
**Volume 43:
Polyynes, Arynes, Enynes, and Alkynes**

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
	Introduction	
	H. Hopf	1
43.1	Product Class 1: Linear Conjugated Diynes, Oligoynes, and Polyynes	
	A. Hirsch and O. Vostrowsky	37
43.2	Product Class 2: Cyclic Conjugated Diynes, Triynes, Tetraynes, and Polyynes	
	F. Diederich, R. R. Tykwinski, and M. B. Nielsen	119
43.3	Product Class 3: Arynes	
	T. L. Gilchrist	151
43.4	Product Class 4: Linear Enynes	
	C. Burmester, O. Haß, and R. Faust	225
43.5	Product Class 5: Cyclic Enynes	
	A. G. Fallis and M. S. Souweha	289
43.6	Product Class 6: Acyclic Arylalkynes	
	A. G. Griesbeck and A. Soldevilla	345
43.7	Product Class 7: Cyclic Arylalkynes	
	Y. Tobe and R. Umeda	393
43.8	Product Class 8: Linear Alkynes	
43.8.1	Synthesis by Elimination	
	S. Sankararaman	435
43.8.2	Synthesis by Rearrangement	
	A. Krueger	469
43.8.3	Synthesis from Other Alkynes	
	R. A. Aitken and K. Aitken	555
43.9	Product Class 9: Cycloalkynes	
	R. Gleiter and D. B. Werz	631

Keyword Index	669
Author Index	707
Abbreviations	739

Table of Contents

Introduction		
H. Hopf		
<hr/>		
	Introduction	1
43.1	Product Class 1: Linear Conjugated Diynes, Oligoynes, and Polyynes	
A. Hirsch and O. Vostrowsky		
<hr/>		
43.1	Product Class 1: Linear Conjugated Diynes, Oligoynes, and Polyynes	37
43.1.1	Product Subclass 1: Alka-1,3-diynes	38
43.1.1.1	Synthesis of Product Subclass 1	38
43.1.1.1.1	Method 1: Copper-Promoted Oxidative Homocoupling of Terminal Alkynes	38
43.1.1.1.1.1	Variation 1: Glaser Coupling	39
43.1.1.1.1.2	Variation 2: Eglinton Coupling	42
43.1.1.1.1.3	Variation 3: Hay Coupling	44
43.1.1.1.1.4	Variation 4: Copper-Promoted Oxidative Homocoupling of Silylacetylenes	48
43.1.1.1.1.5	Variation 5: Copper-Mediated Solid-State Coupling	49
43.1.1.1.1.6	Variation 6: Silver(I) 4-Toluenesulfonate/Copper(II) Chloride/ <i>N,N,N',N'</i> -Tetramethylethylenediamine Catalytic System and Solid-Phase On-Bead Coupling	49
43.1.1.1.2	Method 2: Heterocoupling of Terminal Alkynes with 1-Haloalkynes	51
43.1.1.1.2.1	Variation 1: The Cadiot–Chodkiewicz Coupling	51
43.1.1.1.2.2	Variation 2: Polymer-Supported Cadiot–Chodkiewicz Coupling	54
43.1.1.1.2.3	Variation 3: Other Copper(I)-Catalyzed Heterocoupling Reactions	55
43.1.1.1.2.4	Variation 4: Cross Coupling of Alkynyl(phenyl)iodonium 4-Toluenesulfonates	56
43.1.1.1.2.5	Variation 5: Copper(I)-Promoted Heterocoupling between Silylalkynes and Chloroalkynes	57
43.1.1.1.3	Method 3: Homocoupling of Alkynyl Grignard Compounds	57
43.1.1.1.4	Method 4: Heterocoupling of Alkynyl Grignard Derivatives with 1-Haloalkynes	58
43.1.1.1.5	Method 5: Homocoupling of Alkynyllithium Compounds	59
43.1.1.1.6	Method 6: Coupling of Alkynylstannanes	60
43.1.1.1.6.1	Variation 1: Homocoupling of Alkynylstannanes	60
43.1.1.1.6.2	Variation 2: Cross Coupling of Alkynylstannanes	60
43.1.1.1.7	Method 7: Homocoupling and Cross Coupling of Alkynylboron Derivatives	61
43.1.1.1.8	Method 8: Dimerization of 1-Selanylalkynes	62
43.1.1.1.9	Method 9: Demercuration of Bis(alkynyl)mercury Compounds	63
43.1.1.1.10	Method 10: Coupling of Alkynylnickel Complexes	63
43.1.1.1.11	Method 11: Buta-1,3-diynes from Alkynylzirconocenes	64
43.1.1.1.12	Method 12: Palladium-Catalyzed Coupling of Terminal Alkynes	64
43.1.1.1.12.1	Variation 1: Homocoupling of Terminal Alkynes	65
43.1.1.1.12.2	Variation 2: Heterocoupling of Terminal Alkynes	67

43.1.1.1.13	Method 13:	Palladium-Catalyzed Coupling of Alkynylstannanes	70
43.1.1.1.14	Method 14:	Other Transition-Metal-Mediated Alkyne Coupling Processes	70
43.1.1.1.15	Method 15:	Elimination of a Hydrogen Halide from 1,4-Dihalobut-2-yne	71
43.1.1.1.16	Method 16:	Elimination of a Hydrogen Halide from Haloalkenyne	72
43.1.1.1.16.1	Variation 1:	Elimination of a Hydrogen Halide from 1-Haloalk-1-en-3-yne	72
43.1.1.1.16.2	Variation 2:	Elimination of a Hydrogen Halide from 2-Haloalk-1-en-3-yne	75
43.1.1.1.16.3	Variation 3:	Elimination of a Hydrogen Halide from 1-Haloalk-3-en-1-yne	76
43.1.1.1.17	Method 17:	Buta-1,3-diyne Formation from Carbenes and Carbenoids (Fritsch–Buttenberg–Wiechell Rearrangement)	77
43.1.1.1.18	Method 18:	Synthesis of Buta-1,3-diyne via Phosphorus Ylides	79
43.1.1.1.18.1	Variation 1:	Wittig Synthesis Using Phosphacumulene Ylides	79
43.1.1.1.18.2	Variation 2:	Flash-Vacuum Pyrolysis of 2-Oxoalk-3-ynylidene-triphenyl- phosphoranes	80
43.1.1.1.19	Method 19:	Base-Catalyzed Triple-Bond Isomerizations (Zipper Reaction)	82
43.1.2	Product Subclass 2: Linear Conjugated Oligoynes and Polyyne		83
43.1.2.1	Synthesis of Product Subclass 2		83
43.1.2.1.1	Method 1:	Convergent Synthesis of Polyyne by Acetylene Coupling Reactions	83
43.1.2.1.1.1	Variation 1:	Glaser Coupling	83
43.1.2.1.1.2	Variation 2:	Eglinton Coupling	84
43.1.2.1.1.3	Variation 3:	Hay Coupling	86
43.1.2.1.2	Method 2:	Cadiot–Chodkiewicz Cross Coupling	91
43.1.2.1.3	Method 3:	Tetraynes from Oxidative Homocoupling of Alkadiynyl Grignard Derivatives	94
43.1.2.1.4	Method 4:	Homocoupling of Transition-Metal-Bound Buta-1,3-diyne	95
43.1.2.1.5	Method 5:	Iterative Synthesis of Polyyne Using Acetylene Coupling Reactions	95
43.1.2.1.6	Method 6:	Dehydrohalogenation of Halogenated Polyyne Precursors	98
43.1.2.1.6.1	Variation 1:	Elimination of Hydrogen Chloride from 1,6-Dichlorohexa-2,4-diyne	98
43.1.2.1.6.2	Variation 2:	Convergent Synthesis of Polyyne by the Alkynylation/ Elimination of 1,1-Dibromoalk-1-en-3-yne	99
43.1.2.1.7	Method 7:	Polyne Formation from Carbenes and Carbenoids (Fritsch–Buttenberg–Wiechell Rearrangement)	100
43.1.2.1.8	Method 8:	Synthesis of Higher Polyyne by Pyrolysis	104
43.1.2.1.8.1	Variation 1:	Flash-Vacuum Pyrolysis of Ethyl 3-Oxo-7-(4-tolyl)- 2-(triphenylphosphoranylidene)hepta-4,6-dienoate	104
43.1.2.1.8.2	Variation 2:	Linear Polyyne from Solution-Spray Flash-Vacuum Pyrolysis of Cyclobutene-1,2-dione	105
43.1.3	Product Subclass 3: Polydisperse Polyene Fractions with Varying Numbers of Triple Bonds		105
43.1.3.1	Synthesis of Product Subclass 3		105
43.1.3.1.1	Method 1:	Laser Ablation of Carbon Particles in Suspension	105
43.1.3.1.2	Method 2:	Synthesis by Electric Arc Discharge	106
43.1.3.1.3	Method 3:	Synthesis of Polydisperse Polyene Solutions from the Hydrolysis of Carbides	107

