Compendium of Organic Synthetic Methods

Volume 3

LOUIS S. HEGEDUS

and

LEROY WADE

DEPARTMENT OF CHEMISTRY
COLORADO STATE UNIVERSITY
FORT COLLINS, COLORADO

A Wiley-Interscience Publication

JOHN WILEY & SONS, New York • Chichester • Brisbane • Toronto

Compendium of Organic Synthetic Methods

Volume 3

LOUIS S. HEGEDUS

and

LEROY WADE

DEPARTMENT OF CHEMISTRY
COLORADO STATE UNIVERSITY
FORT COLLINS, COLORADO

A Wiley-Interscience Publication

JOHN WILEY & SONS, New York · Chichester · Brisbane · Toronto

Library of Congress Catalog Card Number: 71-162800

ISBN 0-471-36752-4

Printed in the United States of America

20 19 18 17 16 15 14 13 12 11

PREFACE

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

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

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

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

Louis S. Hegedus
Leroy Wade

Fort Collins, Colorado
June, 1977

ABBREVIATIONS

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

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

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

CONTENTS

ABBREVIATIONS vii
INDEX, MONOFUNCTIONAL COMPOUNDS ix
INDEX, DIFUNCTIONAL COMPOUNDS x
INTRODUCTION xi

1 PREPARATION OF ACETYLENES 1
2 PREPARATION OF CARBOXYLIC ACIDS, ACID HALIDES, AND ANHYDRIDES 8
3 PREPARATION OF ALCOHOLS AND PHENOLS 24
4 PREPARATION OF ALDEHYDES 66
5 PREPARATION OF ALKYLS, METHYLENES, AND ARYLS 88
6 PREPARATION OF AMIDES 134
7 PREPARATION OF AMINES 149
8 PREPARATION OF ESTERS 178
9 PREPARATION OF ETHERS AND EPOXIDES 204
10 PREPARATION OF HALIDES AND SULFONATES 218
11 PREPARATION OF HYDRIDES 235
12 PREPARATION OF KETONES 248
13 PREPARATION OF NITRILES 296
14 PREPARATION OF OLEFINS 305
15 PREPARATION OF DIFUNCTIONAL COMPOUNDS 336

INDEX, MONOFUNCTIONAL COMPOUNDS

Sections—heavy type
Pages—light type

PREPARATION OF →
FROM ↓

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

PROTECTION

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

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

INDEX, DIFUNCTIONAL COMPOUNDS

Sections—**heavy type**

Pages—*light type*

	Acetylene	Carboxylic acid	Alcohol	Aldehyde	Amide	Amine	Ester	Ether, epoxide	Halide	Ketone	Nitrile	Olefin
Acetylene	**300** 336											
Carboxylic acid		**312** 342										
Alcohol	**302** 337	**313** 343	**323** 353									
Aldehyde	**303** 338		**324** 356									
Amide	**304** 338	**315** 345	**325** 357		**342** 395							
Amine		**316** 346	**326** 360			**350** 401						
Ester	**306** 338	**317** 348	**327** 361	**336** 386	**344** 396	**351** 401	**357** 412					
Ether, epoxide	**307** 339		**328** 364	**337** 386		**352** 404	**358** 412	**363** 441				
Halide	**308** 340	**319** 348	**329** 365		**346** 398	**353** 405	**359** 413	**364** 441	**368** 450			
Ketone	**309** 340	**320** 350	**330** 365	**339** 387	**347** 398	**354** 405	**360** 415	**365** 442	**369** 452	**372** 458		
Nitrile		**321** 351	**331** 375	**340** 388		**355** 407	**361** 422	**366** 444	**370** 454	**373** 467	**375** 489	
Olefin	**311** 341	**322** 351	**332** 376	**341** 388	**349** 399	**356** 407	**362** 423	**367** 444	**371** 455	**374** 468	**376** 489	**377** 491

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

INTRODUCTION

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

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

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

The terms hydrides, alkyls, and aryls classify compounds containing reacting hydrogens, alkyl groups, and aryl groups, respectively; for example, $RCH_2\text{-}H \rightarrow RCH_2COOH$ (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). Alkylations which involve additions across a double bond are found in section 74, Alkyls from Olefins.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Chapter 1 PREPARATION OF ACETYLENES

Section 1 Acetylenes from Acetylenes

$$\mathrm{PhC{\equiv}CH} \xrightarrow[\substack{\text{2) Bu}_3\text{B} \\ \text{3) MeSOCl}}]{\text{1) BuLi}} \mathrm{PhC{\equiv}CBu} \qquad 80\%$$

