

**Volume 9:
Fully Unsaturated Small-Ring Heterocycles and Mono-
cyclic Five-Membered Heteroarenes with One Heteroatom**

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
	Introduction	
	G. Maas	1
9.1	Product Class 1: Oxirenes	
	K.-P. Zeller	19
9.2	Product Class 2: Thiirenes and Their Derivatives	
	N. Tokitoh and W. Ando	43
9.3	Product Class 3: Selenirenes	
	N. Tokitoh and W. Ando	61
9.4	Product Class 4: Tellurirenes	
	N. Tokitoh and W. Ando	65
9.5	Product Class 5: 1<i>H</i>-Azirines	
	K.-P. Zeller	67
9.6	Product Class 6: Phosphirenes	
	H. Heydt	85
9.7	Product Class 7: Three-Membered Rings with Phosphorus and One or More Heteroatoms	
	H. Heydt	125
9.8	Product Class 8: Four-Membered Rings with One or More Heteroatoms	
	M. Regitz and U. Bergsträßer	135
9.9	Product Class 9: Furans	
	B. König	183
9.10	Product Class 10: Thiophenes, Thiophene 1,1-Dioxides, and Thiophene 1-Oxides	
	J. Schatz	287
9.11	Product Class 11: Selenophenes	
	J. Schatz	423
9.12	Product Class 12: Tellurophenes	
	J. Schatz	433
9.13	Product Class 13: 1<i>H</i>-Pyrroles	
	D. StC. Black	441
9.14	Product Class 14: Phospholes	
	F. Mathey	553
	Keyword Index	601
	Author Index	613
	Abbreviations	659

Table of Contents

	Introduction	
	G. Maas	
	<hr/>	
	Introduction	1
9.1	Product Class 1: Oxirenes	
	K.-P. Zeller	
	<hr/>	
9.1	Product Class 1: Oxirenes	19
9.1.1	Synthesis by Ring-Closure Reactions	21
9.1.1.1	By Formation of Two O—C Bonds	21
9.1.1.1.1	Fragments C—C and O	21
9.1.1.1.1.1	Method 1: Oxidation of Alkynes	21
9.1.1.1.1.1.1	Variation 1: With Peroxy Acids	21
9.1.1.1.1.1.2	Variation 2: With Dioxiranes	23
9.1.1.1.1.1.3	Variation 3: With Atomic and Molecular Oxygen	25
9.1.1.1.1.1.4	Variation 4: Enzymatic Oxidation	26
9.1.1.2	By Formation of One O—C Bond	27
9.1.1.2.1	Fragment O—C—C	27
9.1.1.2.1.1	Method 1: Isomerization of α -Oxo Carbenes	27
9.1.1.2.1.2	Method 2: Isomerization of Ketene	34
9.1.2	Synthesis by Ring Transformation	35
9.1.2.1	Method 1: From Larger Heterocycles by Extrusion Reactions	35
9.1.3	Aromatization	36
9.1.3.1	Method 1: Isomerization of Oxiranylidene	36
9.1.3.2	Method 2: β -Elimination Reactions of Oxiranes	37
9.1.3.3	Method 3: Cycloreversion Reactions of Fused Oxiranes	38
9.2	Product Class 2: Thiirenes and Their Derivatives	
	N. Tokitoh and W. Ando	
	<hr/>	
9.2	Product Class 2: Thiirenes and Their Derivatives	43
9.2.1	Product Subclass 1: Thiirenes	44
9.2.1.1	Synthesis by Ring Transformation	46
9.2.1.1.1	Method 1: From 1,2,3-Thiadiazoles	46
9.2.1.1.1.1	Variation 1: Photochemical Decomposition in Matrixes	46
9.2.1.1.1.2	Variation 2: Photochemical Decomposition in Solution	47

9.2.2	Product Subclass 2: Thiirene 1,1-Dioxides	48
9.2.2.1	Synthesis by Ring-Closure Reactions	49
9.2.2.1.1	Method 1: From α,α' -Dihalo-Substituted Sulfones	49
9.2.2.2	Aromatization	50
9.2.2.2.1	Method 1: Dehydrohalogenation of 2-Halothiiranes	50
9.2.3	Product Subclass 3: Thiirene 1-Oxides	52
9.2.3.1	Synthesis by Ring-Closure Reactions	53
9.2.3.1.1	Method 1: From α,α' -Dihalo-Substituted Sulfoxides	53
9.2.3.2	Aromatization	54
9.2.3.2.1	Method 1: Fused Thiirene 1-Oxides from Diels–Alder Reactions of 2,3-Bis(alkylidene)thiirane 1-Oxides	54
9.2.4	Product Subclass 4: Thiirenium Ions	55
9.2.4.1	Synthesis by Ring-Closure Reactions	56
9.2.4.1.1	Method 1: Addition of a Sulfonium Ion to Alkynes	56
9.2.4.1.2	Method 2: From 1-Halo-2-sulfanylethenes	57
9.3	Product Class 3: Selenirenes N. Tokitoh and W. Ando	
9.3	Product Class 3: Selenirenes	61
9.3.1	Synthesis by Ring Transformation	61
9.3.1.1	Method 1: From 1,2,3-Selenadiazoles	61
9.3.1.1.1	Variation 1: Photochemical Decomposition in a Matrix	61
9.3.1.1.2	Variation 2: Photochemical Decomposition in Solution	62
9.4	Product Class 4: Tellurirenes N. Tokitoh and W. Ando	
9.4	Product Class 4: Tellurirenes	65
9.5	Product Class 5: 1H-Azirines K.-P. Zeller	
9.5	Product Class 5: 1H-Azirines	67
9.5.1	Synthesis by Ring-Closure Reactions	68
9.5.1.1	By Formation of Two N—C Bonds	68
9.5.1.1.1	Fragments C—C and N	68
9.5.1.1.1.1	Method 1: Reactions of Alkynes with Nitrenes or Nitrene Equivalents ...	68
9.5.1.1.1.1.1	Variation 1: Generation of Nitrene (NH) from Hydrazoic Acid	68
9.5.1.1.1.1.2	Variation 2: Generation of Nitrenes from Organic Azides	68
9.5.1.1.1.1.3	Variation 3: Oxidation of <i>N</i> -Aminophthalimides in the Presence of Alkynes	69

9.5.1.2	By Formation of One N—C Bond	70
9.5.1.2.1	Fragment N—C—C	70
9.5.1.2.1.1	Method 1: Cyclization of α -Imino Carbenes	70
9.5.1.2.1.1.1	Variation 1: Generation of α -Imino Carbenes from 1 <i>H</i> -1,2,3-Triazoles	71
9.5.1.2.1.1.2	Variation 2: Generation of α -Imino Carbenes from α -Diazo Imines	74
9.5.1.2.1.1.3	Variation 3: Generation of Cyclic α -Imino Carbenes from 1 <i>H</i> -1,2,3-Benzotriazoles (Formation of 1 <i>H</i> -Benzo[<i>b</i>]azirines)	75
9.5.1.2.1.1.4	Variation 4: Generation of Cyclic α -Imino Carbenes from Isatin and Its Derivatives (Formation of 1 <i>H</i> -Benzo[<i>b</i>]azirines)	75
9.5.1.2.1.2	Method 2: Cyclization of Vinylnitrenes	77
9.5.1.3	By Formation of One C—C Bond	79
9.5.1.3.1	Fragment C—N—C	79
9.5.2	Synthesis by Ring Transformation	79
9.5.2.1	Method 1: Extrusion Reactions of Larger Heterocycles	79
9.5.3	Aromatization	80
9.5.3.1	Method 1: Isomerization of Cyclic Isomers	80
9.5.3.2	Method 2: β -Elimination from Aziridines	80
9.5.3.3	Method 3: Cycloreversion Reactions of Fused Aziridines	81
9.6	Product Class 6: Phosphirenes H. Heydt	
9.6	Product Class 6: Phosphirenes	85
9.6.1	Product Subclass 1: λ^5-1<i>H</i>-Phosphirenes	85
9.6.1.1	Synthesis by Substituent Modification	86
9.6.1.1.1	Method 1: Reaction of λ^3 -1 <i>H</i> -Phosphirenes with Benzo-1,2-quinones	86
9.6.1.1.2	Method 2: Reaction of λ^3 -1 <i>H</i> -Phosphirenes with Azodicarboxylates	87
9.6.1.1.3	Method 3: Modification of an Existing λ^5 -1 <i>H</i> -Phosphirene	87
9.6.2	Product Subclass 2: λ^5-1<i>H</i>-Phosphirene Imides, Oxides, and Homologues	87
9.6.2.1	Synthesis by Ring-Closure Reactions	88
9.6.2.1.1	By Formation of Two P—C Bonds	88
9.6.2.1.1.1	Method 1: Cycloaddition of Iminophosphines to Alkynes	88
9.6.2.2	Synthesis by Substituent Modification	89
9.6.2.2.1	Method 1: Oxidative Addition to λ^3 -1 <i>H</i> -Phosphirenes	89
9.6.3	Product Subclass 3: λ^5-1<i>H</i>-Phosphirenium Salts	90
9.6.3.1	Synthesis by Ring-Closure Reactions	91
9.6.3.1.1	By Formation of Two P—C Bonds	91
9.6.3.1.1.1	Method 1: Cycloaddition of Electrophilic Phosphorus Compounds to Alkynes	91
9.6.3.1.1.1.1	Variation 1: Cycloaddition with Phosphenium Cations	91
9.6.3.1.1.1.2	Variation 2: Cycloaddition with Halophosphines	92