43.1.3.1.4	Method 4: Polydisperse α,ω -Dicyanopolyne Fractions from Electric Arcing	108
43.2	Product Class 2: Cyclic Conjugated Diynes, Triynes, Tetraynes, and Polyynes F. Diederich, R. R. Tykwinski, and M. B. Nielsen	
43.2	Product Class 2: Cyclic Conjugated Diynes, Triynes, Tetraynes, and Polyynes	119
43.2.1	Product Subclass 1: Cyclic Conjugated Diynes	119
43.2.1.1	Synthesis of Product Subclass 1	119
43.2.1.1.1	Oxidative Homocoupling	119
43.2.1.1.1.1	Method 1: Glaser–Eglinton Conditions with Terminal Alkynes	120
43.2.1.1.1.1.1	Variation 1: Synthesis via Oligomerization under Standard Conditions ...	120
43.2.1.1.1.1.2	Variation 2: Synthesis via Oligomerization with Addition of Copper(I) Chloride	122
43.2.1.1.1.1.3	Variation 3: Synthesis via Oligomerization under Oxygen-Free Conditions	123
43.2.1.1.1.1.4	Variation 4: Synthesis via Oligomerization in Acetonitrile	123
43.2.1.1.1.1.5	Variation 5: Stepwise Synthesis under Standard Conditions	124
43.2.1.1.1.1.6	Variation 6: Stepwise Synthesis with Addition of Copper(I) Chloride	125
43.2.1.1.1.1.7	Variation 7: Stepwise Synthesis under Oxygen-Free Conditions	126
43.2.1.1.1.2	Method 2: Hay Conditions with Terminal Alkynes	127
43.2.1.1.1.2.1	Variation 1: Synthesis via Oligomerization	127
43.2.1.1.1.2.2	Variation 2: Stepwise Synthesis	129
43.2.1.1.2	Oxidative Heterocoupling of Terminal Alkynes and Bromoalkynes	130
43.2.1.1.2.1	Method 1: Cadiot–Chodkiewicz Conditions	130
43.2.1.1.2.1.1	Variation 1: With Pyridine as Solvent	130
43.2.1.1.2.1.2	Variation 2: Under Palladium Catalysis	132
43.2.1.1.3	Nucleophilic Substitution	133
43.2.1.1.3.1	Method 1: Reaction of Sodium Acetylides with Alkyl Bromides	133
43.2.1.1.3.1.1	Variation 1: Synthesis of Symmetrical Diynes	133
43.2.1.1.3.1.2	Variation 2: Synthesis of Unsymmetrical Diynes	134
43.2.1.1.4	Cumulene Dimerization	135
43.2.1.1.4.1	Method 1: Dimerization under Copper Catalysis	135
43.2.1.1.4.2	Method 2: Dimerization without Copper Catalysis	135
43.2.1.1.4.3	Method 3: 1,6-Elimination from 1,6-Dibromohexa-2,4-diyne Followed by Dimerization	136
43.2.1.1.5	Iodolactonization	136
43.2.1.2	Applications of Product Subclass 1 in Organic Synthesis	137
43.2.1.2.1	Method 1: Reaction with Sulfur	137
43.2.1.2.2	Method 2: Reaction with Tetrachlorothiophene 1,1-Dioxide	137
43.2.1.2.3	Method 3: Palladium-Catalyzed Enyne–Diyne Cross-Benzannulation ...	138
43.2.1.2.4	Method 4: Hydrogenation	138

43.2.1.2.5	Method 5: Reduction with a Trialkylborane	139
43.2.1.2.6	Method 6: Annulene Formation	139
43.2.1.2.7	Method 7: Radialene Formation	139
43.2.1.2.8	Method 8: Transannular Cyclization	140
43.2.1.2.8.1	Variation 1: With Potassium Hydroxide	140
43.2.1.2.8.2	Variation 2: With Potassium Hydroxide and Heat	140
43.2.1.2.8.3	Variation 3: With Sodium Bis(2-methoxyethoxy)aluminum Hydride	141
43.2.2	Product Subclass 2: Cyclic Conjugated Triynes	141
43.2.2.1	Synthesis of Product Subclass 2	141
43.2.2.1.1	Nucleophilic Substitution	141
43.2.2.1.1.1	Method 1: Reaction of Sodium Acetylides with Alkyl Bromides	142
43.2.3	Product Subclass 3: Cyclic Conjugated Tetraynes	142
43.2.3.1	Synthesis of Product Subclass 3	142
43.2.3.1.1	Oxidative Homocoupling	142
43.2.3.1.1.1	Method 1: Glaser–Eglinton Conditions	142
43.2.3.1.2	Carbenoid Rearrangement	143
43.2.3.1.2.1	Method 1: Fritsch–Buttenberg–Wiechell Conditions	143
43.2.4	Product Subclass 4: Cyclic Conjugated Polyynes	144
43.2.4.1	Synthesis of Product Subclass 4	144
43.2.4.1.1	Method 1: Decarbonylation	144
43.2.4.1.2	Method 2: Retro-Diels–Alder Reactions	145
43.2.4.1.3	Method 3: Retro-[2+2] Reactions	145
43.2.4.1.4	Method 4: [2+1]-Cheletropic Fragmentation	146
43.2.4.2	Applications of Product Subclass 4 in Organic Synthesis	146
43.2.4.2.1	Method 1: Reaction with Furan	146
43.2.4.2.2	Method 2: Fullerene Formation	147
43.3	Product Class 3: Arynes	
	T. L. Gilchrist	
43.3	Product Class 3: Arynes	151
43.3.1	Product Subclass 1: 1,2-Didehydroarenes and 1,2-Didehydroheterarenes	156
43.3.1.1	Synthesis of Product Subclass 1	156
43.3.1.1.1	Method 1: Elimination of Hydrogen	156
43.3.1.1.2	Method 2: Elimination of a Hydrogen and a Halogen Function	156
43.3.1.1.3	Method 3: Elimination of a Hydrogen and a Nitrogen Function	162
43.3.1.1.4	Method 4: Elimination of a Hydrogen and an Oxygen Function	162
43.3.1.1.5	Method 5: Elimination of a Hydrogen and a Sulfur or Selenium Function	163
43.3.1.1.6	Method 6: Elimination of a Silicon and a Halogen Function	163
43.3.1.1.7	Method 7: Elimination of a Silicon and an Oxygen Function	166
43.3.1.1.8	Method 8: Elimination of Two Carbon Functions	168
43.3.1.1.8.1	Variation 1: From Benzocyclobutene-1,2-diones	168

