
**Volume 44:
Cumulenes and Allenes**

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
	Introduction	
	N. Krause	1
44.1	Product Class 1: Cumulenes	
	M. Ogasawara	9
44.2	Product Class 2: Linear Allenes	
44.2.1	Synthesis by Substitution	
	H. Ohno and K. Tomioka	71
44.2.2	Synthesis by Elimination	
	V. Gandon and M. Malacria	175
44.2.3	Synthesis by Addition	
	K. K. Wang	229
44.2.4	Synthesis by Rearrangement	
	A. S. K. Hashmi	287
44.2.5	Synthesis from Other Allenes	
	H.-U. Reissig and R. Zimmer	301
44.2.6	Applications of Allenes in Organic Synthesis	
	M. A. Tius	353
44.3	Product Class 3: Cyclic Allenes	
	T. Kawase	395
	Keyword Index	451
	Author Index	485
	Abbreviations	503

Table of Contents

	Introduction	
	N. Krause	
	<hr/>	
	Introduction	1
44.1	Product Class 1: Cumulenes	
	M. Ogasawara	
	<hr/>	
44.1	Product Class 1: Cumulenes	9
44.1.1	Product Subclass 1: [6]- and Higher Cumulenes	10
44.1.1.1	Synthesis of Product Subclass 1	10
44.1.1.1.1	Synthesis by Elimination	10
44.1.1.1.1.1	Method 1: Reduction of α,ω -Dihydroxypolyynes	10
44.1.1.1.1.2	Method 2: Double Elimination of Methanol from 1,7-Dimethoxy- hepta-2,4-diyne	11
44.1.2	Product Subclass 2: Hexapentaenes ([5]Cumulenes)	12
44.1.2.1	Synthesis of Product Subclass 2	12
44.1.2.1.1	Synthesis by Elimination	12
44.1.2.1.1.1	Method 1: Dehydroxylation of Hexa-2,4-diyne-1,6-diols	12
44.1.2.1.1.2	Method 2: Debromination of 3,4-Dibromohexa-1,2,4,5-tetraenes	13
44.1.2.1.1.3	Method 3: Other Methods Involving Elimination	14
44.1.2.1.2	Synthesis Mediated by Carbene Species	15
44.1.2.1.2.1	Method 1: Dimerization of Allenylidene Species	15
44.1.2.1.2.1.1	Variation 1: Dimerization of Allenylidene Species Generated from Propargylic Precursors	15
44.1.2.1.2.1.2	Variation 2: Dimerization of Allenylidene Species Generated from Bromoallenes	17
44.1.2.1.2.1.3	Variation 3: Dimerization of Allenylidene–Chromium Species	17
44.1.2.1.2.2	Method 2: Trapping of Hexapentaenylidene Species	17
44.1.3	Product Subclass 3: Pentatetraenes ([4]Cumulenes)	18
44.1.3.1	Synthesis of Product Subclass 3	18
44.1.3.1.1	Synthesis by Substitution	18
44.1.3.1.1.1	Method 1: Lithiation and Silylation of Hexa-2,4-diyne	18
44.1.3.1.1.2	Method 2: S_N2'' Substitution on Penta-2,4-diynyl Esters	19
44.1.3.1.2	Synthesis by Elimination	20
44.1.3.1.2.1	Method 1: Double Dehydrobromination of 2,4-Dibromopenta-1,4-dienes	20
44.1.3.1.2.2	Method 2: 1,2- and 1,4-Elimination from 5-Methoxypent-2-yn-1-ols	20

