

Table of Contents

Volume 10: Fused Five-Membered Heteroarenes with One Heteroatom

| | | |
|-------------------|---|-----|
| 10.21 | Product Class 21: Five–Five-Fused Heteroarenes with One Heteroatom in Each Ring | New |
| | S. P. Stanforth | |
| 10.21 | Product Class 21: Five–Five-Fused Heteroarenes with One Heteroatom in Each Ring | 1 |
| 10.21.1 | Product Subclass 1: Hetaryl[3,2-<i>b</i>]heteroarenes (1,4-Diheteropentalenes) .. | 4 |
| 10.21.1.1 | Synthesis by Ring-Closure Reactions | 4 |
| 10.21.1.1.1 | By Annulation to a Heteroarene | 4 |
| 10.21.1.1.1.1 | By Formation of Two Heteroatom–Carbon Bonds | 4 |
| 10.21.1.1.1.1.1 | Method 1: Synthesis from Alkynyldiols | 4 |
| 10.21.1.1.1.1.2 | Method 2: Synthesis from 2-Alkynyl-3-bromoheteroarenes | 5 |
| 10.21.1.1.1.1.3 | Method 3: Synthesis from 3-Bromo-2-(2-bromoalkenyl)heteroarenes | 7 |
| 10.21.1.1.1.2 | By Formation of One Heteroatom–Carbon Bond and One C–C Bond | 8 |
| 10.21.1.1.1.2.1 | Method 1: Synthesis from 2-Acetyl-3-halothiophenes | 8 |
| 10.21.1.1.1.3 | By Formation of One Heteroatom–Carbon Bond | 8 |
| 10.21.1.1.1.3.1 | Method 1: Formation of a Ring-Junction Heteroatom–Carbon Bond | 8 |
| 10.21.1.1.1.3.1.1 | Variation 1: From 2-(2-Sulfanylalkenyl)heteroarenes | 8 |
| 10.21.1.1.1.3.1.2 | Variation 2: From 2-(2-Azidoalkenyl)heteroarenes | 8 |
| 10.21.1.1.1.3.2 | Method 2: Formation of a Non-Ring-Junction Heteroatom–Carbon Bond | 10 |
| 10.21.1.1.1.3.2.1 | Variation 1: From 2-Alkynyl-3-(<i>tert</i> -butylsulfanyl)heteroarenes | 10 |
| 10.21.1.1.1.3.2.2 | Variation 2: From 2-Alkynyl-3-aminoheteroarenes | 10 |
| 10.21.1.1.1.3.2.3 | Variation 3: From 2-Alkenyl-3-nitroheteroarenes and Related Compounds | 11 |
| 10.21.1.1.1.3.2.4 | Variation 4: From 2-Alkenyl-3-azidoheteroarenes | 13 |
| 10.21.1.1.1.3.2.5 | Variation 5: From 3-Amino-2-(2,2-dichlorovinyl)heteroarenes | 15 |
| 10.21.1.1.1.3.2.6 | Variation 6: From 3-Hydroxy-2-(2-oxoalkyl)heteroarenes | 15 |
| 10.21.1.1.1.4 | By Formation of One C–C Bond | 17 |
| 10.21.1.1.1.4.1 | Method 1: Formation of a C–C Bond between Two Non-Ring-Junction Carbons | 17 |
| 10.21.1.1.1.4.2 | Method 2: Formation of a C–C Bond between One Ring-Junction Carbon and One Non-Ring-Junction Carbon | 20 |
| 10.21.1.1.1.4.2.1 | Variation 1: By a Cyclodehydration or Equivalent Reaction | 20 |
| 10.21.1.1.1.4.2.2 | Variation 2: By a Dehydrohalogenation Reaction | 22 |
| 10.21.1.1.1.4.2.3 | Variation 3: By an Oxidative Cyclization Reaction | 23 |
| 10.21.1.2 | Synthesis by Ring Transformation | 23 |

| | | | |
|-------------------|--------------|---|----|
| 10.21.1.2.1 | Method 1: | Ring Contraction of 1 λ^4 ,2-Thiazine | 23 |
| 10.21.1.3 | | Aromatization | 24 |
| 10.21.1.3.1 | Method 1: | Dehydrogenation | 24 |
| 10.21.1.3.2 | Method 2: | Dehydration | 25 |
| 10.21.1.4 | | Synthesis by Substituent Modification | 26 |
| 10.21.1.4.1 | | Substitution of Existing Substituents | 26 |
| 10.21.1.4.1.1 | | Of C-Hydrogen | 26 |
| 10.21.1.4.1.1.1 | Method 1: | Formation of C-Metal Compounds | 26 |
| 10.21.1.4.1.1.1.1 | Variation 1: | Formation of C-Lithium | 26 |
| 10.21.1.4.1.1.1.2 | Variation 2: | Formation of C-Magnesium | 29 |
| 10.21.1.4.1.1.2 | Method 2: | Formation of C-Carbon Compounds | 29 |
| 10.21.1.4.1.1.2.1 | Variation 1: | Formation of C-Nitrile | 29 |
| 10.21.1.4.1.1.2.2 | Variation 2: | Formation of C-Alkene | 29 |
| 10.21.1.4.1.1.2.3 | Variation 3: | Formation of C-Carbonyl | 31 |
| 10.21.1.4.1.1.2.4 | Variation 4: | Formation of C-(Aminoalkyl) | 32 |
| 10.21.1.4.1.1.2.5 | Variation 5: | Oxidative Coupling Giving Heterene Polymers | 33 |
| 10.21.1.4.1.1.3 | Method 3: | Formation of C-Halogen Compounds | 34 |
| 10.21.1.4.1.1.4 | Method 4: | Formation of C-Nitrogen Compounds | 38 |
| 10.21.1.4.1.2 | | Of N-Hydrogen | 38 |
| 10.21.1.4.1.2.1 | Method 1: | N-Alkylation | 38 |
| 10.21.1.4.1.3 | | Of Metals | 40 |
| 10.21.1.4.1.3.1 | Method 1: | Formation of C-Hydrogen Compounds | 40 |
| 10.21.1.4.1.3.2 | Method 2: | Formation of Different C-Metal Compounds | 41 |
| 10.21.1.4.1.3.2.1 | Variation 1: | Formation of C-Boron | 41 |
| 10.21.1.4.1.3.2.2 | Variation 2: | Formation of C-Silicon | 42 |
| 10.21.1.4.1.3.2.3 | Variation 3: | Formation of C-Tin | 44 |
| 10.21.1.4.1.3.3 | Method 3: | Formation of C-Carbon Compounds | 47 |
| 10.21.1.4.1.3.3.1 | Variation 1: | Formation of C-Carboxylic Acid and C-Ester | 47 |
| 10.21.1.4.1.3.3.2 | Variation 2: | Formation of C-Carbonyl | 49 |
| 10.21.1.4.1.3.3.3 | Variation 3: | Formation of C-(1-Hydroxyalkyl) | 52 |
| 10.21.1.4.1.3.3.4 | Variation 4: | Formation of C-Alkyl | 52 |
| 10.21.1.4.1.3.3.5 | Variation 5: | Reductive Elimination Giving Heterene Oligomers | 54 |
| 10.21.1.4.1.3.3.6 | Variation 6: | Formation of C-Aryl: Suzuki–Miyaura Reaction | 56 |
| 10.21.1.4.1.3.3.7 | Variation 7: | Formation of C-Aryl: Stille Reaction | 57 |
| 10.21.1.4.1.3.4 | Method 4: | Formation of C-Heteroatom Compounds | 59 |
| 10.21.1.4.1.3.4.1 | Variation 1: | Formation of C-Halogen | 59 |
| 10.21.1.4.1.3.4.2 | Variation 2: | Formation of C-Oxygen: Oxidation of Boronic Acids | 60 |
| 10.21.1.4.1.3.4.3 | Variation 3: | Formation of C-Sulfur, C-Selenium, or C-Tellurium | 60 |
| 10.21.1.4.1.4 | | Of Carbon Functionalities | 63 |
| 10.21.1.4.1.4.1 | | Of C-Carboxylic Acid | 63 |
| 10.21.1.4.1.4.1.1 | Method 1: | Formation of C-Hydrogen Compounds | 63 |
| 10.21.1.4.1.4.1.2 | Method 2: | Formation of C-Aldehydes | 66 |
| 10.21.1.4.1.4.1.3 | Method 3: | Formation of C-Bromides | 66 |