43.3.1.1.8.2	Variation 2:	From Phthalic Anhydrides	170
43.3.1.1.8.3	Variation 3:	From Phthaloyl Peroxide	173
43.3.1.1.8.4	Variation 4:	From 1 <i>H</i> -2,3-Benzoxazin-1-ones	173
43.3.1.1.9	Method 9:	Elimination of a Carbon and a Halogen Function	174
43.3.1.1.10	Method 10:	Elimination of a Carbon and an Oxygen Function	175
43.3.1.1.11	Method 11:	Elimination of a Carbon and a Nitrogen Function	175
43.3.1.1.11.1	Variation 1:	From <i>ortho</i> -Diazonioarene-carboxylates	175
43.3.1.1.11.2	Variation 2:	From <i>ortho</i> -(3,3-Dimethyltriaz-1-enyl)arene-carboxylic Acids	177
43.3.1.1.12	Method 12:	Elimination of Two Halogen Functions	178
43.3.1.1.12.1	Variation 1:	From <i>ortho</i> -Haloarylmagnesium Halides	178
43.3.1.1.12.2	Variation 2:	From <i>ortho</i> -Haloarylithium Species	179
43.3.1.1.13	Method 13:	Elimination of a Halogen and an Oxygen Function	181
43.3.1.1.13.1	Variation 1:	From <i>ortho</i> -(Arylsulfonyloxy)arylmagnesium Chlorides	181
43.3.1.1.13.2	Variation 2:	From <i>ortho</i> -Sulfonylarylithium Compounds	183
43.3.1.1.14	Method 14:	Elimination of a Halogen and a Sulfur Function	184
43.3.1.1.15	Method 15:	Elimination of a Nitrogen and a Sulfur Function	184
43.3.1.1.16	Method 16:	Elimination of Two Nitrogen Functions	185
43.3.1.2	Applications of Product Subclass 1 in Organic Synthesis		187
43.3.1.2.1	Method 1:	Diels–Alder Reactions	188
43.3.1.2.2	Method 2:	1,3-Dipolar Cycloaddition Reactions	191
43.3.1.2.3	Method 3:	[2 + 2]-Cycloaddition Reactions	194
43.3.1.2.4	Method 4:	Ene Reactions	196
43.3.1.2.5	Method 5:	Reactions with Nucleophiles	197
43.3.1.2.6	Method 6:	Reactions Catalyzed by Palladium	203
43.3.2	Product Subclass 2: 1,3-Didehydroarenes and 1,3-Didehydroheterarenes		206
43.3.2.1	Synthesis of Product Subclass 2		207
43.3.2.1.1	Method 1:	Elimination of Two Carbon Functions	207
43.3.2.1.1.1	Variation 1:	From Diacetyl Isophthaloyl Peroxide	207
43.3.2.1.1.2	Variation 2:	From Cyclophanediones	208
43.3.2.1.2	Method 2:	Elimination of Two Halogen Functions	208
43.3.2.1.3	Method 3:	Elimination of Two Nitrogen Functions	209
43.3.2.1.4	Method 4:	Routes Applicable to Specific <i>meta</i> -Arynes	209
43.3.2.1.4.1	Variation 1:	Synthesis of 2-Chloro-1,3-didehydronaphthalene by Elimination of Hydrogen and Halogen Functions	209
43.3.2.1.4.2	Variation 2:	Synthesis of 2,4-Didehydrophenol by Elimination of a Carbon and a Nitrogen Function	210
43.3.2.1.4.3	Variation 3:	Synthesis of 2-Phenyl-1,3-didehydrobenzene by Rearrangement	210
43.3.2.1.4.4	Variation 4:	Synthesis of 1,8-Didehydronaphthalene by Elimination of Two Nitrogen Functions	211
43.3.2.1.4.5	Variation 5:	Synthesis of 1,2,3-Tridehydrobenzene by Elimination of One Halogen and Two Carbon Functions	211
43.3.2.1.4.6	Variation 6:	Synthesis of Trifluoro-1,3,5-tridehydrobenzene by Elimination of Three Halogen Functions	212
43.3.3	Product Subclass 3: 1,4-Didehydroarenes and 1,4-Didehydroheterarenes		212
43.3.3.1	Synthesis of Product Subclass 3		213

43.3.3.1.1	Method 1:	Elimination of Two Carbon Functions	213
43.3.3.1.1.1	Variation 1:	From Diacyl Terephthaloyl Peroxides	213
43.3.3.1.1.2	Variation 2:	From Propellanes	213
43.3.3.1.2	Method 2:	Elimination of Two Halogen Functions	214
43.3.3.1.3	Method 3:	Rearrangement Reactions	215
43.4	Product Class 4: Linear Enynes		
	C. Burmester, O. Haß, and R. Faust		
43.4	Product Class 4: Linear Enynes		225
43.4.1	Synthesis of Product Class 4		225
43.4.1.1	Method 1:	Palladium-Catalyzed Cross-Coupling Reactions	225
43.4.1.1.1	Variation 1:	Using Terminal Alkynes	225
43.4.1.1.2	Variation 2:	Using Organoboron Compounds	228
43.4.1.1.3	Variation 3:	Using Organomagnesium Compounds	230
43.4.1.1.4	Variation 4:	Using Organotin Compounds	232
43.4.1.1.5	Variation 5:	Using Organozinc Compounds	234
43.4.1.2	Method 2:	Copper-Mediated Reactions	235
43.4.1.2.1	Variation 1:	Copper(I) Catalysis with Terminal Alkynes	236
43.4.1.2.2	Variation 2:	Starting from Vinylboranes	237
43.4.1.2.3	Variation 3:	Starting from Other Vinyl Organometallic Compounds	239
43.4.1.2.4	Variation 4:	Starting from Alkynylcopper Species	240
43.4.1.3	Method 3:	Carbene Reactions	241
43.4.1.4	Method 4:	Elimination Reactions To Form the Alkene	244
43.4.1.4.1	Variation 1:	From Propargylic Systems	244
43.4.1.4.2	Variation 2:	From Cyclic Carbonates	247
43.4.1.4.3	Variation 3:	Coupling–Elimination Reactions	248
43.4.1.4.4	Variation 4:	By Carbonyl Alkenation	249
43.4.1.4.5	Variation 5:	From Silicon or Sulfur Compounds	252
43.4.1.5	Method 5:	Elimination Reactions To Form the Alkyne	254
43.4.1.5.1	Variation 1:	From 1,1-Dibromobutadienes	254
43.4.1.5.2	Variation 2:	From Vinyl Sulfones	255
43.4.1.6	Method 6:	Addition Reactions to Diynes	257
43.4.1.6.1	Variation 1:	Addition of Complex Aluminum and Boron Hydrides	257
43.4.1.6.2	Variation 2:	Hydrosilylation, Hydrostannylation, and Stannylcupration of Diynes	258
43.4.1.6.3	Variation 3:	Hydroaminations, Hydrophosphinylations, and the Addition of Alcohols, Thiols, and Higher Group 16 Analogues	260
43.4.1.6.4	Variation 4:	Addition of Carbon Fragments	263
43.4.1.7	Method 7:	Synthesis from Heterocyclic Compounds	266
43.4.1.8	Method 8:	Synthesis by Rearrangement	268
43.4.1.9	Method 9:	Alkyne Dimerizations	273
43.4.1.9.1	Variation 1:	Base-Induced Dimerizations	273
43.4.1.9.2	Variation 2:	Transition-Metal-Catalyzed Alkyne Dimerizations	274
43.4.1.9.3	Variation 3:	Rare Earth and Main Group Metal Catalyzed Dimerizations	279