44.1.3.1.2.3	Method 3:	Oxidation of Hexapentaenes Followed by Carbon Monoxide Elimination	21
44.1.3.1.2.4	Method 4:	Reductive 1,4-Dechlorination of a 2,5-Dichloropent-1-en-3-yne	22
44.1.3.1.2.5	Method 5:	1,1-Dehalogenation and Rearrangement of 1,1-Dihalocyclopropanes	22
44.1.3.1.2.6	Method 6:	Sulfur Elimination from Penta-1,2,3,4-tetraene Episulfides	23
44.1.3.1.2.7	Method 7:	Wittig Reaction	24
44.1.3.1.2.7.1	Variation 1:	Wittig Reaction of Carbon Suboxide with Alkylidenephosphoranes	24
44.1.3.1.2.7.2	Variation 2:	Wittig Reaction of Alka-2,3-dienoyl Chlorides with Alkylidenephosphoranes	25
44.1.3.1.2.8	Method 8:	Retro-Diels–Alder Reaction	25
44.1.4	Product Subclass 4: Butatrienes ([3]Cumulenes)		26
44.1.4.1	Synthesis of Product Subclass 4		26
44.1.4.1.1	Synthesis by Substitution		26
44.1.4.1.1.1	Method 1:	S _N 2'' Substitution on Pent-4-en-2-ynyl Derivatives and Related Reactions	26
44.1.4.1.1.1.1	Variation 1:	On Pent-4-en-2-ynyl Methanesulfonates with Alkylsilver(I) Reagents	26
44.1.4.1.1.1.2	Variation 2:	On 2-(But-3-en-1-ynyl)oxiranes with Alkylsilver(I) Reagents	27
44.1.4.1.1.1.3	Variation 3:	Reduction of Alka-4,5-dien-2-ynols or Related Alcohols by Lithium Aluminum Hydride	27
44.1.4.1.1.2	Method 2:	S _N 2' Substitution on 2-Bromo-1-en-3-yne	28
44.1.4.1.1.2.1	Variation 1:	With Alkylcopper Reagents	28
44.1.4.1.1.2.2	Variation 2:	With Soft Carbon Nucleophiles Catalyzed by a Palladium Complex	29
44.1.4.1.1.3	Method 3:	Synthesis of Phosphinobutatrienes from 2-Vinyl-1 <i>H</i> -phosphirenes and Alkylolithium Reagents	30
44.1.4.1.2	Synthesis by Elimination		30
44.1.4.1.2.1	Method 1:	Dehydrohalogenation	30
44.1.4.1.2.1.1	Variation 1:	Single Dehydrohalogenation of Haloallenes	30
44.1.4.1.2.1.2	Variation 2:	Double Dehydrohalogenation of 2,3-Dihalobut-2-enes	31
44.1.4.1.2.1.3	Variation 3:	Double Dehydrohalogenation of 1,4-Dihalobut-2-enes	32
44.1.4.1.2.1.4	Variation 4:	Double Dehydrochlorination and Ring Opening of 1,1-Dichlorocyclopropanes	33
44.1.4.1.2.2	Method 2:	Dehydration	34
44.1.4.1.2.2.1	Variation 1:	1,2-Dehydration of Alka-2,3-dienols	34
44.1.4.1.2.2.2	Variation 2:	Rearrangement and Dehydration of Epoxyalkynols	34
44.1.4.1.2.3	Method 3:	Elimination of Alcohols and Related Reactions	35
44.1.4.1.2.3.1	Variation 1:	1,4-Elimination of Alcohols	35
44.1.4.1.2.3.2	Variation 2:	1,6-Elimination of Alcohols	37
44.1.4.1.2.4	Method 4:	Pyrolysis of Hexakis(trimethylsilyl)but-2-yne	37
44.1.4.1.2.5	Method 5:	Dehalogenation	37
44.1.4.1.2.5.1	Variation 1:	1,4-Dehalogenation of 1,4-Dihaloalk-2-yne	37
44.1.4.1.2.5.2	Variation 2:	1,2-Dehalogenation of 2,3-Dihalo-1,3-dienes	39

44.1.4.1.2.6	Method 6:	1,1-Dehalogenation and Rearrangement of 2-Alkenylidene-1,1-dihalocyclopropanes	40
44.1.4.1.2.7	Method 7:	Dehydroxylation of Alk-2-yne-1,4-diols	41
44.1.4.1.2.8	Method 8:	1,4-Elimination from 4-Hydroxybut-2-ynylsilanes or -stannanes	42
44.1.4.1.2.8.1	Variation 1:	From 4-Hydroxybut-2-ynylsilanes	42
44.1.4.1.2.8.2	Variation 2:	From 4-Hydroxybut-2-ynylstannanes	44
44.1.4.1.2.9	Method 9:	Desulfurization of Cyclic Trithiocarbonates	44
44.1.4.1.2.10	Method 10:	Sulfur Elimination from Alkylidenecyclopropanethiones	45
44.1.4.1.2.11	Method 11:	Wittig and Related Reactions	46
44.1.4.1.2.11.1	Variation 1:	Wittig Reaction of Aldehydes or Ketones with Allenylidenephosphoranes	46
44.1.4.1.2.11.2	Variation 2:	Double Wittig Reaction of a Phosphorus Dilyde with an Aldehyde	47
44.1.4.1.2.11.3	Variation 3:	Horner–Emmons-Type Reactions of Aldehydes or Ketones	48
44.1.4.1.2.11.4	Variation 4:	Wittig Reaction of a Ketene with a Vinylidenephosphorane	49
44.1.4.1.2.12	Method 12:	Base-Induced Borane Elimination from Bis(1-iodoalkenyl)boranes	49
44.1.4.1.2.13	Method 13:	Retro-Diels–Alder Reactions	50
44.1.4.1.2.14	Method 14:	Thermal Decomposition of a Disodium Salt of a Cyclobutane-1,3-dione Bis(tosylhydrazone)	51
44.1.4.1.3	Synthesis by Addition		51
44.1.4.1.3.1	Method 1:	Electrophilic 1,4-Addition to 1,3-Diynes	51
44.1.4.1.3.2	Method 2:	1,4-Disilylation of 1,4-Disilyl-1,3-diynes	52
44.1.4.1.3.2.1	Variation 1:	1,4-Disilylation of 1,4-Disilyl-1,3-diynes by a Silylmanganese Reagent	52
44.1.4.1.3.2.2	Variation 2:	Palladium-Catalyzed 1,4-Disilylation of 1,4-Disilyl-1,3-diynes	53
44.1.4.1.3.3	Method 3:	Palladium-Catalyzed Double Arylation of 1,4-Diaryl-1,3-diynes	54
44.1.4.1.3.4	Method 4:	1,6-Addition of Bromine to 1,5-Dien-3-yne	54
44.1.4.1.4	Synthesis by Rearrangement		55
44.1.4.1.4.1	Method 1:	Base-Promoted Rearrangement of a Conjugated Bisallene to an Alkenylbutatriene	55
44.1.4.1.4.2	Method 2:	Photorearrangement of Vinylidenecyclopropanes to Butatriene Derivatives	55
44.1.4.1.5	Synthesis Mediated by Carbene Species		56
44.1.4.1.5.1	Method 1:	Dimerization of Vinylidene Species or Vinylidene Equivalents	56
44.1.4.1.5.1.1	Variation 1:	Dimerization of Vinylidene Species or Vinylidene Equivalents Generated from <i>gem</i> -Dihaloalkenes	56
44.1.4.1.5.1.2	Variation 2:	Dimerization of Vinylidene Species or Vinylidene Equivalents Generated from 1-Halo-1-hydroalkenes	57
44.1.4.1.5.1.3	Variation 3:	Formation of a Butatriene from 2-Nitro-1,1-diphenylethene	58
44.1.4.1.5.1.4	Variation 4:	Dimerization of Alkenylidene Species Generated from Dialkenylcuprates	59
44.1.4.1.5.1.5	Variation 5:	Desulfurization–Dimerization of Dithioacetals with Hexacarbonyltungsten(0)	59
44.1.4.1.5.1.6	Variation 6:	Dimerization of Vinylidene–Tungsten Species	59
44.1.4.1.5.2	Method 2:	Reactions Involving Allenylidene Species	60