| | | |
|-------------------|---|----|
| 10.21.1.4.1.5 | Of Heteroatoms | 66 |
| 10.21.1.4.1.5.1 | Of C-Halogen | 66 |
| 10.21.1.4.1.5.1.1 | Method 1: Formation of C-Hydrogen Compounds | 66 |
| 10.21.1.4.1.5.1.2 | Method 2: Formation of C-Metal Compounds | 68 |
| 10.21.1.4.1.5.1.3 | Method 3: Formation of C-Alkyl Compounds | 68 |
| 10.21.1.4.1.5.1.4 | Method 4: Formation of C-Aryl Compounds: Suzuki–Miyaura Reaction | 69 |
| 10.21.1.4.1.5.1.5 | Method 5: Formation of C-Aryl Compounds: Stille Reaction | 70 |
| 10.21.1.4.1.5.1.6 | Method 6: Formation of C-Heteroatom Compounds | 70 |
| 10.21.1.4.2 | Addition Reactions | 72 |
| 10.21.1.4.2.1 | Addition of Heteroatoms | 72 |
| 10.21.1.4.2.1.1 | Method 1: Synthesis of S,S-Dioxides | 72 |
| 10.21.1.4.3 | Rearrangement of Substituents | 74 |
| 10.21.1.4.3.1 | Method 1: “Halogen Dance” Isomerization | 74 |
| 10.21.1.4.4 | Modification of Substituents | 74 |
| 10.21.1.4.4.1 | Method 1: O-Alkylation | 74 |
| 10.21.2 | Product Subclass 2: Hetaryl[2,3-<i>c</i>]hetarenes and Hetaryl[3,4-<i>b</i>]hetarenes (1,5-Diheteropentalenes) | 76 |
| 10.21.2.1 | Synthesis by Ring-Closure Reactions | 76 |
| 10.21.2.1.1 | By Annulation to a Hetarene | 76 |
| 10.21.2.1.1.1 | By Formation of Two Heteroatom—Carbon Bonds | 76 |
| 10.21.2.1.1.1.1 | Method 1: Synthesis from 4-Oxoprolines | 76 |
| 10.21.2.1.1.1.2 | Method 2: Synthesis from 2(3)-Acetylthiophene-3(2)-carbaldehydes | 76 |
| 10.21.2.1.1.1.3 | Method 3: Synthesis from 2-[Hydroxy(aryl)methyl]thiophene-3-carbaldehydes | 77 |
| 10.21.2.1.1.1.4 | Method 4: Synthesis from 3-Aroyl-2-(bromomethyl)hetarenes | 77 |
| 10.21.2.1.1.1.5 | Method 5: Synthesis from 4-Bromo-3-(2-bromoalkenyl)hetarenes | 78 |
| 10.21.2.1.1.1.6 | Method 6: Synthesis from 2-[[2(3)-(Bromomethyl)-3(2)-hetaryl]methylene]malonates | 79 |
| 10.21.2.1.1.2 | By Formation of One Heteroatom—Carbon and One C—C Bond | 80 |
| 10.21.2.1.1.2.1 | Method 1: Synthesis from 2-Thioaroylhetarenes | 80 |
| 10.21.2.1.1.3 | By Formation of One Heteroatom—Carbon Bond | 80 |
| 10.21.2.1.1.3.1 | Method 1: Synthesis from 2-Alkynyl-3-bromohetarenes | 80 |
| 10.21.2.1.1.3.2 | Method 2: Synthesis from 2-[[2(3)-(Azidomethyl)-3(2)-hetaryl]methylene]malonates | 82 |
| 10.21.2.1.1.3.3 | Method 3: Synthesis from 2-Benzoyl-3-[(ethylsulfinyl)methyl]thiophene and Related Compounds | 83 |
| 10.21.2.1.1.3.4 | Method 4: Synthesis from 3-Carbonyl-2-(hydroxymethyl)hetarene Derivatives | 84 |
| 10.21.2.1.1.3.5 | Method 5: Synthesis from 2-(4,4-Dimethyldihydrooxazolium)-3-[hydroxy(phenyl)methyl]thiophene Iodide | 86 |
| 10.21.2.1.1.3.6 | Method 6: Synthesis from 3-Alkynyl-2-(2-oxiranyl)hetarenes | 86 |

| | | |
|-------------------|---|-----|
| 10.21.2.1.1.4 | By Formation of One C—C Bond | 87 |
| 10.21.2.1.1.4.1 | Method 1: Formation of a C—C Bond between Two Non-Ring-Junction Carbons | 87 |
| 10.21.2.1.1.4.2 | Method 2: Formation of a C—C Bond between One Ring-Junction Carbon and One Non-Ring-Junction Carbon | 89 |
| 10.21.2.1.1.4.2.1 | Variation 1: By a Cyclodehydration or Equivalent Reaction | 89 |
| 10.21.2.1.1.4.2.2 | Variation 2: By a Dehydrohalogenation Reaction | 90 |
| 10.21.2.2 | Aromatization | 90 |
| 10.21.2.2.1 | Method 1: Dehydrogenation | 90 |
| 10.21.2.2.2 | Method 2: Dehydration | 91 |
| 10.21.2.2.3 | Method 3: Elimination of Dimethyl Sulfide | 92 |
| 10.21.2.3 | Synthesis by Substituent Modification | 93 |
| 10.21.2.3.1 | Substitution of Existing Substituents | 93 |
| 10.21.2.3.1.1 | Of C-Hydrogen | 93 |
| 10.21.2.3.1.1.1 | Method 1: Formation of C-Carbon Compounds | 93 |
| 10.21.2.3.1.1.1.1 | Variation 1: Formation of C-Aldehyde | 93 |
| 10.21.2.3.1.1.1.2 | Variation 2: Oxidative Coupling Giving Hetarene Polymers | 94 |
| 10.21.2.3.1.1.2 | Method 2: Formation of C-Bromides | 94 |
| 10.21.2.3.1.2 | Of Carbon Functionalities | 95 |
| 10.21.2.3.1.2.1 | Of C-Carboxylic Acid | 95 |
| 10.21.2.3.1.2.1.1 | Method 1: Formation of C-Hydrogen Compounds | 95 |
| 10.21.2.3.1.3 | Of Heteroatoms | 96 |
| 10.21.2.3.1.3.1 | Of C-Bromine | 96 |
| 10.21.2.3.1.3.1.1 | Method 1: Formation of C-Aryl Compounds: Stille Reaction | 96 |
| 10.21.3 | Product Subclass 3: Hetaryl[2,3-<i>b</i>]hetarenes (1,6-Diheteropentalenes) | 97 |
| 10.21.3.1 | Synthesis by Ring-Closure Reactions | 97 |
| 10.21.3.1.1 | By Annulation to a Hetarene | 97 |
| 10.21.3.1.1.1 | By Formation of Two Heteroatom—Carbon Bonds | 97 |
| 10.21.3.1.1.1.1 | Method 1: Synthesis from 2-Bromo-3-(2-bromoalkenyl)hetarenes | 97 |
| 10.21.3.1.1.1.2 | Method 2: Synthesis from 3-(3-Thienyl)acrylic Acids | 98 |
| 10.21.3.1.1.1.3 | Method 3: Synthesis from Dihydrothiophen-3(2 <i>H</i>)-ones | 98 |
| 10.21.3.1.1.2 | By Formation of One Heteroatom—Carbon and One C—C Bond | 99 |
| 10.21.3.1.1.3 | By Formation of One Heteroatom—Carbon Bond | 99 |
| 10.21.3.1.1.3.1 | Method 1: Formation of a Ring-Junction Heteroatom—Carbon Bond | 99 |
| 10.21.3.1.1.3.1.1 | Variation 1: From 3-(2-Sulfanylalkenyl)hetarenes | 99 |
| 10.21.3.1.1.3.1.2 | Variation 2: From 2-Bromo-3-(2-sulfanylalkenyl)hetarenes | 99 |
| 10.21.3.1.1.3.1.3 | Variation 3: From 3-(2-Azidoalkenyl)hetarenes | 100 |
| 10.21.3.1.1.3.2 | Method 2: Formation of a Non-Ring-Junction Heteroatom—Carbon Bond | 101 |
| 10.21.3.1.1.3.2.1 | Variation 1: From 2-(Butylselanyl)- and 2-(Butyltellanyl)-3-(ethynyl)thiophenes | 101 |
| 10.21.3.1.1.3.2.2 | Variation 2: From 3-Alkynyl-2-aminohetarenes | 102 |

