 89 7009



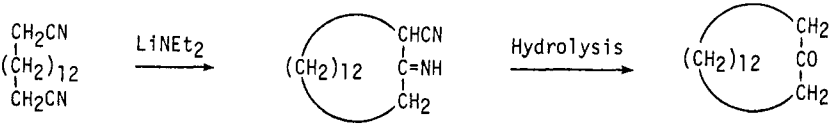
89%

Ber (1964) 97 2661



47%

Tetr Lett (1967) 437

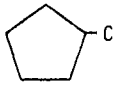


Annalen (1933) 504 94
(1934) 513 43

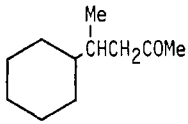
Section 179 Ketones from Olefins

$EtCH{=}CH_2$ → (1 B_2H_6 THF; 2 $BrCH_2COMe$ potassium 2,6-di-t-butylphenoxide) → $Et(CH_2)_3COMe$ 84%

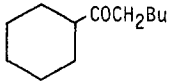
JACS (1969) 91 6852 2147

(1 B_2H_6 THF; 2 $N_2CHCOMe$; 3 NaOH H_2O) →  67%

JACS (1968) 90 5936

(1 B_2H_6 THF; 2 $MeCH{=}CHCOMe$ air i-PrOH) →  98%

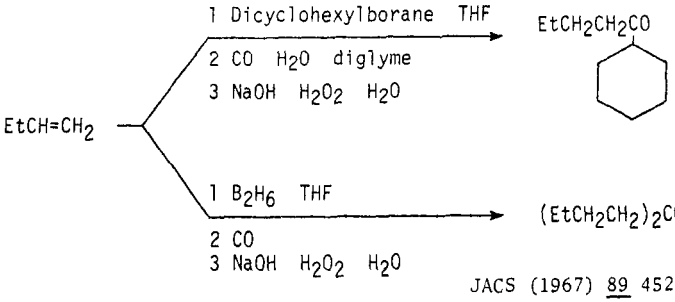
JACS (1970) 92 714

(1 B_2H_6 THF; 2 $BuC{\equiv}CBr$; 2 NaOH H_2O_2 H_2O) →  79%

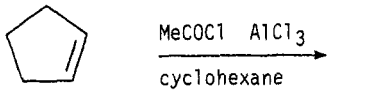
JACS (1967) 89 5086

$C_6H_{13}CH{=}CH_2$ → (B_2H_6) → $(C_6H_{13}CH_2CH_2)_3B$ → (1 NaCN diglyme; 2 $(CF_3CO)_2O$; 3 NaOH H_2O_2 H_2O) → $(C_6H_{13}CH_2CH_2)_2CO$ ~95%

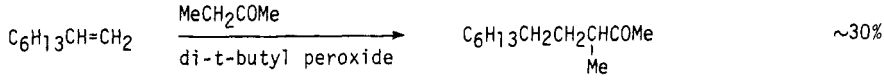
Chem Comm (1970) 1529



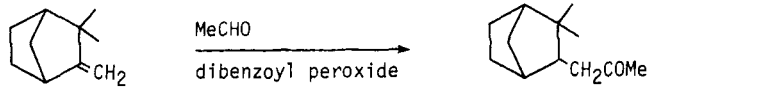
JACS (1967) 89 4528 4530 5285



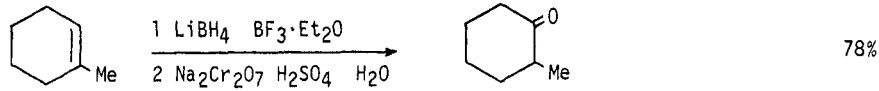
Ber (1936) 69B 1820



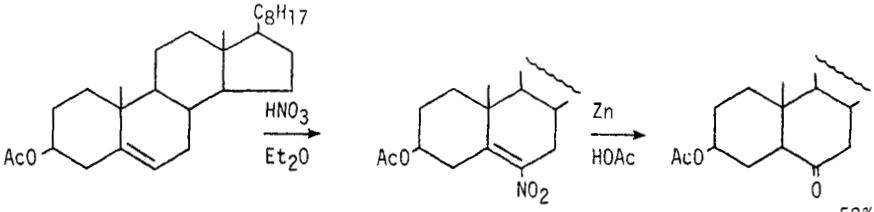
JCS (1965) 1918



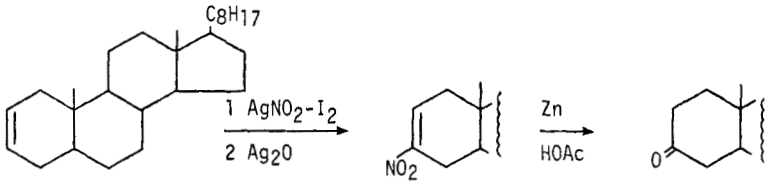
Aust J Chem (1967) 20 2033
JOC (1964) 29 245
(1949) 14 248



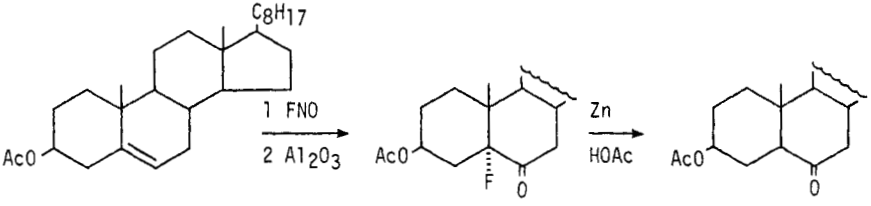
JACS (1961) 83 2951
JOC (1962) 27 2938
Org React (1963) 13 1



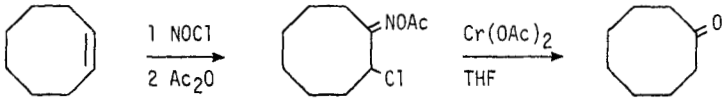
JACS (1954) 76 532



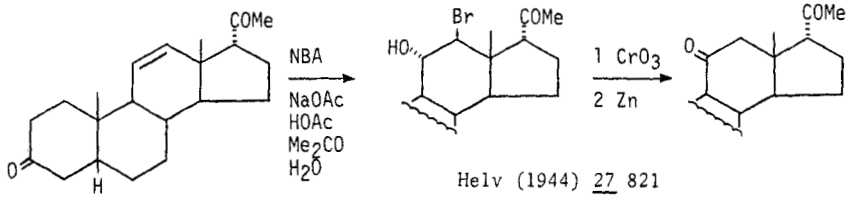
JOC (1969) 34 2628



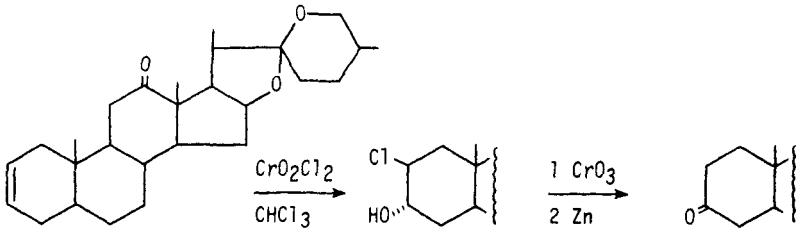
Chem Ind (1965) 1929



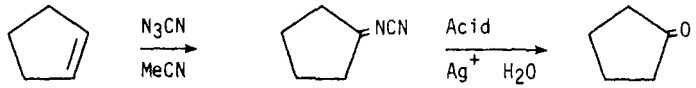
JACS (1970) 92 5276
Zh Org Khim (1966) 2 2178
(Chem Abs 66 75730)



Helv (1944) 27 821

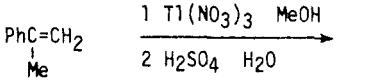


JACS (1956) 78 3749
JOC (1968) 33 3970



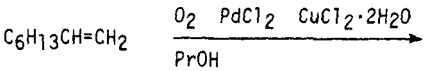
91%

JACS (1964) 86 4506



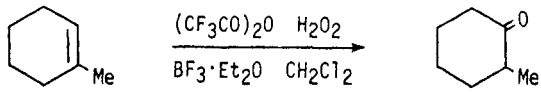
81%

Tetr Lett (1970) 5275



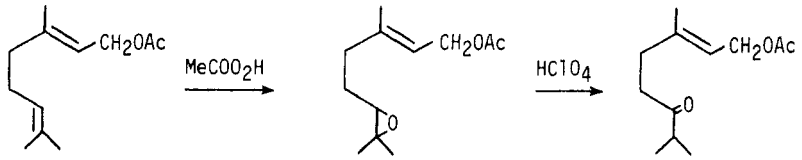
68%

JOC (1969) 34 3949
Synthesis (1970) 225



41%

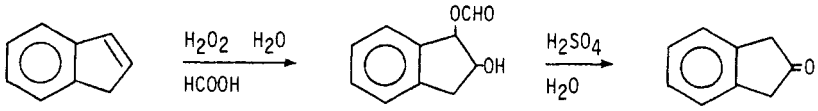
JOC (1967) 32 2669
(1962) 27 666



60%

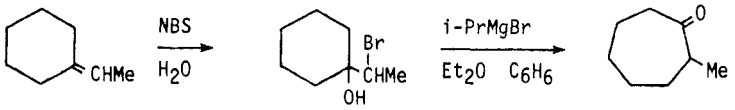
Tetr Lett (1964) 3481

Further examples of the epoxidation of olefins and the conversion of epoxides into ketones are included in section 134 (Ethers and Epoxides from Olefins) and section 174 (Ketones from Ethers and Epoxides)



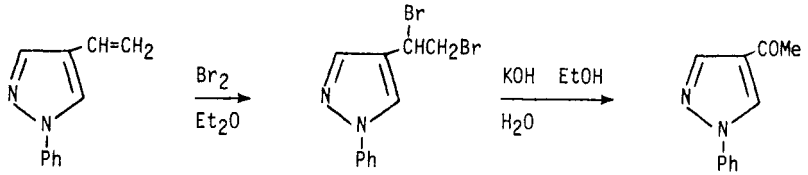
69-81%

Org Synth (1961) 41 53



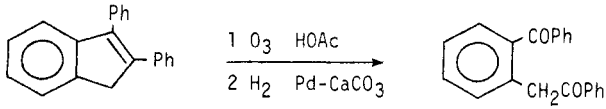
40%

JOC (1970) 35 2670



71%

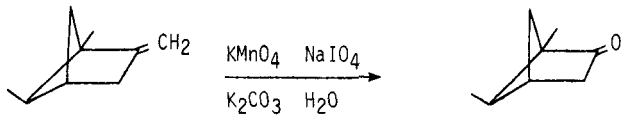
JCS (1963) 3967



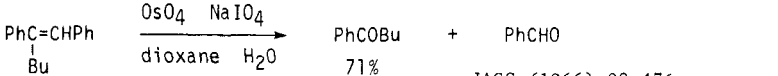
Ber (1954) 87 993

Ozonides may also be reduced by the following reagents:

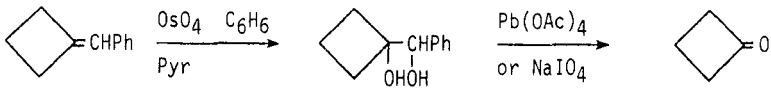
Zn-HOAc	JACS (1943) 65 752
Ni	JACS (1941) 63 3540
HCOOH	JACS (1948) 70 4069
Tetracyanoethylene	Ber (1963) 96 1564 Bull Soc Chim Fr (1964) 729
Ph_3P	Angew (1956) 68 473
$P(OMe)_3$-MeOH	JOC (1960) 25 1031
NaI-HOAc	JOC (1968) 33 1656 Ber (1955) 88 795
$PhNHNH_2$	Ber (1954) 87 993



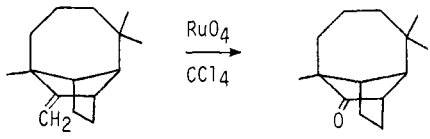
JOC (1966) 31 3028



JACS (1966) 88 476
(1957) 79 6313
JCS C (1966) 655

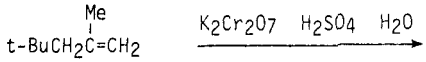


JCS C (1966) 655

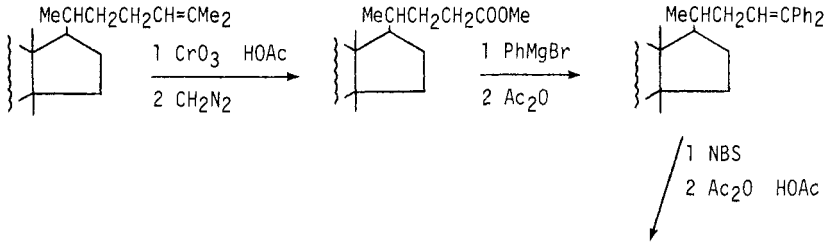


27%

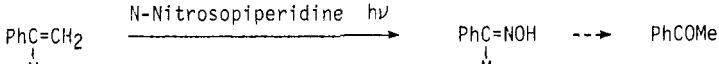
Bull Soc Chim Fr (1964) 729
JCS (1962) 4745



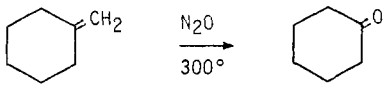
JACS (1950) 72 3701



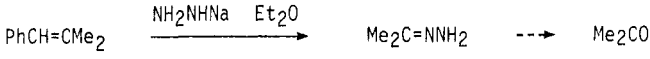
JACS (1970) 92 2059



JACS (1965) 87 4642



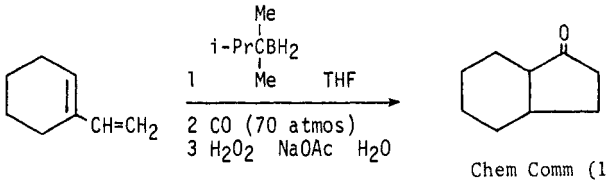
JCS (1951) 2999 3009



Angew (1962) 74 650
(Internat Ed 1 456)

$Ph_2C{=}CHEt \xrightarrow{NaN_3\ \ H_2SO_4} PhCOCH_2Et$ 64%

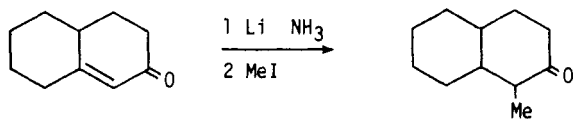
JACS (1950) 72 5777



60%

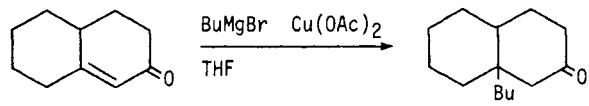
Chem Comm (1968) 594

Section 180 Ketones from Miscellaneous Compounds



< 83%

JACS (1965) 87 275
Tetrahedron (1964) 20 357
JOC (1967) 32 2851
Bull Soc Chim Fr (1969) 4356 4348

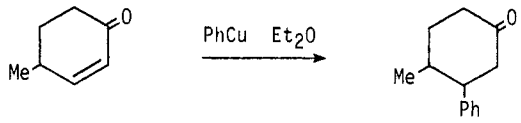


71%

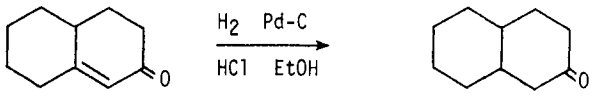
JACS (1965) 87 82
JOC (1966) 31 3128
JCS (1943) 501

$MeCH{=}CHCOMe \xrightarrow[Et_2O]{MeMgBr\text{-}Bu_3PCuI} Me_2CHCH_2COMe$ 99%

JOC (1966) 31 3128



Tetr Lett (1970) 1579



JOC (1958) 23 1853
Chem Ind (1966) 1796

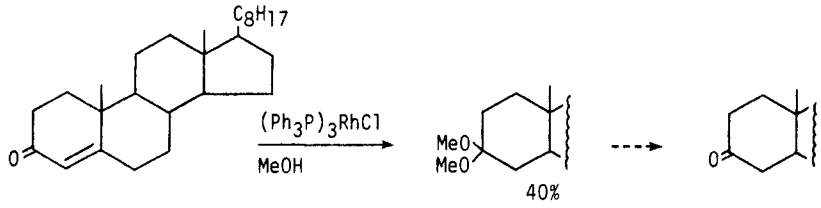
For reduction of enones with H_2 and Rh see JOC (1968) 33 3695

$PhCH{=}CHCOMe \xrightarrow{H_2\ Ni\ CH_2Cl_2} PhCH_2CH_2COMe$ 93-96%

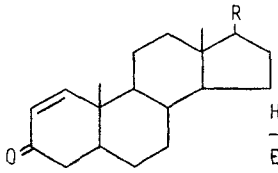
Bull Soc Chim Fr (1954) 522

$Me_2C{=}CHCOMe \xrightarrow{Ni\ \ H_2O} Me_2CHCH_2COMe$ 95%

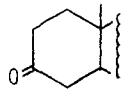
Bull Chem Soc Jap (1967) 40 1548



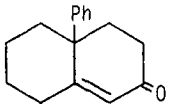
Ber (1968) 101 1154



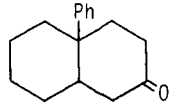
H_2 $(Ph_3P)_3RhCl$ NaI
EtOH C_6H_6



JACS (1966) 88 4537



1 Li NH_3 Et_2O
2 MeOH
3 CrO_3 H_2SO_4 Me_2CO

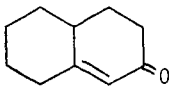


trans 63%

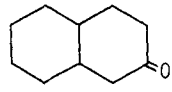
JOC (1970) 35 753
JACS (1965) 87 275

t-BuCH=CHCOBu-t —(Na HMPA THF)→ t-$BuCH_2CH_2$COBu-t

JACS (1970) 92 2783
Bull Soc Chim Fr (1968) 595



1 Na trimesitylborane
$MeOCH_2CH_2OMe$
2 MeOH



85-95%

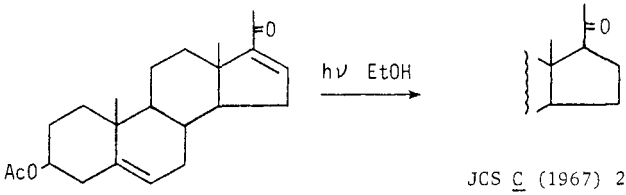
JACS (1970) 92 696

Me_2C=CHCOMe —($CrCl_2$ NH_3 H_2O)→ Me_2CHCH_2COMe

Angew (1968) 80 271
(Internat Ed 7 247)

PhCH=CHCOPh —(Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate, 156°)→ $PhCH_2CH_2$COPh

JCS (1960) 3257

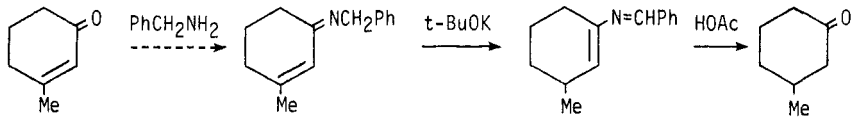


40%

JCS C (1967) 2032

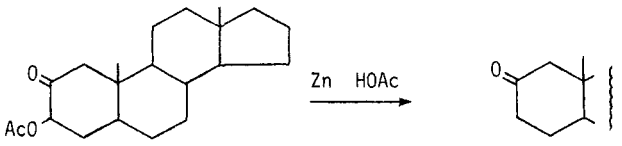
$Me_2C{=}CHCOMe \xrightarrow{Ph_3SnH} Me_2CHCH_2COMe$

Compt Rend (1965) 260 581

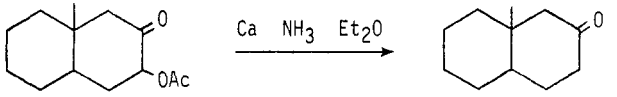


40-70%

JACS (1967) 89 2794

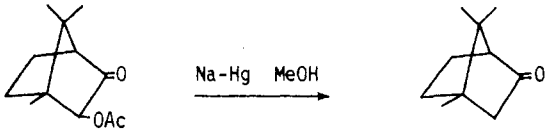


JCS C (1970) 244
JACS (1955) 77 4367



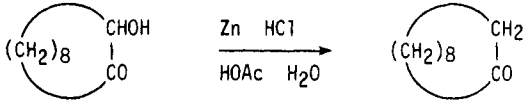
80%

JOC (1969) 34 4188
JCS (1956) 4344



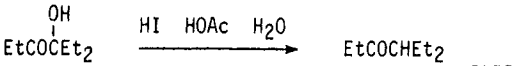
95%

Bull Chem Soc Jap (1969) 42 2068



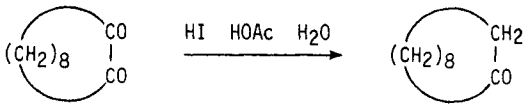
75-78%

Org Synth (1963) Coll Vol 4 218
JACS (1964) 86 3068



80%

JACS (1964) 86 3068
JOC (1938) 3 456



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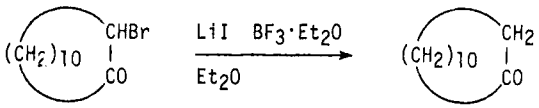
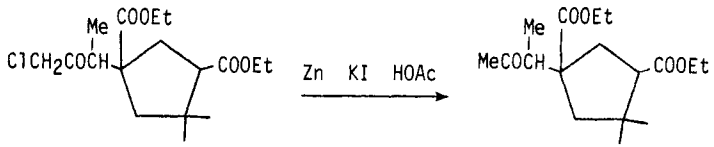
JACS (1964) 86 3068