9.6.3.1.1.1.3	Variation 3: Reaction with Dichlorophosphines	93
9.6.3.1.1.1.4	Variation 4: Reaction with Phosphiranium Cations	93
9.6.3.2	Synthesis by Substituent Modification	94
9.6.3.2.1	Method 1: Alkylation of λ^3 -1 <i>H</i> -Phosphirenes	94
9.6.3.2.1.1	Variation 1: Alkylation with Alkyl Triflates	94
9.6.3.2.1.2	Variation 2: Alkylation with Trimethyloxonium Tetrafluoroborate	95
9.6.3.2.2	Method 2: Protonation of λ^5 -1 <i>H</i> -Phosphirene Imides	95
9.6.4	Product Subclass 4: η^1-1<i>H</i>-Phosphirene–Metal Complexes	95
9.6.4.1	Synthesis by Ring-Closure Reactions	96
9.6.4.1.1	By Formation of Two P–C Bonds	96
9.6.4.1.1.1	Method 1: Cycloaddition of Phosphinidene Complexes to Alkynes	96
9.6.4.1.1.1.1	Variation 1: With Phosphinidene Complexes Generated from 7-Phosphabicyclo[2.2.1]hepta-2,5-diene Complexes	96
9.6.4.1.1.1.2	Variation 2: With Phosphinidene Complexes Generated from λ^3 -1 <i>H</i> -Phosphirane Complexes	99
9.6.4.1.1.1.3	Variation 3: With Phosphinidene Complexes Generated from λ^3 -2 <i>H</i> -1,2-Azaphosphirene Complexes	100
9.6.4.1.1.1.4	Variation 4: With Phosphinidene Complexes Generated from Secondary λ^3 -Phosphine Complexes	101
9.6.4.1.1.1.5	Variation 5: With Phosphinidene Complexes Generated from Disodium Tetracarbonylferrate (Collman’s Reagent) and an Aminodichlorophosphine	102
9.6.4.2	Synthesis by Substituent Modification	102
9.6.4.2.1	Method 1: Exchange Reactions with the Substituent at Phosphorus	102
9.6.4.2.2	Method 2: Modification of the Metal Fragment	103
9.6.4.2.3	Method 3: Formation of η^1 -1 <i>H</i> -Phosphirene–Metal Complexes by Complexation of λ^3 -1 <i>H</i> -Phosphirenes	104
9.6.5	Product Subclass 5: λ^3-1<i>H</i>-Phosphirenes	105
9.6.5.1	Synthesis by Ring-Closure Reactions	106
9.6.5.1.1	By Formation of Two P–C Bonds	106
9.6.5.1.1.1	Method 1: Cycloaddition of Phosphinidenes to Alkynes	106
9.6.5.1.1.2	Method 2: λ^3 -1 <i>H</i> -Phosphirenes from Metallacyclopropenes	107
9.6.5.1.1.3	Method 3: λ^3 -1 <i>H</i> -Phosphirenes from a Vinylcarbene–Cobalt Complex	107
9.6.5.1.2	By Formation of One P–C and One C–C Bond	108
9.6.5.1.2.1	Method 1: Cycloaddition of Carbenes to Phosphaalkynes	108
9.6.5.1.2.1.1	Variation 1: Cycloaddition with Halocarbenes	109
9.6.5.1.2.1.2	Variation 2: Cycloaddition with Chloro(vinyl)carbenes	110
9.6.5.1.2.1.3	Variation 3: Cycloaddition with a Stable Phosphino(silyl)carbene	111
9.6.5.2	Synthesis by “Aromatization”	111
9.6.5.2.1	Elimination Reactions with λ^3 -Phosphiranes	112
9.6.5.2.1.1	Method 1: Cycloaddition of Halocarbenes to Phosphaalkenes Followed by HX Elimination	112

9.6.5.2.1.2	Method 2: Cyclization of Bis(methylene)phosphoranes Followed by 1,2-Elimination	112
9.6.5.3	Synthesis by Substituent Modification	113
9.6.5.3.1	Method 1: Decomplexation of η^1 -1 <i>H</i> -Phosphirene–Metal Complexes	113
9.6.5.3.1.1	Variation 1: Decomplexation with Iodine and 1-Methyl-1 <i>H</i> -imidazole	113
9.6.5.3.1.2	Variation 2: Decomplexation with 1,2-Bis(diphenylphosphino)ethane	114
9.6.5.3.2	Method 2: Reduction of 1-Halo- λ^5 -1 <i>H</i> -phosphirenium Salts with Tertiary Phosphines	114
9.6.5.3.3	Method 3: Substitution of Hydrogen at the λ^3 -1 <i>H</i> -Phosphirene Double Bond	115
9.6.5.3.4	Method 4: Substitution of Chlorine in 1-Chloro- λ^3 -1 <i>H</i> -phosphirenes	116
9.6.5.3.4.1	Variation 1: Substitution by Hydrogen with Complex Hydrides	116
9.6.5.3.4.2	Variation 2: Substitution by Lithium and Grignard Nucleophiles	116
9.6.5.3.4.3	Variation 3: Substitution by Boron Functionalities with Lithium, Sodium, or Silver Borates	117
9.6.5.3.4.4	Variation 4: Substitution with Silylated and Stannylated Nucleophiles	118
9.6.6	Product Subclass 6: λ^3-1<i>H</i>-Phosphirenium Salts	119
9.7	Product Class 7: Three-Membered Rings with Phosphorus and One or More Heteroatoms H. Heydt	
9.7	Product Class 7: Three-Membered Rings with Phosphorus and One or More Heteroatoms	125
9.7.1	Product Subclass 1: 2λ^3-2<i>H</i>-1,2-Azaphosphirenes	125
9.7.1.1	Synthesis by Ring-Closure Reactions	126
9.7.1.1.1	By Formation of One P–N and One P–C Bond	126
9.7.1.1.1.1	Method 1: From Amino(aryl)carbene Complexes and a P ₁ Reagent	126
9.7.1.1.1.1.1	Variation 1: Reactions of Amino(aryl)carbene Complexes with Chlorophosphaalkenes	126
9.7.1.1.1.1.2	Variation 2: Reactions of Amino(aryl)carbene Complexes with Dichlorophosphines	127
9.7.2	Product Subclass 2: 1λ^3,2λ^3-1<i>H</i>-Diphosphirenes	128
9.7.2.1	Synthesis by Ring-Closure Reactions	128
9.7.2.1.1	By Formation of One P–P and One P–C Bond	129
9.7.2.1.1.1	Method 1: Cycloaddition of Phosphinidenes or Phosphinidene Equivalents to Phosphaalkynes	129
9.7.2.1.1.1.1	Variation 1: Cycloaddition with Iminophosphines	129
9.7.2.1.1.1.2	Variation 2: Cycloaddition with Phosphinidene Complexes	129
9.7.2.1.1.1.3	Variation 3: Cycloaddition with Halo(silyl)phosphines	130
9.7.2.1.1.2	Method 2: Cyclooligomerization of Phosphaalkynes under the Influence of Lewis Acids	130
9.7.2.1.2	By Formation of One P–P Bond	131
9.7.2.1.2.1	Method 1: Cyclization of Aminophosphino-Substituted Phosphaalkenes	131

9.7.2.2	Synthesis by Substituent Modification	131
9.7.3	Product Subclass 3: 1<i>H</i>-Triphosphirenes	132
9.8	Product Class 8: Four-Membered Rings with One or More Heteroatoms M. Regitz and U. Bergsträßer	
9.8	Product Class 8: Four-Membered Rings with One or More Heteroatoms	135
9.8.1	Product Subclass 1: Azetes	135
9.8.1.1	Synthesis by Ring Transformation	137
9.8.1.1.1	Method 1: Ring Enlargement of Azidocyclopropenes	137
9.8.2	Product Subclass 2: λ^5-Phosphetes	138
9.8.2.1	Synthesis by Ring-Closure Reactions	138
9.8.2.1.1	By Formation of One P—C Bond	138
9.8.2.1.1.1	Method 1: From (Arylmethylene)phosphoranes	138
9.8.3	Product Subclass 3: λ^3-Phosphetes	139
9.8.3.1	Synthesis by Ring-Closure Reactions	139
9.8.3.1.1	By Formation of One P—C and One C—C Bond	139
9.8.3.1.1.1	Method 1: From Phosphaalkynes and Alkynes in the Coordination Sphere of Transition Metals	139
9.8.4	Product Subclass 4: 1,2-Dithietes	140
9.8.4.1	Synthesis by Ring-Closure Reactions	141
9.8.4.1.1	By Formation of Two S—C Bonds	141
9.8.4.1.1.1	Method 1: From Alkynes and Sulfur	141
9.8.4.1.1.1.1	Variation 1: From Alkynes and Molten Sulfur	142
9.8.4.1.1.1.2	Variation 2: From Alkynes and Sulfur in Solution	142
9.8.4.1.2	By Formation of One S—S Bond	143
9.8.4.1.2.1	Method 1: From an α -Thioxo Ketone and Lawesson's Reagent	143
9.8.4.2	Synthesis by Ring Transformation	143
9.8.4.2.1	Synthesis by Ring Contraction	143
9.8.4.2.1.1	Method 1: From 1,3-Dithiol-2-ones	143
9.8.4.2.1.2	Method 2: Dimethyl 1,2-Dithiete-3,4-dicarboxylate by Oxidative Ring Contraction of a 2-Titana-1,3-dithiole	144
9.8.5	Product Subclass 5: 1,2-Diselenetes	144
9.8.5.1	Synthesis by Ring Transformation	145
9.8.5.1.1	Synthesis by Ring Contraction	145
9.8.5.1.1.1	Method 1: From a 1,3,2-Diselenazolylium Salt	145
9.8.6	Product Subclass 6: 1,2λ^5-Azaphosphetes	145
9.8.6.1	Synthesis by Ring Transformation	146