43.5	Product Class 5: Cyclic Enynes A. G. Fallis and M. S. Souweha	
43.5	Product Class 5: Cyclic Enynes	289
43.5.1	Product Subclass 1: Cyclooctenyne	290
43.5.1.1	Synthesis of Product Subclass 1	290
43.5.1.1.1	Method 1: Alkyne Formation Post Ring Closure	290
43.5.1.1.1.1	Variation 1: Base-Mediated Cycloelimination Reaction	290
43.5.2	Product Subclass 2: Cyclononyne	291
43.5.2.1	Synthesis of Product Subclass 2	293
43.5.2.1.1	Method 1: Ring Closure by Alkynylmetal Condensations with Carbonyl Groups and Related Electrophiles	293
43.5.2.1.2	Method 2: Ring Closure by Condensation of Alkyne–Hexacarbonyl- dicobalt Complexes (Nicholas Reaction)	294
43.5.2.1.3	Method 3: Ring-Contraction Reactions	295
43.5.2.1.3.1	Variation 1: Wittig Rearrangement	295
43.5.2.1.3.2	Variation 2: Photochemical Sulfur Dioxide Extrusion	295
43.5.2.1.4	Method 4: Alkene Formation Post Ring Closure	296
43.5.2.1.4.1	Variation 1: Elimination Reactions with Base	296
43.5.2.1.4.2	Variation 2: Decomplexation Reactions	296
43.5.2.1.5	Method 5: Alkyne Formation Post Ring Closure	297
43.5.3	Product Subclass 3: Cyclodecyne	297
43.5.3.1	Synthesis of Product Subclass 3	298
43.5.3.1.1	Method 1: Base-Mediated Ring Closure by Alkynylmetal Condensations with Carbonyl Groups and Related Electrophiles	298
43.5.3.1.1.1	Variation 1: Aldol Condensation Reaction	301
43.5.3.1.1.2	Variation 2: Carbene Insertion–Elimination Reaction	302
43.5.3.1.1.3	Variation 3: Chromium(II) Chloride/Nickel(II) Chloride Condensation Reactions	302
43.5.3.1.1.4	Variation 4: Alkynyltrimethylsilane Condensations with Fluoride Ion	305
43.5.3.1.1.5	Variation 5: Condensations from Enol Ethers with a Lewis Acid	306
43.5.3.1.2	Method 2: Ring Closure by Condensation of Alkyne–Hexacarbonyl- dicobalt Complexes (Nicholas Reaction)	306
43.5.3.1.2.1	Variation 1: With In Situ Enolization	308
43.5.3.1.3	Method 3: Pinacol Ring-Closure Reactions	309
43.5.3.1.3.1	Variation 1: Pinacol Ring Closure–Alkene Formation	310
43.5.3.1.4	Method 4: Palladium Coupling Reactions	311
43.5.3.1.4.1	Variation 1: Double Palladium Coupling Reactions	312
43.5.3.1.5	Method 5: Ring-Contraction Reactions	313
43.5.3.1.5.1	Variation 1: Sulfur Dioxide Extrusion	313
43.5.3.1.6	Method 6: Intramolecular Diels–Alder Reactions	314
43.5.3.1.7	Method 7: Alkene Formation Post Ring Closure	315
43.5.3.1.7.1	Variation 1: Thermolysis Reactions	315
43.5.3.1.7.2	Variation 2: Enzyme-Mediated Reactions	316
43.5.3.1.7.3	Variation 3: Allylic Rearrangement Reactions	316

43.5.3.1.7.4	Variation 4:	Dehydrogenation Reactions	317
43.5.3.1.7.5	Variation 5:	Retro-Diels–Alder Reactions	317
43.5.3.1.8	Method 8:	Alkyne Formation Post Ring Closure	318
43.5.3.1.9	Method 9:	Ruthenium Coupling Reactions	318
43.5.4	Product Subclass 4: Cycloundecenynes		319
43.5.4.1	Synthesis of Product Subclass 4		319
43.5.4.1.1	Method 1:	Ring Closure by Alkynylmetal Condensations with Carbonyl Groups and Related Electrophiles	319
43.5.4.1.1.1	Variation 1:	Chromium(II) Chloride/Nickel(II) Chloride Condensations	320
43.5.4.1.2	Method 2:	Ring Closure by Condensation of Alkyne–Hexacarbonyl-dicobalt Complexes (Nicholas Reaction)	320
43.5.4.1.3	Method 3:	Palladium Coupling Reactions	321
43.5.4.1.4	Method 4:	Ring-Contraction Reactions	321
43.5.4.1.4.1	Variation 1:	Sulfur Dioxide Extrusion	321
43.5.4.1.4.2	Variation 2:	Sigmatropic Rearrangements	322
43.5.4.1.5	Method 5:	Intramolecular Diels–Alder Reactions	323
43.5.4.1.6	Method 6:	Alkene Formation Post Ring Closure	323
43.5.4.1.6.1	Variation 1:	Thermolysis Reactions	323
43.5.5	Product Subclass 5: Cyclododecenynes		324
43.5.5.1	Synthesis of Product Subclass 5		324
43.5.5.1.1	Method 1:	Ring Closure by Chromium(II) Chloride/Nickel(II) Chloride Condensations	324
43.5.5.1.2	Method 2:	Copper Coupling Reactions	325
43.5.5.1.3	Method 3:	Ruthenium Coupling Reactions	326
43.5.5.1.4	Method 4:	Ring-Contraction Reactions	326
43.5.5.1.4.1	Variation 1:	Sulfur Dioxide Extrusion	326
43.5.5.1.5	Method 5:	Alkene Formation Post Ring Closure	327
43.5.5.1.5.1	Variation 1:	Thermolysis Reactions	327
43.5.5.1.6	Method 6:	Alkyne Formation Post Ring Closure	327
43.5.6	Product Subclass 6: Cyclotridecenynes		328
43.5.6.1	Synthesis of Product Subclass 6		328
43.5.6.1.1	Method 1:	Ring-Contraction Reactions	328
43.5.6.1.1.1	Variation 1:	Sulfur Dioxide Extrusion	328
43.5.6.1.1.2	Variation 2:	Sigmatropic Rearrangement Reaction	328
43.5.7	Product Subclass 7: Cyclotetradecenynes		329
43.5.7.1	Synthesis of Product Subclass 7		329
43.5.7.1.1	Method 1:	Ring-Contraction Reactions	329
43.5.7.1.1.1	Variation 1:	Sulfur Dioxide Extrusion	329
43.5.7.1.2	Method 2:	Copper Coupling Reactions	329
43.5.7.1.3	Method 3:	Ruthenium Coupling Reactions	330
43.5.8	Product Subclass 8: Cyclopentadecenynes		330
43.5.8.1	Synthesis of Product Subclass 8		330
43.5.8.1.1	Method 1:	Ring-Contraction Reactions	330