100%

Tetr Lett (1971) 137

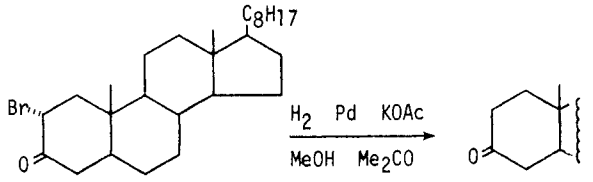


88%

JACS (1961) 83 3114
Helv (1944) 27 821
Tetr Lett (1968) 1575

$PhCOCH_2Cl \xrightarrow{CrSO_4\ \ DMF\ \ H_2O} PhCOMe$ 79%

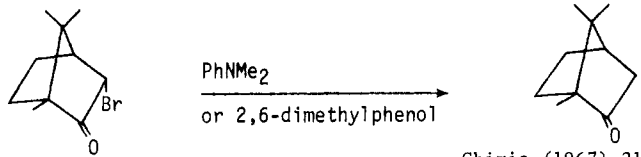
JACS (1963) 85 2768
(1945) 67 1728
Angew (1968) 80 271
(Internat Ed 7 247)



JCS (1964) 5535

$PhCOCH_2Cl \xrightarrow{Bu_2SnH_2\ \ Et_2O} PhCOMe$ 95%

JOC (1963) 28 2165



70-76%

Chimia (1967) 21 464
JCS C (1969) 301

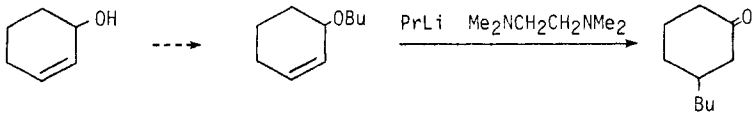
$i\text{-}PrCH_2COCHPr\text{-}i \xrightarrow[2\ EtOH]{1\ Ph_3P\ \ C_6H_6} i\text{-}PrCH_2COCH_2Pr\text{-}i$
(Br)

JCS (1962) 2337
Tetr Lett (1962) 471

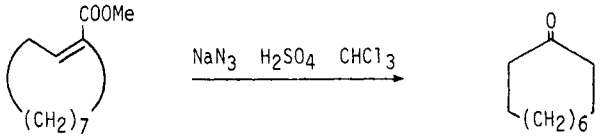
$PhCOCHMe \xrightarrow{Ph_2PH\ \ CCl_4} PhCOCH_2Me$
(Br)

100%

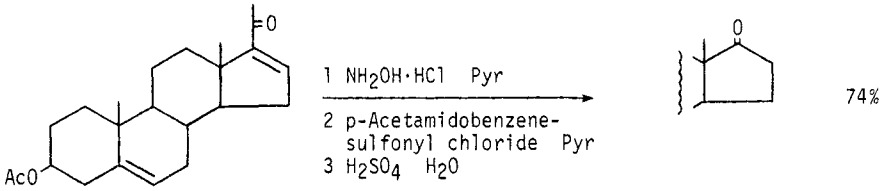
JOC (1969) 34 2687



Tetr Lett (1969) 821

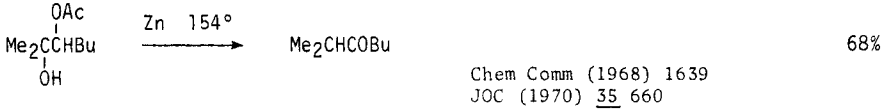


JOC (1968) 33 2157



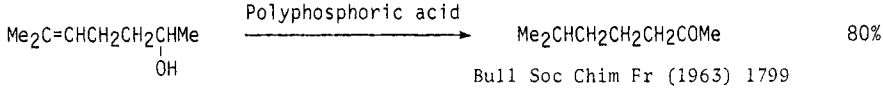
74%

JOC (1956) 21 520
Org React (1960) 11 1



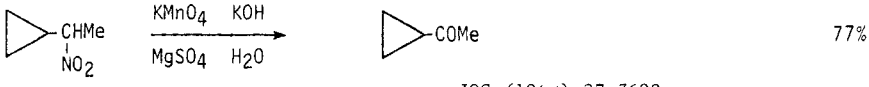
68%

Chem Comm (1968) 1639
JOC (1970) 35 660



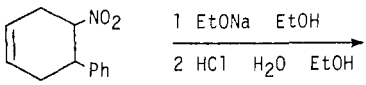
80%

Bull Soc Chim Fr (1963) 1799
JACS (1965) 87 2772



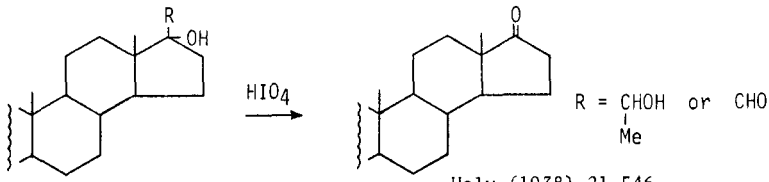
77%

JOC (1962) 27 3699



78%

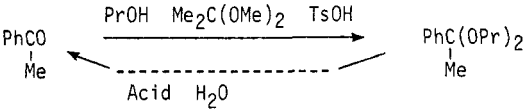
JOC (1952) 17 581
Chem Rev (1955) 55 137



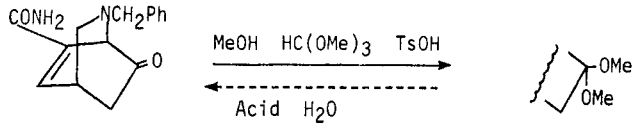
Helv (1938) 21 546
(1940) 23 170
(1941) 24 945
Org React (1944) 2 341

Section 180A Protection of Ketones

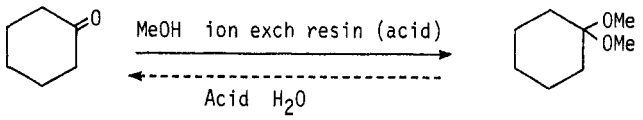
Ketals are stable to the following reagents: NaOH, NaH, Na-NH_3, RMgX, $NaBH_4$, $LiAlH_4$, H_2-Pd, CrO_3 and $SOCl_2$-Pyr



JOC (1960) 25 521 525



JACS (1968) 90 2448
Annalen (1962) 656 97

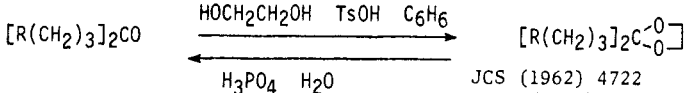


JOC (1959) 24 1731

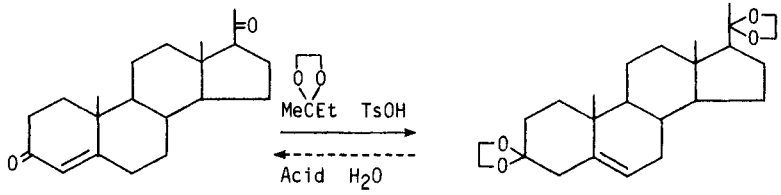
The following catalysts may also be used for the preparation of ketals:

$(Ph_3P)_3RhCl$ . .Ber (1968) 101 1154

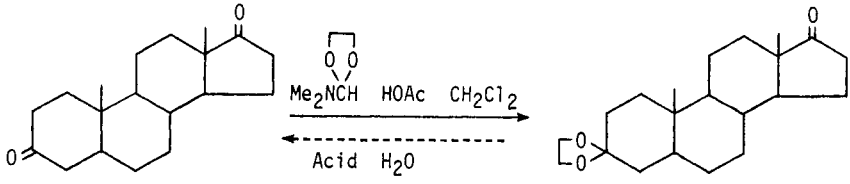
SeO_2 . . . . .JACS (1954) 76 6113



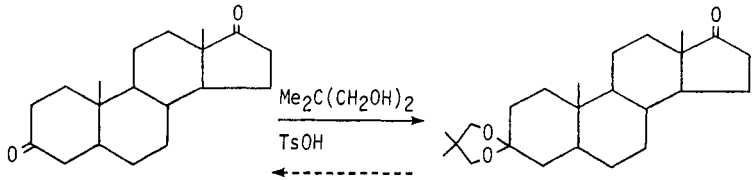
JCS (1962) 4722
JACS (1964) 86 2183



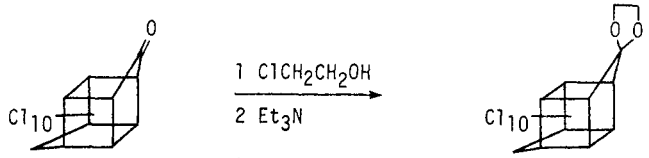
JACS (1954) 76 1359
(1953) 75 1716



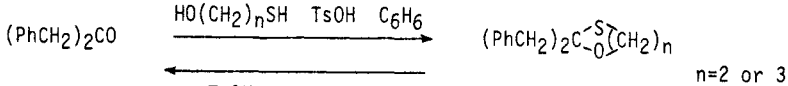
Steroids (1963) 1 45



JACS (1968) 90 1253

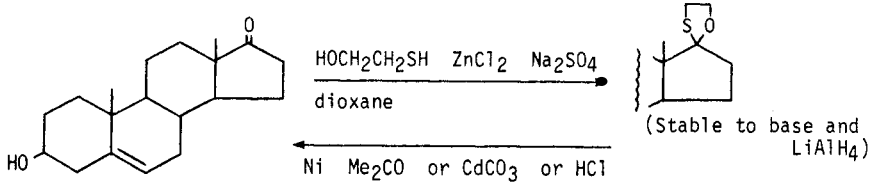


JOC (1968) 33 1280

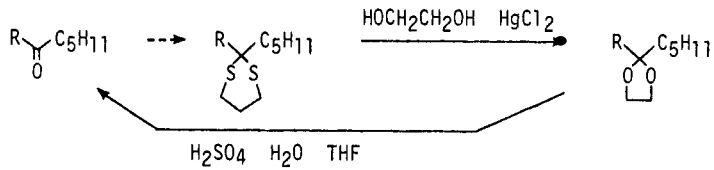


JACS (1953) 75 3704
(1954) 76 1945

For cleavage with Ni see JACS (1958) 80 4723

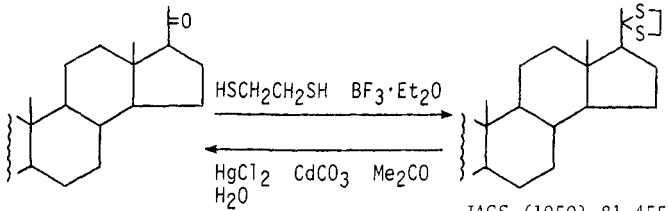


JACS (1951) 73 4961

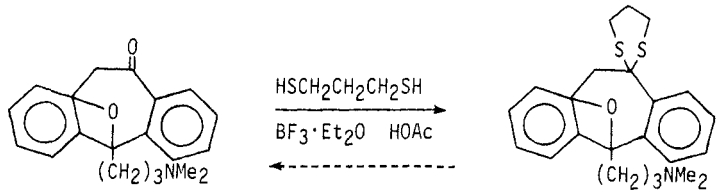


JACS (1968) 90 3245

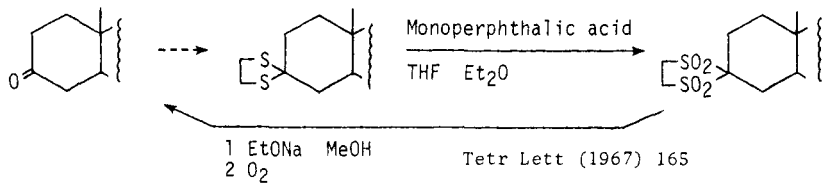
Thioketals are stable to the following reagents: NaOH, $LiAlH_4$, RMgX, CrO_3-Pyr



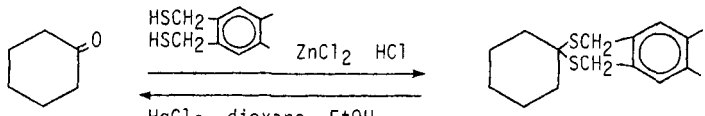
JACS (1959) 81 4556
Can J Chem (1955) 33 716



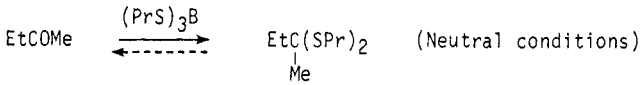
J Med Chem (1970) 13 191



Tetr Lett (1967) 165



JCS C (1966) 1005

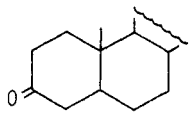


Can J Chem (1969) 47 859
(1965) 43 307

$(RCOOCH_2)_2CO$ —EtSH $ZnCl_2$→ $(RCOOCH_2)_2C(SEt)_2$

$(RCOOCH_2)_2C(SEt)_2$ —$HgCl_2$ Me_2CO H_2O→ $(RCOOCH_2)_2CO$

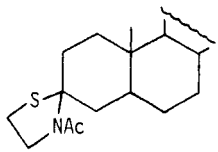
Can J Chem (1955) 33 716



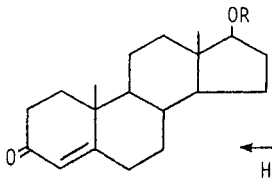
1 $HSCH_2CH_2NH_2$ TsOH C_6H_6

2 Acetylation

Ni Me_2CO



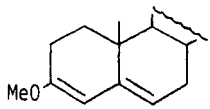
JOC (1962) 27 1112



$Me_2C(OMe)_2$ TsOH

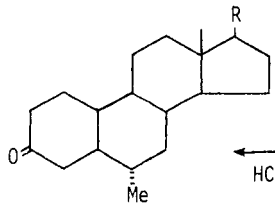
MeOH DMF

HCl MeOH H_2O



(Stable to base, RMgX and $LiAlH_4$)

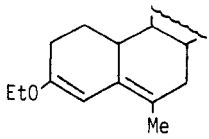
JOC (1961) 26 3925



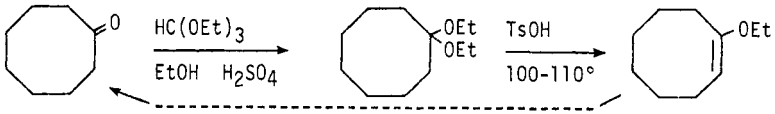
$HC(OEt)_3$ TsOH

EtOH dioxane

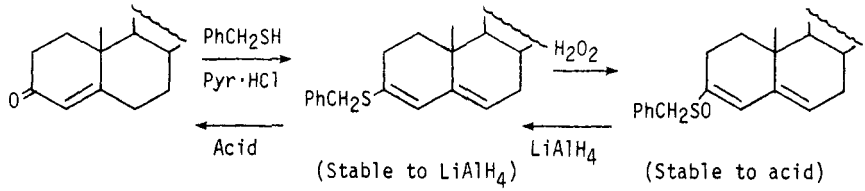
HCl MeOH H_2O



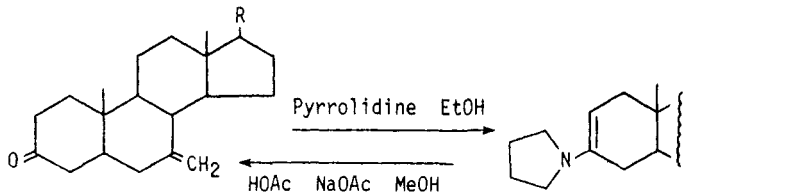
JACS (1959) 81 4566



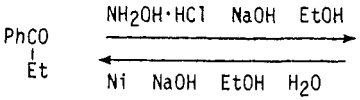
Annalen (1962) 656 97
Gazz (1962) 92 309
(Chem Abs 57 12572)



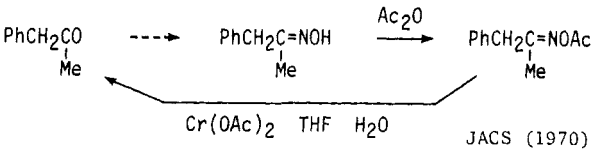
JACS (1951) 73 1528



Coll Czech (1961) 26 1646
JACS (1956) 78 430
(1952) 74 3627



JCS C (1966) 531

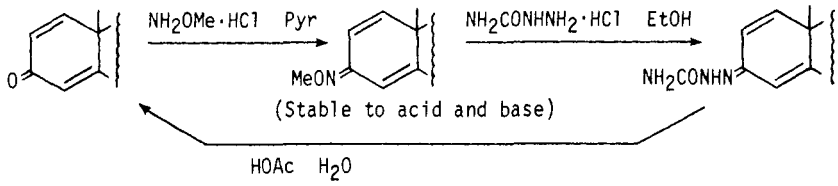


JACS (1970) 92 5276

Oximes may also be cleaved by the following reagents:

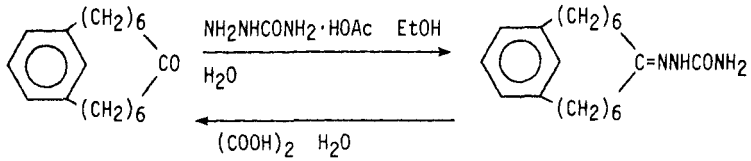
$NaHSO_3$	JOC (1966) 31 3446
$MeCOCH_2CH_2COOH$-HCl	JACS (1959) 81 4629
Zn-HOAc	J Indian Chem Soc (1969) 46 44
$TiCl_3$	Tetr Lett (1971) 195
$(NH_4)_2Ce(NO_3)_6$	Can J Chem (1969) 47 145
$Fe(CO)_5$-BF_3·Et_2O	JOC (1967) 32 2938

For preparation of oximes of unreactive and acid or base sensitive ketones (using Me_2SO-NH_2OH·HCl) see Chem Ind (1969) 240



JOC (1962) 27 914
For cleavage of methoximes with O_3 see JOC (1969) 34 2961

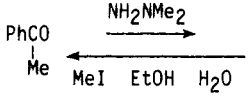
Semicarbazones are stable to $NaBH_4$ and Oppenauer oxidation



Helv (1932) 15 1220

Semicarbazones may also be cleaved by the following reagents:

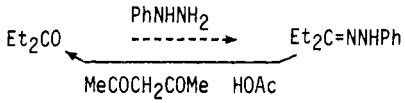
H_2SO_4-H_2O	JCS (1946) 27
HCl-H_2O	JACS (1950) 72 1751
MeCOCOOH	JCS (1953) 3864 JACS (1955) 77 1221
$MeCOCH_2COMe$-HCl	Annalen (1962) 656 119
Ac_2O-Pyr	JOC (1956) 21 795
$(NH_4)_2Ce(NO_3)_6$	Can J Chem (1969) 47 145
$MeCOO_2H$	Ber (1961) 94 712
$NaNO_2$-HOAc	Rec Trav Chim (1946) 65 796 JACS (1955) 77 4781 (1961) 83 4249



(Stable to base, B_2H_6, $LiAlH_4$ and CrO_3)

Chem Comm (1969) 445

For cleavage of dimethylhydrazones with O_3 see JOC (1969) 34 2961
" " " " " peracid see Ber (1961) 94 712

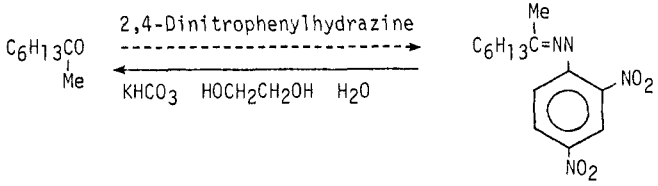


Annalen (1962) 656 119

Phenylhydrazones may also be cleaved by the following reagents:

MnO_2	JOC (1967) 32 2252
$MeCOO_2H$	JOC (1967) 32 2865

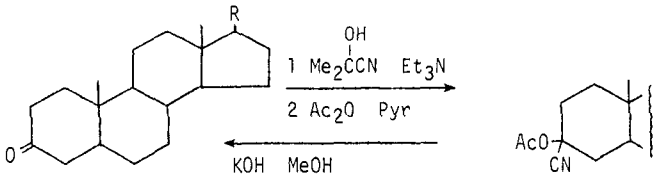
2,4-Dinitrophenylhydrazones are stable to CrO_3 and B_2H_6



Aust J Chem (1968) 21 271

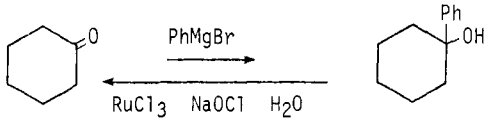
2,4-Dinitrophenylhydrazones may also be cleaved by the following reagents:

$MeCOCH_2CH_2COOH$-HCl	JACS (1959) 81 4629
$SnCl_2$-HCl-Me_2CO	Nature (1954) 173 266
$CrCl_2$-HCl	JCS (1962) 4729
O_3	Chem Comm (1968) 433 JOC (1951) 16 556
$CuCO_3 \cdot Cu(OH)_2$-HCOOH	Nature (1954) 173 541