Tetrahedron (1974) 30 2159

$$\mathrm{HC{\equiv}CCH_2OH} \xrightarrow[\text{2) } \underline{n}\text{-C}_6\text{H}_{13}\text{Br}]{\text{1) LiNH}_2\text{, NH}_3} \underline{n}\text{-}\mathrm{C_6H_{13}\text{-}C{\equiv}CCH_2OH} \qquad 60\%$$

JOC USSR (1975) 11 517

$$\mathrm{PhC{\equiv}CH} + \mathrm{PhI} \xrightarrow[\text{Et}_2\text{NH}]{(\text{Ph}_3\text{P})_2\ \text{PdCl}_2/\text{CuI}} \mathrm{PhC{\equiv}CPh} \qquad 90\%$$

Tetr Lett (1975) 4467

$$\mathrm{PhI} + \underline{n}\text{-}\mathrm{PrC{\equiv}CH} \xrightarrow[\text{NaOMe, DMF}]{\text{Pd(PPh}_3)_4} \mathrm{PhC{\equiv}C}\text{-}\underline{n}\text{-}\mathrm{Pr} \qquad 97\%$$

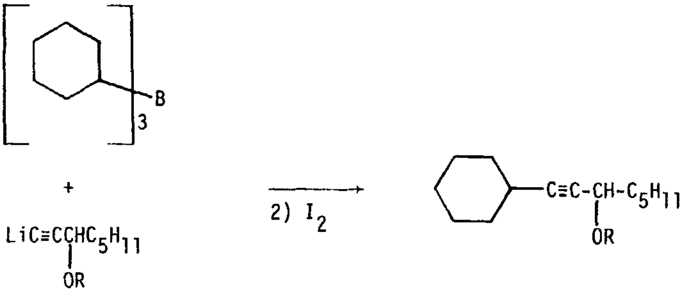
J Organometal Chem (1975) 93 253, 259

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

JOC (1974) 39 731

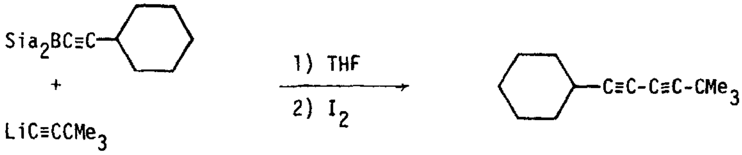
$\underline{i}\text{-}Bu_3B + LiC\equiv CCl \xrightarrow[\text{2) } NaOH/H_2O_2]{\text{1) } I_2\text{, -78°}} \underline{i}\text{-}BuC\equiv C\text{-}Bu\text{-}\underline{i}$ 85%

Tetr Lett (1975) 1961



65%

JOC (1976) 41 3947

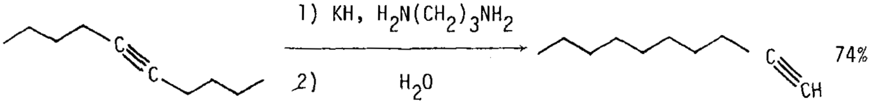


70%

JOC (1976) 41 1078

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

JACS (1975) 97 7385



JACS (1975) 97 891

Section 2 Acetylenes from Carboxylic Acids

No additional examples

Section 3 Acetylenes from Alcohols

No additional examples

Section 4 Acetylenes from Aldehydes

No additional examples

Section 5 Acetylenes from Alkyls, Methylenes and Aryls

No examples

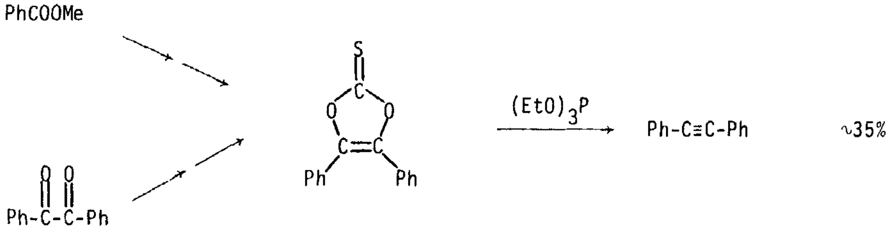
Section 6 Acetylenes from Amides

No additional examples

Section 7 Acetylenes from Amides

No additional examples

Section 8 Acetylenes from Esters



JOC (1976) 41 2640

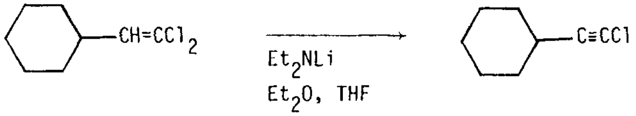
Section 9 Acetylenes from Ethers

No examples

Section 10 Acetylenes from Halides

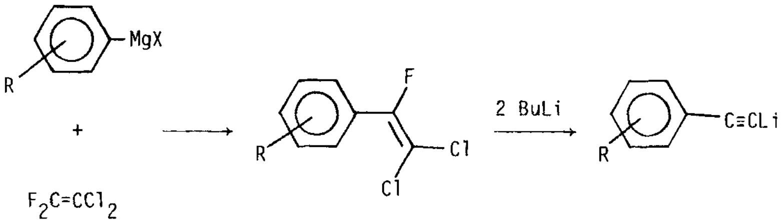
$$HCBr{=}CBrH \xrightarrow[\text{rfx}]{\text{2 eq. Ph}_2\text{PLi, THF}} HC{\equiv}CH \qquad 80\%$$