43.5.8.1.1.1	Variation 1: Sulfur Dioxide Extrusion	330
43.5.8.1.2	Method 2: Alkyne Formation Post Ring Closure	331
43.5.9	Product Subclass 9: Cyclohexadecenynes	331
43.5.9.1	Synthesis of Product Subclass 9	331
43.5.9.1.1	Method 1: Ruthenium Coupling Reactions	331
43.5.9.1.2	Method 2: Ring-Contraction Reactions	332
43.5.10	Product Subclass 10: Cyclophanes and Annulenes with Enyne Bridge Components	332
43.5.10.1	Synthesis of Product Subclass 10	332
43.5.10.1.1	Method 1: Copper Coupling Reactions	332
43.5.10.1.2	Method 2: Palladium Coupling Reactions	338
43.6	Product Class 6: Acyclic Arylalkynes A. G. Griesbeck and A. Soldevilla	
43.6	Product Class 6: Acyclic Arylalkynes	345
43.6.1	Synthesis of Product Class 6	347
43.6.1.1	Synthesis from Metalated Arenes and Haloalkynes	347
43.6.1.1.1	Method 1: Cross Coupling of Aryl Cuprates and Haloalkynes	347
43.6.1.1.2	Method 2: Cross Coupling of Aryl Stannanes and Haloalkynes	348
43.6.1.2	Synthesis from Haloarenes and Metal Alkynides	349
43.6.1.2.1	Method 1: Palladium-Catalyzed Cross Coupling with Tin Alkynides	349
43.6.1.2.2	Method 2: Palladium-Catalyzed Cross Coupling with Zinc Alkynides	350
43.6.1.2.3	Method 3: Palladium-Catalyzed Cross Coupling with Copper Alkynides (The Stephens–Castro Reaction)	351
43.6.1.2.4	Method 4: Palladium-Catalyzed Cross Coupling with Silicon Alkynides	352
43.6.1.2.5	Method 5: Palladium-Catalyzed Cross Coupling with Aluminum Alkynides	353
43.6.1.2.6	Method 6: Palladium-Catalyzed Cross Coupling with Magnesium Alkynides (Kumada–Corriu-Type Coupling)	355
43.6.1.2.7	Method 7: Palladium-Catalyzed Cross Coupling with Boron Alkynides	355
43.6.1.3	Synthesis from Haloarenes and Terminal Alkynes	357
43.6.1.3.1	Method 1: Silver/Palladium-Catalyzed Cross Coupling of Haloarenes and Terminal Alkynes	357
43.6.1.3.2	Method 2: Indium/Palladium-Catalyzed Cross Coupling of Haloarenes and Terminal Alkynes	358
43.6.1.3.3	Method 3: Zinc/Palladium-Catalyzed Cross Coupling of Haloarenes and Terminal Alkynes	359
43.6.1.3.4	Method 4: Copper/Palladium-Catalyzed Cross Coupling of Haloarenes and Terminal Alkynes (The Sonogashira–Hagihara Cross-Coupling Reaction)	359
43.6.1.3.4.1	Variation 1: Sonogashira Cross-Coupling Reactions for Bromoarenes Using Specially Designed Ligands	361

43.6.1.3.4.2	Variation 2:	Sonogashira Reaction under Microwave-Irradiation Conditions	362
43.6.1.3.4.3	Variation 3:	Sonogashira Reaction under Phase-Transfer Conditions	363
43.6.1.3.4.4	Variation 4:	Sonogashira Reactions in Water or Aqueous Mixtures of Solvents	364
43.6.1.3.5	Method 5:	Palladium-Catalyzed Cross Coupling (Copper-Free Sonogashira Reaction)	365
43.6.1.3.5.1	Variation 1:	Domino Halogen-Exchange (Halex) and Copper-Free Sonogashira Reaction	368
43.6.1.3.5.2	Variation 2:	Palladium-Catalyzed Cross Coupling in Water	369
43.6.1.3.5.3	Variation 3:	Palladium-Catalyzed Cross Coupling in Ionic Liquids	370
43.6.1.3.5.4	Variation 4:	Palladium-Catalyzed Coupling Using Palladium(0) Nanoparticles	371
43.6.1.3.5.5	Variation 5:	Solvent-Free Palladium-Catalyzed Cross Coupling	372
43.6.1.3.5.6	Variation 6:	Palladium-Catalyzed Cross Coupling Using Microwave Irradiation	373
43.6.1.3.6	Method 6:	Metal-Free Cross Coupling (Metal-Free Sonogashira Reaction)	374
43.6.1.4		Synthesis by Elimination	375
43.6.1.4.1	Method 1:	Elimination of Arylalkanes	375
43.6.1.4.1.1	Variation 1:	Halogenation Followed by Double Dehydrohalogenation	375
43.6.1.4.1.2	Variation 2:	Benzylation Followed by Double Dehydrohalogenation	376
43.6.1.4.2	Method 2:	Elimination from Vinylarenes	376
43.6.1.4.2.1	Variation 1:	1,1-Dehydrohalogenation and 1,1-Dehalogenation	376
43.6.1.4.3	Method 3:	Elimination of Carbon Monoxide from Cyclopropenones	377
43.6.1.4.4	Method 4:	Elimination of Dinitrogen from Five-Membered Heterocycles	379
43.6.1.4.5	Method 5:	Synthesis from Aromatic Aldehydes	380
43.6.1.4.5.1	Variation 1:	Alkenylation and Subsequent Elimination	380
43.6.1.4.5.2	Variation 2:	Corey–Fuchs Modification	381
43.6.1.4.5.3	Variation 3:	Seyferth–Gilbert Modification	382
43.6.1.4.5.4	Variation 4:	Bestmann–Ohira Modification	383
43.6.1.5		Synthesis by Metathesis Reactions	385
43.6.1.5.1	Method 1:	Alkyne Homodimerization	385
43.6.1.5.2	Method 2:	Alkyne Cross Metathesis	386
43.6.1.5.3	Method 3:	Ring-Closure Alkyne Metathesis	386
43.6.1.5.4	Method 4:	Acyclic Diyne Metathesis	387
43.7		Product Class 7: Cyclic Arylalkynes Y. Tobe and R. Umeda	
43.7		Product Class 7: Cyclic Arylalkynes	393
43.7.1		Synthesis of Product Class 7	393
43.7.1.1		Formation of Triple-Bond-Containing Rings by C–C Bond Formation	393
43.7.1.1.1	Method 1:	Formation of C(sp ³)–C(sp ³) Bonds by Wurtz-Type Coupling Reactions	393