44.1.4.1.5.2.1	Variation 1:	Reactions of Allenylidene Species with Diazoalkanes	60
44.1.4.1.5.2.2	Variation 2:	Reactions of Allenylidene–Rhodium Complexes with Diazomethane	60
44.1.4.1.5.3	Method 3:	Reactions of 1,2,3-Trienylidene Species	61
44.1.4.1.5.3.1	Variation 1:	Reactions of 1,2,3-Trienylidene Species with Alkenes	61
44.1.4.1.5.3.2	Variation 2:	Reactions of 1,2,3-Trienylidene Species with Group 14 Hydrides	61
44.1.4.1.6	Other Methods	for the Synthesis of Butatrienes	62
44.1.4.1.6.1	Method 1:	Dimerization of Terminal Alkynes by Transition-Metal Catalysts	62
44.1.4.1.6.2	Method 2:	Coupling Reactions between 1,1-Dichloroalkenes and Terminal Alkenes	64
44.1.4.1.6.3	Method 3:	Zirconium-Mediated Coupling Reactions of 1,3-Diynes with Aldehydes or Ketones	64
44.1.4.1.6.3.1	Variation 1:	Reactions of Zirconacycles with Aldehydes To Form Butatrienyl Monoalcohols	64
44.1.4.1.6.3.2	Variation 2:	Reactions of Zirconacycles with Ketones To Form Butatrienyl Diols	65

44.2 Product Class 2: Linear Allenes

44.2.1 Synthesis by Substitution

H. Ohno and K. Tomioka

44.2.1	Synthesis by Substitution	71	
44.2.1.1	Method 1:	Organocopper-Mediated Reactions of Propargylic and Related Substrates	71
44.2.1.1.1	Variation 1:	Reactions of Various Propargylic Substrates	75
44.2.1.1.2	Variation 2:	Reactions Using Various Copper Nucleophiles	81
44.2.1.1.3	Variation 3:	Synthesis of Enantiomerically Enriched Allenes	83
44.2.1.1.4	Variation 4:	Ring-Opening Reactions	94
44.2.1.1.5	Variation 5:	1,5-Substitution Reactions	100
44.2.1.1.6	Variation 6:	Halogenation of Propargylic Substrates	101
44.2.1.2	Method 2:	Aluminum-Mediated Reactions of Propargylic Substrates	102
44.2.1.2.1	Variation 1:	Reactions of Propargylic Halides	102
44.2.1.2.2	Variation 2:	Reactions of Propargylic Alcohols	103
44.2.1.2.3	Variation 3:	Reactions of Propargylic Sulfonates	106
44.2.1.2.4	Variation 4:	Reactions of Propargylic Ethers	108
44.2.1.2.5	Variation 5:	Reactions of Propargylic Amine Derivatives	110
44.2.1.2.6	Variation 6:	Ring-Opening Reactions	111
44.2.1.2.7	Variations 7:	Miscellaneous Reactions	115
44.2.1.3	Method 3:	Lithium-, Magnesium-, or Zinc-Mediated Reactions of Propargylic and Related Substrates	115
44.2.1.3.1	Variation 1:	Lithium-Mediated Reactions	115
44.2.1.3.2	Variation 2:	Magnesium-Mediated Reactions	117
44.2.1.3.3	Variation 3:	Zinc-Mediated Reactions	119