(Stable to acids, peracids, CrO_3 and Br_2)

Gazz (1961) 91 1250
(Chem Abs 56 10211)
Steroids (1967) 10 411
JACS (1953) 75 650

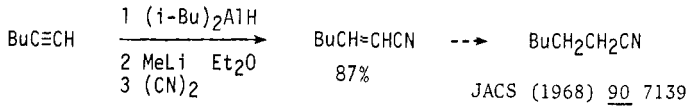


Chem Comm (1970) 1420

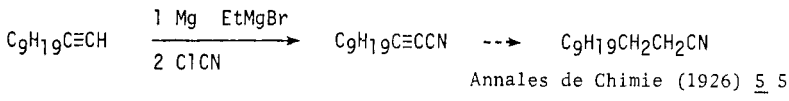
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 13 PREPARATION OF NITRILES

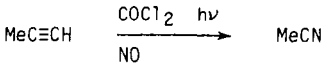
Section 181 Nitriles from Acetylenes



JACS (1968) 90 7139

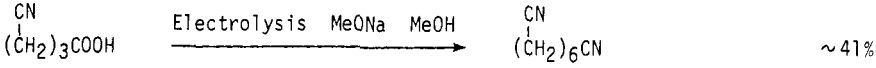


Annales de Chimie (1926) 5 5



JACS (1963) 85 3506

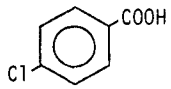
Section 182 Nitriles from Carboxylic Acids



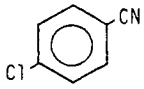
Z. Naturforsch (1947) 2b 185
Advances in Org Chem (1960) 1 1

i-PrCOOH $\xrightarrow{PhCH_2CN \quad H_2SO_4}$ i-PrCN 40%

JCS (1956) 1686



$\xrightarrow[259\text{-}294°]{\text{Isophthalonitrile}}$

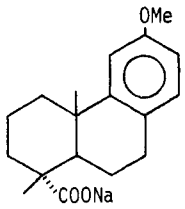


93%

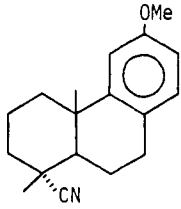
JOC (1958) 23 1350

$PhCH{=}CHCOOZn_{1/2}$ $\xrightarrow{Pb(CNS)_2 \quad \Delta}$ PhCH=CHCN 27-36%

JACS (1916) 38 2120



$\xrightarrow[250°]{ClCN}$

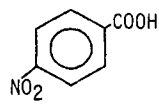


26%

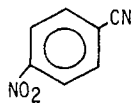
JCS (1961) 3185

t-BuCOOH $\xrightarrow[2 \text{ DMF}]{1 \ ClSO_2NCO \quad \text{pentane}}$ t-BuCN 68%

Ber (1967) 100 2719
Tetr Lett (1968) 1631

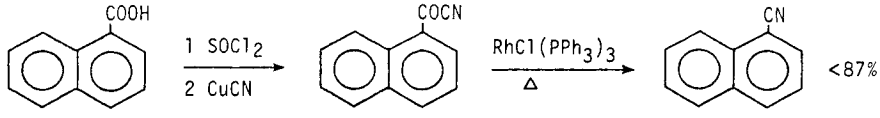


$\xrightarrow[200\text{-}205°]{\text{p-toluenesulfonamide} \quad PCl_5}$

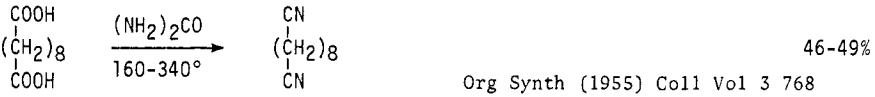


85-90%

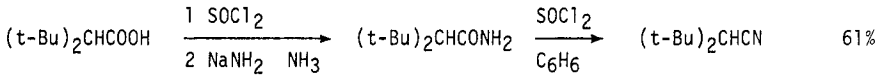
Org Synth (1955) Coll Vol 3 646
JCS (1946) 763



JACS (1967) 89 2338

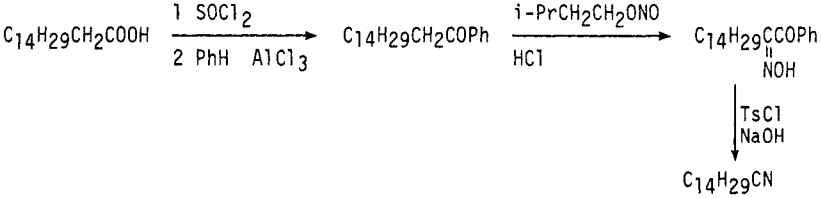


Org Synth (1955) Coll Vol 3 768
(1963) Coll Vol 4 62



JACS (1960) 82 2498

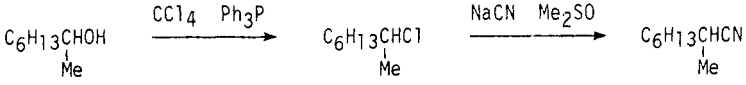
Further examples of the preparation of nitriles from amides are included in section 186 (Nitriles from Amides)



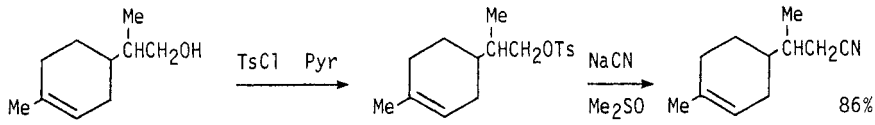
JACS (1953) 75 2347
JOC (1961) 26 3507

Section 183 Nitriles from Alcohols

Annalen (1963) 661 157



JOC (1967) 32 855

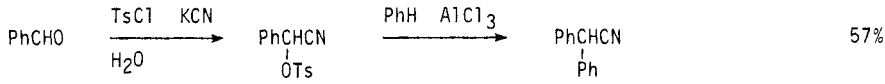


JACS (1970) 92 336

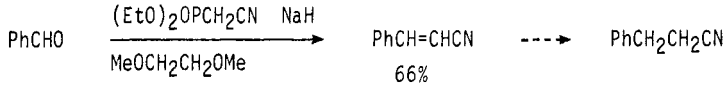
Further examples of the preparation of nitriles from halides and sulfonates are included in section 190 (Nitriles from Halides and Sulfonates)

Rec Trav Chim (1963) 82 757

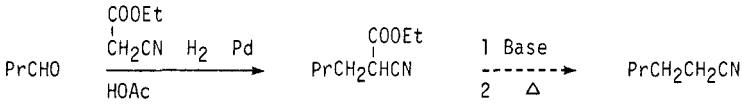
Section 184 Nitriles from Aldehydes



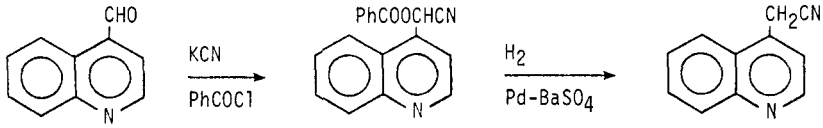
JOC (1954) 19 1699



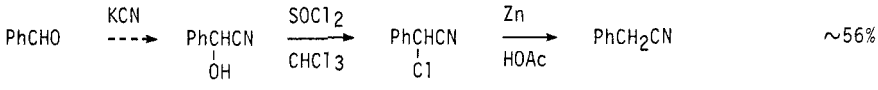
JACS (1961) 83 1733



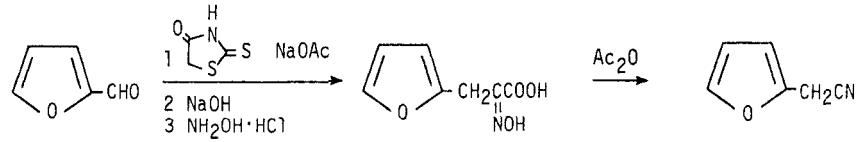
Org Synth (1955) Coll Vol 3 385
JACS (1959) 81 5397



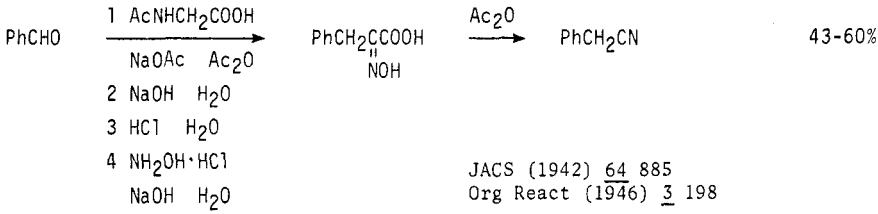
Arch Pharm (1957) 290 218



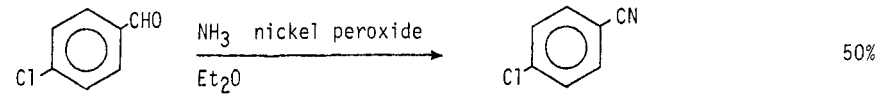
J Soc Chem Ind (1935) 54 98T



JACS (1940) 62 1512
JCS (1946) 958
Org React (1942) 1 210



JACS (1942) 64 885
Org React (1946) 3 198



Chem Comm (1966) 17

$C_6H_{13}CHO \xrightarrow{NH_3\ \ Pb(OAc)_4\ \ C_6H_6} C_6H_{13}CN$ 59%

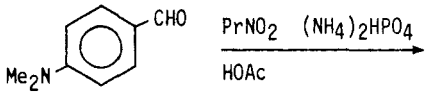
Chem Ind (1965) 988

$C_6H_{13}CHO \xrightarrow[MeONa\ \ MeOH]{NH_3\ \ O_2\ \ CuCl_2} C_6H_{13}CN$ 63%

Rec Trav Chim (1963) 82 757

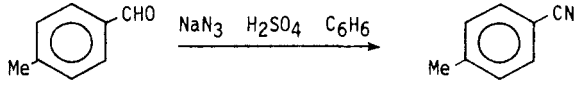
$PhCHO \xrightarrow[2\ I_2]{1\ NH_3\ \ MeONa\ \ MeOH} PhCN$ 50%

Bull Chem Soc Jap (1966) 39 854



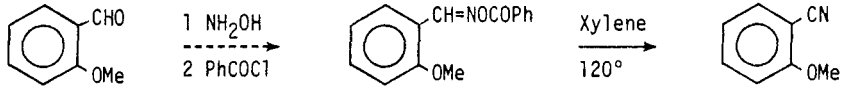
77%

JACS (1961) 83 2203



44%

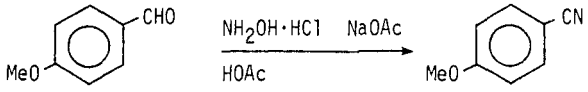
JACS (1952) 74 1168
Org React (1946) 3 307



JCS (1950) 1243

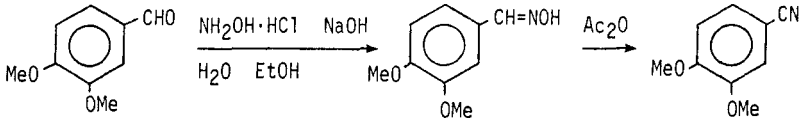
$$PhCH{=}CHCHO \xrightarrow[Pyr\ \ C_6H_6]{CF_3COONHCOCF_3} PhCH{=}CHCN \qquad 88\%$$

JACS (1959) 81 6340



67%

Chem Ind (1961) 1873
JCS (1965) 1564



70-76%

Org Synth (1943) Coll Vol 2 622

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

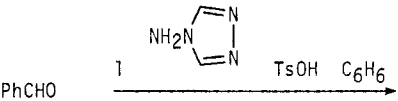
HCl-EtOH	Can J Chem (1967) 45 1014
MsCl-Pyr-collidine	Tetr Lett (1965) 2497
$PhNCO\text{-}Et_3N$	JOC (1961) 26 782
$PhN{=}CCl_2$	Bull Chem Soc Jap (1962) 35 1104
$(PhO)_2POH\text{-}CCl_4\text{-}Et_3N$	JOC (1969) 34 2805
p-chlorophenyl chlorothionoformate	Chem Comm (1970) 1014

$$BuCHO \xrightarrow[C_6H_6]{NH_2NMe_2} BuCH{=}NNMe_2 \xrightarrow[2\ MeONa\ \ MeOH\ \text{or}\ H_2O_2\ \ H_2O]{1\ MeI} BuCN \qquad 42\text{-}47\%$$

JOC (1962) 27 4372
(1966) 31 4100

$$PhCH_2CHO \xrightarrow{Ph_2NNH_2} PhCH_2CH{=}NNPh_2 \xrightarrow{O_2\ \ h\nu} PhCH_2CN \qquad 41\%$$

Tetr Lett (1970) 2085



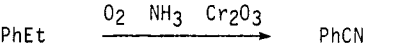
69%

Z Chem (1964) 4 304

Some of the methods listed in section 192 (Nitriles from Ketones) may also be used for the preparation of nitriles from aldehydes

Section 185 Nitriles from Alkyls

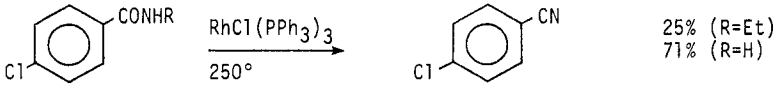
This section lists examples of the replacement of alkyl groups by nitriles. For the replacement of hydrogen by nitrile, RH ⟶ RCN, see section 191 (Nitriles from Hydrides)



8%

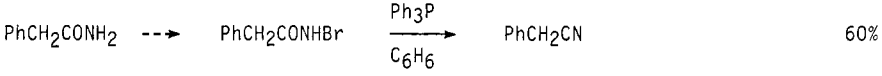
Tetrahedron (1968) 24 6277

Section 186 Nitriles from Amides



25% (R=Et)
71% (R=H)

Tetr Lett (1970) 1963

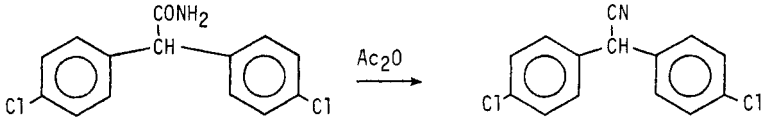


60%

JCS (1960) 2976

$PhCONH_2 \xrightarrow{Ph_3P \quad CCl_4 \quad THF} PhCN$ 82%

Tetr Lett (1970) 4383

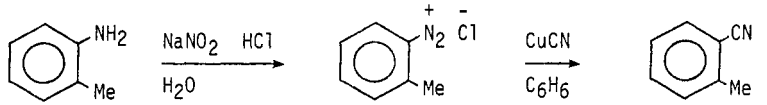


JACS (1949) 71 2650

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

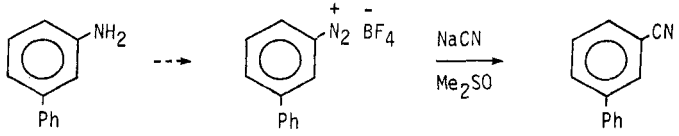
$SOCl_2$	Org Synth (1963) Coll Vol 4 436
$SOCl_2$-DMF	Chem Ind (1964) 752
TsCl-Pyr	JACS (1955) 77 1701
$COCl_2$-Pyr	JCS (1954) 3730
$PhSO_3H$ (235°)	JCS (1946) 763
P_2O_5	Org Synth (1963) Coll Vol 4 144
$POCl_3$-$NaHSO_3$	JOC (1957) 22 1142
$AlCl_3$	JACS (1940) 62 1432
Et_3SiH-$ZnCl_2$	Compt Rend (1962) 254 2357
Catechyl phosphorus trichloride	Ber (1963) 96 1387
Me_2NCHF_2	Coll Czech (1963) 28 2047
DCC-Pyr	JOC (1961) 26 3356
$NaBH_4$-Pyr	Chem Pharm Bull (1969) 17 98 JOC (1967) 32 846
BuLi	JOC (1967) 32 3640 (1966) 31 3873

Section 187 Nitriles from Amines



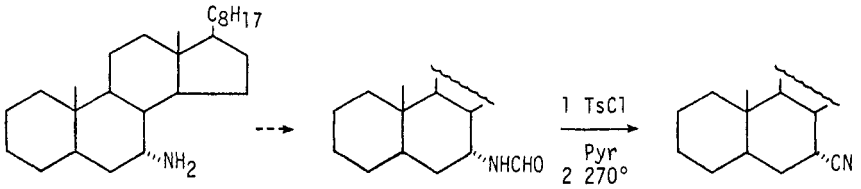
64-70%

Org Synth (1932) Coll Vol 1 514
Rec Trav Chim (1961) 80 1075



<50%

Org Prep and Procedures (1969) 1 221



Tetr Lett (1966) 5087
JOC (1958) 23 1221

$C_7H_{15}CH_2NH_2$ —(Nickel peroxide, C_6H_6)→ $C_7H_{15}CN$ 96%

Chem Pharm Bull (1963) 11 296

$PhCH_2NH_2$ —($Pb(OAc)_4$ C_6H_6)→ PhCN 59%

Tetrahedron (1967) 23 721

$BuCH_2NH_2$ —(AgO H_2O)→ BuCN 87%

Tetr Lett (1968) 5685

$PrCH_2NH_2$ —(1 Cl_2 $NaHCO_3$ H_2O; 2 CsF MeCN)→ PrCN >81%

JOC (1968) 33 1008

$C_5H_{11}CH_2NH_2 \xrightarrow{IF_5\ \ Pyr\ \ CH_2Cl_2} C_5H_{11}CN$ 36%

JOC (1961) 26 2531

Section 188 Nitriles from Esters

The reaction ROTs ⟶ RCN is included in section 190 (Nitriles from Halides and Sulfonates)

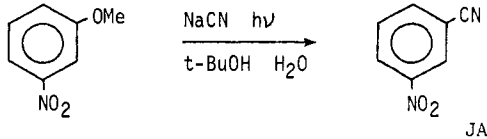
$EtCH_2COOMe \xrightarrow{MeONO\ \ MeONa\ \ DMF} EtCN$ 18%

J Prakt Chem (1969) 311 370

$PhCH{=}CHCH_2CH(COOEt)_2 \xrightarrow[NaOEt]{C_5H_{11}ONO} PhCH{=}CHCH_2C(=NOH)COOH \xrightarrow{Ac_2O} PhCH{=}CHCH_2CN$

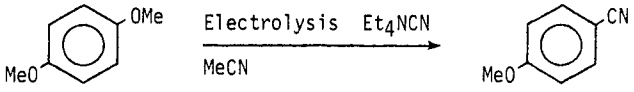
JCS (1950) 926

Section 189 Nitriles from Ethers



30%

JACS (1966) 88 2884



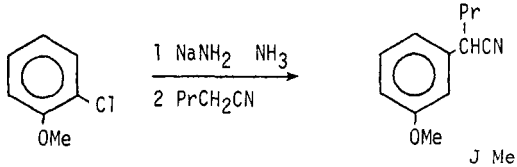
45%

JACS (1969) 4181

$$ArOMe \xrightarrow{KCN} MeCN$$

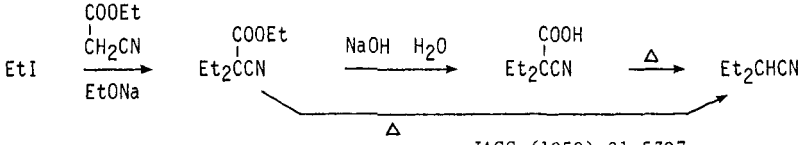
Ber (1933) 66B 1623

Section 190 Nitriles from Halides and Sulfonates

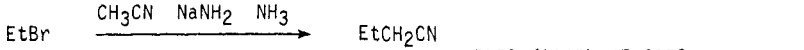


30%

J Med Chem (1971) 14 72



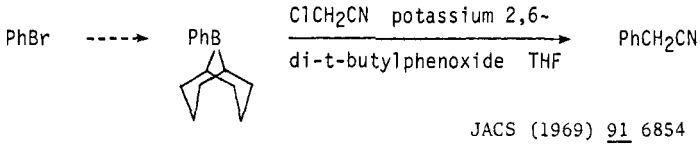
JACS (1959) 81 5397
(1938) 60 131
Org React (1957) 9 107



58%

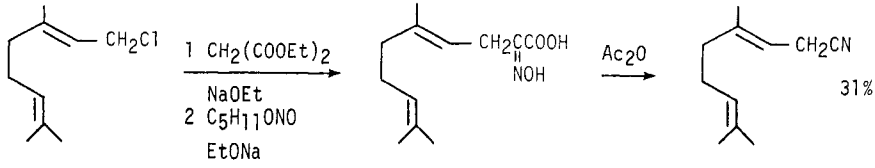
JACS (1945) 67 2152
Ber (1968) 101 3113
Org React (1957) 9 107

Further examples of the alkylation of nitriles with halides are included in section 193 (Nitriles from Nitriles)