Tetr Lett (1975) 4709

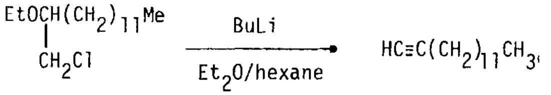


80%

Synthesis (1975) 458



JOC (1976) 41 1487 ∿60-80%



$$EtOCH(CH_2)_{11}Me \text{ (with } CH_2Cl\text{)} \xrightarrow[\text{Et}_2\text{O/hexane}]{\text{BuLi}} HC{\equiv}C(CH_2)_{11}CH_3 \qquad 81\%$$

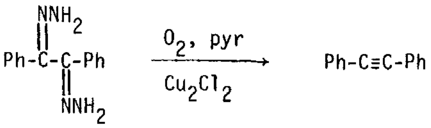
Synth Comm (1975) 5 331

Section 11 Acetylenes from Hydrides

No examples

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

Section 12 Acetylenes from Ketones



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

90%

Chem Lett (1976) 147

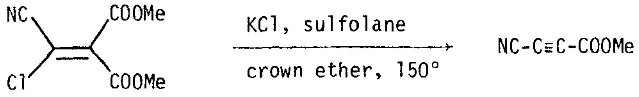
Section 13 Acetylenes from Nitriles

No examples

Section 14 Acetylenes from Olefins

No additional examples

Section 15 Acetylenes from Miscellaneous Compounds



16%

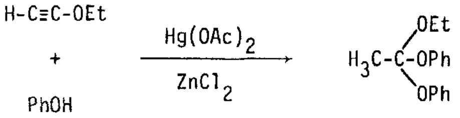
Tetr Lett (1975) 2429

Section 15A Protection of Acetylenes

No additional examples

Chapter 2 PREPARATION OF CARBOXYLIC ACIDS ACID HALIDES AND ANHYDRIDES

Section 16 Carboxylic Acids from Acetylenes



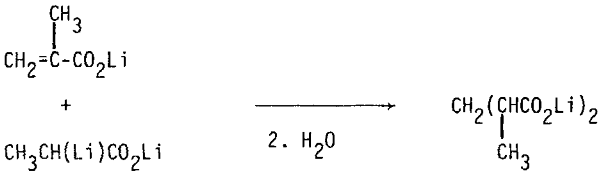
$$H\text{-}C{\equiv}C\text{-}OEt + PhOH \xrightarrow[ZnCl_2]{Hg(OAc)_2} H_3C\text{-}C(OEt)(OPh)_2$$

75%

Rec Trav Chim (1975) 94 209

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

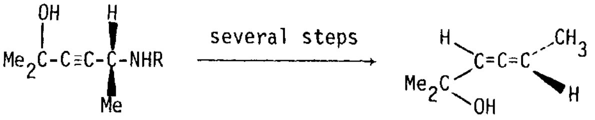
Section 17 Carboxylic Acids, Acid Halides and Anhydrides from Carboxylic Acids



$$CH_2{=}C(CH_3)\text{-}CO_2Li + CH_3CH(Li)CO_2Li \xrightarrow[2.\ H_2O]{} CH_2(CH(CH_3)CO_2Li)_2$$