43.7.1.1.2	Method 2:	Formation of C(sp ³)–C(sp) Bonds by Nucleophilic Substitution Reactions of Metal Acetylides with Haloalkanes	394
43.7.1.1.3	Method 3:	Formation of C(sp ²)–C(sp ²) Bonds by Copper(II)-Catalyzed Coupling Reactions of Aryllithiums	395
43.7.1.1.4	Method 4:	Formation of C(sp ²)–C(sp) Bonds by Transition-Metal-Catalyzed Cross-Coupling Reactions	396
43.7.1.1.4.1	Variation 1:	Stephens–Castro Reactions of Copper(I) Acetylides with Aryl and Vinyl Halides	396
43.7.1.1.4.2	Variation 2:	Copper(I)-Catalyzed Coupling of Acetylenes with Aryl Halides	398
43.7.1.1.4.3	Variation 3:	Hagihara–Sonogashira Reactions of Acetylenes with Aryl and Vinyl Halides	399
43.7.1.1.4.4	Variation 4:	Palladium(0)-Catalyzed Cross-Coupling Reactions of Acetylenes with Vinyl Trifluoromethanesulfonates	401
43.7.1.1.4.5	Variation 5:	In Situ Deprotection–Palladium(0)-Catalyzed Cross-Coupling Reactions	402
43.7.1.1.5	Method 5:	Formation of C(sp)–C(sp) Bonds by Transition-Metal-Mediated Oxidative Coupling Reactions	405
43.7.1.1.5.1	Variation 1:	Hay Coupling Reactions	406
43.7.1.1.5.2	Variation 2:	Eglinton Coupling Reactions	408
43.7.1.1.5.3	Variation 3:	Breslow’s Modification of Eglinton Coupling Reactions	412
43.7.1.1.5.4	Variation 4:	Preparation of Macrocyclic Arylacetylenes Using Covalently Bound Templates	415
43.7.1.1.5.5	Variation 5:	In Situ Deprotection–Eglinton-Type Coupling Reactions	416
43.7.1.1.5.6	Variation 6:	Palladium(II)-Catalyzed Oxidative Coupling Reactions of Terminal Alkynes	417
43.7.1.1.5.7	Variation 7:	Palladium(0)-Catalyzed Cross Coupling of Terminal Alkynes with Bromoalkynes	419
43.7.1.1.6	Method 6:	Alkyne Metathesis	420
43.7.1.1.7	Method 7:	Cycloaddition Reaction of Cumulenic Quinodimethanes	423
43.7.1.2		Formation of Triple-Bond-Containing Rings by Elimination Reactions	423
43.7.1.2.1	Method 1:	Double Dehydrohalogenation Reactions	424
43.7.1.2.2	Method 2:	Double Elimination Reactions of β-Substituted Sulfones	426
43.7.1.2.3	Method 3:	Oxidative Fragmentation of Bishydrazones	427
43.7.1.3		Formation of Aromatic Rings	428
43.7.1.3.1	Method 1:	Metal-Catalyzed Cyclotrimerizations	428
43.7.1.3.2	Method 2:	Palladium(0)-Catalyzed Enyne–Diyne [4+2] Cross Benzannulation	429
43.7.1.3.3	Method 3:	Valence Isomerization	430

43.8	Product Class 8: Linear Alkynes	
43.8.1	Synthesis by Elimination S. Sankararaman	
43.8.1	Synthesis by Elimination	435
43.8.1.1	1,2-Elimination	435
43.8.1.1.1	Method 1: Dehydrogenation of Alkanes and Alkenes	435
43.8.1.1.2	Method 2: Dehydrohalogenation of Vicinal Dihalalkanes	437
43.8.1.1.3	Method 3: Elimination Reactions of Heteroatom-Substituted Vinyl Derivatives	438
43.8.1.1.4	Method 4: Elimination of Vicinal Heteroatom Groups	441
43.8.1.2	1,1-Elimination	442
43.8.1.2.1	Method 1: Dehalogenation of 1,1-Dihaloalkenes (Corey–Fuchs Reaction)	442
43.8.1.2.1.1	Variation 1: Normal Corey–Fuchs Reactions	442
43.8.1.2.1.2	Variation 2: Modified Corey–Fuchs Reactions	444
43.8.1.2.2	Method 2: Rearrangement of Vinyl Carbenoids (Fritsch–Buttenburg– Wiechell Rearrangement)	445
43.8.1.3	Thermolytic Elimination	447
43.8.1.3.1	Method 1: Elimination Reactions of Vinyl Selenoxides	447
43.8.1.3.2	Method 2: Elimination Reactions of Thiirene Dioxides (Ramberg–Bäck- lund Reaction), Phosphirene Oxides, and α -Oxo Ylides	448
43.8.1.3.3	Method 3: Elimination Reactions of Cyclic 1,2,3-Selenadiazoles	450
43.8.1.4	Photolytic Elimination	451
43.8.1.4.1	Method 1: Cycloreversion of Fused Benzocyclobutene Derivatives	451
43.8.1.4.2	Method 2: Elimination of Carbon Monoxide from Cyclopropenone and Cyclobutenedione Derivatives	452
43.8.1.5	Double Elimination Reactions of 1,2-Disubstituted Motifs from Aldol-Type Condensations	454
43.8.1.5.1	Method 1: Wittig Reactions of (Halomethylene)phosphoranes and (Halomethyl)phosphonates	454
43.8.1.5.1.1	Variation 1: Wittig Reactions of (α -Halomethylene)phosphoranes	454
43.8.1.5.1.2	Variation 2: Wittig Reactions of (Halomethyl)phosphonates	455
43.8.1.5.2	Method 2: Synthesis Using α -Diazo β -Oxo Phosphonates (Bestmann–Ohira Reagent)	456
43.8.1.5.2.1	Variation 1: One-Pot Oxidation of Benzyl Alcohols and Subsequent Treatment with the Bestmann–Ohira Reagent	458
43.8.1.5.2.2	Variation 2: Reaction Using a Gel-Supported Bestmann–Ohira Reagent	459
43.8.1.5.3	Method 3: Aldol Condensation of α -Sulfonyl Anions with Aldehydes, Followed by Double Elimination	461
43.8.1.5.3.1	Variation 1: Double Elimination of Acetoxy and Siloxy Derivatives	461
43.8.1.5.3.2	Variation 2: Double Elimination Involving Peterson Elimination	461