9.8.6.1.1	Synthesis by Ring Contraction	146
9.8.6.1.1.1	Method 1: From 1,2,3,4 λ^5 -Triazaphosphinines	146
9.8.6.1.2	Synthesis by Ring Enlargement	147
9.8.6.1.2.1	Method 1: From 2-[Bis(dialkylamino)phosphino]-2 <i>H</i> -azirines	147
9.8.7	Product Subclass 7: 1λ^5,3λ^5-Diphosphetes	149
9.8.7.1	Synthesis by Ring-Closure Reactions	150
9.8.7.1.1	By Formation of Two P—C Bonds	150
9.8.7.1.1.1	Method 1: From Alkylidenephosphoranes	150
9.8.7.1.1.1.1	Variation 1: From [Chloro(phosphino)methylene]phosphoranes	150
9.8.7.1.1.1.2	Variation 2: From (Alkylidene)fluorophosphoranes	151
9.8.7.1.1.2	Method 2: From Diazo(phosphino)(phosphoryl)methanes	152
9.8.7.1.1.3	Method 3: From Diazo(phosphino)(trimethylsilyl)methanes	152
9.8.7.1.1.4	Method 4: From [Bis(trimethylsilyl)methyl]dichlorophosphine	153
9.8.7.2	Synthesis by Substituent Modification	154
9.8.7.2.1	Method 1: From 1,1,3,3-Tetrakis(dimethylamino)-1 λ^5 ,3 λ^5 -diphosphete by Substitution at Ring Carbon Atoms	154
9.8.8	Product Subclass 8: 1λ^5,2λ^3-Diphosphetes	156
9.8.8.1	Synthesis by Ring Transformation	157
9.8.8.1.1	Synthesis by Ring Enlargement	157
9.8.8.1.1.1	Method 1: From a 2-Phosphino-2 <i>H</i> -phosphirene	157
9.8.9	Product Subclass 9: 1λ^3,2λ^3-Diphosphetes	157
9.8.9.1	Synthesis by Ring-Closure Reactions	158
9.8.9.1.1	By Formation of Two P—C Bonds	158
9.8.9.1.1.1	Method 1: From Phosphaalkynes in the Coordination Sphere of Titanium	158
9.8.9.2	Aromatization	159
9.8.9.2.1	Method 1: From a 1,2-Dichloro-1,2-dihydro-1,2-diphosphete–Diiron Complex	159
9.8.10	Product Subclass 10: 1λ^3,3λ^3-Diphosphetes	159
9.8.10.1	Synthesis by Ring-Closure Reactions	160
9.8.10.1.1	By Formation of Two P—C Bonds	160
9.8.10.1.1.1	Method 1: From Phosphaalkynes in the Coordination Sphere of Transition Metals	160
9.8.10.1.1.1.1	Variation 1: From Phosphaalkynes and Transition-Metal–Alkene Complexes	161
9.8.10.1.1.1.2	Variation 2: From Phosphaalkynes and Transition-Metal Carbonyls	163
9.8.10.1.1.1.3	Variation 3: From Phosphaalkynes and Transition-Metal–Arene Complexes	164
9.8.10.1.1.1.4	Variation 4: From Phosphaalkynes and Metal Vapor	165
9.8.10.1.1.1.5	Additional Variations	166
9.8.11	Product Subclass 11: 1,3,2λ^5-Diazaphosphetes	167
9.8.11.1	Synthesis by Ring-Closure Reactions	167

9.8.11.1.1	By Formation of Two N—P Bonds	167
9.8.11.1.1.1	Method 1: From 3-Bromo-3-phenyl-3 <i>H</i> -diazirine and a Stannylphosphine	167
9.8.12	Product Subclass 12: 1λ^5,2λ^3,3λ^5-Triphosphetes	168
9.8.12.1	Synthesis by Ring-Closure Reactions	168
9.8.12.1.1	By Formation of Two P—P Bonds	168
9.8.12.1.1.1	Method 1: From Lithium Bis(diphenylphosphino)(trimethylsilyl)methanide and Phosphorus Trichloride	168
9.8.13	Product Subclass 13: 1λ^3,2λ^3,3λ^3-Triphosphetes	169
9.8.13.1	Synthesis by Ring Transformation	169
9.8.13.1.1	By Ring Contraction	169
9.8.13.1.1.1	Method 1: From a (η^8 -Cyclooctatetraene)(1,4-dihydro-1,2,4-triphosphinine-1,4-diyl)hafnium Complex	169
9.8.14	Product Subclass 14: 1,3,2λ^5,4λ^5-Diazadiphosphetes	170
9.8.14.1	Synthesis by Ring-Closure Reactions	171
9.8.14.1.1	By Formation of Two N—P Bonds	171
9.8.14.1.1.1	Method 1: From Azidobis(diisopropylamino)phosphine	171
9.8.14.1.1.2	Method 2: From <i>N</i> -[Bis(diisopropylamino)phosphino]-C[bis(diisopropylamino)thiophosphoryl]nitrilimine	171
9.8.15	Product Subclass 15: 1λ^5,3λ^5,2λ^3,4λ^3-Tetraphosphetes	172
9.8.15.1	Synthesis by Ring-Closure Reactions	172
9.8.15.1.1	By Formation of Four P—P Bonds	172
9.8.15.1.1.1	Method 1: From Cyclic Bis(amino)chlorophosphines	172
9.8.16	Product Subclass 16: 1,2,3,4-Tetraphosphetes	173
9.8.16.1	Synthesis by Ring-Closure Reactions	174
9.8.16.1.1	By Formation of Four P—P Bonds	174
9.8.16.1.1.1	Method 1: From White Phosphorus in the Coordination Sphere of Transition Metals	174
9.9	Product Class 9: Furans B. König	
9.9	Product Class 9: Furans	183
9.9.1	Synthesis by Ring-Closure Reactions	187
9.9.1.1	By Formation of One O—C and One C—C Bond	187
9.9.1.1.1	Fragments O—C—C and C—C	187
9.9.1.1.1.1	From α -Heterofunctionalized Ketones	187
9.9.1.1.1.1.1	Method 1: Transition-Metal-Catalyzed Reaction of α -Diazoalkanones with Alkynes	187