| | | | |
|-------------------|---------------------------------------|---|-----|
| 10.21.3.1.1.3.2.3 | Variation 3: | From Diynes and Carbon Disulfide | 102 |
| 10.21.3.1.1.3.2.4 | Variation 4: | From 3-Substituted 2-Nitrothiophenes | 103 |
| 10.21.3.1.1.3.2.5 | Variation 5: | From 2-Amino-3-(2,2-dichlorovinyl)thiophenes | 104 |
| 10.21.3.1.1.4 | By Formation of One C—C Bond | | 105 |
| 10.21.3.1.1.4.1 | Method 1: | Formation of a C—C Bond between Two Non-Ring-Junction Carbons | 105 |
| 10.21.3.1.1.4.2 | Method 2: | Formation of a C—C Bond between One Ring-Junction Carbon and One Non-Ring-Junction Carbon | 112 |
| 10.21.3.1.1.4.2.1 | Variation 1: | By a Cyclodehydration Reaction | 112 |
| 10.21.3.1.1.4.2.2 | Variation 2: | By a Fischer-Indole-Type Synthesis | 113 |
| 10.21.3.1.1.4.2.3 | Variation 3: | From 2-(But-2-ynylsulfanyl)thiophenes | 114 |
| 10.21.3.1.1.4.2.4 | Variation 4: | By a Dehydrohalogenation Reaction | 115 |
| 10.21.3.1.1.4.2.5 | Variation 5: | By an Oxidative Cyclization Reaction | 117 |
| 10.21.3.2 | Aromatization | | 117 |
| 10.21.3.2.1 | Method 1: | Dehydration | 117 |
| 10.21.3.3 | Synthesis by Substituent Modification | | 118 |
| 10.21.3.3.1 | Substitution of Existing Substituents | | 118 |
| 10.21.3.3.1.1 | Of C-Hydrogen | | 118 |
| 10.21.3.3.1.1.1 | Method 1: | Formation of C-Lithium Compounds | 118 |
| 10.21.3.3.1.1.2 | Method 2: | Formation of C-Carbon Compounds | 118 |
| 10.21.3.3.1.1.2.1 | Variation 1: | Formation of C-Carbonyl | 118 |
| 10.21.3.3.1.1.2.2 | Variation 2: | Formation of C-(Aminoalkyl) | 120 |
| 10.21.3.3.1.1.3 | Method 3: | Formation of C-Halides | 121 |
| 10.21.3.3.1.1.4 | Method 4: | Formation of C-Nitrogen Compounds | 123 |
| 10.21.3.3.1.2 | Of N-Hydrogen | | 123 |
| 10.21.3.3.1.3 | Of C-Metals | | 124 |
| 10.21.3.3.1.3.1 | Method 1: | Formation of Different C-Metal Compounds | 124 |
| 10.21.3.3.1.3.1.1 | Variation 1: | Formation of C-Silicon | 124 |
| 10.21.3.3.1.3.1.2 | Variation 2: | Formation of C-Tin | 125 |
| 10.21.3.3.1.3.2 | Method 2: | Formation of C-Carbon Compounds | 126 |
| 10.21.3.3.1.3.2.1 | Variation 1: | Formation of C-Carboxylic Acid | 126 |
| 10.21.3.3.1.3.2.2 | Variation 2: | Formation of C-Carbonyl | 126 |
| 10.21.3.3.1.3.2.3 | Variation 3: | Formation of C-(1-Hydroxyalkyl) | 128 |
| 10.21.3.3.1.3.2.4 | Variation 4: | Formation of C-Alkyl | 128 |
| 10.21.3.3.1.3.3 | Method 3: | Formation of C-Heteroatom Compounds | 129 |
| 10.21.3.3.1.3.3.1 | Variation 1: | Formation of C-Halogen | 129 |
| 10.21.3.3.1.3.3.2 | Variation 2: | Formation of C-Sulfur | 130 |
| 10.21.3.3.1.4 | Of Carbon Functionalities | | 131 |
| 10.21.3.3.1.4.1 | Of C-Carboxylic Acid | | 131 |
| 10.21.3.3.1.4.1.1 | Method 1: | Formation of C-Hydrogen Compounds | 131 |
| 10.21.3.3.1.4.1.2 | Method 2: | Formation of C-Bromides | 132 |
| 10.21.3.3.1.5 | Of Heteroatoms | | 133 |
| 10.21.3.3.1.5.1 | Of C-Halogen | | 133 |

| | | | |
|-------------------|---|--|-----|
| 10.21.3.3.1.5.1.1 | Method 1: | Formation of C-Hydrogen Compounds | 133 |
| 10.21.3.3.1.5.1.2 | Method 2: | Formation of C-Metal Compounds | 134 |
| 10.21.3.3.1.5.1.3 | Method 3: | Formation of C-Aryl Compounds: Suzuki–Miyaura Reaction | 134 |
| 10.21.3.3.1.5.1.4 | Method 4: | Formation of C-Aryl Compounds: Stille Reaction | 135 |
| 10.21.3.4 | Addition Reactions | | 136 |
| 10.21.3.4.1 | Addition of Heteroatoms | | 136 |
| 10.21.3.4.1.1 | Method 1: | Synthesis of S,S-Dioxides | 136 |
| 10.21.3.5 | Modification of Substituents | | 136 |
| 10.21.3.5.1 | Method 1: | O-Alkylation | 136 |
| 10.21.4 | Product Subclass 4: Hetaryl[3,4-c]hetarenes (2,5-Diheteropentalenes) | | 137 |
| 10.21.4.1 | Synthesis by Ring-Closure Reactions | | 137 |
| 10.21.4.1.1 | By Annulation to a Hetarene | | 137 |
| 10.21.4.1.1.1 | By Formation of Two Heteroatom—Carbon Bonds | | 137 |
| 10.21.4.1.1.1.1 | Method 1: | Synthesis from 2,3-Dibenzoylhetarenes | 137 |
| 10.21.4.1.1.1.2 | Method 2: | Synthesis from 3,4-Bis(cyanomethyl)hetarenes | 138 |
| 10.21.4.2 | Synthesis by Ring Transformation | | 139 |
| 10.21.4.2.1 | Method 1: | Dimerization of Cyclopropenethiones | 139 |
| 10.21.4.3 | Aromatization | | 140 |
| 10.21.4.3.1 | Method 1: | Dehydration | 140 |
| 10.21.4.3.2 | Method 2: | Elimination of Trifluoroacetate | 141 |
| 10.21.4.3.3 | Method 3: | Debromination | 142 |

Volume 17: Six-Membered Hetarenes with Two Unlike or More than Two Heteroatoms and Fully Unsaturated Larger- Ring Heterocycles

| | | | |
|------------------|--|---|------|
| 17.1 | Product Class 1: Six-Membered Hetarenes with Two Unlike Heteroatoms | | |
| 17.1.2.5 | One Oxygen and One Nitrogen or Phosphorus Atom | | 2014 |
| | R. A. Aitken and A. Meehan | | |
| 17.1.2.5 | One Oxygen and One Nitrogen or Phosphorus Atom | | 149 |
| 17.1.2.5.1 | 1,4-Oxazines | | 149 |
| 17.1.2.5.1.1 | Synthesis by Ring-Closure Reactions | | 149 |
| 17.1.2.5.1.1.1 | By Formation of One O—C Bond | | 149 |
| 17.1.2.5.1.1.1.1 | Method 1: | Reaction of <i>N</i> -(Hydroxyalkyl)- <i>N</i> -propargyl-4-toluenesulfonamides with Base | 149 |
| 17.1.2.5.1.2 | Synthesis by Ring Transformation | | 150 |

| | | | |
|--------------------|--|--|-----|
| 17.1.2.5.1.2.1 | Method 1: | Reaction of 2 <i>H</i> -Azirines with 2-Diazo-1,3-dicarbonyl Compounds | 150 |
| 17.1.2.5.1.3 | Aromatization | | 152 |
| 17.1.2.5.1.3.1 | Method 1: | Reaction of 5,6-Dihydro-2 <i>H</i> -1,4-oxazin-2-ones with <i>p</i> -Chloranil | 152 |
| 17.1.2.5.1.4 | Synthesis by Substituent Modification | | 152 |
| 17.1.2.5.1.4.1 | Substitution of Existing Substituents | | 152 |
| 17.1.2.5.1.4.1.1 | Of Hydrogen | | 152 |
| 17.1.2.5.1.4.1.1.1 | Method 1: | Reaction of 3,5-Disubstituted 2 <i>H</i> -1,4-Oxazines with Acetic Anhydride | 152 |
| 17.1.2.5.1.4.1.1.2 | Method 2: | Reaction of Substituted 4 <i>H</i> -1,4-Oxazines with Butyllithium Followed by an Electrophile | 153 |
| 17.1.2.5.1.4.1.1.3 | Method 3: | Reaction of 3,5-Bis[(diphenoxyphosphoryl)oxy]-4 <i>H</i> -1,4-oxazines with Butyllithium Followed by an Aldehyde | 155 |
| 17.1.2.5.1.4.1.2 | Of <i>tert</i> -Butoxycarbonyl | | 156 |
| 17.1.2.5.1.4.1.2.1 | Method 1: | Thermal Decomposition of 4-(<i>tert</i> -Butoxycarbonyl)-4 <i>H</i> -1,4-oxazines | 156 |
| 17.1.2.5.1.4.1.3 | Of Halogen | | 157 |
| 17.1.2.5.1.4.1.3.1 | Method 1: | Sonogashira Coupling of 3,4,5-Trisubstituted 2-Iodo-4 <i>H</i> -1,4-oxazines with Alkynes | 157 |
| 17.1.2.5.1.4.1.4 | Of (Diphenoxyphosphoryl)oxy | | 158 |
| 17.1.2.5.1.4.1.4.1 | Method 1: | Reduction of 3,5-Bis[(diphenoxyphosphoryl)oxy]-4 <i>H</i> -1,4-oxazines with Formic Acid | 158 |
| 17.1.2.5.1.4.1.4.2 | Method 2: | Stille Reaction of 3,5-Bis[(diphenoxyphosphoryl)oxy]-4 <i>H</i> -1,4-oxazines with Organotin Compounds | 158 |
| 17.1.2.5.1.4.1.4.3 | Method 3: | Suzuki–Miyaura Reaction of 3,5-Bis[(diphenoxyphosphoryl)oxy]-4 <i>H</i> -1,4-oxazines with Arylboronic Acids | 159 |
| 17.1.2.5.1.4.2 | Modification of Substituents | | 160 |
| 17.1.2.5.1.4.2.1 | Method 1: | Reaction of 4-Acetyl-4 <i>H</i> -1,4-oxazines with Lithium Aluminum Hydride | 160 |
| 17.1.2.5.1.4.2.2 | Method 2: | Wittig Reaction of 3,4,5-Trisubstituted 4 <i>H</i> -1,4-Oxazine-2-carbaldehydes | 161 |
| 17.1.2.5.1.4.2.3 | Method 3: | Reaction of Morpholine-3,5-diones with Potassium Hexamethyldisilazanide and Diphenyl Chlorophosphate | 161 |
| 17.1.2.5.2 | 1,4-Benzoxazines | | 162 |
| 17.1.2.5.2.1 | Synthesis by Ring-Closure Reactions | | 162 |
| 17.1.2.5.2.1.1 | By Formation of One O—C and One N—C Bond | | 162 |
| 17.1.2.5.2.1.1.1 | From 2-Aminophenols | | 162 |
| 17.1.2.5.2.1.1.1.1 | Method 1: | Reaction of 2-Aminophenols with α -Oxo Esters | 162 |
| 17.1.2.5.2.1.1.1.2 | Method 2: | Reaction of 2-Aminophenols with 1,2-Diketones | 163 |
| 17.1.2.5.2.1.1.2 | From 2-Nitrosophenols | | 164 |
| 17.1.2.5.2.1.1.2.1 | Method 1: | Reaction of 2-Nitrosophenols with Electron-Rich Alkenes | 164 |