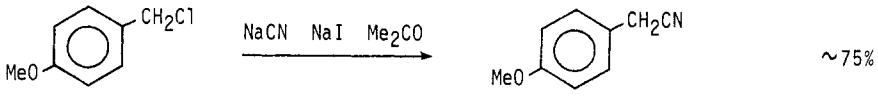


<75%

JACS (1969) 91 6854

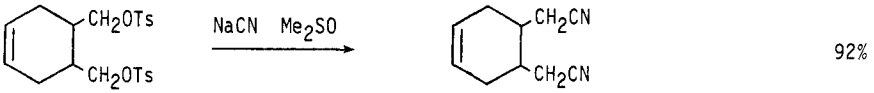


JCS (1950) 926



Org Synth (1963) Coll Vol 4 576

JOC (1960) 25 257 877



Tetr Lett (1964) 2273
JACS (1970) 92 336
JOC (1958) 23 797

Chem Pharm Bull (1962) 10 427

JOC (1963) 28 698

$C_7H_{15}C{\equiv}CCH{=}CHCH_2Br \xrightarrow[\text{xylene}]{\text{CuCN NaI}} C_7H_{15}C{\equiv}CCH{=}CHCH_2CN$ 31%

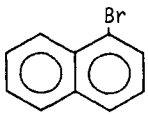
JACS (1953) 75 3430
Ber (1954) 87 712

$RBr \xrightarrow[\text{2 ClCN or } (CN)_2]{\text{1 Mg } Et_2O} RCN$ 63% (R=$PhCH_2CH_2$)
80% (R=Ph)

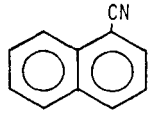
Annales de Chimie (1915) 4 28
Compt Rend (1911) 152 388

$PhCH{=}CHBr \xrightarrow[\text{MeOH}]{K_4Ni_2(CN)_6\ KCN} PhCH{=}CHCN$ 78%

JACS (1969) 91 1233
JOC (1969) 34 3626

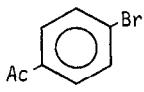


CuCN Pyr
215-225°

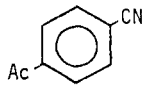


82-90%

Org Synth (1955) Coll Vol 3 631 212
JACS (1966) 88 3318
JOC (1952) 17 298



1 CuCN DMF
2 $FeCl_3$ HCl H_2O



88%

JOC (1961) 26 2522

The following solvents may also be used in the above reaction:

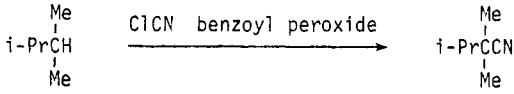
N-Methylpyrrolidone	JOC (1961) 26 2525
HMPA	JOC (1969) 34 3626
Me_2SO	Proc Chem Soc (1962) 113

$PhCH_2Br \xrightarrow[\text{2 } NaNH_2\ NH_3]{\text{1 } Ph_3P} PhCH{=}PPh_3 \xrightarrow{NO} PhCN$ 24%

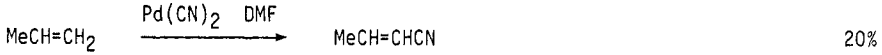
Chem Comm (1969) 166
Annalen (1969) 721 34
Bull Chem Soc Jap (1967) 40 2983

Section 191 Nitriles from Hydrides (RH)

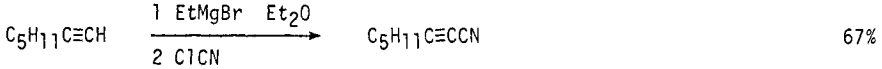
This section lists examples of the replacement of hydrogen by CN, RH ⟶ RCN. For the replacement of alkyl groups by CN, RR ⟶ RCN see section 185(Nitriles from Alkyls)



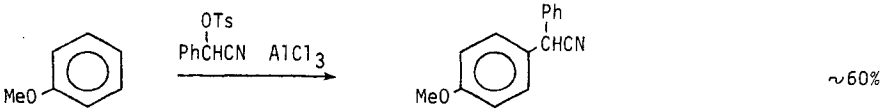
JACS (1969) 91 3028
Ber (1963) 96 670



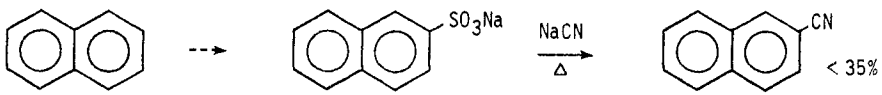
JACS (1966) 88 4105



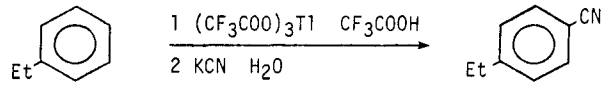
Bull Soc Chim Fr (1915) 17 228



JOC (1954) 19 1699
(1949) 14 839

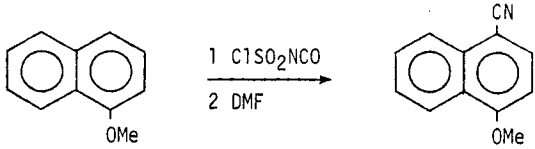


JACS (1921) 43 898
JCS (1954) 678
Chem Met Eng (1921) 24 638
(Chem Abs 15 1703)



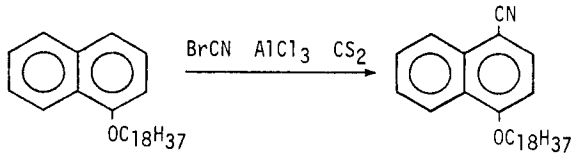
80%

JACS (1970) 92 3520



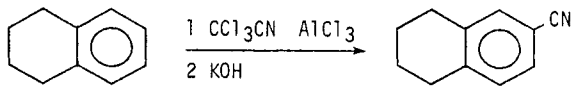
81%

Ber (1967) 100 2719



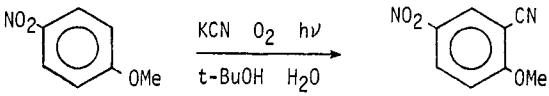
80%

JCS (1954) 678



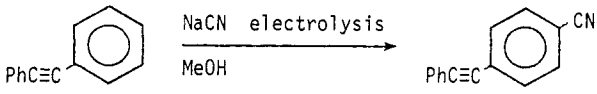
65%

Ber (1933) 66B 339



53%

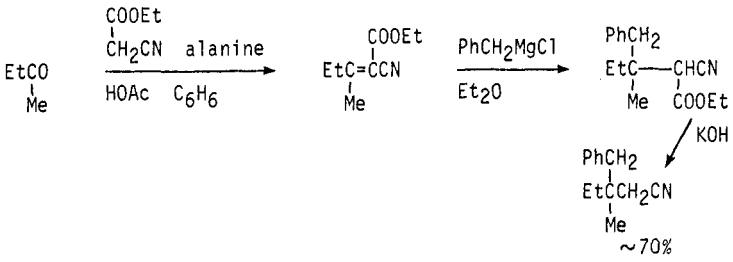
JACS (1966) 88 2884



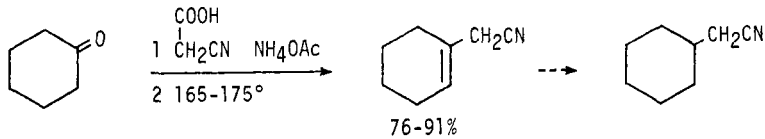
35%

Chem Comm (1970) 711
JACS (1969) 91 4181

Section 192 Nitriles from Ketones

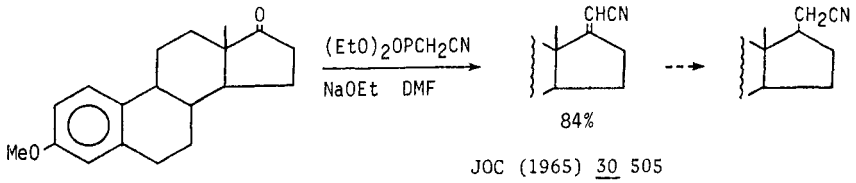


Org Synth (1963) Coll Vol 4 93
JCS C (1969) 121

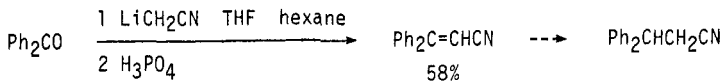


Org Synth (1963) Coll Vol 4 234

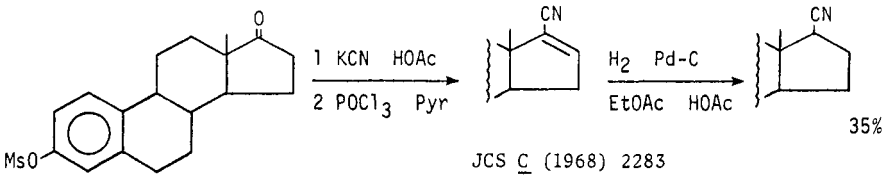
JACS (1959) 81 5397



JOC (1965) 30 505

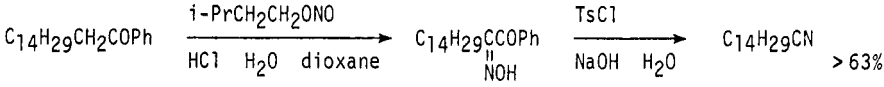


JOC (1968) 33 3402



35%

JCS C (1968) 2283



>63%

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

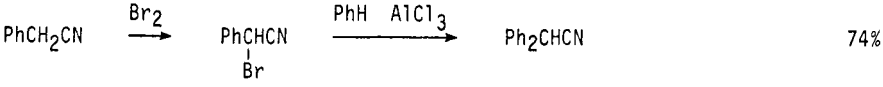
Some of the methods listed in section 184 (Nitriles from Aldehydes) may also be applied to the preparation of nitriles from ketones

Section 193 Nitriles from Nitriles

Review: The Alkylation of Esters and Nitriles Org React (1957) 9 107

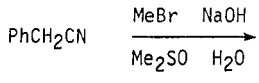
80%

JACS (1948) 70 3091



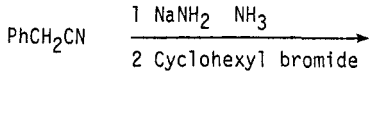
74%

JOC (1949) 14 839



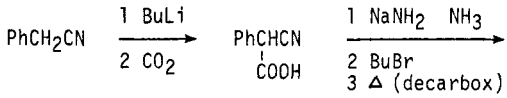
79%

JOC (1969) 34 226



65-77%

Org Synth (1955) Coll Vol 3 219
JCS (1946) 25
JOC (1958) 23 1346

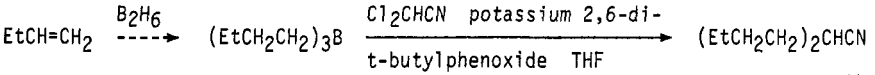


< 70%

JOC (1966) 31 3873

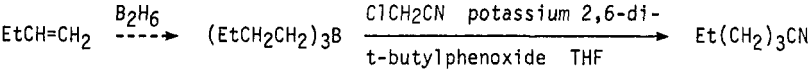
For further examples of the alkylation of nitriles with halides see section 190 (Nitriles from Halides and Sulfonates)

Section 194 Nitriles from Olefins

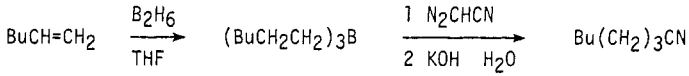


~85%

JACS (1970) 92 5790

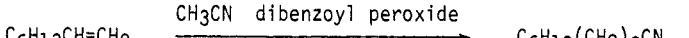


JACS (1969) 91 6854



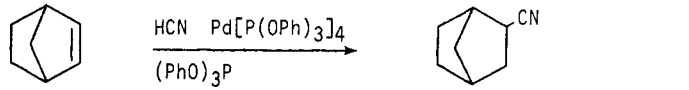
95%

JACS (1968) 90 6891



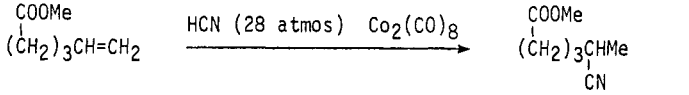
17%

JCS (1965) 1918 1932



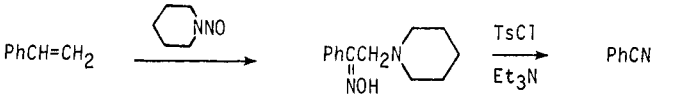
83%

Chem Comm (1969) 112



~19%

JACS (1954) 76 5364

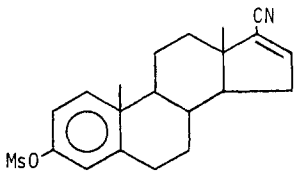


JACS (1965) 87 4642

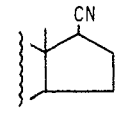
Section 195 Nitriles from Miscellaneous Compounds

90%

Tetr Lett (1967) 4805
(1969) 489



H_2 Pd-C
EtOAc HOAc

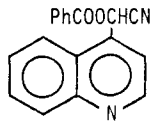


92%

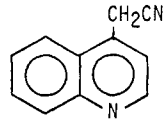
JCS C (1968) 2283

$PhCHCN$ (Cl) $\xrightarrow{Zn\ \ HOAc}$ $PhCH_2CN$

J Soc Chem Ind (1935) 54 98T



H_2 Pd-$BaSO_4$
EtOH



51%

Arch Pharm (1957) 290 218

$C_7H_{15}CH_2NO_2$ $\xrightarrow[2\ Br_2\ \ CCl_4]{1\ Base}$ $C_7H_{15}CHNO_2$ (Br) $\xrightarrow[C_6H_6]{Ph_3P}$ $C_7H_{15}CN$

50%

JCS (1960) 2976

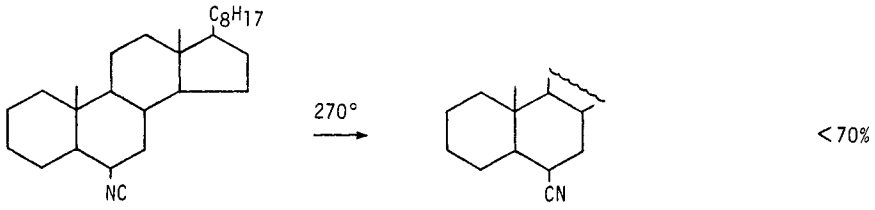
$PhC{\equiv}CCONH_2$ $\xrightarrow{NaOCl\ \ H_2O}$ $PhCH_2CN$

Rec Trav Chim (1920) 39 704
(1927) 46 268

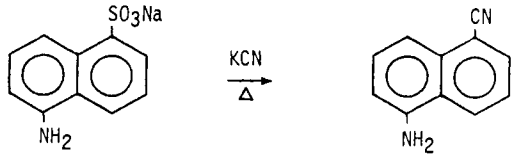
$PhCH_2COCOOH$ $\xrightarrow{NH_2OH{\cdot}HCl\ \ H_2O}$ $PhCH_2CN$

90%

Can J Chem (1961) 39 1340
JCS (1950) 926



Tetr Lett (1966) 5087

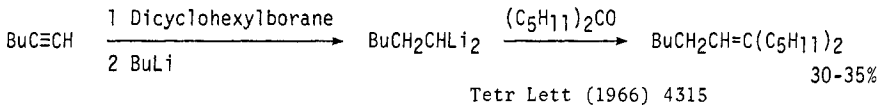


JCS (1954) 678

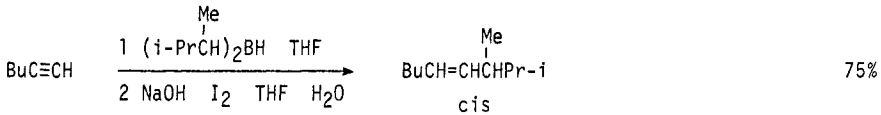
Compendium of Organic Synthetic Methods, Volume 1
Edited by Ian T. Harrison, Shuyen Harrison

Chapter 14 PREPARATION OF OLEFINS

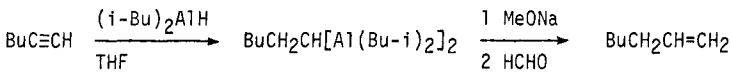
Section 196 Olefins from Acetylenes



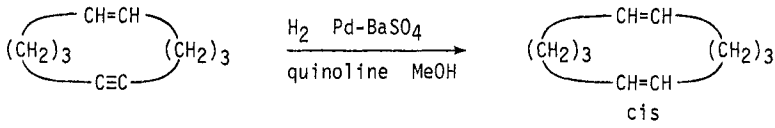
Tetr Lett (1966) 4315



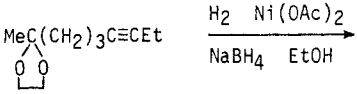
JACS (1967) 89 3652



Tetr Lett (1966) 6021

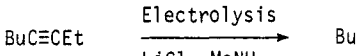


JACS (1956) 78 2518



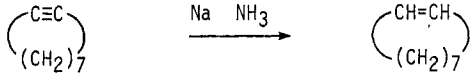
80%

Tetrahedron (1969) 25 5149



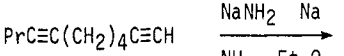
58%

JOC (1968) 33 2727



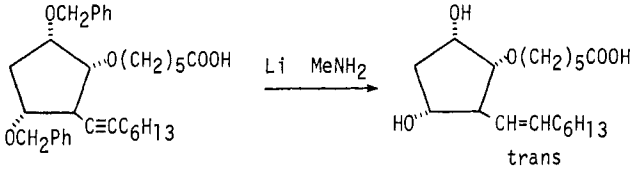
<86%

JACS (1952) 74 3643
(1963) 85 622

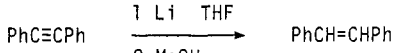


75%

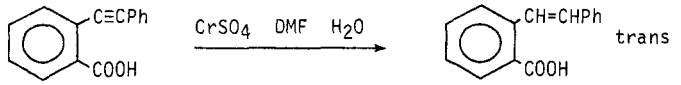
JCS (1955) 3558



Chem Comm (1968) 634

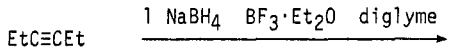


JOC (1970) 35 1702



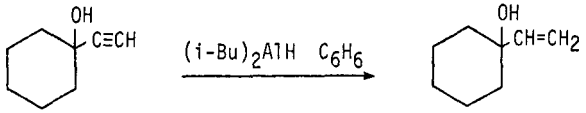
85%

JACS (1964) 86 4358



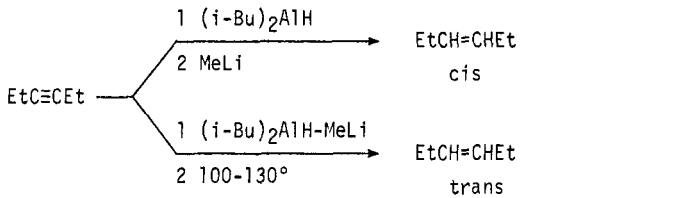
68%

JACS (1959) 81 1512



48%

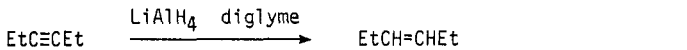
JOC (1959) 24 627
(1963) 28 1254
Ber (1956) 89 444



90%

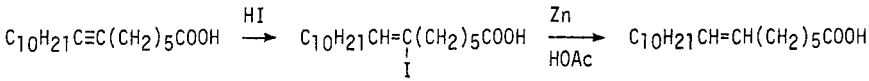
88%

JACS (1967) 89 5085 5086

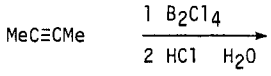


97%

Tetrahedron (1967) 23 4509



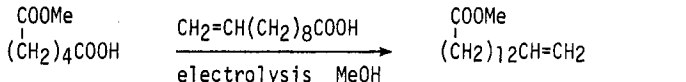
Compt Rend (1916) 162 944



JACS (1967) 89 4217

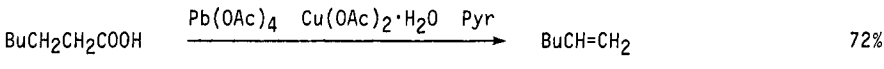
Section 197 Olefins from Carboxylic Acids, Acid Halides and Anhydrides

The decarboxylation of αβ- and βγ-unsaturated acids, $RCH{=}CHCOOH \longrightarrow RCH{=}CH_2$ and $RCH{=}CHCH_2COOH \longrightarrow RCH_2CH{=}CH_2$, is included in section 152 (Hydrides from Carboxylic Acids)

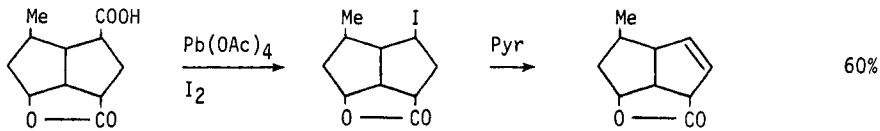


JCS (1953) 2393
(1954) 448 4219

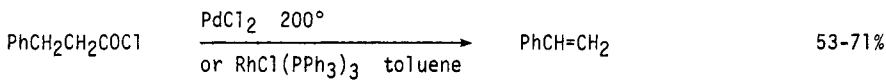
For further examples of the Kolbe electrolysis see section 62 (Alkyls from Carboxylic Acids)



Tetrahedron (1968) 24 2215
JCS C (1969) 1047



Tetr Lett (1968) 2471



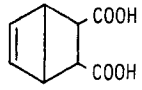
JACS (1968) 90 94 99

$Bu_2\overset{COOH}{\overset{|}{C}}CH_2Pr \xrightarrow[220\text{-}240°]{CuCN} Bu_2C{=}CHPr$ 73%