9.9.1.1.1.1.2	Method 2:	From α -Halo Ketones and 3-Oxoalkanoates (Feist–Benary Reaction)	188
9.9.1.1.1.1.3	Method 3:	From 1,1-Dialkoxy-2-bromoalkanes and Dicarbonyl Compounds or 1-(Trimethylsiloxy)alk-1-enes	189
9.9.1.1.1.1.4	Method 4:	From α -Hydroxy Ketones and Dialkyl But-2-ynedioate	190
9.9.1.1.1.1.5	Method 5:	From α -Hydroxy Ketones and Dicarbonyl Compounds and Derivatives	191
9.9.1.1.1.1.6	Method 6:	From α -Haloalkanones and α -Trimethylstannyl Ketones	192
9.9.1.1.1.2		From 1,3-Dicarbonyl Compounds	192
9.9.1.1.1.2.1	Method 1:	From 1,3-Dicarbonyl Compounds and 3-Bromoalkynes	192
9.9.1.1.1.2.2	Method 2:	Palladium-Catalyzed Reaction of Alkyl 3-Oxoalkanoates with 2-(Alk-1-ynyl)oxiranes	193
9.9.1.1.1.2.3	Method 3:	Manganese-Mediated Reaction of Alkyl 3-Oxoalkanoates with Enol Ethers	194
9.9.1.1.1.2.4	Method 4:	Knoevenagel Condensation of 1,3-Dicarbonyl Compounds and Aldehydes Followed by Bromination and Cyclization	194
9.9.1.1.1.2.5	Method 5:	From 1,3-Dicarbonyl Compounds and 1-Nitroalk-1-enes	195
9.9.1.1.1.2.6	Method 6:	Palladium-Catalyzed Reaction of 1,3-Dicarbonyl Compounds with Prop-2-ynyl Carbonate	196
9.9.1.1.1.3		From Functionalized Alkenes and Alkynes with C,C,O Building Blocks	196
9.9.1.1.1.3.1	Method 1:	From 1-Haloalk-1-enes and Methylene Ketones	196
9.9.1.1.1.3.2	Method 2:	From Alk-2-ynylsulfonium Salts and Carbonyl Compounds	197
9.9.1.1.1.3.3	Method 3:	From 1-Aminoalk-1-ynes and Sulfonylalk-1-ynes	197
9.9.1.1.2		Fragments C—C—C and O—C	198
9.9.1.1.2.1	Method 1:	From 3-Bromopropenal Acetals and Alkanals	198
9.9.1.1.2.2	Method 2:	From Silylallenes and Acid Chlorides	199
9.9.1.1.3		Fragments O—C—C—C and C	200
9.9.1.1.3.1	Method 1:	From α,β -Unsaturated Carbonyl Compounds and Sulfonium Ylides	200
9.9.1.1.3.2	Method 2:	From 1-Aryl-3-chloroalkan-1-ones and Potassium Cyanide	200
9.9.1.1.3.3	Method 3:	From Selectively Protected 1,3-Dicarbonyl Compounds	201
9.9.1.1.3.4	Method 4:	2,3-Disubstituted Furans from 1-(Benzyloxy)-3-tosylalkenes and Aldehydes	202
9.9.1.2		By Formation of Two C—C Bonds	203
9.9.1.2.1		Fragments C—O—C and C—C	203
9.9.1.2.1.1	Method 1:	From Dialkyl Oxalate and Bis(alkoxycarbonylmethyl) Ethers	203
9.9.1.3		By Formation of One O—C Bond	203
9.9.1.3.1		Fragment O—C—C—C—C	203
9.9.1.3.1.1		By Cyclization of 1,4-Diheterofunctional C ₄ Compounds	203
9.9.1.3.1.1.1	Method 1:	Cyclization of 4-Oxobutanamides or 4-Oxobutanenitriles to Furan-2-amines	203
9.9.1.3.1.1.2	Method 2:	Cyclization of 4-Hydroxybut-2-enenitriles	204
9.9.1.3.1.1.3	Method 3:	Reductive Cyclization of Alkene-1,4-diones and Cyclization of 4-Hydroxyalk-2-en-1-ones	205

9.9.1.3.1.1.4	Method 4:	Cyclization of 4-Diazoalk-2-en-1-ones	206
9.9.1.3.1.1.5	Method 5:	Cyclization of 4,4-Dialkoxyalkan-1-ones	206
9.9.1.3.1.1.6	Method 6:	Cyclization of Alkane-1,4-diones (The Paal–Knorr Synthesis)	207
9.9.1.3.1.1.7	Method 7:	Cyclization of γ -Hydroxy Ketone or Their Derivatives	208
9.9.1.3.1.1.8	Method 8:	Cyclization of 1,4-Dihydroxyalk-2-yne	210
9.9.1.3.1.1.9	Method 9:	Oxidative Cyclization of 1,4-Dihydroxyalk-2-enes	210
9.9.1.3.1.2		By Cyclization of Monofunctionalized C ₄ Compounds	211
9.9.1.3.1.2.1	Method 1:	Palladium-Catalyzed Cyclization of Alk-1(2)-yn-4-ones	211
9.9.1.3.1.2.2	Method 2:	Cyclization of Alka-1,2-dien-4-ones	212
9.9.1.3.1.2.3	Method 3:	Cyclization of α -Substituted β,γ -Unsaturated Ketones with Diphenyl Diselenide	213
9.9.1.3.1.2.4	Method 4:	Cyclization of 5-Hydroxyalk-3-en-1-yne	214
9.9.1.3.1.2.5	Method 5:	Base-Assisted Cyclization of 1-(4-Hydroxyalk-2-ynyl)benzotriazoles	216
9.9.1.3.1.2.6	Method 6:	Cyclization of Alkynyloxiranes	216
9.9.1.3.1.2.7	Method 7:	Cyclization of 4-Hydroxyalk-1-yne and Substituted 4-Hydroxyalk-1-enes	218
9.9.1.3.1.2.8	Method 8:	Oxidative Cyclization of Alk-1-en-4-ones	219
9.9.1.4		By Formation of One C–C Bond	220
9.9.1.4.1		Fragment C–O–C–C	220
9.9.1.4.1.1	Method 1:	McMurry-type Cyclization of 1-Acyloxyalk-1-en-3-ones	220
9.9.1.4.2		Fragment C–C–O–C–C	220
9.9.1.4.2.1	Method 1:	Cyclization of 1-(Alk-2-ynyloxy)-2-bromo-1-(organooxy)alkanes via a Radical Mechanism	220
9.9.2		Synthesis by Ring Transformation	221
9.9.2.1		Ring Enlargement	221
9.9.2.1.1	Method 1:	From Epoxides	221
9.9.2.2		From Five-Membered Heterocycles	222
9.9.2.2.1	Method 1:	Cycloaddition of Alkynes to Furans Followed by Retro-Diels–Alder Reaction	222
9.9.2.2.2	Method 2:	Cycloaddition of Alkynes to Oxazoles Followed by Retro-Diels–Alder Reaction	224
9.9.2.2.3	Method 3:	Cycloaddition of Alkynes to Mesoionic Heterocycles Followed by Retro-Diels–Alder Reaction	226
9.9.2.2.4	Method 4:	Decomposition of 4-(Benzoyloxy)-1,3-dioxolanes	227
9.9.2.2.5	Method 5:	Reduction and Rearrangement of 4,5-Dihydroisoxazoles	227
9.9.2.3		Ring Contraction	228
9.9.2.3.1	Method 1:	Synthesis from 2 <i>H</i> -Pyrones	228
9.9.2.3.2	Method 2:	Synthesis from 2 <i>H</i> -Pyrans and Pyrylium Salts	229
9.9.2.3.3	Method 3:	Synthesis from 3,6-Dihydro-1,2-dioxins	230
9.9.2.3.4	Method 4:	Synthesis from Sugar Derivatives	231
9.9.3		Aromatization	232
9.9.3.1	Method 1:	Reduction and Elimination of Water from Furan-2(5 <i>H</i>)-ones	232

9.9.3.2	Method 2: Oxidation of Dihydro- and Tetrahydrofurans	233
9.9.4	Synthesis by Substituent Modification	234
9.9.4.1	Substitution of Hydrogen	234
9.9.4.1.1	Method 1: Replacement by Deuterium	234
9.9.4.1.2	Method 2: Metalation	235
9.9.4.1.2.1	Variation 1: Replacement of Hydrogen by Lithium	235
9.9.4.1.2.2	Variation 2: Replacement of a Halogen by Lithium	238
9.9.4.1.3	Method 3: Introduction of Formyl Groups	239
9.9.4.1.4	Method 4: Introduction of Acyl Groups	241
9.9.4.1.5	Method 5: Introduction of Chloromethyl and Hydroxymethyl Groups	243
9.9.4.1.6	Method 6: Introduction of Aminoalkyl Groups (Mannich Reaction)	243
9.9.4.1.7	Method 7: Introduction of Allyl Groups	244
9.9.4.1.8	Method 8: Introduction of Alk-1-enyl Groups	245
9.9.4.1.9	Method 9: Introduction of Aryl Groups	246
9.9.4.1.10	Method 10: Introduction of Alkyl Groups by Reaction with Alkyl Halides (Friedel–Crafts Reaction)	248
9.9.4.1.11	Method 11: Introduction of Alkyl Groups by Reaction with α,β -Unsaturated Carbonyl Compounds	249
9.9.4.1.12	Method 12: Introduction of Halogen Substituents	249
9.9.4.1.13	Method 13: Sulfonation	252
9.9.4.1.14	Method 14: Nitration	253
9.9.4.2	Substitution of Metals	254
9.9.4.2.1	Method 1: Replacement of Lithium by Hydrogen or Deuterium	254
9.9.4.2.2	Method 2: Replacement of Lithium by a Silyl Group	254
9.9.4.2.3	Method 3: Replacement of Lithium by a Carboxy Group	255
9.9.4.2.4	Method 4: Replacement of Lithium by an Acyl Group	256
9.9.4.2.5	Method 5: Replacement of Lithium by a Hydroxymethyl Group	256
9.9.4.2.6	Method 6: Replacement of Lithium by an Aryl Group via Intermediate Boronates (Suzuki Coupling)	257
9.9.4.2.7	Method 7: Replacement of Lithium by an Aryl or Alkenyl Group via Intermediate Stannanes (Stille Coupling)	258
9.9.4.2.8	Method 8: Replacement of Lithium by an Acyl Group via Intermediate Furylcopper Compounds (Including Ullmann Coupling)	259
9.9.4.2.9	Method 9: Replacement of Lithium by Aryl, Alkenyl, or Alkynyl Groups via Intermediate Furylzinc Compounds	260
9.9.4.2.10	Method 10: Replacement of Lithium by an Alkyl Group	261
9.9.4.2.11	Method 11: Replacement of Lithium by a Halogen	261
9.9.4.2.12	Method 12: Replacement of Lithium by an Alkylsulfanyl or Arylsulfanyl Group	262
9.9.4.3	Substitution of Carbon Functionalities	263
9.9.4.3.1	Method 1: Decarboxylation of Furoic Acids	263
9.9.4.4	Substitution of Heteroatoms	263
9.9.4.4.1	Method 1: Substitution of a Halogen by Hydrogen	263
9.9.4.4.2	Method 2: Reaction of Halo- or Nitrofurans with Carbon Nucleophiles	264