| | | |
|--------------------|---|-----|
| 17.1.2.5.2.2 | Aromatization | 167 |
| 17.1.2.5.2.2.1 | Dehydrogenation | 167 |
| 17.1.2.5.2.2.1.1 | Method 1: Polonovski Reaction of 2,4-Disubstituted 3,4-Dihydro-2 <i>H</i> -1,4-benzoxazines | 167 |
| 17.1.2.5.2.2.1.2 | Method 2: Swern Oxidation of Substituted (3,4-Dihydro-2 <i>H</i> -1,4-benzoxazin-2-yl)methanols | 168 |
| 17.1.2.5.2.2.2 | Elimination | 168 |
| 17.1.2.5.2.2.2.1 | Method 1: Elimination of Hydrogen Bromide | 168 |
| 17.1.2.5.2.2.2.2 | Method 2: Elimination of Ethanol | 169 |
| 17.1.2.5.2.3 | Synthesis by Substituent Modification | 170 |
| 17.1.2.5.2.3.1 | Substitution of Existing Substituents | 170 |
| 17.1.2.5.2.3.1.1 | Of Hydrogen | 170 |
| 17.1.2.5.2.3.1.1.1 | Method 1: N-Alkylation of 4 <i>H</i> -1,4-Benzoxazine-2-carbaldehydes | 170 |
| 17.1.2.5.2.3.1.1.2 | Method 2: N-Acylation of 4 <i>H</i> -1,4-Benzoxazine-2-carbaldehydes | 171 |
| 17.1.2.5.2.3.1.2 | Of Methylsulfanyl | 172 |
| 17.1.2.5.2.3.1.2.1 | Method 1: Reaction of 3-(Methylsulfanyl)-2 <i>H</i> -1,4-benzoxazines with Amine Nucleophiles | 172 |
| 17.1.2.5.2.3.2 | Modification of Substituents | 172 |
| 17.1.2.5.2.3.2.1 | Method 1: Reduction of Methyl 4 <i>H</i> -1,4-Benzoxazine-2-carboxylates with Sodium Bis(2-methoxyethoxy)aluminum Hydride | 172 |
| 17.1.2.5.2.3.2.2 | Method 2: Wittig Reaction of 4 <i>H</i> -1,4-Benzoxazine-2-carbaldehydes | 173 |
| 17.1.2.5.2.3.2.3 | Method 3: Nitrosation of 3-Substituted 2 <i>H</i> -1,4-Benzoxazin-2-ones | 174 |
| 17.1.2.5.2.3.2.4 | Method 4: Reaction of 4-Acetyl-4 <i>H</i> -1,4-benzoxazines with Sulfonyl Isocyanates | 174 |
| 17.1.2.5.2.3.2.5 | Method 5: Reaction of 4 <i>H</i> -1,4-Benzoxazine-2-carboxamides with Chlorosulfonyl Isocyanate and Triethylamine | 175 |
| 17.1.2.5.2.3.2.6 | Method 6: Reaction of 2 <i>H</i> -1,4-Benzoxazine-3(4 <i>H</i>)-thiones with Alkyl Halides | 175 |
| 17.1.3.9 | One Sulfur, Selenium, or Tellurium Atom and One Nitrogen or Phosphorus Atom 2014 R. A. Aitken and A. Meehan | |
| 17.1.3.9 | One Sulfur, Selenium, or Tellurium Atom and One Nitrogen or Phosphorus Atom | 179 |
| 17.1.3.9.1 | 1,4-Thiazines | 179 |
| 17.1.3.9.1.1 | Synthesis by Ring-Closure Reactions | 179 |
| 17.1.3.9.1.1.1 | Formation of Two S—C and Two N—C Bonds | 179 |
| 17.1.3.9.1.1.1.1 | Method 1: Reaction of Ynamines and <i>N</i> -Sulfonylamines | 179 |
| 17.1.3.9.1.1.2 | Formation of Two S—C Bonds and One N—C Bond | 179 |
| 17.1.3.9.1.1.2.1 | Method 1: Reaction of β -Aminoacrylates with 1,2,3-Dithiazol-5-ones or 1,2,3-Dithiazole-5-thiones | 179 |

| | | |
|--------------------|---|-----|
| 17.1.3.9.1.1.3 | Formation of Two N—C Bonds | 180 |
| 17.1.3.9.1.1.3.1 | Method 1: Reaction of Bis(2-oxoalkyl)sulfones and Related Compounds | 180 |
| 17.1.3.9.1.1.4 | Formation of One N—C Bond | 181 |
| 17.1.3.9.1.1.4.1 | Method 1: Reaction of 2-(Aminocarbonyl)ethyl 2-Oxopropyl Sulfides | 181 |
| 17.1.3.9.1.2 | Synthesis by Ring Transformation | 182 |
| 17.1.3.9.1.2.1 | Ring Enlargement | 182 |
| 17.1.3.9.1.2.1.1 | Method 1: Reaction of Thiirene 1,1-Dioxides | 182 |
| 17.1.3.9.1.3 | Aromatization | 183 |
| 17.1.3.9.1.3.1 | Method 1: Pummerer Reaction of 3,4-Dihydro-2 <i>H</i> -1,4-thiazine 1-Oxides | 183 |
| 17.1.3.9.1.3.2 | Method 2: Oxidation of 3,4-Dihydro-2 <i>H</i> -1,4-thiazines | 184 |
| 17.1.3.9.1.3.3 | Method 3: Elimination of Amines from 3,4-Dihydro-2 <i>H</i> -1,4-thiazin-4-amines | 185 |
| 17.1.3.9.1.4 | Synthesis by Substituent Modification | 185 |
| 17.1.3.9.1.4.1 | Substitution of Existing Substituents | 185 |
| 17.1.3.9.1.4.1.1 | Of Hydrogen | 185 |
| 17.1.3.9.1.4.1.1.1 | Method 1: Ring Bromination of λ^6 -Thiazine 1-Oxides | 185 |
| 17.1.3.9.1.4.1.1.2 | Method 2: N-Alkylation of Thiazine 1,1-Dioxides | 186 |
| 17.1.3.9.1.4.1.2 | Of Halogen or Alkylsulfanyl | 187 |
| 17.1.3.9.1.4.1.2.1 | Method 1: Nucleophilic Displacement of Existing 3-Substituents | 187 |
| 17.1.3.9.1.4.2 | Modification of Substituents | 189 |
| 17.1.3.9.1.4.2.1 | Method 1: Silylation of 2 <i>H</i> -1,4-Thiazin-3(4 <i>H</i>)-ones | 189 |
| 17.1.3.9.1.4.2.2 | Method 2: Chlorination of 5-Methyl-2 <i>H</i> -1,4-thiazine-2,3(4 <i>H</i>)-diones | 190 |
| 17.1.3.9.2 | 1,4-Benzothiazines and Related Compounds | 190 |
| 17.1.3.9.2.1 | Synthesis by Ring-Closure Reactions | 190 |
| 17.1.3.9.2.1.1 | Formation of Two S—C Bonds | 190 |
| 17.1.3.9.2.1.1.1 | Method 1: Reaction of Benzil Monoarylimines with Phosphorus Pentasulfide | 190 |
| 17.1.3.9.2.1.2 | Formation of One S—C Bond | 191 |
| 17.1.3.9.2.1.2.1 | Method 1: Reaction of 2-(Vinylamino)phenyl Sulfoxides and Related Compounds | 191 |
| 17.1.3.9.2.1.2.2 | Method 2: Reaction of 3-(Arylimino)-4,4,4-trifluoro-1-methoxy-1-oxobutane-2-thiolates via Oxidative Intramolecular Cyclization Using Iodine | 193 |
| 17.1.3.9.2.2 | Synthesis by Substituent Modification | 194 |
| 17.1.3.9.2.2.1 | Substitution of Existing Substituents | 194 |
| 17.1.3.9.2.2.1.1 | Of Halogens | 194 |
| 17.1.3.9.2.2.1.1.1 | Method 1: Reaction of 3-Chloro-4 <i>H</i> -1,4-benzothiazines and Their 1,1-Dioxides | 194 |
| 17.1.3.9.2.2.1.2 | Of (Diphenoxyphosphoryl)oxy | 195 |