JACS (1950) 72 2792

$C_{13}H_{27}CH_2CH_2COOH \xrightarrow{SeO_2\ \Delta} C_{13}H_{27}CH{=}CH_2$

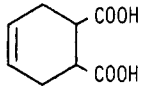
J Chem Soc Jap (1938) 59 262 271



$\xrightarrow[Et_3N\ \ Pyr\ \ H_2O]{\text{Electrolysis}}$

35%

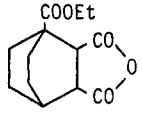
Tetr Lett (1968) 5117 5123



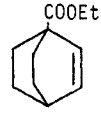
$\xrightarrow{Pb(OAc)_4\ \ O_2\ \ Pyr}$

76%

JACS (1968) 90 113
Helv (1958) 41 1191

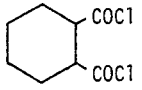


$\xrightarrow{PbO_2\ \ 170\text{-}190°}$

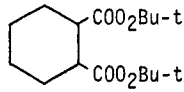


30-37%

Helv (1958) 41 1191
JACS (1952) 74 4370



$\xrightarrow{t\text{-}BuOOH}$



$\xrightarrow[\text{or } h\nu]{\Delta}$

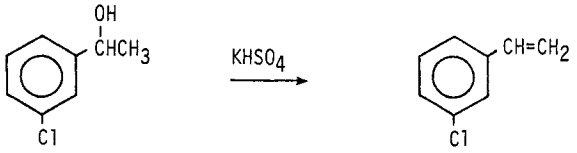
38%

Chem Comm (1969) 98

Section 198 Olefins from Alcohols

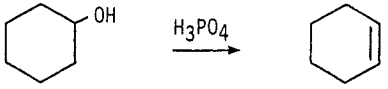
$$BuOH \dashrightarrow BuOCH_2CH{=}CH_2 \xrightarrow{PrLi\ \ pentane} BuCH{=}CH_2 \qquad \sim 73\%$$

Tetr Lett (1969) 821



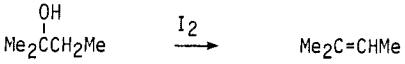
80-82%

Org Synth (1955) Coll Vol 3 204
(1943) Coll Vol 2 606
(1941) Coll Vol 1 430

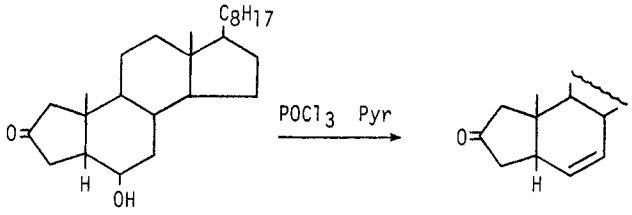


79-84%

Org Synth (1943) Coll Vol 2 151

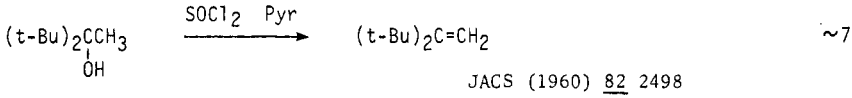


JACS (1915) 37 1748

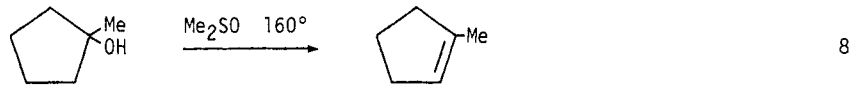


83%

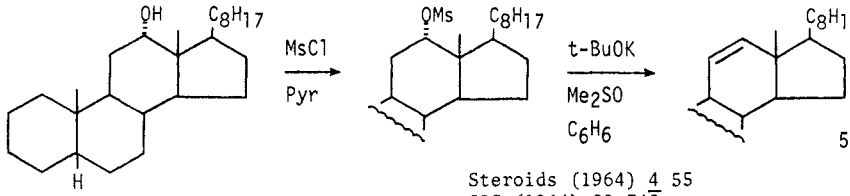
JACS (1961) 83 5003
Chem Pharm Bull (1961) 9 854
JCS C (1967) 1115



JACS (1960) 82 2498

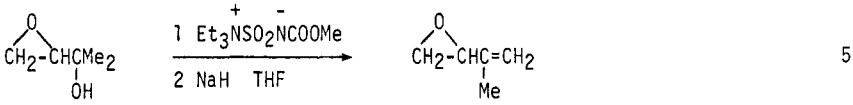


JOC (1964) 29 123

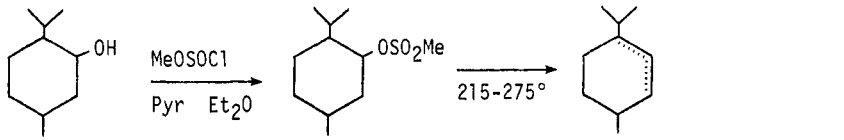


Steroids (1964) 4 55
JOC (1964) 29 742
(1961) 26 2883

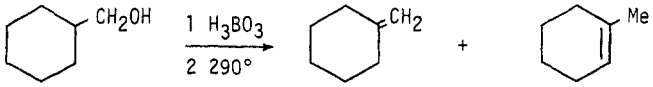
Further examples of the preparation of olefins from sulfonates are included in section 205 (Olefins from Halides and Sulfonates)



JACS (1970) 92 5224
JOC (1970) 35 2594



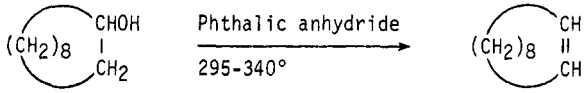
JACS (1954) 76 1213



JOC (1961) 26 4193
Chem Rev (1960) 60 431

$C_{16}H_{33}CH_2CH_2OH \xrightarrow[\text{(vapor phase)}]{Ac_2O\ (600°)} C_{16}H_{33}CH{=}CH_2$ 68%

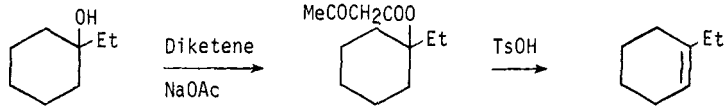
Chem Ind (1965) 681



80%

JACS (1952) 74 3636

For examples of the preparation of olefins from esters, by pyrolysis and by other methods, see section 203 (Olefins from Esters)



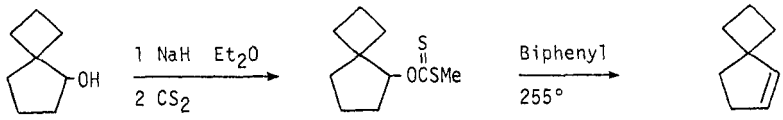
69%

Arkiv Kemi (1961) 17 401

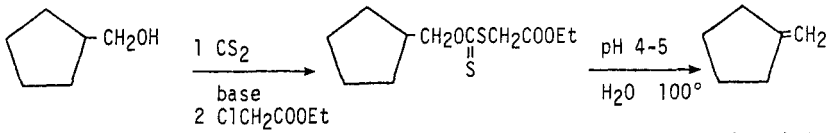
$C_6H_{13}CH_2CH_2OH \xrightarrow[2\ Bu_3P]{1\ BrCH_2COCl\ \ Pyr} C_6H_{13}CH_2CH_2OCOCH_2\overset{+}{P}Bu_3\ \overset{-}{Br} \xrightarrow{170°} C_6H_{13}CH{=}CH_2$

~72%

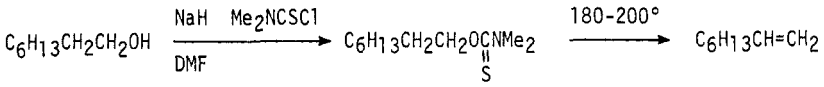
JOC (1964) 29 1003
JACS (1961) 83 3336



JOC (1967) 32 2933
(1968) 33 2214
Can J Chem (1970) 48 970
Org React (1962) 12 1

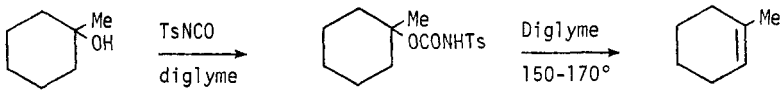


Ind Eng Chem Prod Res Dev (1970) 9 230

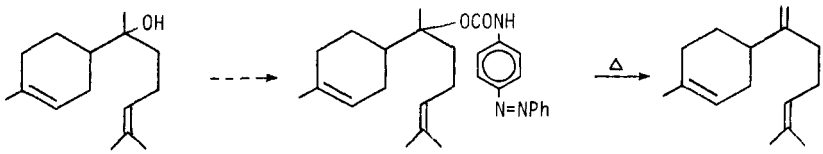


86%

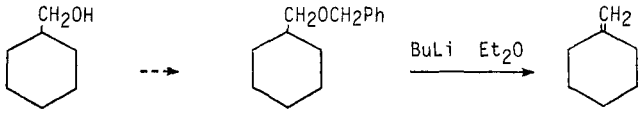
JOC (1969) 34 3604



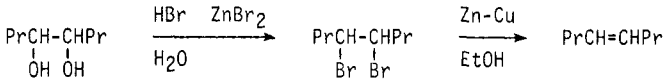
Chem Comm (1970) 606



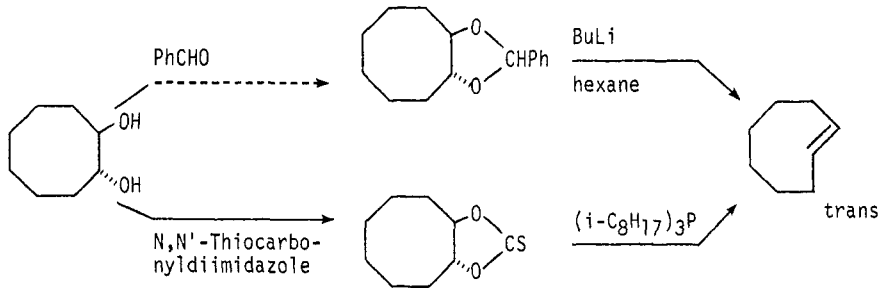
Aust J Chem (1954) 7 298
JACS (1953) 75 2118



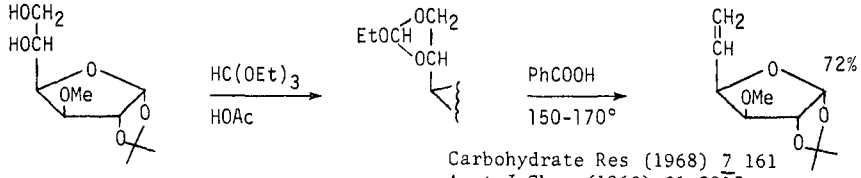
JCS (1958) 843



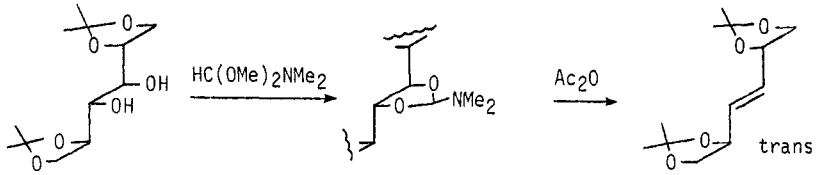
JACS (1937) 59 403
JCS (1951) 1079



Chem Comm (1968) 1593
Tetr Lett (1968) 3655
JACS (1965) 87 934
(1963) 85 2677



Carbohydrate Res (1968) 7 161
Aust J Chem (1968) 21 2013

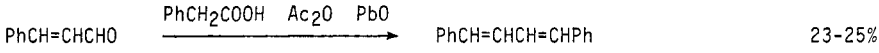


Tetr Lett (1970) 5223

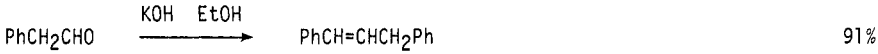
For the preparation of olefins from diols via bis sulfonates see section 205 (Olefins from Halides and Sulfonates)

Section 199 Olefins from Aldehydes

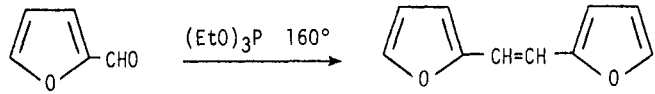
Examples of the decarbonylation of αβ-unsaturated aldehydes, RCH=CHCHO ⟶ RCH=CH_2, are included in section 154 (Hydrides from Aldehydes)



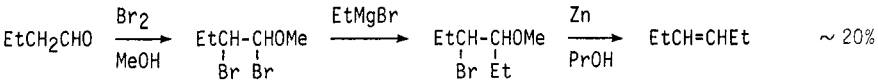
Org Synth (1943) Coll Vol 2 229



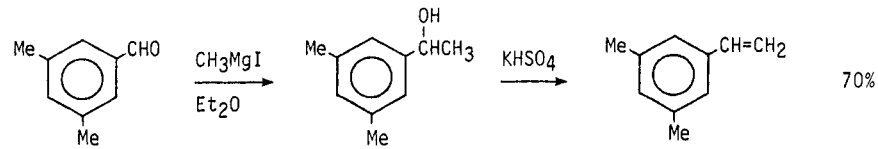
JOC (1966) 31 396



Izv (1960) 1030
(Chem Abs 54 24627)



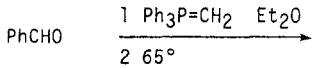
JACS (1932) 54 751



JACS (1946) 68 1085

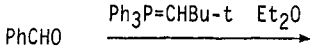
Reviews: The Wittig Reaction
Org React (1965) 14 270
Quart Rev (1963) 17 406

New Reactions of Alkylidenephosphoranes and their Preparative Uses
Angew (1965) 77 850
(Internat Ed 4 830)



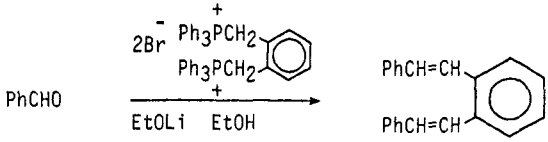
67%

Ber (1954) 87 1318



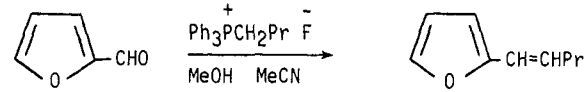
84%

JACS (1965) 87 4156



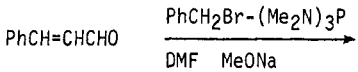
84%

Org React (1965) 14 270



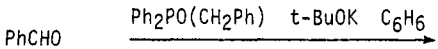
41%

Ber (1970) 103 2077



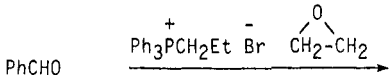
89%

Annalen (1965) 682 58

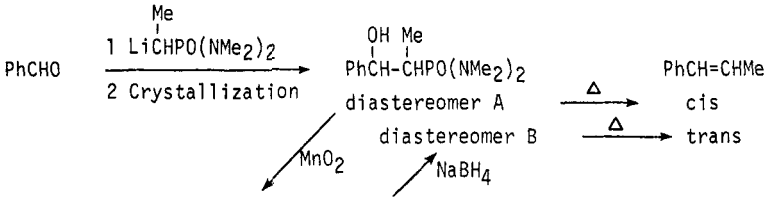


70%

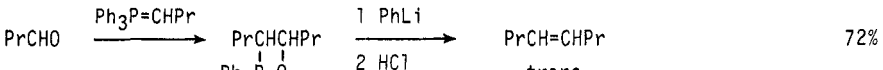
Ber (1959) 92 2499



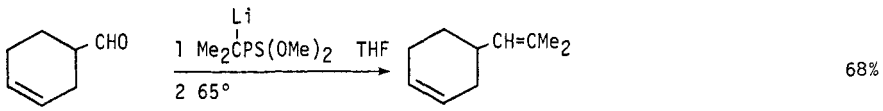
Angew (1968) 80 535
(Internat Ed 7 536)



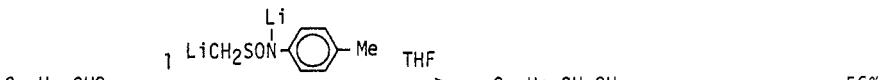
JACS (1966) 88 5653 5652
(1968) 90 6816
JOC (1969) 34 3053



Angew (1966) 78 115
(Internat Ed 5 126)
JACS (1970) 92 226

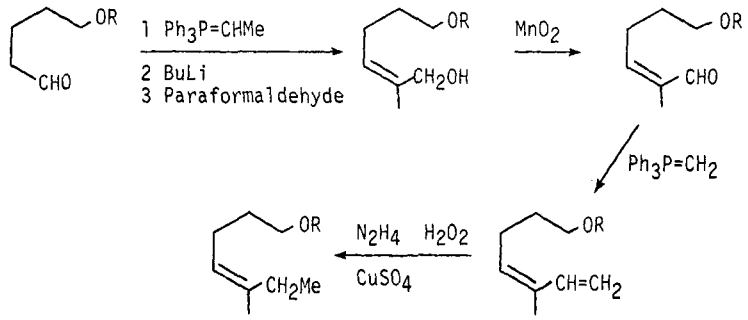


JACS (1966) 88 5654



JACS (1966) 88 5656
(1968) 90 5548

Further examples of the Wittig Reaction and a list of bases which may be used for the generation of Wittig reagents are included in section 207 (Olefins from Ketones)



JACS (1970) 92 6635

$C_6H_{13}CHO$ → (1 $Ph_3P=CHMe$ THF; 2 BuLi) → $C_6H_{13}CH(OLi)-C(Me)=PPh_3$ → (MeI) → $C_6H_{13}CH=CMe_2$ <50%

JACS (1970) 92 226

$C_6H_{13}CHO$ → (1 $Ph_3P=CHMe$; 2 $Hg(OAc)_2$; 3 LiI I_2) → C_6H_{13}, H, C=C, I, Me → (R_2CuLi) → C_6H_{13}, H, C=C, R, Me (R=alkyl)

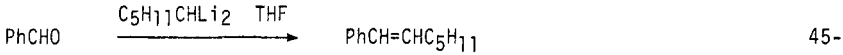
Tetr Lett (1970) 447

PhCHO → (Me_3SiCH_2Ph BuLi; HMPA) → PhCH=CHPh >50%

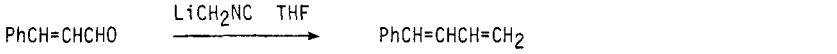
Tetr Lett (1970) 1137

$C_{11}H_{23}CHO$ → (CH_2I_2 Mg-Hg Et_2O) → $C_{11}H_{23}CH=CH_2$ 65%

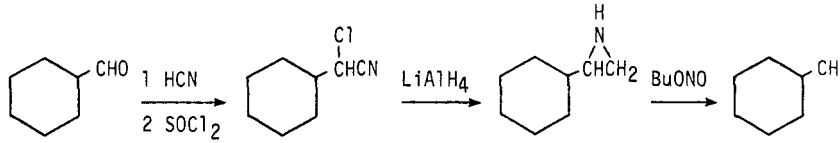
Tetrahedron (1970) 26 1281
J Organometallic Chem (1968) 12 263



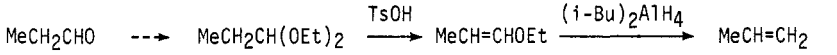
Tetr Lett (1966) 4315



Angew (1968) 80 842
(Internat Ed 7 805)



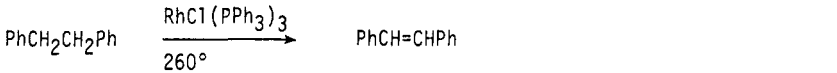
Tetr Lett (1969) 4001



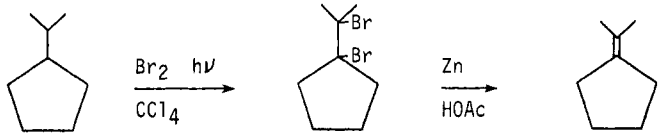
JOC (1966) 31 329

Some of the methods included in section 207 (Olefins from Ketones) may also be applied to the preparation of olefins from aldehydes

Section 200 Olefins from Alkyls, Methylenes and Aryls

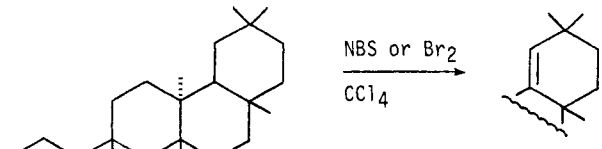


Tetr Lett (1970) 1825



~37%

Rec Trav Chim (1964) 83 67



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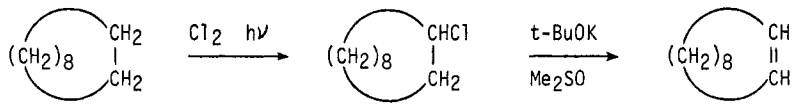
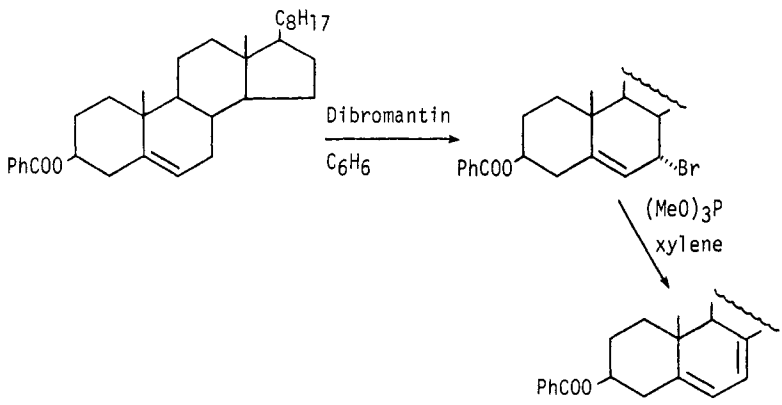
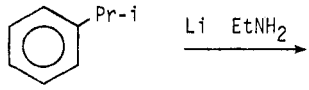
JOC (1965) 30 2479