9.9.4.4.3	Method 3:	Metal-Catalyzed Cross Coupling of Halofurans with Alkenes, Arenes, and Alkynes	265
9.9.4.4.4	Method 4:	Reaction of Halo- or Nitrofurans with Hetero Nucleophiles	267
9.9.4.5		Modification of α -Substituents	269
9.9.4.5.1	Method 1:	Enolization of Furan-2(5 <i>H</i>)-ones and Dihydrofuran-2,5-diones	269
9.9.4.5.2	Method 2:	Ene Reaction of 3-Methylene-2,3-dihydrofurans	269
9.9.4.5.3	Method 3:	Wittig Rearrangement of Alkyl 3-Furylmethyl Ether	270
9.9.4.5.4	Method 4:	Anionic Oxy-Cope Reaction of a 2-But-3-enylfuran	271
9.10	Product Class 10: Thiophenes, Thiophene 1,1-Dioxides, and Thiophene 1-Oxides		
	J. Schatz		
9.10	Product Class 10: Thiophenes, Thiophene 1,1-Dioxides, and Thiophene 1-Oxides		287
9.10.1	Product Subclass 1: Thiophenes		287
9.10.1.1	Synthesis by Ring-Closure Reactions		291
9.10.1.1.1	By Formation of Two S—C Bonds and One C—C Bond		291
9.10.1.1.1.1	Fragment S and Two C—C Fragments		291
9.10.1.1.1.1.1	Method 1:	Oxidative Coupling of Aryl Methyl and Related Ketones and a Source of Sulfur	291
9.10.1.1.1.1.2	Method 2:	Reaction of Alkenes or Alkynes with a Source of Sulfur	292
9.10.1.1.1.1.2.1	Variation 1:	Reaction of Alkynes with a Source of Sulfur	292
9.10.1.1.1.1.2.2	Variation 2:	Reaction of Alkenes with a Source of Sulfur	293
9.10.1.1.1.1.3	Method 3:	Thionation of <i>N</i> -(Phenylacetyl)thiobenzamides	293
9.10.1.1.2	By Formation of Two S—C Bonds		294
9.10.1.1.2.1	Fragments C—C—C and S		294
9.10.1.1.2.1.1	Method 1:	Reaction of Buta-1,3-diynes with Sulfuration Reagents	294
9.10.1.1.2.1.1.1	Variation 1:	Reaction of Buta-1,3-diynes with Sulfides	294
9.10.1.1.2.1.1.2	Variation 2:	Reaction of Buta-1,3-diynes with Sulfur Dichloride	295
9.10.1.1.2.1.2	Method 2:	Reaction of Buta-1,3-dienes with a Source of Sulfur	296
9.10.1.1.2.1.3	Method 3:	Reaction of But-2-enes or Butanes with Sulfur	296
9.10.1.1.2.1.4	Method 4:	Cyclization of Sulfinylalkenes	297
9.10.1.1.2.1.4.1	Variation 1:	Reaction of Buta-1,2-dienes with Sulfur Dioxide	297
9.10.1.1.2.1.4.2	Variation 2:	Reaction of 1-Siloxypenta-1,4-dienes with Thionyl Chloride	298
9.10.1.1.2.1.5	Method 5:	Reaction of 1,4-Diketones with Sulfur Reagents and Cyclization (The Paal Synthesis)	298
9.10.1.1.2.1.6	Method 6:	Reaction of α,β -Unsaturated Nitriles with Sulfur (The Gewald Synthesis)	300
9.10.1.1.3	By Formation of One S—C and One C—C Bond		301
9.10.1.1.3.1	Fragments S—C—C and C		301
9.10.1.1.3.1.1	Method 1:	S-Alkylation of β -Thioxo Carbonyl Compounds or β -Thioxonitriles Followed by Ring Closure	301

9.10.1.1.3.1.1.1	Variation 1:	S-Alkylation of Enolizable β -Thioxo Carbonyl Compounds or β -Thioxonitriles	301
9.10.1.1.3.1.1.2	Variation 2:	Reaction of β -Oxo Dithioesters and β -Oxothioamides with a 4-Bromobut-2-enoate	303
9.10.1.1.3.1.1.3	Variation 3:	Reaction of Active Methylene Compounds with Carbon Disulfide Followed by S-Alkylation and Ring Closure	304
9.10.1.1.3.1.2	Method 2:	Carbene Addition to α -Oxoketene Dithioacetals and α -Oxoketene Monothioacetals	305
9.10.1.1.3.2	Fragments S—C—C and C—C		306
9.10.1.1.3.2.1	Method 1:	From α -Sulfanyl Ketones	306
9.10.1.1.3.2.1.1	Variation 1:	Reaction of α -Sulfanyl Ketones with 2-(Diethoxyphosphoryl)-Substituted Alk-2-enoates	306
9.10.1.1.3.2.1.2	Variation 2:	From α -Sulfanyl Ketones and Cyanoacetates	307
9.10.1.1.3.2.2	Method 2:	Reaction of α -Alkylsulfanyl Ketones with Grignard Reagents	308
9.10.1.1.3.2.3	Method 3:	From Vinyl Sulfides and Alkynes	309
9.10.1.1.3.2.4	Method 4:	From 1,2,3-Thiadiazoles and Alkynes	310
9.10.1.1.3.3	Fragments S—C and C—C—C		311
9.10.1.1.3.3.1	Method 1:	Reaction of Dithioesters with Alk-1-ynes	311
9.10.1.1.3.3.2	Method 2:	Reaction of Isothiocyanates with Allyl or Alkynyl Compounds	312
9.10.1.1.3.3.2.1	Variation 1:	Reaction of Isothiocyanates with (Cyanomethyl)ketene Dithioacetals	312
9.10.1.1.3.3.2.2	Variation 2:	Reaction of Isothiocyanates with Alk-1-ynyllithium Compounds	313
9.10.1.1.3.3.3	Method 3:	Reaction of Thioglycolates with β -Electrophilic Carbonyl Compounds or Equivalents	314
9.10.1.1.3.3.3.1	Variation 1:	Reaction of Thioglycolates with β,β -Dihalo or α,β -Dihalo Carbonyl Compounds	314
9.10.1.1.3.3.3.2	Variation 2:	Reaction of Thioglycolates with β -Chlorovinyl Carbonyl Compounds and Equivalents (The Fiesselmann Synthesis)	315
9.10.1.1.3.3.3.3	Variation 3:	Reaction of Thioglycolates with β -Chloro-Substituted Cinnamionitriles	316
9.10.1.1.3.3.3.4	Variation 4:	Reaction of Thioglycolates with α -Oxoalkynes	317
9.10.1.1.3.3.3.5	Variation 5:	Reaction of Thioglycolates or α -Sulfanyl Ketones with Acetylenic Esters	318
9.10.1.1.3.3.3.6	Variation 6:	Reaction of Thioglycolic Acid or Esters with β -Oxo Esters	320
9.10.1.1.3.3.4	Method 4:	Reaction of Benzyl Thiols with Butadiynes	321
9.10.1.1.3.3.5	Method 5:	Reaction of Thiocarboxylic Acids with a Cyclopropyl(triphenyl)phosphonium Salt	322
9.10.1.1.3.3.6	Method 6:	Reaction of Dithiocarbonates or Equivalents and Cyclopropenylium Salts	323
9.10.1.1.4	By Formation of Two C—C Bonds		324
9.10.1.1.4.1	Fragments C—S—C—C and C		324
9.10.1.1.4.1.1	Method 1:	S-Alkylation of Thioamides and Reaction with a Chloromethaniminium Salt	324
9.10.1.1.4.2	Fragments C—S—C and C—C		325
9.10.1.1.4.2.1	Method 1:	Reaction of 3-Thia-1,5-dicarbonyl Compounds or Equivalents with 1,2-Dicarbonyl Compounds (The Hinsberg Synthesis)	325