44.2.1.4	Method 4:	Borane- or Gallium-Mediated Reactions of Propargylic Substrates	120
44.2.1.4.1	Variation 1:	Borane-Mediated Reactions	120
44.2.1.4.2	Variation 2:	Gallium-Mediated Reactions	123
44.2.1.5	Method 5:	Iron-Catalyzed Reactions of Propargylic Substrates	123
44.2.1.5.1	Variation 1:	Ring-Opening Reactions of Epoxides	125
44.2.1.6	Method 6:	Palladium-Catalyzed Reactions of Propargylic Substrates	126
44.2.1.6.1	Variation 1:	Reactions with Grignard Reagents	127
44.2.1.6.2	Variation 2:	Reactions with Zinc Reagents	127
44.2.1.6.3	Variation 3:	Reactions with Borane Reagents	129
44.2.1.6.4	Variation 4:	Reactions with Aluminum or Tin Reagents	131
44.2.1.6.5	Variation 5:	Reactions with Copper Acetylides	132
44.2.1.6.6	Variation 6:	Reactions with Samarium Reagents	133
44.2.1.6.7	Variation 7:	Carbonylation Reactions	134
44.2.1.6.8	Variation 8:	Reactions with Hydride Reagents	138
44.2.1.6.9	Variations 9:	Miscellaneous Reactions	141
44.2.1.7	Methods 7:	Miscellaneous Reactions of Propargylic Substrates	145
44.2.1.7.1	Variation 1:	Reactions with Nitrogen Nucleophiles	145
44.2.1.7.2	Variation 2:	Reactions with Enol Ethers	146
44.2.1.7.3	Variation 3:	Chromium-Catalyzed Reactions	146
44.2.1.7.4	Variation 4:	Nickel-Mediated Reactions	147
44.2.1.7.5	Variation 5:	Reactions with Copper Cyanide	147
44.2.1.7.6	Variation 6:	Zirconocene-Mediated Reactions	148
44.2.1.7.7	Variation 7:	Ruthenium-Catalyzed Reactions	148
44.2.1.7.8	Variation 8:	Samarium-Mediated Reactions	149
44.2.1.8	Method 8:	Substitution of Haloallenes	150
44.2.1.8.1	Variation 1:	Copper-Mediated Reactions	150
44.2.1.8.2	Variation 2:	Palladium-Catalyzed Reactions	155
44.2.1.8.3	Variation 3:	Other Reactions with Carbon Nucleophiles	161
44.2.1.8.4	Variation 4:	Reactions with Nitrogen Nucleophiles	163
44.2.1.8.5	Variation 5:	Reactions with Oxygen Nucleophiles	166
44.2.1.8.6	Variation 6:	Reactions with Sulfur Nucleophiles	166
44.2.1.9	Method 9:	Substitution of 2-Halobuta-1,3-dienes and Related Compounds	166
44.2.1.9.1	Variation 1:	Copper-Mediated Reactions	166
44.2.1.9.2	Variation 2:	Palladium-Catalyzed Reactions	167
44.2.2	Synthesis by Elimination V. Gandon and M. Malacria		
44.2.2	Synthesis by Elimination		175
44.2.2.1	1,3-Elimination from Substituted Vinylic or Allylic Derivatives		176
44.2.2.1.1	Method 1:	Dehydrohalogenation of 2-Halopropenes	176
44.2.2.1.1.1	Variation 1:	From Nonactivated Substrates	176
44.2.2.1.1.2	Variation 2:	From α,β -Unsaturated Substrates	178
44.2.2.1.2	Method 2:	Dehydrosilylation of Silyl Enol Ethers	178
44.2.2.1.3	Method 3:	Dehydrosulfonylation of Vinyl Trifluoromethanesulfonates	180

44.2.2.1.4	Method 4:	Dehydration of Allylic Alcohols	181
44.2.2.1.5	Method 5:	Elimination from Vinyl Sulfoxides and Vinyl Sulfones	182
44.2.2.1.6	Method 6:	Elimination from Phenyl Vinyl Selenoxides	182
44.2.2.1.6.1	Variation 1:	Oxidation with 3-Chloroperoxybenzoic Acid	182
44.2.2.1.6.2	Variation 2:	Asymmetric Elimination Using Sharpless Oxidation	183
44.2.2.1.6.3	Variation 3:	Asymmetric Elimination Using Chiral Diferrocenyl Diselenides	185
44.2.2.1.7	Method 7:	Elimination from Enol Phosphates	186
44.2.2.1.8	Method 8:	Elimination from Vinylsilanes and Vinylstannanes	188
44.2.2.1.9	Method 9:	Peterson Reaction	190
44.2.2.1.10	Method 10:	Elimination from Vinyl- and Allylmetal Intermediates	192
44.2.2.1.10.1	Variation 1:	Vinylcopper and Vinylmagnesium Intermediates from Propargyl Ethers and Organocopper and Organomagnesium Reagents	192
44.2.2.1.10.2	Variation 2:	Allylzinc Intermediates from Alkynyl Sulfoxides and Alkynyl Sulfones	194
44.2.2.1.10.3	Variation 3:	Vinylpalladium Intermediates from <i>N</i> -Propargylsulfonamides	194
44.2.2.1.10.4	Variation 4:	Vinylzirconium and Vinyltitanium Intermediates from Propargyl Ethers and Propargyl Bromides	195
44.2.2.1.11	Method 11:	Dehalogenation of 2,3-Dihalopropenes and Deoxyhalogenation of β -Haloallyl Alcohol Derivatives	197
44.2.2.1.12	Method 12:	Debromosulfonylation of 1-(Bromomethyl)vinyl Sulfoxides and Sulfimides	197
44.2.2.1.12.1	Variation 1:	Using Tributyltin Hydride	198
44.2.2.1.12.2	Variation 2:	Using Tris(trimethylsilyl)silane	199
44.2.2.1.13	Method 13:	Debromosulfonylation from 1-(Bromomethyl)vinyl Sulfides	200
44.2.2.1.14	Method 14:	Elimination from β -Sulfinylallyl Alcohol Derivatives and 1-(Sulfinylalkyl)vinyl Trifluoromethanesulfonates	201
44.2.2.1.14.1	Variation 1:	Elimination from 1-(Sulfinylalkyl)vinyl Trifluoromethanesulfonates	201
44.2.2.1.14.2	Variation 2:	Elimination from β -Sulfinylallyl Alcohol Derivatives	202
44.2.2.2		Wittig Alkenations and Related Reactions	203
44.2.2.2.1	Method 1:	Synthesis Using or via (Hydroxyalkenyl)phosphonate and (Hydroxyalkenyl)phosphine Oxide Intermediates	204
44.2.2.2.1.1	Variation 1:	Baylis–Hillman-Type Reaction of Alkenylphosphorus Compounds with Aldehydes	204
44.2.2.2.1.2	Variation 2:	Sulfanyl-, Selanyl-, or Carbometalation of Alkynylphosphine Oxides and Reaction with Aldehydes	205
44.2.2.2.2	Method 2:	Synthesis via β -Hydroxyallylphosphonate Derivatives Prepared from Ketenes or Ketene Equivalents	207
44.2.2.2.2.1	Variation 1:	Using Acid Chlorides	208
44.2.2.2.2.2	Variation 2:	Using Aryl Esters	209
44.2.2.3		Metal–Vinylidene Routes to Allenes	211
44.2.2.3.1	Method 1:	Synthesis from 1,1-Dimetalloalkenes	211
44.2.2.3.2	Method 2:	Synthesis via Alkenyltitanocene Derivatives	212
44.2.2.3.3	Method 3:	Double Alkenation Using Titanium-Substituted Ylides	214
44.2.2.3.4	Method 4:	Synthesis via Alkenylidenemagnesium Intermediates	215