JOC (1967) 32 510

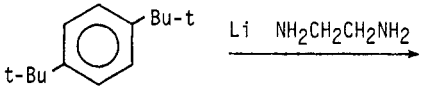


Helv (1958) 41 70



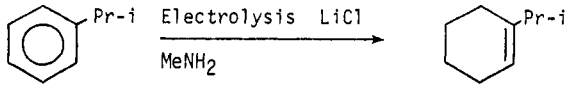
69%

JOC (1963) 28 1094



44%

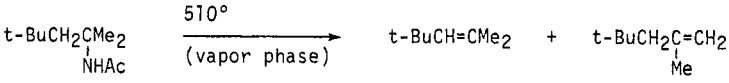
JOC (1966) 31 965
Aust J Chem (1964) 17 55



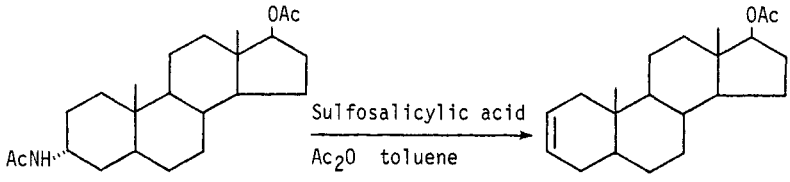
<81%

JACS (1964) 86 5272

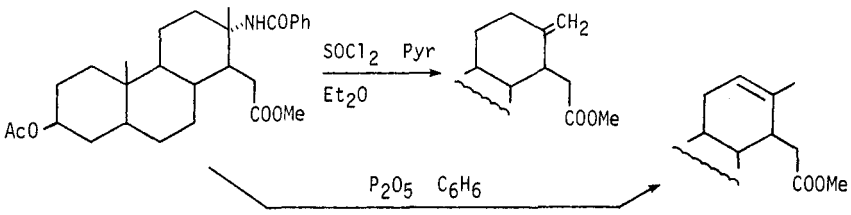
Section 201 Olefins from Amides



JOC (1958) 23 996
JACS (1959) 81 651
(1958) 80 4588



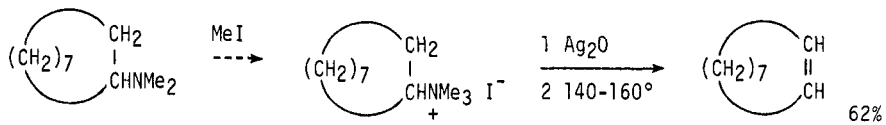
Tetr Lett (1965) 2369



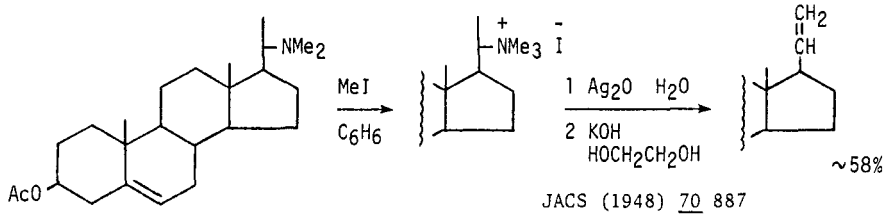
Bull Soc Chim Fr (1966) 2404

Section 202 Olefins from Amines

Review: The Hofmann Elimination Reaction and Amine Oxide Pyrolysis
Org React (1960) 11 317

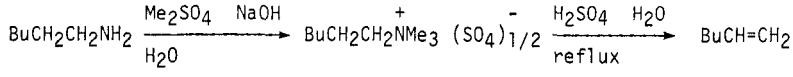


JACS (1952) 74 3643
JCS (1955) 4016

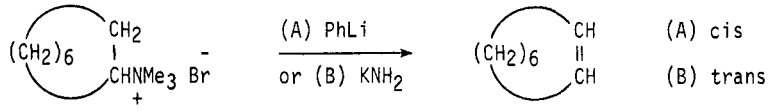


JACS (1948) 70 887

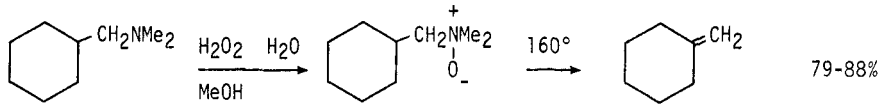
The following bases may also be used in place of Ag_2O in the Hofmann degradation of amines:
Ag_2SO_4-$Ba(OH)_2$, NaOH, TlOH, ion exchange resin Org React (1960) 11 317
Ag_2CO_3 JCS (1935) 1685



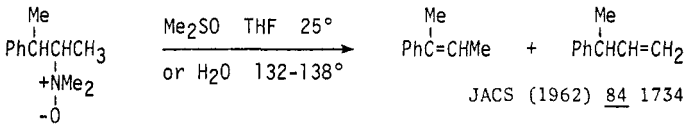
Org React (1960) 11 317



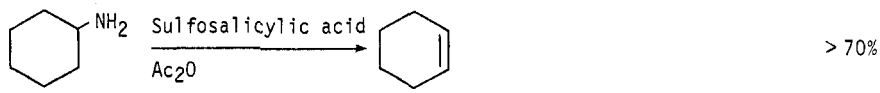
Annalen (1958) 612 102



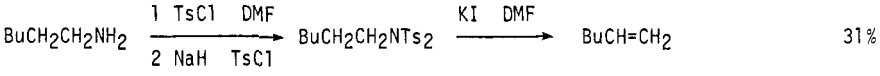
Org Synth (1963) Coll Vol 4 612



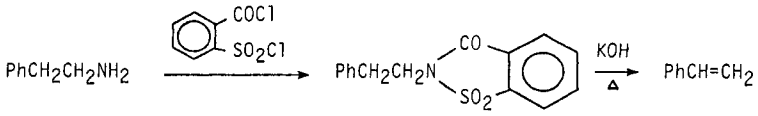
JACS (1962) 84 1734



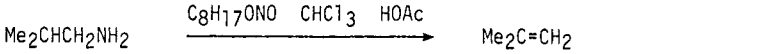
Tetr Lett (1965) 2369



JACS (1969) 91 2384



Tetr Lett (1967) 3027
JACS (1969) 91 2384

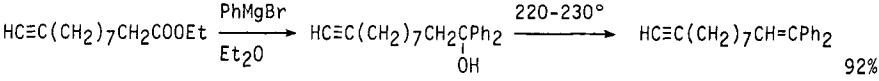


JACS (1969) 91 1790

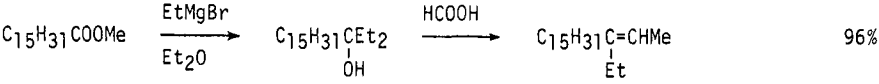
Tetr Lett (1969) 4001

Section 203 Olefins from Esters

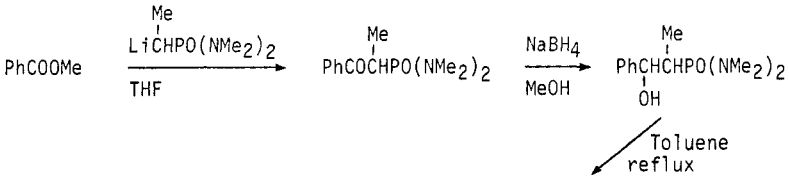
For the preparation of olefins from sulfonic esters see section 205 (Olefins from Halides and Sulfonates)



JCS (1957) 1622



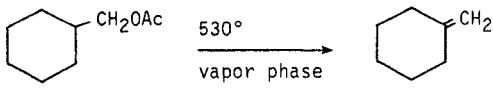
JACS (1945) 67 2239



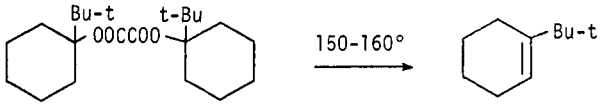
JACS (1966) 88 5653

Review: Pyrolytic Cis Eliminations Chem Rev (1960) 60 431

JACS (1959) 81 1968



JACS (1959) 81 647 651



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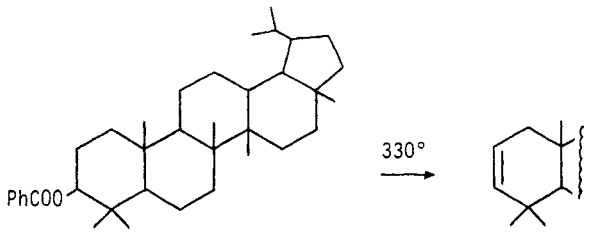
JACS (1969) 91 3324
JOC (1965) 30 689



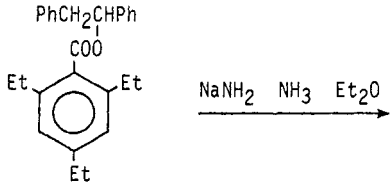
71%

JCS (1965) 4379

Esters of the following acids have also been used for the preparation of olefins by liquid-phase pyrolysis:

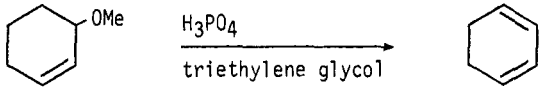
Stearic	JACS (1948) 70 2690 JCS (1957) 1998
d-Camphoric	JACS (1952) 74 3944
2,4,6-Triethylbenzoic	JACS (1953) 75 6011
2-Naphthoic	JACS (1954) 76 5692
3,5-Dinitrobenzoic	Chem Ind (1954) 1426
Anthraquinone-2-carboxylic	Helv (1944) 27 713 821
Ethyl carbonic	JACS (1952) 74 5454
2-Naphthyl carbonic	JACS (1954) 76 6108
Phenylcarbamic	JACS (1953) 75 2118 Can J Chem (1953) 31 688

Further examples of the preparation of olefins by pyrolysis of esters are included in section 198 (Olefins from Alcohols)



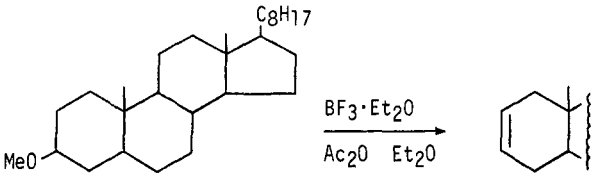
JACS (1953) 75 6011

Section 204 Olefins from Ethers and Epoxides



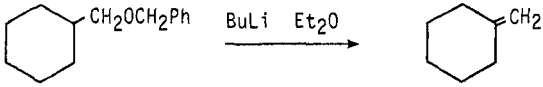
82%

Ber (1967) 100 1764



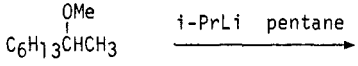
24%

Tetr Lett (1964) 759

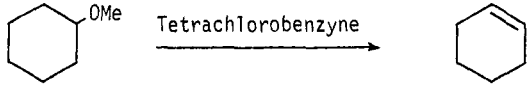


~60%

JCS (1958) 843



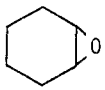
JACS (1951) 73 5708 1263



Tetr Lett (1968) 4455

$EtCH_2CH_2OBu \xrightarrow[140\text{-}150°]{N_2CHCOOEt} EtCH{=}CH_2$ 6%

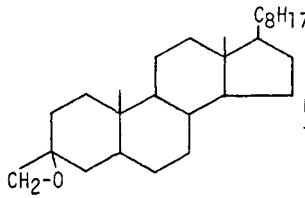
Rec Trav Chim (1955) 74 143



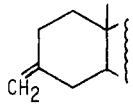
$\xrightarrow[DMF \quad H_2O]{Cr(ClO_4)_2 \quad NH_2CH_2CH_2NH_2}$

92%

Tetrahedron (1968) 24 3503

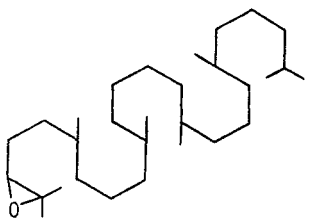


$\xrightarrow[THF]{Mg\text{-}Hg \quad MgBr_2}$

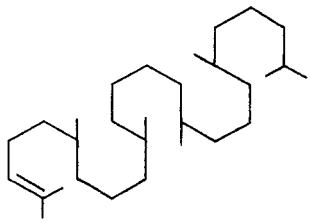


80%

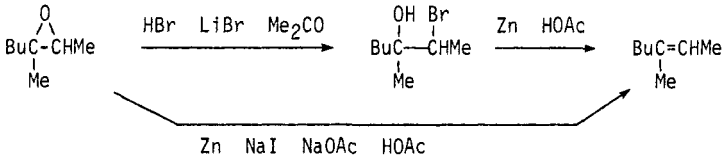
Chem Comm (1970) 144



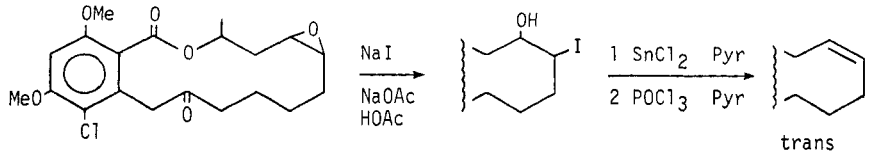
$\xrightarrow[HOAc]{Zn}$



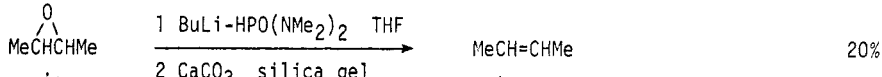
Chem Comm (1970) 1450



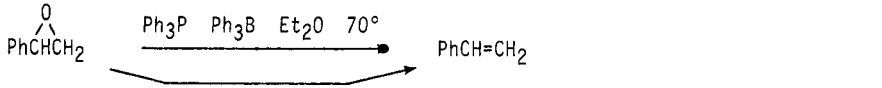
JCS (1959) 112
(1955) 1370



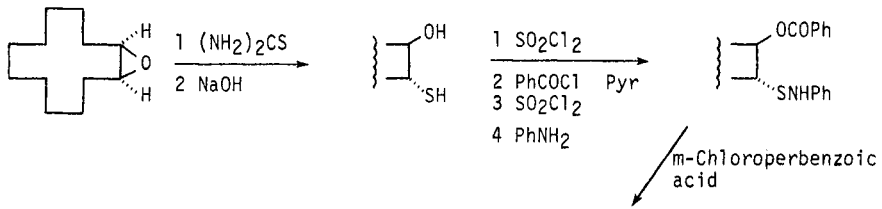
Aust J Chem (1966) 19 1265
JCS (1959) 112



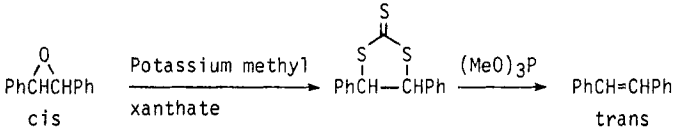
JOC (1969) 34 3053



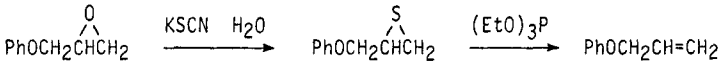
Ber (1955) 88 1654
Chem Ind (1959) 330



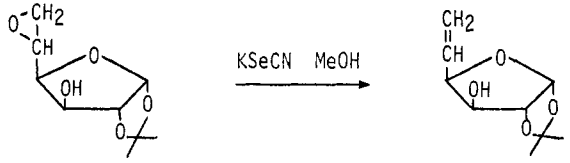
JACS (1968) 90 5553



JACS (1965) 87 934



JOC (1961) 26 3467

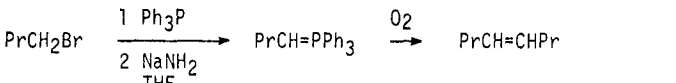


64%

Carbohydrate Res (1967) 5 282

Section 205 Olefins from Halides and Sulfonates

The reduction of vinyl halides, $R_2C{=}\overset{R}{\overset{|}{C}}X \longrightarrow R_2C{=}\overset{R}{\overset{|}{C}}H$, is included in section 160 (Hydrides from Halides and sulfonates)



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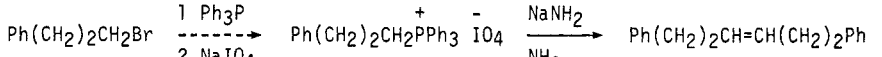
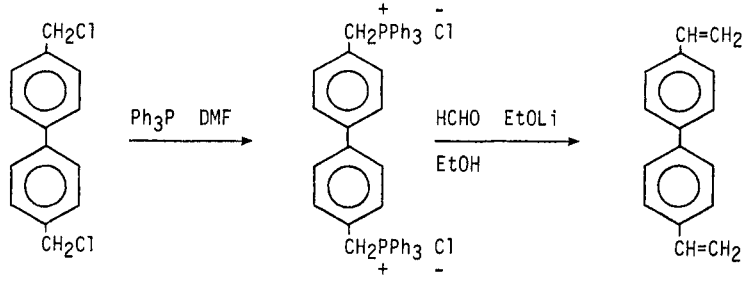
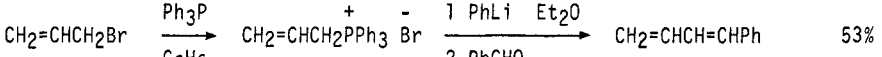
Ber (1963) 96 1899
(1966) 99 2848
(1961) 94 1987
Annalen (1969) 721 34



Ber (1969) 102 2259

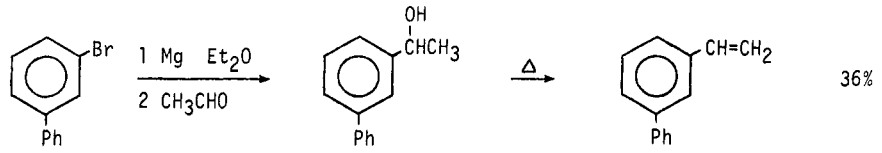


Org React (1965) 14 270

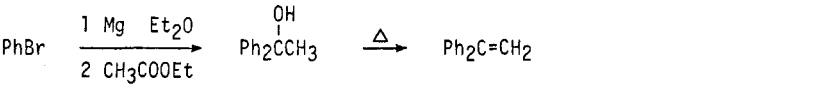


Ber (1954) 87 1318
Annalen (1965) 682 58

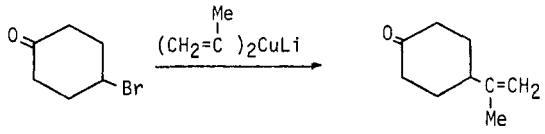
Further examples of the Wittig reaction are included in section 199 (Olefins from Aldehydes) and section 207 (Olefins from Ketones)



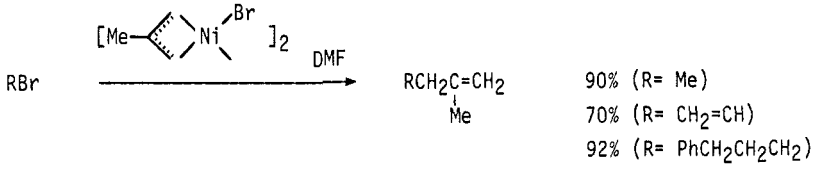
JACS (1946) 68 1109



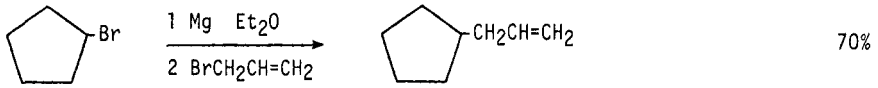
Org Synth (1932) Coll Vol 1 226



J Indian Chem Soc (1968) 45 1026

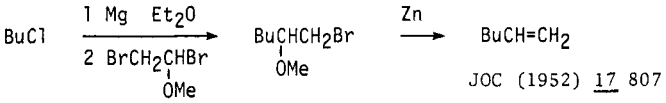


JACS (1967) 89 2755

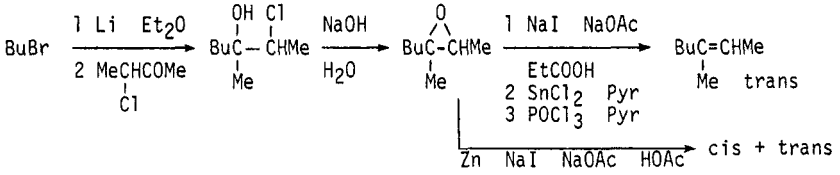


JACS (1946) 68 1101
JOC (1970) 35 22

Further examples of the coupling of halides are included in section 70 (Alkyls and Aryls from Halides and Sulfonates)