43.8.1.5.3.3	Variation 3: Double Elimination Using a Chlorophosphonate as a Trapping Agent	462
43.8.1.6	Oxidative Elimination	463
43.8.1.6.1	Method 1: Oxidative Elimination of 1,2-Bis(hydrazones)	463
43.8.1.6.2	Method 2: Oxidative Elimination of Vinylstannanes	465
43.8.2	Synthesis by Rearrangement A. Krueger	
43.8.2	Synthesis by Rearrangement	469
43.8.2.1	Thermal Rearrangements	469
43.8.2.1.1	Method 1: Thermal Isomerization of Cyclopropenes	469
43.8.2.1.2	Method 2: Cope and Claisen Rearrangements and Related Reactions	471
43.8.2.1.3	Method 3: Ene Reaction and Related Conversions	476
43.8.2.1.4	Method 4: Rearrangement of Alkylidenecarbenes	478
43.8.2.1.5	Method 5: Fritsch–Buttenberg–Wiechell Rearrangement and Related Carbenoid Reactions	483
43.8.2.1.5.1	Variation 1: Fritsch–Buttenberg–Wiechell Rearrangement of 1-Haloalkenes and 1,1-Dihaloalkenes	483
43.8.2.1.5.2	Variation 2: Photo-Fritsch–Buttenberg–Wiechell Rearrangement	486
43.8.2.1.5.3	Variation 3: Electrochemical-Fritsch–Buttenberg–Wiechell Rearrangement	487
43.8.2.1.5.4	Variation 4: Carbenoid Rearrangement of Other Metalated Species	488
43.8.2.1.5.5	Variation 5: Carbenoid Rearrangements of α -Halo- β,β -diarylacrylic Acids and α -Halocinnamic Acids	489
43.8.2.1.5.6	Variation 6: Carbenoid Rearrangement of 3-Nitrosooxazolidin-2-ones and Related Compounds	491
43.8.2.1.5.7	Variation 7: Carbenoid Rearrangement of 5-Methyltetrazoles	492
43.8.2.1.5.8	Variation 8: Carbenoid Rearrangement of Ketene Adducts with Phosphites	493
43.8.2.1.6	Method 6: Miscellaneous Thermal Rearrangements	493
43.8.2.1.6.1	Variation 1: Alkynes by a Hydrogen-Shift Reaction	493
43.8.2.1.6.2	Variation 2: Alkynes by Retro-Diels–Alder Reaction	494
43.8.2.1.6.3	Variation 3: Alkynes by [2,3]-Sigmatropic Rearrangement	495
43.8.2.2	Photochemical Rearrangements	495
43.8.2.2.1	Method 1: Photochemical Rearrangement of Allenes	495
43.8.2.2.2	Method 2: Photochemical Vinylidenecarbene Rearrangements	497
43.8.2.2.3	Method 3: Photochemical Rearrangement of Cyclopropenes	498
43.8.2.2.4	Method 4: Formal Cycloreversion of Cyclobutenes	499
43.8.2.3	Base-Catalyzed Rearrangements	500
43.8.2.3.1	Method 1: Alk-2-yne by Base-Catalyzed Rearrangement of Alk-1-yne	500
43.8.2.3.2	Method 2: Alk-1-yne by Base-Catalyzed Rearrangement of Internal Alkynes	503
43.8.2.3.3	Method 3: Base-Catalyzed Rearrangement of Internal Alkynes	506
43.8.2.3.4	Method 4: Base-Catalyzed Rearrangement of Allenes	507
43.8.2.4	Acid-Catalyzed Rearrangements	509

43.8.2.4.1	Method 1:	Acid-Catalyzed Rearrangement of Alkynes and Allenes	510
43.8.2.4.2	Method 2:	Dienol–Benzene and Dienone–Benzene Rearrangements	511
43.8.2.4.3	Method 3:	Anomeric Oxygen-to-Carbon Rearrangement of Alkynyltributylstannanes	514
43.8.2.5		Metal-Catalyzed Rearrangements	516
43.8.2.5.1	Method 1:	Alkyne Metathesis	516
43.8.2.5.2	Method 2:	Gold-Catalyzed Rearrangements	524
43.8.2.5.3	Method 3:	Tandem Zinc-Promoted Brook Rearrangement and Ene–Allene Cyclization	525
43.8.2.5.4	Method 4:	Metal-Catalyzed Rearrangements with Other Metals	527
43.8.2.6		Coarctate Rearrangements	532
43.8.2.6.1	Method 1:	Diazirine Rearrangement	533
43.8.2.6.2	Method 2:	Spiroozonide Conversion	533
43.8.2.6.3	Method 3:	Rearrangement of Cyclopropylcarbenes	534
43.8.2.6.4	Method 4:	The Eschenmoser–Tanabe Fragmentation of Epoxy Ketones	537
43.8.2.6.5	Method 5:	Fragmentation of 1,3,4-Oxadiazolidin-2-ones	543
43.8.2.6.6	Method 6:	Cyclopropenylcarbene Fragmentation	544
43.8.2.6.7	Method 7:	Furfurylidene Rearrangement	546
43.8.2.7		Enzyme-Catalyzed Rearrangements	547
43.8.3		Synthesis from Other Alkynes	
		R. A. Aitken and K. Aitken	
43.8.3		Synthesis from Other Alkynes	555
43.8.3.1		Conversion into an Alkynylmetal Followed by Reaction with an Electrophile	555
43.8.3.1.1	Method 1:	Reaction of an Alkynyllithium with an Alkyl Halide or Equivalent	555
43.8.3.1.1.1	Variation 1:	With a Chloroalkane	555
43.8.3.1.1.2	Variation 2:	With a Bromoalkane	558
43.8.3.1.1.3	Variation 3:	With an Iodoalkane	569
43.8.3.1.1.4	Variation 4:	With a Dialkyl Sulfate	577
43.8.3.1.1.5	Variation 5:	With an Alkyl Methanesulfonate	578
43.8.3.1.1.6	Variation 6:	With an Alkyl Arenesulfonate	579
43.8.3.1.1.7	Variation 7:	With an Alkyl Trifluoromethanesulfonate	581
43.8.3.1.1.8	Variation 8:	With an Allyl Ester or Carbonate	582
43.8.3.1.1.9	Variation 9:	With an Alcohol	583
43.8.3.1.1.10	Variation 10:	With a Trialkylborane	583
43.8.3.1.1.11	Variation 11:	With an Alkylzirconium Reagent	585
43.8.3.1.2	Method 2:	Reaction of an Alkynylsodium with an Alkyl Halide or Equivalent	586
43.8.3.1.2.1	Variation 1:	With a Chloroalkane	586
43.8.3.1.2.2	Variation 2:	With a Bromoalkane	586
43.8.3.1.2.3	Variation 3:	With an Iodoalkane	589
43.8.3.1.2.4	Variation 4:	With a Dialkyl Sulfate	590
43.8.3.1.2.5	Variation 5:	With an Alkyl Arenesulfonate	591