44.2.2.4	Elimination from 1,1-Disubstituted Cyclopropane Derivatives	218
44.2.2.4.1	Method 1: Dehalogenation of 1,1-Dihalocyclopropanes through Carbenoid Intermediates	218
44.2.2.4.2	Method 2: Synthesis from 1-Halo-1-(phenylsulfinyl)cyclopropanes via Carbenoid Intermediates	219
44.2.2.5	Miscellaneous Methods	221
44.2.2.5.1	Method 1: Nitrogen Elimination by Oxidation of Pyrazol-3-ones Using Lead(IV) Acetate	221
44.2.2.5.2	Method 2: Dehydration of Ketones	222
44.2.3	Synthesis by Addition K. K. Wang	
44.2.3	Synthesis by Addition	229
44.2.3.1	Method 1: Reduction of Pent-2-en-4-yn-1-ols with Lithium Aluminum Hydride	229
44.2.3.2	Method 2: 1,4-Addition of Hydroboranes to Conjugated Enynes	233
44.2.3.3	Method 3: 1,4-Addition of Hydrosilanes to Conjugated Enynes	233
44.2.3.4	Method 4: 1,4-Addition of Hydrogen Halides and Halogens to Conjugated Enynes	236
44.2.3.5	Method 5: Conjugate Addition of Organometallic Reagents to Acceptor-Substituted Enynes	237
44.2.3.5.1	Variation 1: 1,6-Addition of Organometallic Reagents to Acceptor-Substituted Enynes	238
44.2.3.5.2	Variation 2: 1,8-, 1,10-, and 1,12-Addition of Organometallic Reagents to Acceptor-Substituted Enynes	250
44.2.3.6	Method 6: 1,4-Addition of Organometallic Reagents to Conjugated Enynes	251
44.2.3.7	Method 7: 1,4-Addition of Carbon Pronucleophiles to Conjugated Enynes	257
44.2.3.8	Method 8: Friedel–Crafts Acylation and Alkylation of Conjugated Enynes	259
44.2.3.9	Method 9: 1,4-Addition of Nucleophiles to Ynones and Ynoates	261
44.2.3.10	Method 10: Condensation of Propargylboranes with Carbonyl and Related Compounds	263
44.2.3.11	Method 11: Condensation of Propargylsilanes with Carbonyl and Related Compounds	268
44.2.3.12	Method 12: Condensation of Propargylstannanes with Carbonyl and Related Compounds	275
44.2.3.13	Method 13: Condensation of Other Propargylic Organometallic Reagents with Carbonyl Compounds	279
44.2.4	Synthesis by Rearrangement A. S. K. Hashmi	
44.2.4	Synthesis by Rearrangement	287
44.2.4.1	Method 1: Prototropic Rearrangements	287
44.2.4.1.1	Variation 1: Stoichiometric Deprotonation Followed by Protonation	287