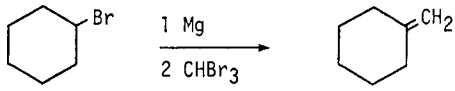
JOC (1952) 17 807



JCS (1959) 112

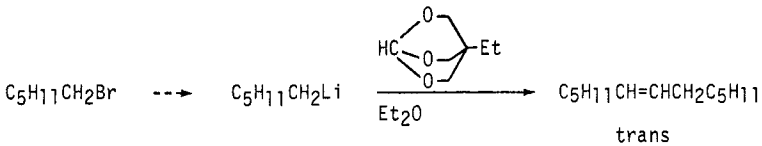
$PrCH_2Br \dashrightarrow PrCH_2MgBr \xrightarrow[Et_2O]{CF_2Br_2} PrCH{=}CHCH_2Pr$ 72%

Ber (1962) 95 1958



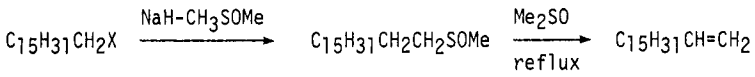
60%

Compt Rend (1965) 260 4535



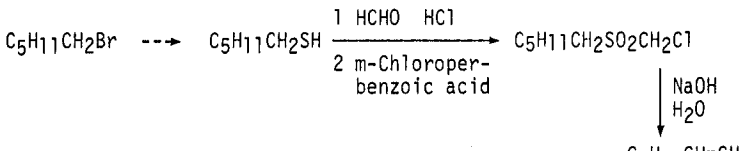
33%

Tetr Lett (1964) 2547



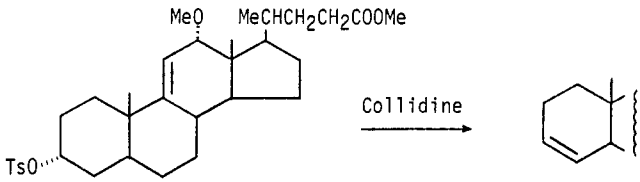
<85%

Chem Comm (1965) 29

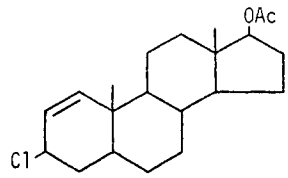


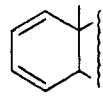
<53%

JACS (1964) 86 4383



JOC (1961) 26 2883



$\xrightarrow[DMF]{Pyr\ or\ CaCO_3}$  80%

JOC (1963) 28 1976

$BuCH_2CH_2Br \xrightarrow{HMPA\ \ 180\text{-}210^\circ} BuCH{=}CH_2$ 61%

Chem Comm (1971) 113

$C_3H_7CHCH_2Et$ (Br) $\xrightarrow[Me_2SO]{1,5\text{-Diazabicyclo[5.4.0]undec-5-ene}} C_3H_7CH{=}CHEt$ 91%

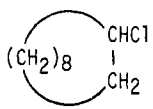
Angew (1967) 79 53
(Internat Ed 6 76)
Ber (1966) 99 2012

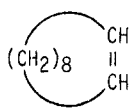
$C_5H_{11}CH_2CH_2Br \xrightarrow{LiF\ \ Li_2CO_3\ \ HMPA} C_5H_{11}CH{=}CH_2$ ~51%

Bull Soc Chim Fr (1967) 2455
(1968) 283
JOC (1970) 35 76 1023

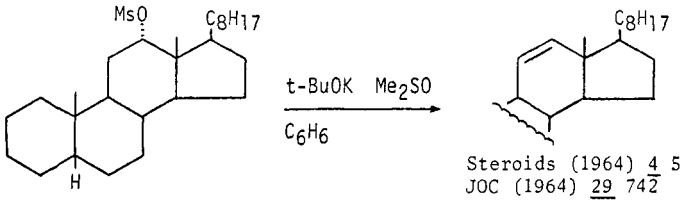
$Ph_3CCH_2CH_2Cl \xrightarrow{EtONa\ \ Me_2SO} Ph_3CCH{=}CH_2$ 90%

JCS C (1967) 1115



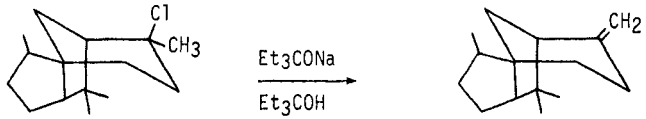
$\xrightarrow{t\text{-}BuOK\ \ Me_2SO}$ 

JOC (1967) 32 510
(1965) 30 2054
Tetr Lett (1967) 2273



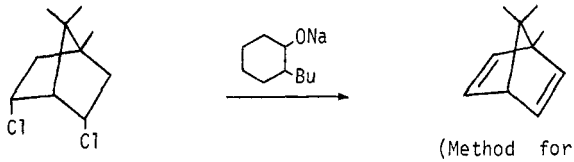
65%

Steroids (1964) 4 55
JOC (1964) 29 742



52%

JOC (1970) 35 196
Chem Comm (1968) 305



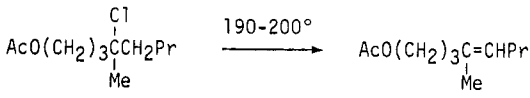
94%

(Method for unreactive halides)

Annalen (1962) 652 96

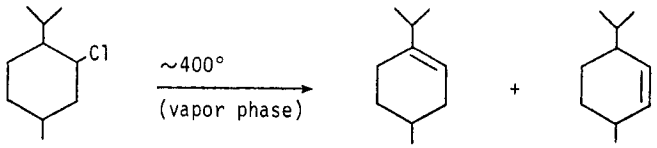
The following bases/solvents may also be used for the elimination of HX from halides and sulfonates:

Lithium dicyclohexylamide	JOC (1967) 32 510
$NaNH_2$-HMPA	Bull Soc Chim Fr (1966) 1293
Potassium t-amylate	Helv (1967) 50 2111
Me_2SO	JACS (1959) 81 5428 Tetr Lett (1968) 4191
$(MeO)_3P$-xylene	Helv (1958) 41 70
$C_{17}H_{35}COOAg$-C_6H_6	Ber (1942) 75B 660
Ag_2O-C_6H_6	Helv (1951) 34 1176

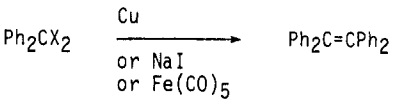


80%

JOC (1948) 13 239

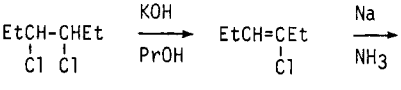


JCS (1952) 453
Chem Rev (1960) 60 431

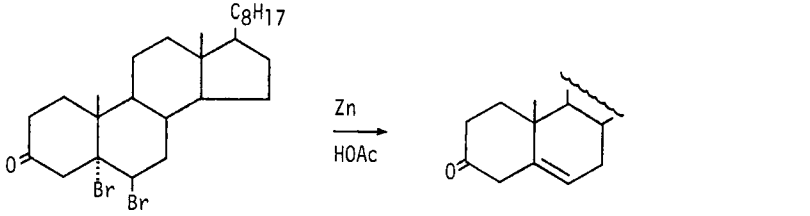


X=Br or Cl

Org Synth (1963) Coll Vol 4 914
JCS (1959) 678
JACS (1961) 83 1623



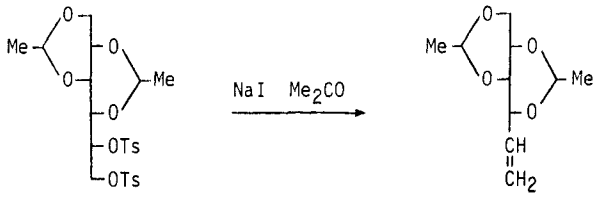
JACS (1951) 73 3329



Org Synth (1963) Coll Vol 4 195
JOC (1970) 35 1733
JCS (1961) 4547

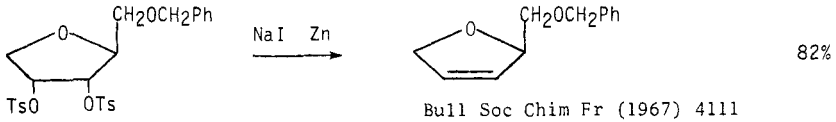
The following reagents may also be used for the conversion of 1,2-dihalides to olefins:

NaI, KI	JOC (1965) 30 1658 (1959) 24 143 Annalen (1967) 705 76
CrX_2 (X=Cl, OAc etc.)	JACS (1968) 90 1582 (1967) 89 6547 (1964) 86 4603 JOC (1959) 24 1621 1629 Tetrahedron (1968) 24 3503
Bu_3SnH	JOC (1963) 28 2165 Acc Chem Res (1968) 1 299
$Na-NH_3$	JACS (1952) 74 4590
Sodium dihydronaphthylide	Chem Comm (1969) 78
Phenanthrene disodium	Angew (1964) 76 432
PhSNa, EtSNa	Rev Chim (Bucharest) (1962) 7 1379 (Chem Abs 61 4208) JOC (1959) 24 143
Na_2Se	JOC (1966) 31 4292
$(NH_2)_2CS$	Chem Ind (1966) 1418
KSCN	Chem Ind (1966) 1418
Potassium cyclohexylphosphide	Ber (1961) 94 2664
$(EtO)_3P$	JOC (1970) 35 3181
$NaH-Me_2SO$	Chem Ind (1965) 345
$LiAlH_4$	Can J Chem (1964) 42 1294
PhLi	Annalen (1967) 705 76
PrMgBr	Bull Soc Chim Fr (1946) 604



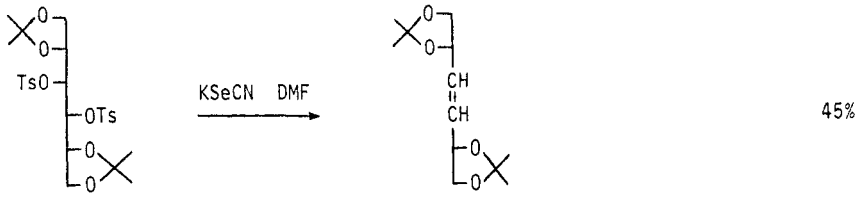
73%

JCS (1950) 598
JACS (1952) 74 4894



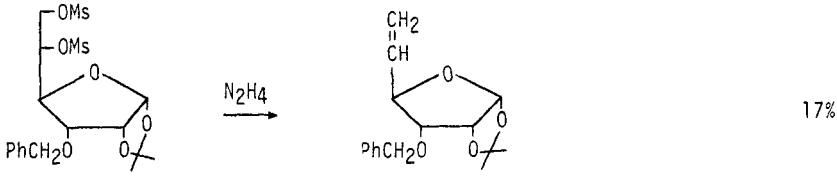
82%

Bull Soc Chim Fr (1967) 4111



45%

Carbohydrate Res (1967) 5 282

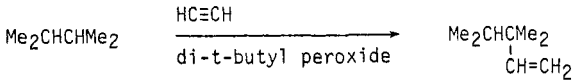


17%

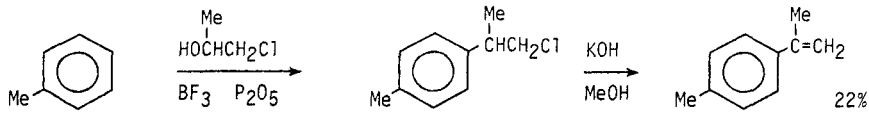
Ber (1969) 102 820

Section 206 Olefins from Hydrides (RH)

This section lists examples of the replacement of hydrogen by olefinic groups. For the dehydrogenation of alkyl groups, e.g. $RCH_2CH_2R \longrightarrow RCH{=}CHR$, see section 200 (Olefins from Alkyls, Methylenes and Aryls)



JOC (1965) 30 3814

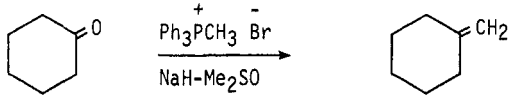


JACS (1948) 70 1772

Section 207 Olefins from Ketones

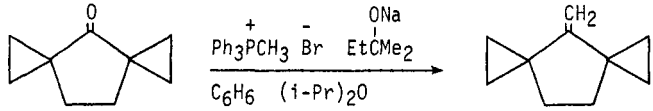
Reviews: The Wittig Reaction Org React (1965) 14 270
Quart Rev (1963) 17 406

New Reactions of Alkylidenephosphoranes and their Preparative Uses
Angew (1965) 77 850
(Internat Ed 4 830)



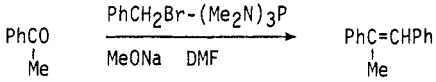
86%

Org React (1965) 14 270
Ber (1954) 87 1318



90%

Bull Soc Chim Fr (1967) 1936



35%

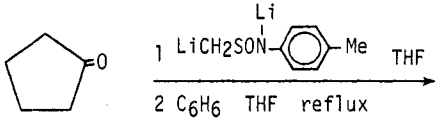
Annalen (1965) 682 58

Ph_2CO —[$Ph_2P(O)CH_2Me$ t-BuOK; toluene]→ $Ph_2C{=}CHMe$ 51%

Ber (1959) 92 2499

Ph_2CO —[1 $LiCHPO(NMe_2)_2$ THF; 2 Silica gel C_6H_6 reflux]→ $Ph_2C{=}CHMe$ 87%

JACS (1966) 88 5652 5653
JOC (1969) 34 3053



~90%

JACS (1966) 88 5656
(1968) 90 5548

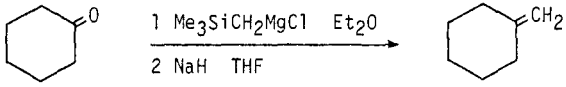
Ph_2CO —[$LiCHPS(OMe)_2$ THF]→ $Ph_2C{=}CHMe$ 93%

JACS (1966) 88 5654

The following reagents/solvents may also be used for the generation of Wittig reagents:

$NaH\text{-}Me_2SO$, $NaNH_2\text{-}NH_3$, PhLi, BuLi, EtOLi-EtOH, EtONa-EtOH	Org React (1965) 14 270
Na	Chem Abs (1940) 34 392
t-BuOK-Me_2SO	Ber (1965) 98 604
PhLi-t-BuOK-t-BuOH	Angew (1964) 76 683 (Internat Ed 3 636)
Ethylene oxide	Angew (1968) 80 535 (Internat Ed 7 536)
Diazabicyclo[3.4.0]non-5-ene	Ber (1966) 99 2012
Electrolysis (non basic)	JACS (1968) 90 2728 Tetr Lett (1969) 3523

Further examples of the Wittig reaction are included in section 199 (Olefins from Aldehydes)



> 50%

Tetr Lett (1970) 1137
JOC (1968) 33 780

$(C_5H_{11})_2CO \xrightarrow{C_5H_{11}CHLi_2\ THF} (C_5H_{11})_2C{=}CHC_5H_{11}$ 30-35%

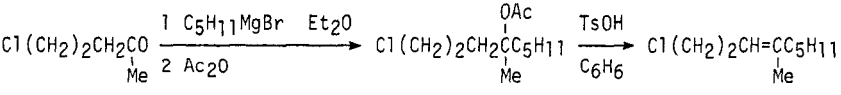
Tetr Lett (1966) 4315

$(C_5H_{11})_2CO \xrightarrow{CH_2I_2\ Mg\ Et_2O} (C_5H_{11})_2C{=}CH_2$ 30%

Tetrahedron (1970) 26 1281

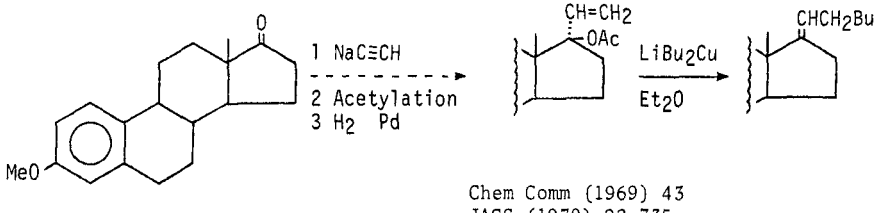
$Ph_2CO \xrightarrow{PhCH(Li)NC\ THF} Ph_2C{=}CHPh$ 74%

Angew (1968) 80 842
(Internat Ed 7 805)

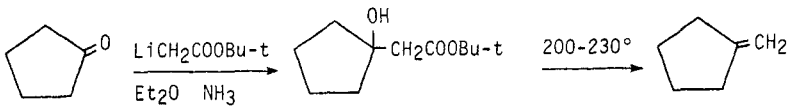


75%

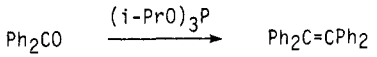
JOC (1948) 13 239
JACS (1949) 71 819



Chem Comm (1969) 43
JACS (1970) 92 735

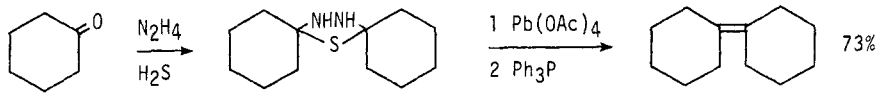


Bull Soc Chim Fr (1960) 1196

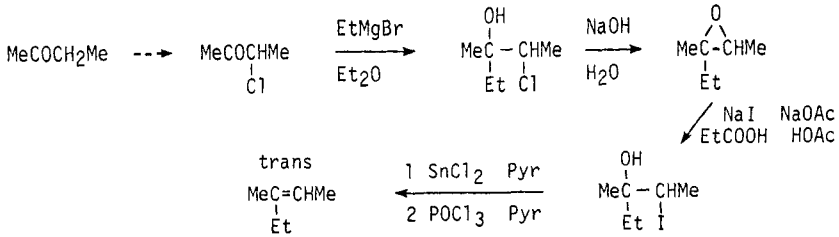


low yield

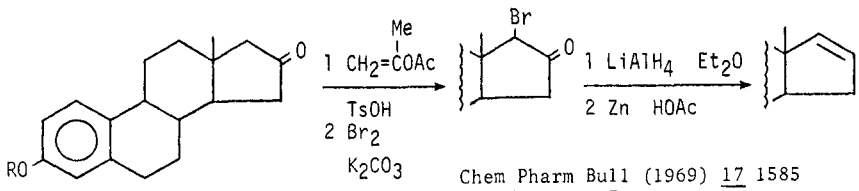
JOC (1964) 29 2567



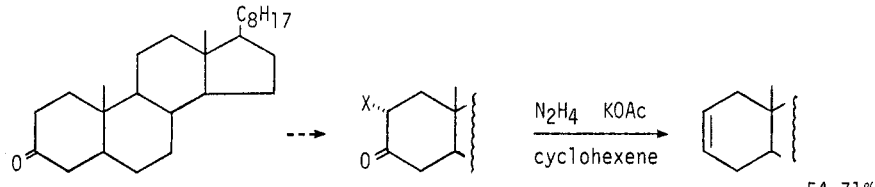
Chem Comm (1970) 1226 1225



JCS (1959) 112



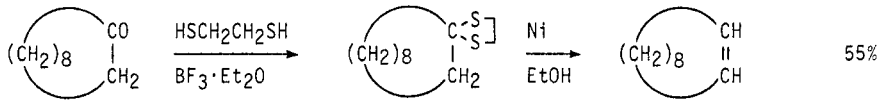
Chem Pharm Bull (1969) 17 1585
JCS (1955) 1370



X=F, Cl, Br or I

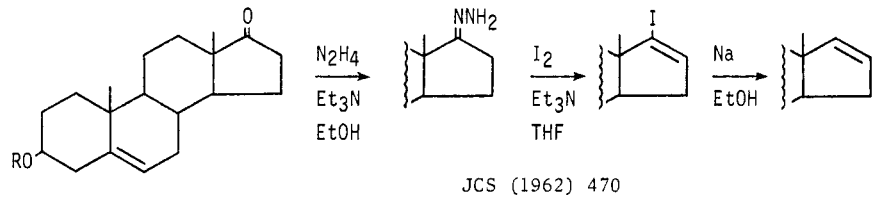
54-71%

JOC (1964) 29 958



55%

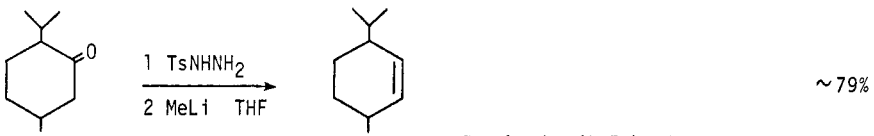
Tetrahedron (1969) 25 2823
JOC (1963) 28 1443