43.8.3.1.3	Method 3:	Reaction of an Alkynylpotassium with an Alkyl Halide or Equivalent	591
43.8.3.1.4	Method 4:	Reaction of an Alkynyl Grignard Reagent with an Alkyl Halide or Equivalent	591
43.8.3.1.4.1	Variation 1:	With a Chloroalkane	591
43.8.3.1.4.2	Variation 2:	With a Bromoalkane	593
43.8.3.1.4.3	Variation 3:	With an Iodoalkane	594
43.8.3.1.4.4	Variation 4:	With a Dialkyl Sulfate	595
43.8.3.1.4.5	Variation 5:	With an Alkyl Methanesulfonate	596
43.8.3.1.4.6	Variation 6:	With an Alkyl Arenesulfonate	597
43.8.3.1.4.7	Variation 7:	With an Allyl Ester	597
43.8.3.1.4.8	Variation 8:	With an Alkylzirconium Reagent	598
43.8.3.1.5	Method 5:	Reaction of an Alkynylcalcium with an Alkyl Halide or Equivalent	599
43.8.3.1.6	Method 6:	Reaction of an Alkynylbarium with an Alkyl Halide or Equivalent	599
43.8.3.1.7	Method 7:	Palladium/Copper-Catalyzed Reaction of an Alk-1-yne with an Alkyl Halide or Equivalent	599
43.8.3.1.7.1	Variation 1:	With a Chloroalkane	599
43.8.3.1.7.2	Variation 2:	With a Bromoalkane	601
43.8.3.1.7.3	Variation 3:	With an Iodoalkane	605
43.8.3.1.7.4	Variation 4:	With an Alkyl Methanesulfonate	605
43.8.3.1.7.5	Variation 5:	With an Alkyl Arenesulfonate	606
43.8.3.1.7.6	Variation 6:	With a Trialkylborane	606
43.8.3.1.8	Method 8:	Reaction of an Alkynylcopper with an Alkyl Halide or Equivalent	606
43.8.3.1.8.1	Variation 1:	With a Bromoalkane	606
43.8.3.1.9	Method 9:	Reaction of an Alkynylmercury with an Alkyl Halide or Equivalent	607
43.8.3.1.9.1	Variation 1:	With a Bromoalkane	607
43.8.3.1.9.2	Variation 2:	With an Iodoalkane	607
43.8.3.1.10	Method 10:	Reaction of an Alkynylboron Reagent with an Alkyl Halide or Equivalent	607
43.8.3.1.11	Method 11:	Reaction of an Alkynylaluminum Reagent with an Alkyl Halide or Equivalent	608
43.8.3.1.11.1	Variation 1:	With a Chloroalkane	608
43.8.3.1.11.2	Variation 2:	With a Bromoalkane	609
43.8.3.1.11.3	Variation 3:	With an Alkyl Methanesulfonate	609
43.8.3.1.11.4	Variation 4:	With an Alkyl Phenyl Sulfone	609
43.8.3.1.11.5	Variation 5:	With a Propiolactone	610
43.8.3.1.12	Method 12:	Reaction of a (Trialkylsilyl)alkyne with an Alkyl Halide or Equivalent	611
43.8.3.1.12.1	Variation 1:	With a Chloroalkane	611
43.8.3.1.13	Method 13:	Reaction of an Alkynyllithium with an Allene or Other Alkene	611
43.8.3.1.13.1	Variation 1:	With a Bromoallene	611
43.8.3.2	Nucleophilic Substitution by an Organometallic Reagent at an Alkyne Derivative	612	
43.8.3.2.1	Method 1:	Reaction of a Chloroalkyne with an Organometallic Reagent	612

43.8.3.2.1.1	Variation 1:	With a Silyl Enol Ether	612
43.8.3.2.1.2	Variation 2:	With an Organozirconium Reagent	612
43.8.3.2.2	Method 2:	Reaction of a Bromoalkyne with an Organometallic Reagent	613
43.8.3.2.2.1	Variation 1:	With a Grignard Reagent	613
43.8.3.2.2.2	Variation 2:	With an Organozinc Reagent	613
43.8.3.2.2.3	Variation 3:	With a Trialkylaluminum Reagent	616
43.8.3.2.2.4	Variation 4:	With an Organozirconium Reagent	617
43.8.3.2.3	Method 3:	Reaction of an Iodoalkyne with an Organometallic Reagent	617
43.8.3.2.3.1	Variation 1:	With a Grignard Reagent	617
43.8.3.2.3.2	Variation 2:	With an Organozinc Reagent	618
43.8.3.2.3.3	Variation 3:	With an Organocopper Reagent	618
43.8.3.2.3.4	Variation 4:	With an Organozirconium Reagent	619
43.8.3.2.4	Method 4:	Reaction of an Alkynyl Aryl Sulfone with an Alkylolithium	620
43.8.3.3	Reactions Involving neither Electrophilic nor Nucleophilic Attack		620
43.8.3.3.1	Method 1:	Reaction of an Alkynyl Trifluoromethyl Sulfone with an Alkane	620
43.8.3.3.2	Method 2:	Reaction of an Alkynyl Phenyl Sulfone with a <i>B</i> -Alkylcatecholborane	621
43.8.3.3.3	Method 3:	Ruthenium-Catalyzed Reaction of an Alkyne with a 1,3-Diene	622
43.8.3.3.4	Method 4:	Nickel-Catalyzed Reaction of an Alkyne with an Allyl Ester	622
43.8.3.3.5	Method 5:	Palladium-Catalyzed Oxidative Coupling of an Alkynyl-stannane Reagent with an Alkylzinc Reagent	623

43.9

Product Class 9: Cycloalkynes

R. Gleiter and D. B. Werz

43.9	Product Class 9: Cycloalkynes	631
43.9.1	Synthesis of Product Class 9	631
43.9.1.1	Method 1: Ring-Closure Reactions	631
43.9.1.1.1	Variation 1: Using sp -Carbon Nucleophiles	631
43.9.1.1.2	Variation 2: Using sp^3 -Carbon Nucleophiles	634
43.9.1.1.3	Variation 3: Using Chalcogen Nucleophiles	638
43.9.1.1.4	Variation 4: Using Nitrogen Nucleophiles	639
43.9.1.1.5	Variation 5: Alkyne Metathesis	644
43.9.1.2	Method 2: Elimination and Fragmentation Reactions	648
43.9.1.2.1	Variation 1: 1,2-Elimination Reactions	648
43.9.1.2.2	Variation 2: Cycloelimination Reactions	653
43.9.1.2.3	Variation 3: Eschenmoser Fragmentation	656
43.9.1.3	Method 3: Isomerization Reactions	657
43.9.1.3.1	Variation 1: Pericyclic Ring-Opening Reactions	657
43.9.1.4	Method 4: Ring-Enlargement Reactions	658
43.9.1.4.1	Variation 1: Fritsch–Buttenberg–Wiechell Rearrangement	658
43.9.1.4.2	Variation 2: Carbene Reactions	658
43.9.1.5	Method 5: Decomplexation Reactions	660
43.9.1.5.1	Variation 1: Cleavage of Hexacarbonyldicobalt Complexes	660
43.9.2	Applications of Product Class 9 in Organic Synthesis	661
43.9.2.1	Method 1: Reactions of Cyclic Alkynes with Organometallic Reagents	661

43.9.2.1.1	Variation 1: Reactions of Cyclic Alkynes with (η^5 -Cyclopentadienyl)cobalt(I)	661
43.9.2.1.2	Variation 2: Reactions of Cyclic Alkynes with Aluminum Trichloride	663
	Keyword Index	669
	Author Index	707
	Abbreviations	739