44.2.4.1.2	Variation 2:	Using Catalytic Potassium <i>tert</i> -Butoxide	289
44.2.4.1.3	Variation 3:	Spontaneous Rearrangement on Chromatographic Workup	290
44.2.4.2	Method 2:	[2,3]-Sigmatropic Rearrangements	291
44.2.4.2.1	Variation 1:	Via In Situ Formation of Propargyl Sulfenates	291
44.2.4.2.2	Variation 2:	Via In Situ Formation of Propargyl Phosphites	292
44.2.4.2.3	Variation 3:	Via In Situ Formation of Propargyl Phosphinites	293
44.2.4.2.4	Variation 4:	Via [2,3]-Wittig Rearrangement	294
44.2.4.3	Method 3:	[3,3]-Sigmatropic Rearrangements	295
44.2.4.3.1	Variation 1:	Thermal Claisen Rearrangement of Propargyl Vinyl Ethers	295
44.2.4.3.2	Variation 2:	In Situ from Ortho Esters and a Propargyl Alcohol	296
44.2.4.3.3	Variation 3:	Flash-Vacuum Pyrolysis of Thiocyanates and Related Compounds	296
44.2.5	Synthesis from Other Allenes		
	H.-U. Reissig and R. Zimmer		
44.2.5	Synthesis from Other Allenes		301
44.2.5.1	Method 1:	Substitution Reactions of Metalated Allenes	301
44.2.5.1.1	Variation 1:	Of Nonactivated Allenes	301
44.2.5.1.2	Variation 2:	Of Acceptor-Substituted Allenes	303
44.2.5.1.3	Variation 3:	Of Donor-Substituted Allenes	304
44.2.5.1.4	Variation 4:	Of α -Functionalized Allenes	307
44.2.5.2	Method 2:	Transition-Metal-Catalyzed Cross-Coupling Reactions of Allenes	308
44.2.5.2.1	Variation 1:	Alkylations	308
44.2.5.2.2	Variation 2:	Arylations and Vinylations	310
44.2.5.2.3	Variation 3:	Alkynylations	313
44.2.5.2.4	Variation 4:	Reactions with CH-Acidic Compounds	313
44.2.5.2.5	Variation 5:	Carbonylations	315
44.2.5.2.6	Variation 6:	Amination, Amidation, and Imidation Reactions	315
44.2.5.3	Method 3:	Substitution Reactions of Oxygen- and Halogen-Substituted Allenes	316
44.2.5.3.1	Variation 1:	Of 1-Halogen-Substituted Allenes	316
44.2.5.3.2	Variation 2:	Of α -Halogen-Substituted Allenes	318
44.2.5.3.3	Variation 3:	Of 1-Oxygen-Substituted Allenes	319
44.2.5.3.4	Variation 4:	Of α -Oxygen-Substituted Allenes	319
44.2.5.4	Method 4:	Oxidation Reactions	320
44.2.5.4.1	Variation 1:	Oxidation of α -Hydroxy-Substituted Allenes	320
44.2.5.4.2	Variation 2:	Oxidation of Carboxy-Substituted Allenes	321
44.2.5.4.3	Variation 3:	Oxidation of Heteroatom-Substituted Allenes	322
44.2.5.4.4	Variation 4:	Oxidation of Alkynyl-Substituted Allenes	324
44.2.5.5	Method 5:	Reductions of Allenes	325
44.2.5.5.1	Variation 1:	Reduction of α -Carbonyl-Substituted Allenes	325
44.2.5.5.2	Variation 2:	Reduction of Heteroatom-Substituted Allenes	326
44.2.5.5.3	Variation 3:	Reduction of Alkynyl-Substituted Allenes	327
44.2.5.5.4	Variation 4:	Reduction of Allenes Bearing an Epoxide Moiety	328
44.2.5.6	Method 6:	Addition Reactions	328

44.2.5.6.1	Variation 1:	Additions on α -Carbonyl-Substituted Allenes	328
44.2.5.6.2	Variation 2:	Alkenation Reactions	330
44.2.5.6.3	Variation 3:	Additions to Heteroatom-Substituted Allenes	333
44.2.5.6.4	Variation 4:	[2 + 1] Cycloadditions	333
44.2.5.6.5	Variation 5:	[2 + 2] Cycloadditions	335
44.2.5.6.6	Variation 6:	[3 + 2] Cycloadditions	336
44.2.5.6.7	Variation 7:	[4 + 2] Cycloadditions	337
44.2.5.6.8	Variation 8:	Aldol Additions of Allenyl Enolate	337
44.2.5.6.9	Variation 9:	Hydrolysis of 1-Cyano-Substituted Allenes	338
44.2.5.7	Method 7:	Elimination Reactions, Rearrangements, and Metathesis Reactions	339
44.2.5.7.1	Variation 1:	Eliminations	339
44.2.5.7.2	Variation 2:	Rearrangements	340
44.2.5.7.3	Variation 3:	Metathesis and Cycloisomerization	341
44.2.6	Applications of Allenes in Organic Synthesis		
	M. A. Tius		
44.2.6	Applications of Allenes in Organic Synthesis		353
44.2.6.1	Method 1:	Diels–Alder Reactions of Allenes	353
44.2.6.1.1	Variation 1:	Intermolecular Reactions To Form Carbocyclic Products	353
44.2.6.1.2	Variation 2:	Intermolecular Reactions To Form Heterocyclic Products	355
44.2.6.1.3	Variation 3:	Intramolecular Reactions	356
44.2.6.2	Method 2:	[2 + 2]-Cycloaddition Reactions of Allenes	359
44.2.6.2.1	Variation 1:	Using Photochemical Methods	359
44.2.6.2.2	Variation 2:	Using Thermal Methods	360
44.2.6.3	Method 3:	Nazarov Reactions	362
44.2.6.3.1	Variation 1:	With Allenes	362
44.2.6.3.2	Variation 2:	With Allenyl Ethers and Ketones	363
44.2.6.3.3	Variation 3:	With Allenyl Ethers and Nitriles	364
44.2.6.3.4	Variation 4:	With Allenyl Ethers and Amides	364
44.2.6.3.5	Variation 5:	Oxidative Cyclizations of Enallenenes	365
44.2.6.4	Method 4:	Pauson–Khand Reactions of Allenes	366
44.2.6.5	Method 5:	[3 + 2] Cycloadditions of Allenes	369
44.2.6.6	Method 6:	[5 + 2] Cycloadditions of Allenes	374
44.2.6.7	Method 7:	Claisen Rearrangement of Allenyl Ethers	375
44.2.6.8	Method 8:	Allenenes as Precursors	376
44.2.6.8.1	Variation 1:	Of Acylsilanes	376
44.2.6.8.2	Variation 2:	Of Lactones	378
44.2.6.8.3	Variation 3:	Of Spiroketals	379
44.2.6.8.4	Variation 4:	Of Spirobisepoxides	380
44.2.6.8.5	Variation 5:	Of Cyclic Ethers, Amines, and Sulfides	382
44.2.6.9	Method 9:	Prins Reaction of Allenes	385
44.2.6.9.1	Variation 1:	With Aldehydes	385
44.2.6.9.2	Variation 2:	With Ketones	387
44.2.6.9.3	Variation 3:	With Imines	388
44.2.6.10	Method 10:	Ene Reactions	390