9.10.1.1.4.2.2	Method 2:	1,3-Dipolar Cycloaddition of Thiocarbonyl Ylides with Alkynes	326
9.10.1.1.4.2.2.1	Variation 1:	Reaction of 1,3-Dithiolylium-4-olates with Alkynes	326
9.10.1.1.4.2.2.2	Variation 2:	Reaction of Bis[(trimethylsilyl)methyl] Sulfoxides with Alkynes	327
9.10.1.1.4.2.3	Method 3:	From 1,3-Thiazoles and Alkynes	328
9.10.1.1.5	By Formation of One S—C Bond		329
9.10.1.1.5.1	Fragment S—C—C—C		329
9.10.1.1.5.1.1	Method 1:	From ω -Sulfanyl Carbonyl Compounds by Ring Closure	329
9.10.1.1.5.1.1.1	Variation 1:	Cyclization of γ -Sulfanyl Ketones	329
9.10.1.1.5.1.1.2	Variation 2:	Oxidative Cyclization of 2-Sulfanylpenta-2,4-dienoic Acids	330
9.10.1.1.5.1.2	Method 2:	Cyclization of 3-Sulfanylprop-1-ynyl Ketones	331
9.10.1.1.5.1.3	Method 3:	From γ,δ -Unsaturated Thioamides	332
9.10.1.1.6	By Formation of One C—C Bond		334
9.10.1.1.6.1	Fragment C—S—C—C—C		334
9.10.1.1.6.1.1	Method 1:	Cyclization of Aroylketene <i>S,N</i> -Acetals	334
9.10.1.1.6.2	Fragment C—C—S—C—C		334
9.10.1.1.6.2.1	Method 1:	From β,β' -Dioxo Sulfides by Reductive Coupling	334
9.10.1.2	Synthesis by Ring Transformation		336
9.10.1.2.1	From Five-Membered Heterocycles		336
9.10.1.2.1.1	Method 1:	From Zirconocenes and Disulfur Dichloride	336
9.10.1.2.1.2	Method 2:	From 1,2-Thiazolium Salts	336
9.10.1.2.1.3	Method 3:	From 3-Amino-1,2-dithiolium Salts	337
9.10.1.2.1.4	Method 4:	From 1,3-Oxathiolium Salts	338
9.10.1.2.1.5	Method 5:	From Furans	340
9.10.1.2.2	Ring Contraction		340
9.10.1.2.2.1	Method 1:	From 1,2- or 1,4-Dithiins	340
9.10.1.2.2.1.1	Variation 1:	From 1,2-Dithiins by Thermal or Photochemical Ring Contraction, or by Use of Thiophilic Phosphorus Reagents	340
9.10.1.2.2.1.2	Variation 2:	From 1,4-Dithiins by Thermal Ring Contraction	341
9.10.1.2.2.1.3	Variation 3:	From 1,4-Dithiins via their <i>S</i> -Oxides	342
9.10.1.2.2.2	Method 2:	From 4 <i>H</i> -Thiopyrans and Thiopyrylium Salts	343
9.10.1.2.3	Ring Expansion		344
9.10.1.2.3.1	Method 1:	From Thiiranes	344
9.10.1.2.3.1.1	Variation 1:	From 2-(1-Hydroxyalk-2-ynyl)thiiranes by Electrophile-Induced Ring Expansion	344
9.10.1.2.3.1.2	Variation 2:	From 2-(2-Oxoalkyl)thiiranes	345
9.10.1.2.3.1.3	Variation 3:	From 2-(2-Oxoalkyl)oxiranes	346
9.10.1.3	Aromatization		347
9.10.1.3.1	Method 1:	From Dihydro- and Tetrahydrothiophenes	347
9.10.1.4	Synthesis by Substituent Modification		349
9.10.1.4.1	Substitution of Hydrogen		349
9.10.1.4.1.1	Method 1:	Hydrogen–Deuterium Exchange	349

9.10.1.4.1.2	Method 2:	Metalation	349
9.10.1.4.1.2.1	Variation 1:	Generation of Organometallic Compounds by Hydrogen–Lithium Exchange	349
9.10.1.4.1.3	Method 3:	Introduction of Formyl Groups	351
9.10.1.4.1.4	Method 4:	Introduction of Acyl Groups	352
9.10.1.4.1.5	Method 5:	Introduction of Chloromethyl and Hydroxymethyl Groups	354
9.10.1.4.1.6	Method 6:	Introduction of Alkylamino Groups (The Mannich Reaction)	355
9.10.1.4.1.7	Method 7:	Introduction of Allyl, Alk-1-enyl, or Alk-1-ynyl Groups	356
9.10.1.4.1.8	Method 8:	Introduction of Aryl Groups	357
9.10.1.4.1.9	Method 9:	Introduction of Alkyl Groups	360
9.10.1.4.1.10	Method 10:	Halogenation	362
9.10.1.4.1.11	Method 11:	Sulfonation	366
9.10.1.4.1.12	Method 12:	Nitration	367
9.10.1.4.2		Substitution of Metals	369
9.10.1.4.2.1	Method 1:	Substitution Reactions Involving Organostannanes (The Stille Reaction)	370
9.10.1.4.2.2	Method 2:	Substitution Reactions Involving Organocopper or Organozinc Derivatives	371
9.10.1.4.2.3	Method 3:	Substitution Reactions Involving Organoboron Derivatives (The Suzuki Reaction)	373
9.10.1.4.2.4	Method 4:	Substitution Reactions Involving Organolithium Derivatives	374
9.10.1.4.2.4.1	Variation 1:	Replacement of Lithium by Hydrogen or Deuterium	374
9.10.1.4.2.4.2	Variation 2:	Replacement of Lithium by a Silyl Group	375
9.10.1.4.2.4.3	Variation 3:	Replacement of Lithium by a Carboxy Group	376
9.10.1.4.2.4.4	Variation 4:	Replacement of Lithium by a Formyl or Acyl Group	376
9.10.1.4.2.4.5	Variation 5:	Replacement of Lithium by a Hydroxymethyl or an Aminomethyl Group	378
9.10.1.4.2.4.6	Variation 6:	Replacement of Lithium by an Alkyl, Alkenyl, Alkynyl, or Aryl Group	380
9.10.1.4.2.4.7	Variation 7:	Replacement of Lithium by a Halogen	381
9.10.1.4.2.4.8	Variation 8:	Replacement of Lithium by a Sulfanyl or Sulfonyl Group	382
9.10.1.4.3		Substitution of Carbon Functionalities	383
9.10.1.4.3.1	Method 1:	Decarboxylation	383
9.10.1.4.4		Substitution of Heteroatoms	384
9.10.1.4.4.1	Method 1:	Substitution of Halogen by Hydrogen	384
9.10.1.4.4.2	Method 2:	Substitution of Halogen by Lithium	385
9.10.1.4.4.3	Method 3:	Substitution of Halogen by Alkoxy or Sulfanyl Groups	386
9.10.1.4.4.4	Method 4:	Metal-Assisted Cross Coupling of Halothiophenes with Alkenes, Arenes, and Alkynes	387
9.10.1.4.4.4.1	Variation 1:	Manganese-Assisted Coupling Reactions	387
9.10.1.4.4.4.2	Variation 2:	Zinc-Assisted Coupling Reactions	388
9.10.1.4.4.4.3	Variation 3:	Palladium-Assisted Coupling Reactions	388
9.10.1.4.5		Modification of α -Substituents	389
9.10.1.4.5.1	Method 1:	Enolization of Dihydrothiophene-2,5-diones	390
9.10.1.4.5.2	Method 2:	Aromatization of Dihydrothiophen-3(2H)-ones	391

9.10.1.4.5.3	Method 3: Side-Chain Bromination of Alkylthiophenes	392
9.10.2	Product Subclass 2: Thiophene 1,1-Dioxides	393
9.10.2.1	Synthesis by Ring Transformation	394
9.10.2.1.1	Oxidation of Thiophenes	394
9.10.2.1.1.1	Method 1: Oxidation of Thiophenes	394
9.10.2.2	Aromatization	395
9.10.2.2.1	Method 1: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Elimination	395
9.10.2.2.1.1	Variation 1: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Hydrogen Halide Elimination	395
9.10.2.2.1.2	Variation 2: From Dihydro- or Tetrahydrothiophene 1,1-Dioxides by Nitrous Acid Elimination	396
9.10.3	Product Subclass 3: Thiophene 1-Oxides	396
9.10.3.1	Synthesis by Ring Transformation	397
9.10.3.1.1	Formal Exchange of Ring Members	397
9.10.3.1.1.1	Method 1: From Zirconocenes	397
9.10.3.1.2	Oxidation of Thiophenes	398
9.10.3.1.2.1	Method 1: Oxidation of Thiophenes	398
9.11	Product Class 11: Selenophenes J. Schatz	
9.11	Product Class 11: Selenophenes	423
9.11.1	Synthesis by Ring-Closure Reactions	425
9.11.1.1	By Formation of Two Se—C Bonds	425
9.11.1.1.1	Fragments C—C—C and Se	425
9.11.1.1.1.1	Method 1: Reaction of C ₄ Building Blocks with Sources of Selenium	425
9.11.1.1.1.1.1	Variation 1: Reaction of 1,4-Dilithio- or 1,4-Diiodobutadienes with a Selenium Source	425
9.11.1.1.1.1.2	Variation 2: Reaction of Butadiynes with Selenides	425
9.11.1.1.1.1.3	Variation 3: Reaction of 1-Alkynyl-2-bromobenzenes with Elemental Selenium	426
9.11.1.1.1.1.4	Variation 4: Reaction of Chloroalkynols or Alkynyloxiranes with Selenides	427
9.11.1.2	By Formation of Two C—C Bonds	428
9.11.1.2.1	Fragments C—Se—C and C—C	428
9.11.1.2.1.1	Method 1: From 1,2-Diketones and a Selenodiacetate (Hinsberg Synthesis)	428
9.11.1.3	By Formation of One C—C Bond	428
9.11.1.3.1	Fragment C—C—Se—C—C	428
9.11.1.3.1.1	Method 1: Reductive Cyclization of Diphenacyl Selenides	428