JCS (1962) 470

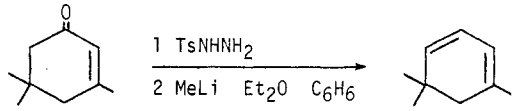
~100%

Annalen (1966) 691 41



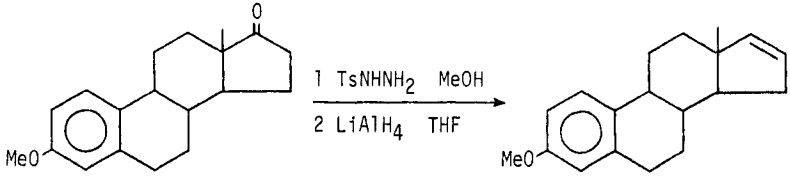
~79%

Synthesis (1970) 595
JACS (1967) 89 5734



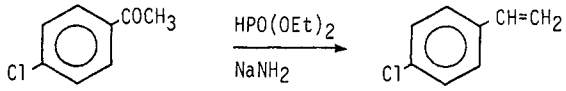
~100%

JACS (1968) 90 4762



70%

Tetrahedron (1963) 19 1127



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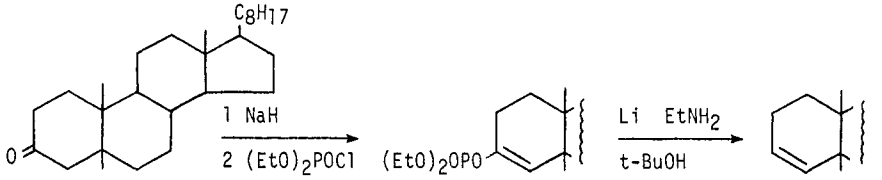
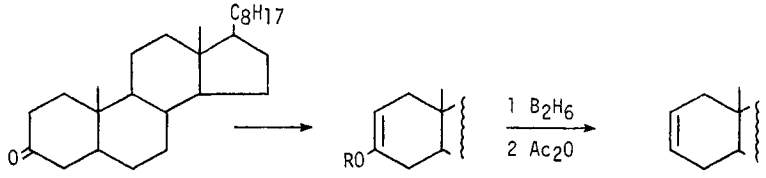
Angew (1963) 75 138
(Internat Ed 2 98)



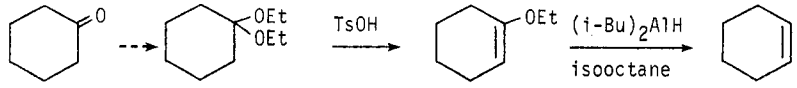
81%

Tetr Lett (1969) 2145
Chem Comm (1969) 112

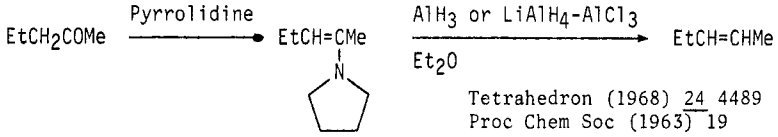


R=Ac or Me

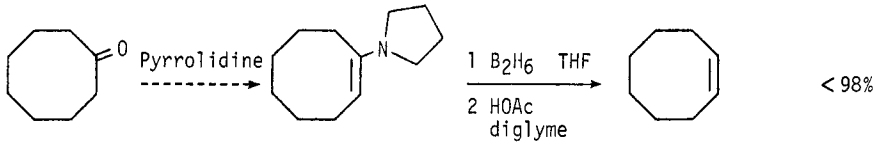
Gazz (1962) 92 309
(Chem Abs 57 12572)



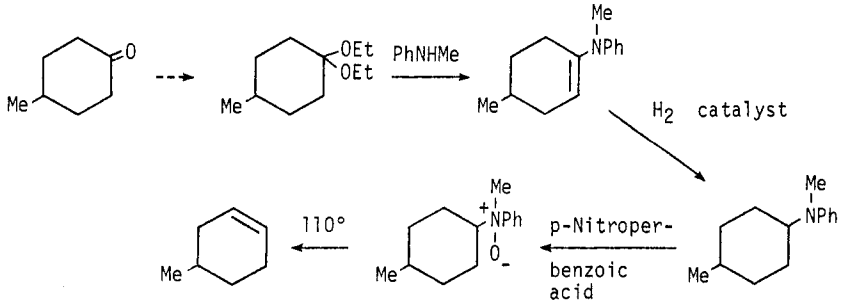
JOC (1966) 31 329



Tetrahedron (1968) 24 4489
Proc Chem Soc (1963) 19

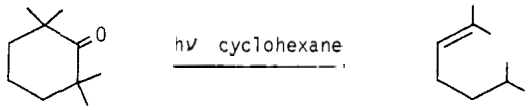


Tetr Lett (1964) 2039

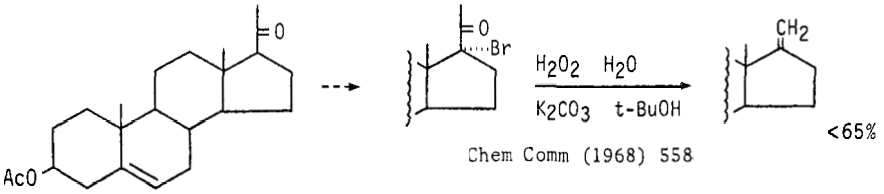


Tetr Lett (1964) 3853
Compt Rend (1967) C 264 710

Chem Comm (1969) 461



JOC (1966) 31 1393

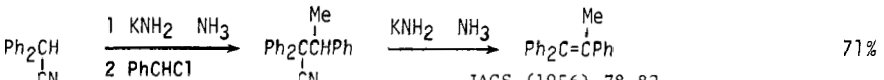


<65%

Chem Comm (1968) 558

Some of the methods listed in section 199 (Olefins from Aldehydes) may also be applied to the preparation of olefins from ketones

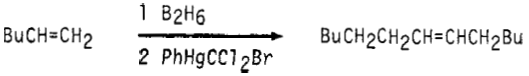
Section 208 Olefins from Nitriles



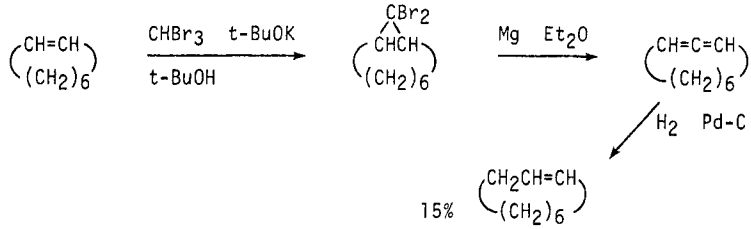
71%

JACS (1956) 78 82
(1960) 82 1786

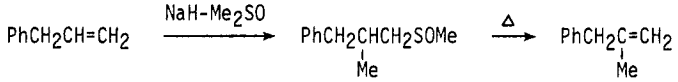
Section 209 Olefins from Olefins



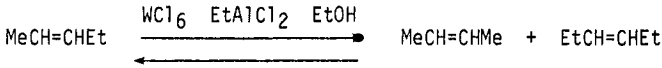
JACS (1966) 88 1834



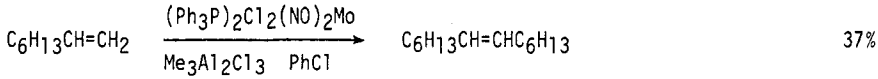
JOC (1961) 26 3518



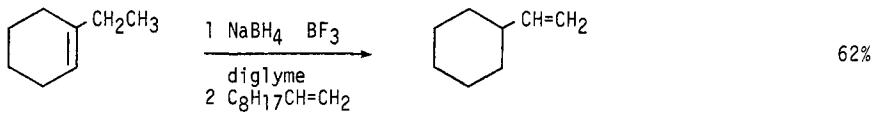
JOC (1964) 29 2699



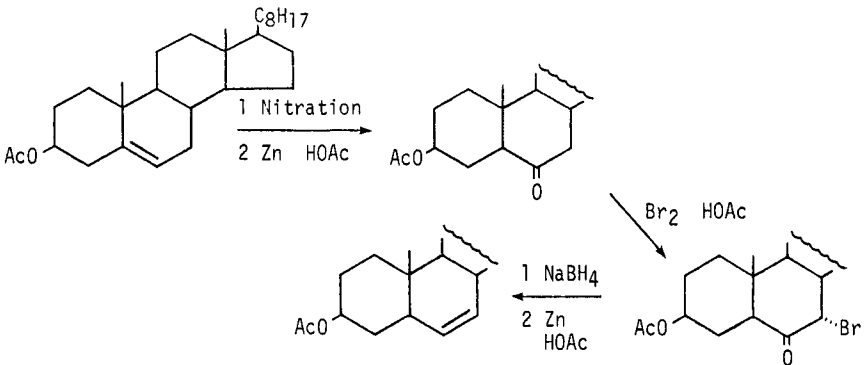
Tetr Lett (1967) 3327
JACS (1968) 90 4133



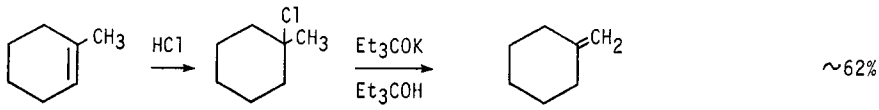
JACS (1970) 92 528



JACS (1967) 89 567 561
(1960) 82 2074

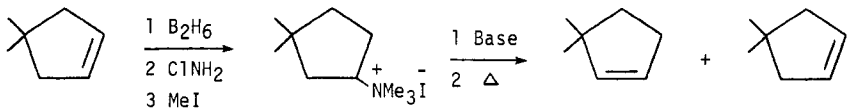


JACS (1956) 78 6269
JOC (1948) 13 424

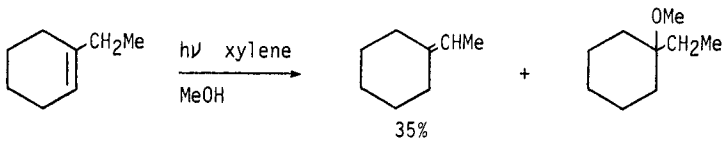


~62%

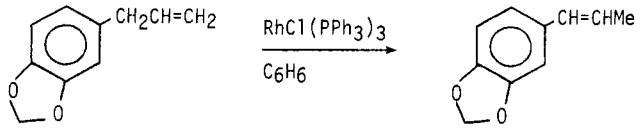
Chem Comm (1968) 305
Helv (1967) 50 2111



Tetr Lett (1968) 2253



JACS (1967) 89 5199



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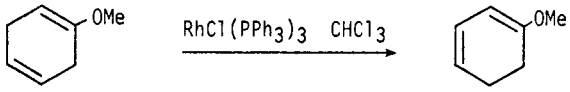
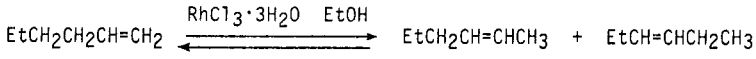
Tetr Lett (1968) 3797

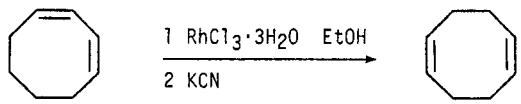


80%

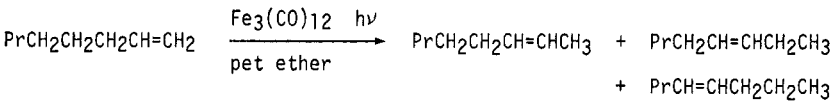
Tetr Lett (1968) 3797



JACS (1964) 86 1776
Helv (1967) 50 2445



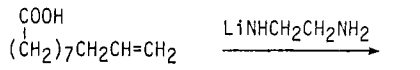
JACS (1964) 86 2516



Proc Chem Soc (1964) 408

Review: The Isomerization of Olefins.
Part I. Base Catalyzed Isomerization of Olefins

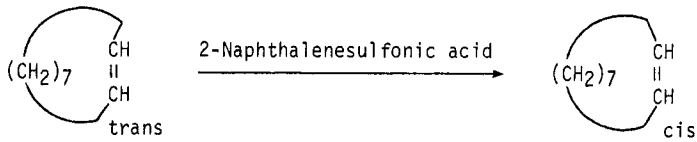
Synthesis (1969) 97



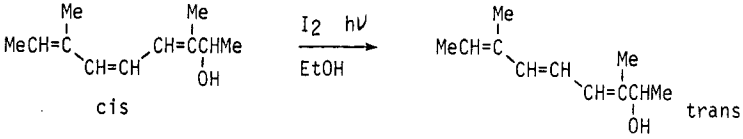
Tetrahedron (1964) 20 2911
JOC (1958) 23 1136

The following bases may also be used for the migration of double bonds:

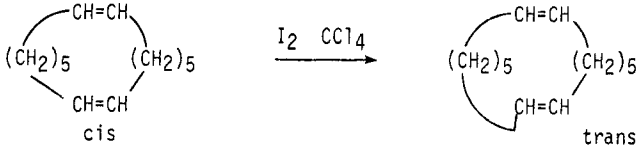
LiNHEt	JACS (1964) 86 5281
t-BuOK-Me_2SO	Ber (1966) 99 1737 JOC (1968) 33 221 JACS (1961) 83 3731
Na-alumina	JACS (1965) 87 4107 JCS C (1967) 2149 (1966) 260
Na-$PhCH_2Na$	Tetr Lett (1964) 467



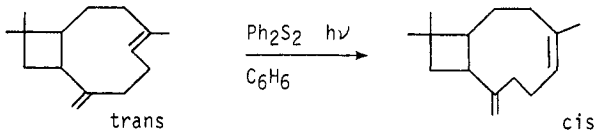
JACS (1952) 74 3643



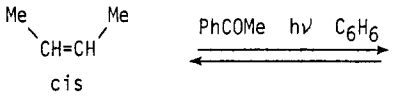
JACS (1954) 76 5719



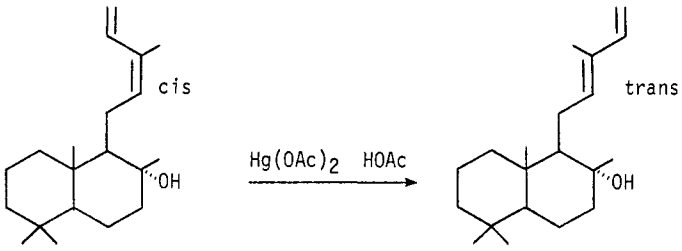
JCS C (1966) 260



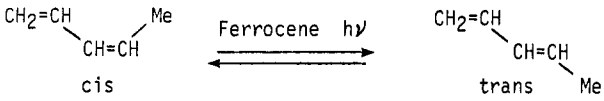
Helv (1968) 51 548
JACS (1967) 89 2758
JCS C (1966) 260



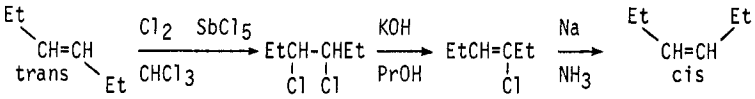
JCS C (1966) 260



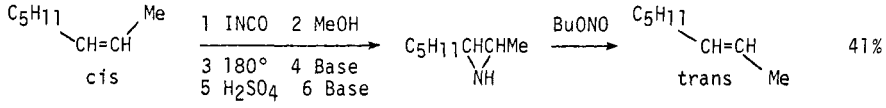
JCS C (1967) 2514



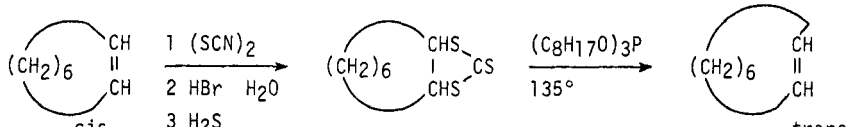
JACS (1965) 87 1626



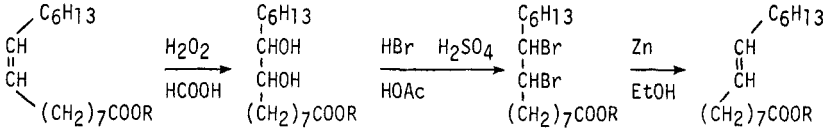
JACS (1951) 73 3329



Tetr Lett (1969) 4001



JACS (1965) 87 934



JCS (1954) 4219
(1953) 2393
(1951) 1079

Further examples of the conversion of diols and dihalides into olefins are included in section 198 (Olefins from Alcohols) and section 205 (Olefins from Halides and Sulfonates)

Section 210 *Olefins from Miscellaneous Compounds*

The reduction of vinyl halides, $R_2C{=}\underset{Cl}{CR} \longrightarrow R_2C{=}CHR$ is included in section 160 (Hydrides from Halides and Sulfonates)

The hydrogenolysis of unsaturated ketones, e.g. $R_2C{=}\underset{R}{\underset{|}{C}}\text{-}\underset{R}{\underset{|}{C}}\text{-}CO \longrightarrow R_2CH\text{-}\underset{R}{\underset{|}{C}}{=}CH$ is included in section 72 (Alkyls, Methylenes and Aryls from Ketones)

$C_{15}H_{31}CH_2CH_2SOMe \xrightarrow[\text{reflux}]{Me_2SO} C_{15}H_{31}CH{=}CH_2$ 85%

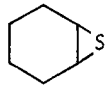
Chem Comm (1965) 29
JOC (1964) 29 2699

$(Me_2CH)_2SO_2 \xrightarrow{\text{t-BuOK}\ \ Me_2SO} MeCH{=}CH_2$ 100%

Chem Ind (1963) 1243
JOC (1967) 32 102

$PhCS(Me) \xrightarrow{Ni\ \ xylene} PhC(Me){=}CPh(Me)$ 18%

JACS (1944) 66 1136



$\xrightarrow{Ph_3P\ \ Et_2O}$  95%

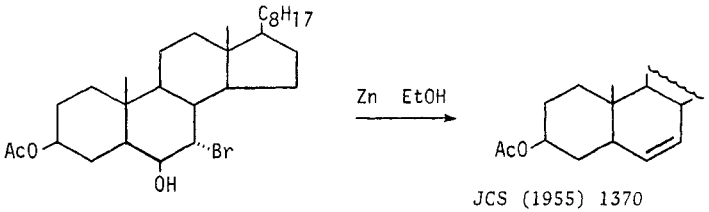
JOC (1958) 23 1767
(1961) 26 3467
Chem Pharm Bull (1960) 8 621

$PhCH_2CH_2SO_2Cl \xrightarrow[Et_2O]{Et_3N\ \ CH_2N_2} PhCH_2CH(SO_2)CH_2 \xrightarrow{80°} PhCH_2CH{=}CH_2$ 96%

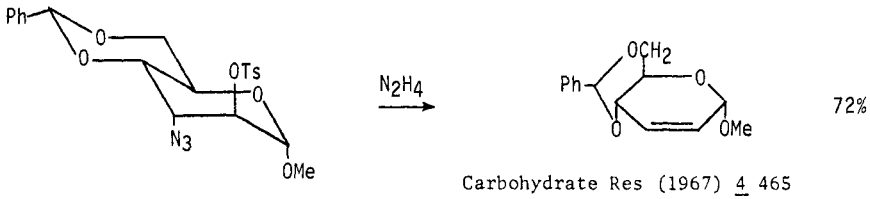
Angew (1965) 77 41
(Internat Ed 4 70)

$BuCH(OMe)CH_2Br \xrightarrow{Zn\ \ PrOH} BuCH{=}CH_2$ 78%

JACS (1932) 54 751

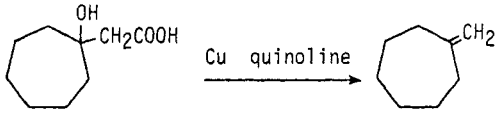


JCS (1955) 1370



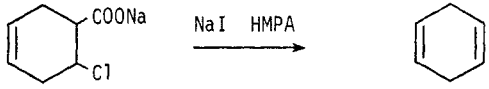
72%

Carbohydrate Res (1967) 4 465



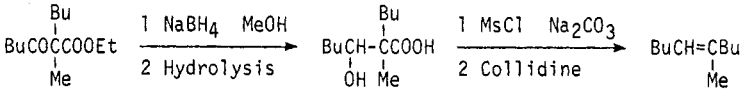
60%

Bull Soc Chim Fr (1960) 1196



70%

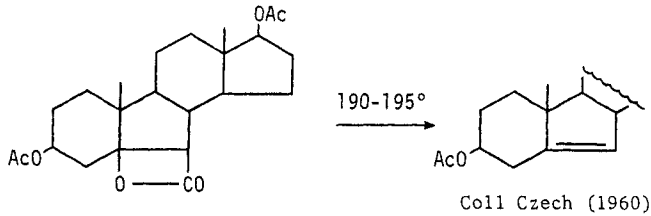
JOC (1968) 33 4540



diastereomer A ⟶ trans

diastereomer B ⟶ cis

Tetr Lett (1968) 4569



91%

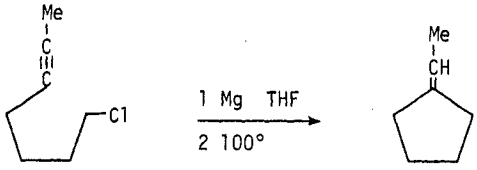
Coll Czech (1960) 25 2341

$C_5H_{11}CH_2CH_2CH_2COCOOH \xrightarrow{h\nu \; C_6H_6} C_5H_{11}CH{=}CH_2$ 88%

JACS (1968) 90 1840

$PhCH{=}CHCH_2\underset{\underset{OH}{|}}{C}Et_2 \xrightarrow{\Delta} PhCH_2CH{=}CH_2$

JCS (1965) 7242



~90%

Tetr Lett (1968) 1457