44.3	Product Class 3: Cyclic Allenes	
	T. Kawase	
44.3	Product Class 3: Cyclic Allenes	395
44.3.1	Product Subclass 1: Cyclohexa-1,2-dienes	396
44.3.1.1	Synthesis of Product Subclass 1	396
44.3.1.1.1	Method 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	396
44.3.1.1.1.1	Variation 1: From 1,1-Dibromocyclopropanes	396
44.3.1.1.1.2	Variation 2: From 1-Bromo-1-fluorocyclopropanes	397
44.3.1.1.2	Method 2: Dehydrohalogenation of 1-Halocyclohexenes	398
44.3.1.1.2.1	Variation 1: Base-Promoted Reactions	398
44.3.1.1.2.2	Variation 2: Photochemical or Thermal Reaction of Intermediate Allyl Anions	399
44.3.1.1.3	Method 3: Dehalogenation of 2,3-Dihalocyclohexenes	399
44.3.1.1.4	Method 4: Elimination from 2-Halo-3-(trimethylsilyl)cyclohexenes	400
44.3.2	Product Subclass 2: Cyclohexa-1,2,4-trienes	400
44.3.2.1	Synthesis of Product Subclass 2	400
44.3.2.1.1	Method 1: [4+2]-Cycloaddition Reactions	401
44.3.2.1.1.1	Variation 1: From Vinylalkynes and Alkynes	401
44.3.2.1.1.2	Variation 2: From Arylalkynes and Alkynes	402
44.3.2.1.1.3	Variation 3: From Diarylacetylenes and Alkynes	404
44.3.2.1.1.4	Variation 4: From Two Arylalkynes	405
44.3.2.1.2	Method 2: Electrocyclization of (Z)-Hexa-1,3-dien-5-yne	406
44.3.2.1.3	Method 3: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	407
44.3.2.1.4	Method 4: Dehydrohalogenation of 1-Halocyclohexa-1,4-dienes	408
44.3.3	Product Subclass 3: Bicyclo[4.4.0]deca-1,3,5,7,8-pentaenes	408
44.3.3.1	Synthesis of Product Subclass 3	408
44.3.3.1.1	Method 1: [4+2]-Cycloaddition Reactions	408
44.3.3.1.1.1	Variation 1: Intermolecular [4+2]-Cycloaddition Reactions	409
44.3.3.1.1.2	Variation 2: Intramolecular [4+2]-Cycloaddition Reactions	409
44.3.3.1.2	Method 2: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	410
44.3.3.1.3	Method 3: Dehydrohalogenation of 3-Bromo-1,2-dihydronaphthalenes	411
44.3.4	Product Subclass 4: Cyclohepta-1,2-dienes	412
44.3.4.1	Synthesis of Product Subclass 4	412
44.3.4.1.1	Method 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	412
44.3.4.1.1.1	Variation 1: From 1,1-Dihalocyclopropanes	412
44.3.4.1.1.2	Variation 2: From 7-Bromo-7-(trimethylstannyl)bicyclo[4.1.0]heptane	413
44.3.4.1.2	Method 2: Ring Enlargement by Cope Rearrangement from 1,2-Diethynylcyclopropanes	414
44.3.4.1.3	Method 3: Ring Enlargement by Thermolysis of Tricyclo[4.1.0.0 ^{2,4}]- hept-5-ylidene or 1-Ethynyl-2-vinylcyclopropane	414
44.3.4.1.4	Method 4: Dehydrohalogenation of 1-Halocycloheptenes	415
44.3.4.1.5	Method 5: Dehalogenation of 1,7-Dihalocycloheptenes	416
44.3.4.1.6	Method 6: Synthesis from 2-Halo-3-(trimethylsilyl)cycloheptenes	417