| | | | |
|--------------------|-----------|--|-----|
| 17.1.3.9.2.2.1.2.1 | Method 1: | Suzuki–Miyaura Reaction of 3-[(Diphenoxyphosphoryl)oxy]-4 <i>H</i> -1,4-benzothiazines | 195 |
| 17.1.3.9.2.2.2 | | Rearrangement of Substituents | 195 |
| 17.1.3.9.2.2.2.1 | Method 1: | Protidealkylation of 1 λ^4 ,4-Benzothiazines | 195 |
| 17.1.3.9.2.2.3 | | Modification of Substituents | 196 |
| 17.1.3.9.2.2.3.1 | Method 1: | Vilsmeier Formylation/Chlorination of 2 <i>H</i> -1,4-Benzothiazin-3(4 <i>H</i>)-ones | 196 |
| 17.1.3.9.2.2.3.2 | Method 2: | Chlorination of 3-Hydroxy-4 <i>H</i> -1,4-benzothiazine-2-carbonitrile 1,1-Dioxides | 196 |
| 17.1.3.9.2.2.3.3 | Method 3: | Phosphorylation of 2 <i>H</i> -1,4-Benzothiazin-3(4 <i>H</i>)-ones | 197 |

Volume 18: Four Carbon–Heteroatom Bonds: $X-C\equiv X$, $X=C=X$, $X_2C=X$, CX_4

18.2 Product Class 2: Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, Isocyanates, Isothiocyanates, Carbodiimides, and Their Selenium, Tellurium, and Phosphorus Analogues

| | | |
|-------------------|---|------|
| 18.2.16 | Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, Isocyanates, Isothiocyanates, Carbodiimides, and Their Selenium, Tellurium, and Phosphorus Analogues | 2014 |
| | S. Braverman and M. Cherkinsky | |
| 18.2.16 | Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, Isocyanates, Isothiocyanates, Carbodiimides, and Their Selenium, Tellurium, and Phosphorus Analogues | 199 |
| 18.2.16.1 | Carbon Dioxide | 199 |
| 18.2.16.1.1 | Applications of Carbon Dioxide in Organic Synthesis | 199 |
| 18.2.16.1.1.1 | Supercritical Carbon Dioxide as a Reaction Medium for Chemical Synthesis | 199 |
| 18.2.16.1.1.1.1 | Method 1: Oxidation Reactions | 201 |
| 18.2.16.1.1.1.1.1 | Variation 1: Oxidation of Alcohols To Give Carbonyl Compounds | 201 |
| 18.2.16.1.1.1.1.2 | Variation 2: Baeyer–Villiger Oxidation of Ketones | 204 |
| 18.2.16.1.1.1.1.3 | Variation 3: Alkene Epoxidation | 206 |
| 18.2.16.1.1.1.1.4 | Variation 4: Wacker-Type and Related Oxidations (Palladium-Catalyzed Oxidation of Alkenes) | 207 |
| 18.2.16.1.1.1.1.5 | Variation 5: Glaser Oxidative Couplings | 209 |
| 18.2.16.1.1.1.1.6 | Variation 6: Diastereocontrolled Sulfur Oxidation | 210 |
| 18.2.16.1.1.1.2 | Method 2: Hydrogenation Reactions | 211 |
| 18.2.16.1.1.1.2.1 | Variation 1: Hydrogenation of Aldehydes and Ketones | 212 |
| 18.2.16.1.1.1.2.2 | Variation 2: Hydrogenation of Alkenes and Alkynes | 214 |
| 18.2.16.1.1.1.2.3 | Variation 3: Hydrogenation of Aromatic Substrates | 216 |
| 18.2.16.1.1.1.3 | Method 3: In Hydroformylation and Related Reactions | 218 |
| 18.2.16.1.1.1.3.1 | Variation 1: Hydroformylation | 218 |
| 18.2.16.1.1.1.3.2 | Variation 2: Hydroaminomethylation | 221 |

| | | | |
|-------------------|--------------|--|-----|
| 18.2.16.1.1.1.4 | Method 4: | Base-Catalyzed Processes | 222 |
| 18.2.16.1.1.1.4.1 | Variation 1: | Baylis–Hillman Reaction | 222 |
| 18.2.16.1.1.1.4.2 | Variation 2: | Henry (Nitroaldol) Reaction | 224 |
| 18.2.16.1.1.1.5 | Method 5: | Acid-Catalyzed Processes | 225 |
| 18.2.16.1.1.1.5.1 | Variation 1: | Friedel–Crafts Reaction | 225 |
| 18.2.16.1.1.1.6 | Method 6: | Palladium-Mediated Coupling Reactions | 226 |
| 18.2.16.1.1.1.6.1 | Variation 1: | Heck Reaction | 227 |
| 18.2.16.1.1.1.6.2 | Variation 2: | Stille Coupling | 230 |
| 18.2.16.1.1.1.6.3 | Variation 3: | Suzuki Coupling | 232 |
| 18.2.16.1.1.1.6.4 | Variation 4: | Sonogashira Reaction | 234 |
| 18.2.16.1.1.1.6.5 | Variation 5: | Palladium-Catalyzed Carbonylation | 235 |
| 18.2.16.1.1.1.7 | Method 7: | Cycloaddition Reactions | 236 |
| 18.2.16.1.1.1.7.1 | Variation 1: | Diels–Alder Reaction | 236 |
| 18.2.16.1.1.1.7.2 | Variation 2: | 1,3-Dipolar Cycloaddition | 239 |
| 18.2.16.1.1.8 | Method 8: | Biotransformations in Supercritical Carbon Dioxide | 240 |
| 18.2.16.1.1.9 | Method 9: | Additional Methods | 244 |
| 18.2.16.1.1.2 | | Reactions of Carbon Dioxide with Oxygen and Nitrogen Nucleophiles | 245 |
| 18.2.16.1.1.3 | | Reactions of Carbon Dioxide with Carbon Nucleophiles | 246 |
| 18.2.16.1.1.3.1 | Method 1: | Carboxylation of Organometallic Derivatives | 246 |
| 18.2.16.1.1.3.2 | Method 2: | Direct Carboxylations of Aromatic Compounds | 250 |
| 18.2.16.2 | | Carbonyl Sulfide | 253 |
| 18.2.16.2.1 | | Applications of Carbonyl Sulfide in Organic Synthesis | 254 |
| 18.2.16.2.1.1 | Method 1: | Thiocarboxylation Reactions | 254 |
| 18.2.16.3 | | Carbonyl Selenide | 256 |
| 18.2.16.3.1 | | Applications of Carbonyl Selenide in Organic Synthesis | 256 |
| 18.2.16.3.1.1 | Method 1: | Synthesis of Symmetrical Diselenides from Imines | 256 |
| 18.2.16.3.1.2 | Method 2: | Synthesis of 1 <i>H</i> -Quinazoline-2,4-diones | 257 |
| 18.2.16.4 | | Isocyanates | 257 |
| 18.2.16.4.1 | | Synthesis of Isocyanates | 258 |
| 18.2.16.4.1.1 | Method 1: | Carbonylation of Primary Amines with Phosgene | 258 |
| 18.2.16.4.1.2 | Method 2: | Carbonylation of Amines with Carbon Dioxide: Dehydration of Carbamate Anions | 258 |
| 18.2.16.4.1.3 | Method 3: | Carbonylation of Primary Amines with Other Carbonyl Transfer Agents | 259 |
| 18.2.16.4.1.3.1 | Variation 1: | By Organic Carbonates | 259 |
| 18.2.16.4.1.3.2 | Variation 2: | By Trichloromethyl Chloroformate | 261 |
| 18.2.16.4.1.3.3 | Variation 3: | By Oxalyl Chloride | 262 |
| 18.2.16.4.1.4 | Method 4: | Carbonylation of Amine Derivatives | 263 |
| 18.2.16.4.1.4.1 | Variation 1: | Phosgenation of <i>N</i> -Silylamines | 263 |
| 18.2.16.4.1.5 | Method 5: | Substitution with Cyanate Anion | 264 |
| 18.2.16.4.1.5.1 | Variation 1: | By Reaction with Tetrabutylammonium Cyanate | 265 |
| 18.2.16.4.1.5.2 | Variation 2: | Synthesis of Phosphoryl Isocyanates | 266 |
| 18.2.16.4.1.6 | Method 6: | Oxidation of Isocyanides | 266 |
| 18.2.16.4.1.7 | Method 7: | Curtius Rearrangement | 267 |