9.11.2	Synthesis by Formal Exchange of Ring Members	429
9.11.2.1	Method 1: Exchange of Zirconium by Selenium	429
9.11.3	Synthesis by Substituent Modification	430
9.12	Product Class 12: Tellurophenes J. Schatz	
9.12	Product Class 12: Tellurophenes	433
9.12.1	Synthesis by Ring-Closure Reactions	435
9.12.1.1	By Formation of Two Te—C Bonds	435
9.12.1.1.1	Fragments C—C—C and Te	435
9.12.1.1.1.1	Method 1: Reaction of C ₄ Building Blocks with Sources of Tellurium	435
9.12.1.1.1.1.1	Variation 1: Reaction of 1,4-Dilithio- or 1,4-Diodobutadienes with a Tellurium Source	435
9.12.1.1.1.1.2	Variation 2: Reaction of Butadiynes with Tellurides	435
9.12.1.1.1.1.3	Variation 3: Reaction of 1-Alkynyl-2-bromobenzenes or But-1-en-3-yne with Elemental Tellurium	436
9.12.1.1.1.1.4	Variation 4: Reaction of Chloroalkynols with Tellurides	437
9.12.1.2	By Formation of One C—C Bond	438
9.12.1.2.1	Fragment C—Te—C—C	438
9.12.1.2.1.1	Method 1: Cyclization of 3-(Alkyltellanyl)propenals	438
9.12.2	Synthesis by Substituent Modification	438
9.13	Product Class 13: 1H-Pyrroles D. StC. Black	
9.13	Product Class 13: 1H-Pyrroles	441
9.13.1	Synthesis by Ring-Closure Reactions	444
9.13.1.1	By Formation of Two N—C Bonds and One C—C Bond	444
9.13.1.1.1	Fragment N and Two C—C Fragments	444
9.13.1.1.1.1	Method 1: Condensation Reaction of β -Dicarbonyl Compounds, α -Halo Carbonyl Compounds and Amines (The Hantzsch Synthesis)	444
9.13.1.1.1.2	Method 2: Condensation Reaction of Benzyl Ketones, Benzoin, and Ammonia	446
9.13.1.1.1.3	Method 3: Condensation Reaction of Aliphatic Aldehydes or Ketones and Hydrazines (The Piloty Synthesis)	447
9.13.1.2	By Formation of One N—C Bond and Two C—C Bonds	449
9.13.1.2.1	Fragments N—C, C—C, and C	449
9.13.1.2.1.1	Method 1: Reaction of Trimethylsilyl Cyanide with Alkynes, Catalyzed by Palladium(II) or Nickel(II) Chloride	449
9.13.1.2.1.2	Method 2: Reaction of Zirconium and Titanium Complexes with Alkynes and Carbonyl Compounds	450

9.13.1.2.1.2.1	Variation 1:	Reaction of Zirconocene Derivatives of Alkylamines with Alkynes and Carbon Monoxide	450
9.13.1.2.1.2.2	Variation 2:	Reaction of Zirconocene Derivatives of C-Silyl Imine Compounds with Alkynes and Acyl Chlorides	451
9.13.1.2.1.2.3	Variation 3:	Reaction of Titanium Alkyne Complexes with Imines and Carbon Monoxide	452
9.13.1.2.1.3	Method 3:	Reaction of Terminal Alkynes with Imines and Tungsten–Carbene Complexes	452
9.13.1.2.1.4	Method 4:	Reaction of Imines with α -Haloacetals and 1-Benzylbenzotriazoles	453
9.13.1.3	By Formation of Three C—C Bonds		454
9.13.1.3.1	Fragment C—N—C and Two C Fragments		454
9.13.1.3.1.1	Method 1:	Reaction of Alkyl Isocyanacetates with Aldehydes	454
9.13.1.4	By Formation of Two N—C Bonds		455
9.13.1.4.1	Fragments C—C—C and N		455
9.13.1.4.1.1	Method 1:	Condensation Reactions of 1,4-Dicarbonyl Compounds or Equivalents with Amines (The Paal–Knorr Synthesis)	455
9.13.1.4.1.2	Method 2:	Reaction of 4-Substituted Carbonyl Compounds or Equivalents with Amines	458
9.13.1.4.1.3	Method 3:	Reaction of Alk-2-enyl Carbonyl Compounds or Equivalents with Amines	459
9.13.1.4.1.4	Method 4:	Reaction of Alk-3-ynyl Carbonyl Compounds with Amines	461
9.13.1.4.1.5	Method 5:	Reaction of Buta-1,3-dienes and Related Compounds with Amines	461
9.13.1.4.1.6	Method 6:	Reaction of Buta-1,3-diynes with Amines	462
9.13.1.4.1.7	Method 7:	Pyrrol-2-amines from the Reaction of Functionalized Nitriles with Amines	463
9.13.1.4.1.8	Method 8:	2-(Benzotriazolylmethyl)pyrroles from the Reaction of Alkynyloxiranes with Amines	464
9.13.1.5	By Formation of One N—C and One C—C Bond		465
9.13.1.5.1	Fragments N—C—C and C		465
9.13.1.5.1.1	Method 1:	Reaction of α,β -Unsaturated Imines with Esters and Niobium(III) Chloride	465
9.13.1.5.1.2	Method 2:	Reaction of α,β -Unsaturated Imine Iron–Tricarbonyl Complexes with Methyllithium	466
9.13.1.5.1.3	Method 3:	Hydroformylation and a Related Reaction of Propargylamines	466
9.13.1.5.1.4	Method 4:	Reaction of β -Amino Ketones with Diazo(trimethylsilyl)methane	467
9.13.1.5.1.5	Method 5:	3-Aminopyrrole-2,4-dicarbonitriles from the Reaction of Alkylidenemalononitriles with Aminoacetoneitriles	468
9.13.1.5.2	Fragments N—C—C and C—C		469
9.13.1.5.2.1	Method 1:	Condensation Reaction of α -Amino Ketones with Methylene-Active Carbonyl Compounds (The Knorr Pyrrole Synthesis)	469
9.13.1.5.2.2	Method 2:	Condensation Reaction of Enamino Esters with α -Electrophilic Carbonyl Compounds and their Synthetic Equivalents	472

9.13.1.5.2.3	Method 3:	Reaction of Enamino Esters with α -Diazo Ketones	474
9.13.1.5.2.4	Method 4:	Reaction of Oximes (and Hydrazones) with Alkynes	474
9.13.1.5.2.5	Method 5:	Reaction of Azoalkenes with Methylene Ketones	475
9.13.1.5.2.6	Method 6:	Combination of α -Amino Carbonyl Compounds and Enolates via Aldol Reactions	476
9.13.1.5.2.7	Method 7:	Reaction of α -Metalated Imines with α -Halo Ketones or α -Diketones	478
9.13.1.5.3		Fragments N—C and C—C—C	481
9.13.1.5.3.1	Method 1:	Reaction of α -Aminoacyl or α -Iminoacyl Compounds with 1,3-Diketones or Equivalents	481
9.13.1.5.3.2	Method 2:	Reaction of Benzotriazole Enamines with Imines	486
9.13.1.5.3.3	Method 3:	Reaction of Allenes with Tosylimines	486
9.13.1.6		By Formation of Two C—C Bonds	487
9.13.1.6.1		Fragments C—N—C—C and C	487
9.13.1.6.1.1	Method 1:	Reaction of 2-Arylvinyl Isocyanides with Carbon Nucleophiles	487
9.13.1.6.2		Fragments C—N—C and C—C	488
9.13.1.6.2.1	Method 1:	Aldol Reaction of α -Diketones with Bis(acceptor-substituted methyl)amines	488
9.13.1.6.2.2	Method 2:	Reaction of α -Amidonitriles with Vinylphosphonium Salts	488
9.13.1.6.2.3	Method 3:	Reaction of Isocyano-Substituted Acetates, Acetonitriles, or Methylphosphonates with Nitroalkenes	489
9.13.1.6.2.4	Method 4:	Reaction of Tosylmethyl Isocyanide with Electrophilic Alkenes	491
9.13.1.6.2.5	Method 5:	Reaction of <i>N</i> -(Tosylmethyl)- or <i>N</i> -(Benzotriazolylmethyl)-Substituted Imidothioates with Electrophilic Alkenes	494
9.13.1.6.2.6	Method 6:	Reaction of Azomethine Ylides or Related Systems with Alkynes or Alkenes	495
9.13.1.6.2.7	Method 7:	Reaction of Chromium-(Alkylidenamino)carbene Complexes with Alkynes	498
9.13.1.7		By Formation of One N—C Bond	498
9.13.1.7.1		Fragment N—C—C—C—C	498
9.13.1.7.1.1	Method 1:	Cyclizative Condensations	498
9.13.1.7.1.2	Method 2:	Cyclization of Alk-4-yn-1-amines	500
9.13.1.7.1.3	Method 3:	Cyclization of Dienyl Azides	501
9.13.1.8		By Formation of One C—C Bond	502
9.13.1.8.1		Fragment C—N—C—C—C	502
9.13.1.8.1.1	Method 1:	Reactions Involving Typical C—C Bond Construction	502
9.13.1.8.2		Fragment C—C—N—C—C	503
9.13.1.8.2.1	Method 1:	Reactions Involving Typical C—C Bond Construction	503
9.13.2		Synthesis by Ring Transformation	504
9.13.2.1		By Ring Enlargement	504
9.13.2.1.1	Method 1:	Rearrangement of an Azabicyclo[2.1.0]pent-2-ene	504
9.13.2.1.2	Method 2:	Rearrangement of 2-Vinyl-2 <i>H</i> -azirines	504