44.3.5	Product Subclass 5: Cyclohepta-1,2,4,6-tetraenes	417
44.3.5.1	Synthesis of Product Subclass 5	417
44.3.5.1.1	Method 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	418
44.3.5.1.2	Method 2: Ring Enlargement by Extrusion of Nitrogen from Phenyldiazomethanes	419
44.3.5.1.3	Method 3: Ring Enlargement by Extrusion of Nitrogen from 7-Diazobicyclo[2.2.1]hepta-2,5-diene	421
44.3.5.1.4	Method 4: Ring Enlargement by Extrusion of Nitrogen from 2-Diazobicyclo[3.2.0]hepta-3,6-diene and Its Benzo Deriva- tive	422
44.3.5.1.5	Method 5: Dehydrohalogenation of Halocycloheptatrienes	423
44.3.5.1.6	Method 6: Thermal and Photochemical Decomposition of Sodium Salts of Cyclohepta-2,4,6-trien-1-one Tosylhydrazone	424
44.3.6	Product Subclass 6: Cycloocta-1,2-dienes	425
44.3.6.1	Synthesis of Product Subclass 6	425
44.3.6.1.1	Method 1: Intramolecular Ene Reaction of Oct-1-ene-7-yne	425
44.3.6.1.2	Method 2: Electrocyclization of Octa-3,5-diene-1,7-diynes	425
44.3.6.1.3	Method 3: Base-Promoted Cyclization of 1-(3-Chloropropyl)-7- (3-phenylprop-2-ynyl)tricyclo[4.1.0.0 ^{2,7}]heptane	426
44.3.6.1.4	Method 4: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	427
44.3.6.1.5	Method 5: Ring Enlargement by Cope Rearrangement from 1,2-Diethynylcyclobutane and 1-Ethynyl-2-vinylcyclobutane	428
44.3.6.1.6	Method 6: Ring Enlargement of Bicyclo[5.1.0]octa-3,5-dien-2-one	428
44.3.6.1.7	Method 7: Ring Enlargement of 2-(Diazomethyl)bicyclo[4.4.1]- undeca-1,3,5,7,9-pentaene	429
44.3.6.1.8	Method 8: Dehydrohalogenation of 1-Halocyclooctenes	430
44.3.6.1.9	Method 9: Dehydrohalogenation of 3-Bromocyclooct-3-en-1-one	430
44.3.7	Product Subclass 7: Cyclonona-1,2-dienes	431
44.3.7.1	Synthesis of Product Subclass 7	431
44.3.7.1.1	Method 1: S _N 2' Substitution of Organocopper Reagents with a 3-Alkoxyalkyne	431
44.3.7.1.2	Method 2: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	431
44.3.7.1.2.1	Variation 1: From 9,9-Dibromobicyclo[6.1.0]nonane Derivatives	431
44.3.7.1.2.2	Variation 2: From (<i>trans</i> -1-Bicyclo[6.1.0]non-9-yl)-1-nitrosourea	433
44.3.7.1.3	Method 3: Ring Enlargement by Photochemical Rearrangement of 2-Ethynylcycloheptanone	434
44.3.7.1.4	Method 4: Dehydrohalogenation of 1-Halocyclononenes	434
44.3.8	Product Subclass 8: Cyclodeca-1,2-dienes	435
44.3.8.1	Synthesis of Product Subclass 8	435
44.3.8.1.1	Method 1: S _N 2' Substitution of Organocopper(I) Reagents with a 3-Alkoxyalkyne	435
44.3.8.1.2	Method 2: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	435
44.3.8.1.3	Method 3: Dehydrohalogenation of 1-Halocyclodecenes	436

44.3.9	Product Subclass 9: Macrocyclic Allenes	437
44.3.9.1	Synthesis of Product Subclass 9	437
44.3.9.1.1	Method 1: Ring-Closure Reactions	437
44.3.9.1.1.1	Variation 1: Wittig-Type Alkenation from Aromatic Dialdehydes	437
44.3.9.1.1.2	Variation 2: Ring-Closing Alkene Metathesis by Using Grubbs' First-Generation Catalyst	438
44.3.9.1.2	Method 2: Ring Transformations	439
44.3.9.1.2.1	Variation 1: Ring Enlargement by the Doering–Moore–Skattebøl Reaction	439
44.3.9.1.2.2	Variation 2: Extrusion of Nitrogen from an Aryldiazomethane	439
44.3.9.1.3	Method 3: Synthesis from 3-Oxo-, 3-Acetoxy-, or 3-Mesyloxy Cyclic Alkynes	440
44.3.9.1.3.1	Variation 1: Base-Promoted Hydrogen Transfer from a Cycloalk-3-ynone	440
44.3.9.1.3.2	Variation 2: S _N 2' Substitution of Organocopper Reagents with 3-Acetyloxycycloalkynes	441
44.3.9.1.3.3	Variation 3: Palladium(0)-Catalyzed Carbonylation of a Macrocyclic Propargylic Methanesulfonate in the Presence of an Alcohol	441
44.3.9.1.4	Method 4: Substituent Modification	442
44.3.9.1.4.1	Variation 1: From 1,1,3,3-Tetraalkylallenes	442
44.3.9.1.4.2	Variation 2: From 1,3-Diarylallenes	443
44.3.9.1.4.3	Variation 3: From 1,3-Diethynylallenes	444
	Keyword Index	451
	Author Index	485
	Abbreviations	503