| | | | |
|-----------------|---|--|-----|
| 18.2.16.4.1.7.1 | Variation 1: | Using Sodium Azide | 267 |
| 18.2.16.4.1.7.2 | Variation 2: | Using Azidotrimethylsilane | 269 |
| 18.2.16.4.1.7.3 | Variation 3: | Using Diphenylphosphoryl Azide | 270 |
| 18.2.16.4.1.8 | Method 8: | Other Rearrangements | 272 |
| 18.2.16.5 | Carbon Disulfide | | 274 |
| 18.2.16.5.1 | Applications of Carbon Disulfide in Organic Synthesis | | 274 |
| 18.2.16.5.1.1 | Method 1: | Synthesis of Dithiocarbonates | 274 |
| 18.2.16.5.1.1.1 | Variation 1: | Reaction with Alcohols: Synthesis of Acyclic Dithiocarbonates | 274 |
| 18.2.16.5.1.1.2 | Variation 2: | Reaction with Epoxides: Synthesis of Cyclic Dithiocarbonates | 276 |
| 18.2.16.5.1.2 | Method 2: | Synthesis of Trithiocarbonates | 278 |
| 18.2.16.5.1.2.1 | Variation 1: | Reaction with Thiols | 278 |
| 18.2.16.5.1.2.2 | Variation 2: | Reaction with Alkyl Halides or Toluenesulfonates | 279 |
| 18.2.16.5.1.3 | Method 3: | Synthesis of Dithiocarbamates by Reaction with Amines | 280 |
| 18.2.16.5.1.3.1 | Variation 1: | One-Pot Synthesis of 2-Hydroxyalkyl Dithiocarbamates | 281 |
| 18.2.16.5.1.3.2 | Variation 2: | Formation of Polymer-Supported Dithiocarbamates for the Solid-Phase Synthesis of Heterocycles | 282 |
| 18.2.16.5.1.4 | Method 4: | Reaction with Aziridines | 283 |
| 18.2.16.5.1.5 | Method 5: | Reaction with Hydrazine and Its Derivatives: Synthesis of Dithiocarbazates | 284 |
| 18.2.16.5.1.6 | Method 6: | Synthesis of Thioureas | 285 |
| 18.2.16.5.1.7 | Method 7: | Reactions with Carbon Nucleophiles | 285 |
| 18.2.16.6 | Isothiocyanates | | 286 |
| 18.2.16.6.1 | Synthesis of Isothiocyanates | | 287 |
| 18.2.16.6.1.1 | Method 1: | Thiocarbonylation of Primary Amines with Thiophosgene | 287 |
| 18.2.16.6.1.2 | Method 2: | Thiocarbonylation of Primary Amines with Carbon Disulfide via Cleavage of Dithiocarbamate Salts | 288 |
| 18.2.16.6.1.3 | Method 3: | Thiocarbonylation of Primary Amines with Other Thiocarbonyl Transfer Agents | 290 |
| 18.2.16.6.1.4 | Method 4: | Thiocarbonylation of Amine Derivatives | 291 |
| 18.2.16.6.1.4.1 | Variation 1: | Thiocarbonylation of Iminophosphoranes | 291 |
| 18.2.16.6.1.5 | Method 5: | Nucleophilic Substitution of Organic Halides with Thiocyanate Anion | 292 |
| 18.2.16.6.1.6 | Method 6: | Nucleophilic Substitution of Alcohols with Thiocyanate Anion via In Situ Activation of the Hydroxy Group of the Alcohol (The One-Pot Conversion) | 295 |
| 18.2.16.6.1.7 | Method 7: | Thionation of Isocyanates | 296 |
| 18.2.16.6.1.8 | Method 8: | Direct Sulfurization of Isocyanides | 297 |
| 18.2.16.6.1.9 | Method 9: | Preparation of Functionalized Isothiocyanates from Other Isothiocyanates | 298 |
| 18.2.16.7 | Isoselenocyanates | | 299 |
| 18.2.16.7.1 | Synthesis of Isoselenocyanates | | 299 |
| 18.2.16.7.1.1 | Method 1: | Addition Reaction of Isocyanides and Elemental Selenium | 299 |
| 18.2.16.7.1.1.1 | Variation 1: | Reaction of Preformed Isocyanides with Selenium | 299 |
| 18.2.16.7.1.1.2 | Variation 2: | Via In Situ Formation of Isocyanides from Formamides | 300 |
| 18.2.16.8 | Carbodiimides | | 301 |

| | | |
|-----------------|--|-----|
| 18.2.16.8.1 | Synthesis of Carbodiimides | 301 |
| 18.2.16.8.1.1 | Method 1: Synthesis via N,N-Disubstituted Ureas and Thioureas | 302 |
| 18.2.16.8.1.1.1 | Variation 1: Dehydration of Ureas | 302 |
| 18.2.16.8.1.1.2 | Variation 2: Dehydrosulfurization of Thioureas | 303 |
| 18.2.16.8.1.2 | Method 2: Synthesis via Aza-Wittig-Type Reaction of Iminophosphanes with Heterocumulenes | 304 |
| 18.2.16.8.1.2.1 | Variation 1: By Aza-Wittig-Type Reaction of Preformed Iminophosphanes | 305 |
| 18.2.16.8.1.2.2 | Variation 2: Tandem Staudinger/Aza-Wittig-Type Reaction | 306 |
| 18.2.16.8.1.3 | Method 3: Synthesis from Isocyanates via Heterocumulene Metathesis .. | 307 |

Volume 24: Three Carbon—Heteroatom Bonds: Ketene Acetals and Yne—X Compounds

| | | |
|--------------|--|------|
| 24.2 | Product Class 2: 1,1-Bis(heteroatom-functionalized) Alk-1-enes | |
| 24.2.1.3 | 1,1-Dihaloalk-1-enes | 2014 |
| | B. Ameduri | |
| 24.2.1.3 | 1,1-Dihaloalk-1-enes | 317 |
| 24.2.1.3.1 | Method 1: Preparation of Functional Fluoro-monomers for Radical Copolymerization with Fluoroalkenes | 317 |
| 24.2.1.3.1.1 | Variation 1: Tetrafluoroethene | 318 |
| 24.2.1.3.1.2 | Variation 2: 1,1-Difluoroethene | 320 |
| 24.2.1.3.1.3 | Variation 3: Chlorotrifluoroethene | 321 |
| 24.2.1.3.1.4 | Variation 4: 1,1,2,3,4,4-Hexafluorobuta-1,3-diene | 323 |
| 24.2.1.3.2 | Method 2: Radical Addition of Halogens to Chlorotrifluoroethene, 1,1-Difluoroethene, and Fluorinated Alkenes | 323 |
| 24.2.1.3.3 | Method 3: Synthesis of Trifluorovinyl Functional Monomers | 328 |
| 24.2.1.3.4 | Method 4: Radical Copolymerization of Fluorinated Functional Monomers with 1,1-Difluoroethene | 332 |
| 24.2.1.3.5 | Method 5: Controlled Radical Copolymerization of 1,1-Difluoroethene with Various Comonomers | 338 |
| 24.2.1.3.6 | Method 6: 2,3-Diaryl-1,1-difluoroprop-1-enes from 2-Aryl-1,1,1-trifluoroprop-2-enes by Rhodium-Catalyzed Addition/Elimination .. | 339 |
| 24.2.1.3.7 | Method 7: Difluoromethylenation of Aldehydes and Ketones | 341 |
| 24.2.1.3.8 | Method 8: Palladium-Catalyzed Cross Coupling of 2,2-Difluorovinyl Organometallic Species | 342 |
| 24.2.1.3.8.1 | Variation 1: (2,2-Difluorovinyl)stannanes | 342 |
| 24.2.1.3.8.2 | Variation 2: (2,2-Difluorovinyl)zinc Reagents | 346 |