66%

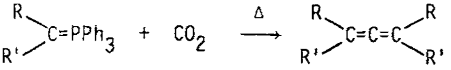
Gazz Chim Ital (1976) 106 201



~30%

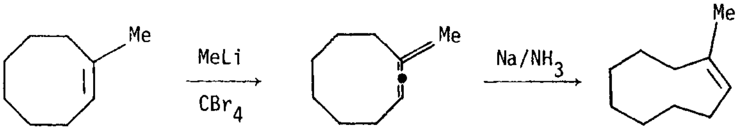
33% ee

JACS (1975) 97 2919



~30%

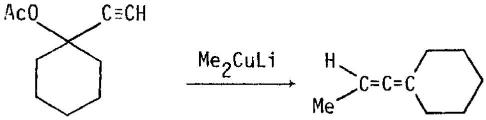
Tetr Lett (1974) 1275



95%

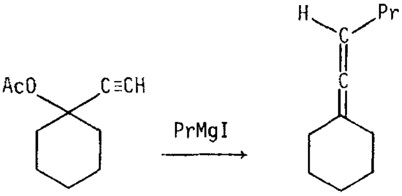
65%

Synthesis (1975) 194



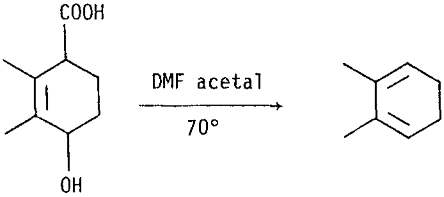
80%

JCS Chem Comm (1976) 183



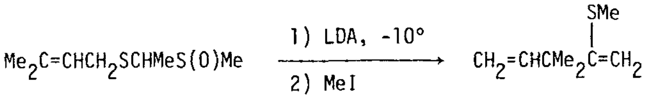
72%

Angew Int Ed (1976) 15 496



94%

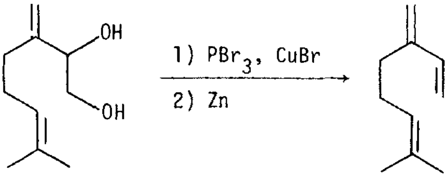
Helv Chim Acta (1975) 58 1450



$$Me_2C{=}CHCH_2SCHMeS(O)Me \xrightarrow[\text{2) MeI}]{\text{1) LDA, -10°}} CH_2{=}CHCMe_2\overset{\overset{\displaystyle SMe}{|}}{C}{=}CH_2$$

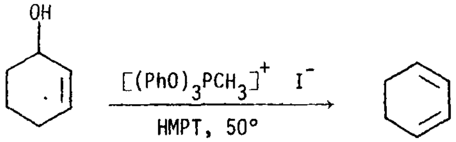
54%

Comptes Rendus (1975) 280 1231;1327



58%

JACS (1975) 97 3252



78%

Synthesis (1976) 108

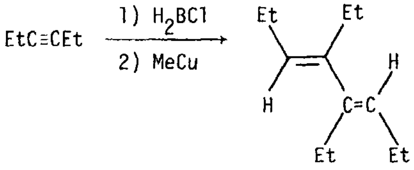
$$R'R^2C{=}CHBr \;+\; R^3CH{=}CHR^4 \xrightarrow[L_2Pd(OAc)_2,\ 100°]{Et_3N} R'R^2C{=}CHCR^3{=}CHR^4$$

JOC (1975) 40 1083

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

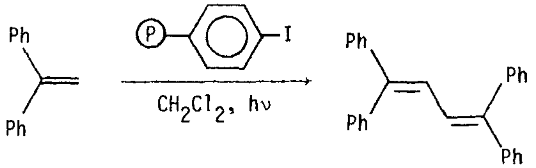
95%

JACS (1975) 97 341



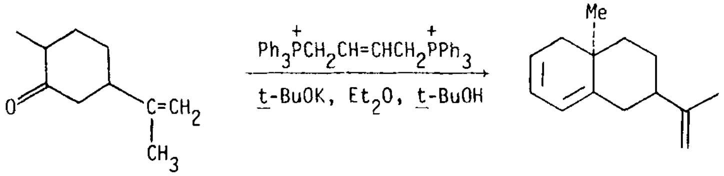
100%

JACS (1975) 97 5606



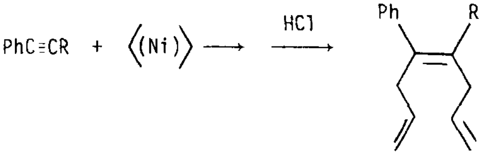
80%

Synth Comm (1976) 6 309



85%

JOC (1975) 40 100



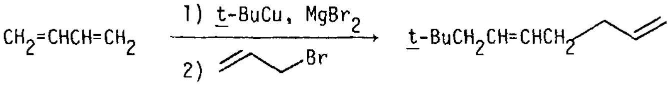
50%

J Organometal Chem (1975) 96 C19

$$\mathrm{PhSe(O)CH_3} \xrightarrow[\substack{\text{2) PhCH=CHCH}_2\text{Br}\\ \text{3) HOAc}\\ \text{4) CH}_2\text{Cl}_2\text{, rfx}}]{\text{1) LDA, THF, -78°}} \mathrm{PhCH{=}CHCH_2CH{=}CHPh}$$

75%

JACS (1975) 97 3250



90%

J Organometal Chem (1975) 92 C28

$$\text{i-PrSCH}_2\text{CH=CH}_2 \xrightarrow[\substack{\text{2) CuI, -78°}\\ \text{3) CH}_2\text{=CHCH}_2\text{Br}}]{\text{1) s-BuLi, -25°}} \text{i-PrSCH=CHCH}_2\text{CH}_2\text{CH=CH}_2$$

88%

Bull Chem Soc Japan (1975) 48 1567