9.13.2.2	By Ring Contraction	505
9.13.2.2.1	Method 1: Rearrangement of Pyridine and 1,3-Oxazepine Derivatives	505
9.13.3	Synthesis by Aromatization	505
9.13.3.1	By Reduction	506
9.13.3.1.1	Method 1: Reduction–Dehydration of 1 <i>H</i> -Pyrrol-2(5 <i>H</i>)-ones and 1 <i>H</i> -Pyrrol-2(3 <i>H</i>)-one	506
9.13.3.2	By Elimination	506
9.13.3.2.1	Method 1: Elimination from Substituted 3,4-Dihydro-2 <i>H</i> -pyrroles	506
9.13.3.3	By Isomerization	508
9.13.3.3.1	Method 1: Rearrangement of 2 <i>H</i> -Pyrroles	508
9.13.3.4	By Dehydrogenation	508
9.13.3.4.1	Method 1: Dehydrogenation of Dihydro- and Tetrahydropyrroles	508
9.13.4	Synthesis by Substituent Modification	509
9.13.4.1	Substitution of Existing Substituents	509
9.13.4.1.1	Substitution of Hydrogen	509
9.13.4.1.1.1	Method 1: Metalation	509
9.13.4.1.1.2	Method 2: C-Acylation	509
9.13.4.1.1.3	Method 3: C-Alkylation	513
9.13.4.1.1.3.1	Variation 1: C-Alkylation by Typical Electrophiles	513
9.13.4.1.1.3.2	Variation 2: C-Alkylation (and Arylation) by Carbenes and Free Radicals	514
9.13.4.1.1.3.3	Variation 3: C-Alkylation by Various Electrophiles	516
9.13.4.1.1.4	Method 4: C-Halogenation	518
9.13.4.1.1.5	Method 5: C-Thiolation	520
9.13.4.1.1.6	Method 6: C-Nitration and Amination	520
9.13.4.1.1.7	Method 7: N-Substitution	521
9.13.4.1.2	Substitution of Metals	524
9.13.4.1.2.1	Method 1: Substitution Reactions Involving Mercury and Thallium Derivatives	525
9.13.4.1.2.2	Method 2: Substitution Reactions Involving Organocopper and Organozinc Derivatives	526
9.13.4.1.2.3	Method 3: Substitution Reactions Involving Organopalladium Derivatives	527
9.13.4.1.2.4	Method 4: Substitution Reactions Involving Organolithium Derivatives	530
9.13.4.1.3	Substitution of Carbon Functionalities	532
9.13.4.1.3.1	Method 1: Reactions Involving Decarboxylation from a Ring Carbon	532
9.13.4.1.3.2	Method 2: Reactions Involving Dealkylation from the Ring Nitrogen	532
9.13.4.1.3.3	Method 3: Reactions Involving Detritylation from the Ring Nitrogen	533
9.13.4.1.4	Substitution of Heteroatoms	534
9.13.4.1.4.1	Method 1: Replacement of Tosyl by Trialkylstannyl Groups on a Ring Carbon	534
9.13.4.1.4.2	Method 2: Replacement of Sulfur and Silyl Groups on the Ring Nitrogen	534
9.13.4.2	Modification of Substituents	535

9.13.4.2.1	Modification of Acyl Substituents	535
9.13.4.2.1.1	Method 1: Reduction of Acyl Groups to Alkyls	535
9.13.4.2.1.2	Method 2: Addition and Condensation Reactions of Acyl Groups	537
9.13.4.2.1.3	Method 3: Rearrangement of Acyl Groups	539
9.13.4.2.2	Modification of Alkyl Substituents	539
9.13.4.2.2.1	Method 1: Substitution Reactions of Mannich Bases	539
9.13.4.2.2.2	Method 2: Alkylation of α -Methylene Substituents	541
9.13.4.2.2.3	Method 3: Halogenation of α -Methylene Substituents	541
9.13.4.2.2.4	Method 4: Oxidation of α -Methylene Substituents	542
9.14	Product Class 14: Phospholes	
	F. Mathey	
9.14	Product Class 14: Phospholes	553
9.14.1	Product Subclass 1: λ^3-1H-Phospholes	555
9.14.1.1	Synthesis by Ring-Closure Reactions	557
9.14.1.1.1	By Formation of Two P—C Bonds and One C—C Bond	557
9.14.1.1.1.1	Fragment P and Two C—C Fragments	557
9.14.1.1.1.1.1	Method 1: Reaction of Dihalophosphines with Enamines	557
9.14.1.1.2	By Formation of Two P—C Bonds	558
9.14.1.1.2.1	Fragments C—C—C and P	558
9.14.1.1.2.1.1	Method 1: Reaction of Dithiophosphines with 1,4-Dihalo-Substituted 1,3-Dienes	558
9.14.1.1.2.1.2	Method 2: Reaction of Dihalophosphines with 1,4-Dithio-Substituted 1,3-Dienes	559
9.14.1.1.2.1.3	Method 3: Reaction of Primary Phosphines with 1,3-Diynes	559
9.14.1.1.2.1.4	Method 4: Thermal Reaction of Dihalophosphines with 1,3-Dienes	560
9.14.1.2	Synthesis by Ring Transformation	561
9.14.1.2.1	Method 1: Reaction of Dihalophosphines with Metallacyclopentadienes	561
9.14.1.2.2	Method 2: Insertion of Alkynes into Phosphirenes	562
9.14.1.3	Aromatization	563
9.14.1.3.1	Method 1: Dehalogenation of <i>P</i> -Halophospholium Salts Obtained from Dihalophosphines and Cyclobutadiene–Aluminum Trichloride Complexes	563
9.14.1.3.2	Method 2: Dehydrohalogenation of 1-Halodihydrophospholium Halides	564
9.14.1.3.2.1	Variation 1: <i>P</i> -Bromination of 2,5-Dihydro- λ^3 -1H-phospholes Followed by Dehydrobromination	566
9.14.1.3.2.2	Variation 2: Quaternization of 1-Bromo-2,5-dihydro-1H-phospholes Followed by Dehydrobromination	568
9.14.1.3.3	Method 3: Dehydrohalogenation of <i>C</i> -Halophospholane 1-Oxides	568
9.14.1.4	Synthesis by Substituent Modification	569
9.14.1.4.1	Addition Reactions	569

9.14.1.4.1.1	Method 1: Reaction of Electrophiles with Phospholide Ions	569
9.14.1.4.1.2	Method 2: α -Functionalization of 1 <i>H</i> -Phosphol-2-ylolithiums	573
9.14.1.4.2	Substitution of Existing Substituents	575
9.14.1.4.2.1	Method 1: Reaction of Nucleophiles with Phospholes	575
9.14.1.4.2.2	Method 2: Transformation of α -Substituents	576
9.14.1.4.2.3	Method 3: Reduction of λ^5 -Phospholes	577
9.14.1.4.3	Decomplexation and Thermolysis	578
9.14.1.4.3.1	Method 1: Decomplexation of Phosphole σ -Complexes	578
9.14.1.4.3.2	Method 2: Thermolysis of λ^3 -Phospholes	579
9.14.2	Product Subclass 2: Phospholide Ions	581
9.14.2.1	Aromatization	582
9.14.2.1.1	Method 1: Cleavage of the Exocyclic P–R Bond of λ^3 -1 <i>H</i> -Phospholes	582
9.14.2.1.1.1	Variation 1: By Alkali Metals	582
9.14.2.1.1.2	Variation 2: By Base	583
9.14.2.1.2	Method 2: Deprotonation of Transient 2 <i>H</i> -Phospholes	584
9.14.3	Product Subclass 3: η^5-Phospholyl Complexes	585
9.14.3.1	Synthesis by Ring-Closure Reactions	588
9.14.3.1.1	Method 1: Assembly of a Phospholyl Ring	588
9.14.3.2	Synthesis by Complexation	588
9.14.3.2.1	Method 1: From Phospholide Ions	588
9.14.3.2.1.1	Variation 1: Via Intermediate 1-Stannyl-1 <i>H</i> -phospholes or 1,1'-Bi-1 <i>H</i> -phospholes	590
9.14.3.2.2	Method 2: From λ^3 -1 <i>H</i> -Phospholes	592
9.14.3.2.3	Method 3: From λ^3 -2 <i>H</i> -Phospholes	593
9.14.3.3	Synthesis by Substituent Modification	594
9.14.3.3.1	Method 1: Electrophilic Substitution	594
9.14.3.3.2	Method 2: Modification of α -Substituents	595
	Keyword Index	601
	Author Index	613
	Abbreviations	659