| | | |
|-----------------|---|------|
| 24.3 | Product Class 3: Bis(heteroatom-functionalized) Acetylenes | |
| 24.3.12 | Bis(heteroatom-functionalized) Acetylenes | 2014 |
| | J. Udmark and M. Brøndsted Nielsen | |
| 24.3.12 | Bis(heteroatom-functionalized) Acetylenes | 353 |
| 24.3.12.1 | Dihaloacetylenes | 353 |
| 24.3.12.1.1 | Synthesis of Dihaloacetylenes | 353 |
| 24.3.12.1.1.1 | Synthesis of Dichloroacetylene | 353 |
| 24.3.12.1.1.1.1 | Method 1: Dehydrochlorination of Trichloroethene Using Sodium Hydride | 354 |
| 24.3.12.1.1.2 | Synthesis of Diiodoacetylene | 354 |
| 24.3.12.1.1.2.1 | Method 1: Iodination of Acetylene Using Hypoiodite under Aqueous Conditions | 355 |
| 24.3.12.1.1.2.2 | Method 2: Iodination of (Trimethylsilyl)acetylene Using <i>N</i> -Iodosuccinimide | 355 |
| 24.3.12.1.2 | Applications of Dihaloacetylenes in Organic Synthesis | 356 |
| 24.3.12.1.2.1 | Method 1: Transformation into Other Acetylenes | 356 |
| 24.3.12.1.2.1.1 | Variation 1: Nucleophilic Acetylenic Substitution | 356 |
| 24.3.12.1.2.1.2 | Variation 2: Transition-Metal-Catalyzed Cross-Coupling Reactions | 357 |
| 24.3.12.1.2.1.3 | Variation 3: Thermally Induced Polymerization | 358 |
| 24.3.12.1.2.2 | Method 2: Transformation into Ethenes | 358 |
| 24.3.12.2 | 1-Heteroatom-Functionalized 2-Haloacetylenes | 359 |
| 24.3.12.2.1 | Synthesis of 1-Heteroatom-Functionalized 2-Haloacetylenes | 359 |
| 24.3.12.2.1.1 | Synthesis of 1-Halo-2-(triorganosilyl)acetylenes | 359 |
| 24.3.12.2.1.1.1 | Method 1: Synthesis of 1-Fluoro-2-(trialkylsilyl)acetylenes from 1,1-Difluoroethene | 359 |
| 24.3.12.2.1.1.2 | Method 2: Halogenation of Lithium Silylacetylides | 360 |
| 24.3.12.2.1.2 | Synthesis of 1-Alkoxy-2-haloacetylenes | 362 |
| 24.3.12.2.1.2.1 | Method 1: Synthesis from Dichloroenoal Ethers by Elimination | 362 |
| 24.3.12.2.1.3 | Synthesis of 1-Halo-2-(organosulfonyl)acetylenes | 362 |
| 24.3.12.2.1.3.1 | Method 1: Electrophilic Chlorination of Sulfonylated Acetylenes | 362 |
| 24.3.12.2.1.4 | Synthesis of 1-Nitrogen-Functionalized 2-Haloacetylenes | 363 |
| 24.3.12.2.1.4.1 | Method 1: Exploitation of 2-Bromoacetylen-1-amines as Reactive Intermediates | 363 |
| 24.3.12.2.1.4.2 | Method 2: Iodination of Acetylen-1-amines | 363 |
| 24.3.12.2.1.5 | Synthesis of 1-Phosphorus-Functionalized 2-Haloacetylenes | 365 |
| 24.3.12.2.1.5.1 | Method 1: Electrophilic Bromination | 365 |
| 24.3.12.2.2 | Applications of 1-Heteroatom-Functionalized 2-Haloacetylenes in Organic Synthesis | 366 |

| | | | |
|-----------------|--------------|--|-----|
| 24.3.12.2.2.1 | Method 1: | C—C Bond Formation | 366 |
| 24.3.12.2.2.1.1 | Variation 1: | Transition-Metal-Catalyzed Alkynylation | 366 |
| 24.3.12.2.2.1.2 | Variation 2: | Gallium-Mediated C—C Bond Formation with 1-Chloro-2-(tri-alkylsilyl)acetylenes | 366 |
| 24.3.12.2.2.1.3 | Variation 3: | Michael and Sulfa-Michael Reactions | 366 |
| 24.3.12.2.2.1.4 | Variation 4: | Cycloadditions | 366 |
| 24.3.12.3 | | Bis(organooxy)acetylenes | 367 |
| 24.3.12.4 | | 1-(Organochalcogeno)-2-(organooxy)acetylenes | 367 |
| 24.3.12.5 | | 1-Nitrogen-Functionalized 2-(Organooxy)acetylenes | 367 |
| 24.3.12.6 | | 1-Phosphorus-Functionalized 2-(Organooxy)acetylenes | 367 |
| 24.3.12.7 | | Bis(organochalcogeno)acetylenes | 367 |
| 24.3.12.7.1 | | Synthesis of Bis(organochalcogeno)acetylenes | 367 |
| 24.3.12.7.1.1 | | Synthesis of Bis(organosulfanyl)acetylenes | 367 |
| 24.3.12.7.1.1.1 | Method 1: | Reaction of Metal Acetylides with Elemental Sulfur and Alkyl Halides | 368 |
| 24.3.12.7.1.1.2 | Method 2: | Reaction of Metal Acetylides with Disulfides | 368 |
| 24.3.12.7.1.2 | | Synthesis of S-Oxidized (Organosulfur)acetylenes | 369 |
| 24.3.12.7.1.2.1 | Method 1: | Selective Oxidation of Bis(organosulfanyl)acetylenes with 3-Chloroperoxybenzoic Acid | 369 |
| 24.3.12.7.2 | | Applications of Bis(organochalcogeno)acetylenes in Organic Synthesis | 369 |
| 24.3.12.8 | | 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes | 370 |
| 24.3.12.8.1 | | Synthesis of 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes | 370 |
| 24.3.12.8.1.1 | Method 1: | Reaction of 1-Chloro-2-(alkylsulfanyl)acetylenes with Sodium Azide | 370 |
| 24.3.12.8.2 | | Applications of 1-Nitrogen-Functionalized 2-(Organochalcogeno)acetylenes in Organic Synthesis | 371 |
| 24.3.12.8.2.1 | Method 1: | Homodimerization and Cyclization of [(Alkylsulfanyl)ethynyl]hydrazines | 371 |
| 24.3.12.8.2.2 | Method 2: | Homocyclization of 2-(Alkylsulfanyl)acetylen-1-amines | 371 |
| 24.3.12.9 | | 1-Phosphorus-Functionalized 2-(Organochalcogeno)acetylenes | 372 |
| 24.3.12.9.1 | | Synthesis of 1-Phosphorus-Functionalized 2-(Organochalcogeno)acetylenes | 372 |
| 24.3.12.9.1.1 | Method 1: | Reaction of 1-Chloro-2-phosphorylacetylenes with Thiols under Neutral Conditions | 372 |
| 24.3.12.10 | | Bis(nitrogen-functionalized) Acetylenes | 372 |
| 24.3.12.10.1 | | Synthesis of Bis(nitrogen-functionalized) Acetylenes | 373 |
| 24.3.12.10.1.1 | Method 1: | Synthesis of Acetylenediamines via a Fritsch–Buttenberg–Wiechell-Type Rearrangement | 373 |
| 24.3.12.10.2 | | Applications of Bis(nitrogen-functionalized) Acetylenes in Organic Synthesis | 374 |
| 24.3.12.10.2.1 | Method 1: | Transformation into 3-Nitrogen-Functionalized 1-Methylindoles | 374 |
| 24.3.12.11 | | 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes and Bis(phosphorus-functionalized) Acetylenes | 374 |

| | | |
|------------------|---|-----|
| 24.3.12.11.1 | Synthesis of 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes | 374 |
| 24.3.12.11.1.1 | Method 1: Synthesis of 1-Phosphoryl-2-(sulfonamido)acetylenes | 374 |
| 24.3.12.11.1.2 | Method 2: Synthesis of 1-[Bis(phosphino)amino]-2-phosphinoacetylenes | 375 |
| 24.3.12.11.1.3 | Method 3: Synthesis of 1-Amino-2-phosphorylacetylenes | 375 |
| 24.3.12.11.2 | Synthesis of Bis(phosphorus-functionalized) Acetylenes | 376 |
| 24.3.12.11.2.1 | Method 1: Reaction of Lithiated 2-(Phosphoryl)acetylenes with P—Cl Electrophiles and Subsequent Oxidation | 377 |
| 24.3.12.11.2.2 | Method 2: Synthesis of Bis(phosphinoyl)acetylenes by Fragmentation .. | 378 |
| 24.3.12.11.2.3 | Method 3: Synthesis of Bis(phosphino)acetylenes | 379 |
| 24.3.12.11.2.3.1 | Variation 1: Synthesis by Alkyne Cross Metathesis | 379 |
| 24.3.12.11.2.3.2 | Variation 2: Synthesis from (<i>E</i>)-1,2-Dichloroethene | 379 |
| 24.3.12.11.3 | Applications of 1-Nitrogen-Functionalized 2-Phosphorus-Functionalized Acetylenes in Organic Synthesis | 380 |
| 24.3.12.11.4 | Applications of Bis(phosphorus-functionalized) Acetylenes in Organic Synthesis | 380 |

24.4

Product Class 4: 1-Heteroatom-Functionalized Alk-1-yne

| | | |
|----------------|--|------|
| 24.4.1.3 | 1-Haloalk-1-yne and Alk-1-yn-1-ols | 2014 |
| | A. U. Petersen and M. Brøndsted Nielsen | |
| 24.4.1.3 | 1-Haloalk-1-yne and Alk-1-yn-1-ols | 385 |
| 24.4.1.3.1 | Synthesis of 1-Haloalk-1-yne and Alk-1-yn-1-ols | 385 |
| 24.4.1.3.1.1 | Method 1: Halogenation of Alk-1-yne | 385 |
| 24.4.1.3.1.1.1 | Variation 1: By Reaction with <i>N</i> -Halosuccinimides | 385 |
| 24.4.1.3.1.1.2 | Variation 2: Halogenation with Molecular Iodine or Bromine | 386 |
| 24.4.1.3.1.1.3 | Variation 3: Iodination with Iodine Formed In Situ | 388 |
| 24.4.1.3.1.1.4 | Variation 4: Iodination Using a Hypervalent Iodine Reagent | 389 |
| 24.4.1.3.1.1.5 | Variation 5: Chlorination Using Arenesulfonyl Chlorides | 389 |
| 24.4.1.3.1.1.6 | Variation 6: Fluorination Using <i>N</i> -Fluorobenzenesulfonimide | 390 |
| 24.4.1.3.1.1.7 | Variation 7: Bromination Using Hypobromite | 390 |
| 24.4.1.3.1.1.8 | Variation 8: Chlorination Using 1,4-Dichloro-1,4-diazoniabicyclo[2.2.2]octane Dichloride | 391 |
| 24.4.1.3.1.2 | Method 2: Direct Transformation of (Trialkylsilyl)alkynes into Haloalkynes | 391 |
| 24.4.1.3.1.2.1 | Variation 1: By Reaction with <i>N</i> -Halosuccinimides | 391 |
| 24.4.1.3.1.2.2 | Variation 2: Chlorination with Trichloroisocyanuric Acid | 393 |
| 24.4.1.3.1.3 | Method 3: Dehydrohalogenation of 1,1-Dihaloalkenes | 394 |
| 24.4.1.3.1.4 | Method 4: Halogenation of Alkynylstannanes | 396 |
| 24.4.1.3.1.5 | Method 5: Halodeboronation of Alkynyltrifluoroborates | 396 |
| 24.4.1.3.1.6 | Method 6: Bromodecarboxylation of Alk-2-ynoic Acids | 396 |
| 24.4.1.3.2 | Applications of 1-Haloalk-1-yne and Alk-1-yn-1-ols in Organic Synthesis | 397 |
| 24.4.1.3.2.1 | Method 1: Variant of the Cadiot–Chodkiewicz Coupling | 397 |

Volume 27: Heteroatom Analogues of Aldehydes and Ketones

| | | |
|---------------|---|------|
| 27.21 | Product Class 21: Diazo Compounds | |
| 27.21.3 | Diazo Compounds | 2014 |
| | H. Heydt | |
| 27.21.3 | Diazo Compounds | 405 |
| 27.21.3.1 | Synthesis of Diazo Compounds | 405 |
| 27.21.3.1.1 | Method 1: Diazo Transfer (Regitz Diazo Group Transfer) | 405 |
| 27.21.3.1.2 | Method 2: Diazotization Reactions | 408 |
| 27.21.3.1.3 | Method 3: Oxidation of Hydrazones | 409 |
| 27.21.3.1.4 | Method 4: Elimination of Hydroxy Anions from Diazenolates (Diazotates) | 412 |
| 27.21.3.1.5 | Method 5: Elimination of Sulfinates from <i>N</i> -Sulfonylhydrazones (Bamford–Stevens Reaction) | 414 |
| 27.21.3.1.6 | Method 6: Substitution Reactions at the Diazo Carbon Atom | 417 |
| 27.21.3.1.6.1 | Variation 1: Alkylation Reactions with Carbonyl Compounds | 417 |
| 27.21.3.1.6.2 | Variation 2: Arylation Reactions | 421 |
| 27.21.3.1.6.3 | Variation 3: Acylation Reactions | 421 |
| 27.21.3.1.7 | Method 7: Diazo Compounds by Reactions at the Periphery of a Given Diazo Compound | 423 |
| 27.21.3.2 | Applications of Diazo Compounds in Organic Synthesis | 426 |

Volume 39: Sulfur, Selenium, and Tellurium

| | | |
|-------------------|---|------|
| 39.19 | Product Class 19: Acyclic Alkaneselenolates | |
| 39.19.2.3 | Alkaneselenolates of Group 3–12 Metals | 2014 |
| | A. Polo and J. Real | |
| 39.19.2.3 | Alkaneselenolates of Group 3–12 Metals | 435 |
| 39.19.2.3.1 | Synthesis of Alkaneselenolates of Group 3–12 Metals | 435 |
| 39.19.2.3.1.1 | Terminal Alkaneselenolates | 435 |
| 39.19.2.3.1.1.1 | Method 1: Reaction of a Metal Complex with a Main Group Alkanesele- nolate | 435 |
| 39.19.2.3.1.1.2 | Method 2: Miscellaneous Methods | 439 |
| 39.19.2.3.1.2 | μ_2 -Alkaneselenolates | 439 |
| 39.19.2.3.1.2.1 | Method 1: Reaction of a Metal Complex with a Main Group Alkanesele- nolate | 439 |
| 39.19.2.3.1.2.1.1 | Variation 1: From Metal Halide Complexes | 439 |
| 39.19.2.3.1.2.2 | Method 2: Oxidative Addition of a Dialkyl Diselenide to a Metal Complex | 441 |

| | | | |
|-----------------|---|---|------|
| 39.19.2.3.1.2.3 | Method 3: | Reaction of a Selenolate–Metal Complex with a Second Metal Complex | 442 |
| 39.19.2.3.1.2.4 | Method 4: | Miscellaneous Methods | 444 |
| 39.19.2.3.1.3 | μ_3 -Alkaneselenolates | | 444 |
| 39.19.2.3.1.3.1 | Method 1: | Reaction of a Metal Salt with an Alkyl Trimethylsilyl Selenide | 444 |
| 39.26 | Product Class 26: Selenolanes, Larger Rings, and Derivatives of Various Oxidation States | | |
| 39.26.6.2 | Cyclic Alkaneselenolates of Group 3–12 Metals | | 2014 |
| | A. Polo and J. Real | | |
| 39.26.6.2 | Cyclic Alkaneselenolates of Group 3–12 Metals | | 447 |
| 39.26.6.2.1 | Synthesis of Cyclic Alkaneselenolates of Group 3–12 Metals | | 447 |
| 39.26.6.2.1.1 | Method 1: | Synthesis of Cyclic Diselenolates | 447 |
| 39.26.6.2.1.1.1 | Variation 1: | Alkylation of Bridging Coordinated Selenides with Dihaloalkanes or Diazomethane | 450 |
| 39.26.6.2.1.2 | Method 2: | Synthesis of Cyclic Selenolates with a Metal–Carbon Bond | 450 |
| 39.26.6.2.1.3 | Method 3: | Synthesis of Cyclic Aminoalkaneselenolates by Reaction of Sodium Aminoalkaneselenolates with a Metal Halide Complex | 451 |
| 39.32 | Product Class 32: Acyclic Alkanetellurolates | | |
| 39.32.2.2 | Alkanetellurolates of Group 3–12 Metals | | 2014 |
| | A. Polo and J. Real | | |
| 39.32.2.2 | Alkanetellurolates of Group 3–12 Metals | | 457 |
| 39.32.2.2.1 | Synthesis of Alkanetellurolates of Group 3–12 Metals | | 457 |
| 39.32.2.2.1.1 | Terminal Alkanetellurolates | | 457 |
| 39.32.2.2.1.1.1 | Method 1: | Reaction of a Metal Complex with a Main Group Alkanetellurolate | 457 |
| 39.32.2.2.1.1.2 | Method 2: | Reaction of Hydridoniobium–Ditelluride Complexes with Methylithium | 458 |
| 39.32.2.2.1.2 | μ_2 -Alkanetellurolates | | 459 |
| 39.32.2.2.1.2.1 | Method 1: | Reaction of Bridging Coordinated Tellurides with Electrophiles | 459 |
| 39.32.2.2.1.2.2 | Method 2: | Oxidative Addition of a Dialkyl Ditelluride to a Metal Complex | 459 |
| 39.32.2.2.1.2.3 | Method 3: | Reaction of a Tellurolate–Metal Complex with a Second Metal Complex | 460 |
| 39.32.2.2.1.3 | μ_3 -Alkanetellurolates | | 461 |
| 39.32.2.2.1.3.1 | Method 1: | Reaction of Bridging Coordinated Tellurides with an Alkylating Agent | 461 |

39.39 **Product Class 39: Tellurolanes, Larger Rings, and Derivatives of Various Oxidation States**

39.39.6.2 **Cyclic Alkanetellurolates of Group 3–12 Metals** 2014
A. Polo and J. Real

| | | |
|---------------|---|-----|
| 39.39.6.2 | Cyclic Alkanetellurolates of Group 3–12 Metals | 465 |
| 39.39.6.2.1 | Synthesis of Cyclic Alkanetellurolates of Group 3–12 Metals | 465 |
| 39.39.6.2.1.1 | Method 1: Cyclic Ditellurolates from Ditellurides | 465 |
| 39.39.6.2.1.2 | Method 2: Cyclic Aminotellurolates by Reaction of an Alkylamino Ditelluride with a Metal Complex | 466 |
| | Author Index | 469 |
| | Abbreviations | 495 |