
Volume 13: Five-Membered Heteroarenes with Three or More Heteroatoms

	Introduction	
	R. C. Storr and T. L. Gilchrist	1
13.1	Product Class 1: 1,2,5-Oxathiazoles, 1,2,3-Dithiazoles, and Related Compounds	
	N. G. Argyropoulos	9
13.2	Product Class 2: 1,2,4-Dioxazoles, 1,2,4-Oxathiazoles, and 1,2,4-Dithiazoles	
	N. G. Argyropoulos	29
13.3	Product Class 3: 1,3,2-Oxathiazoles, 1,3,2-Dithiazoles, and Related Compounds	
	N. G. Argyropoulos	73
13.4	Product Class 4: 1,4,2-Oxathiazoles and Related Compounds	
	N. G. Argyropoulos	95
13.5	Product Class 5: 1,2,3-Oxadiazoles	
	T. L. Gilchrist	109
13.6	Product Class 6: 1,2,4-Oxadiazoles	
	K. Hemming	127
13.7	Product Class 7: 1,2,5-Oxadiazoles	
	R. M. Paton	185
13.8	Product Class 8: 1,3,4-Oxadiazoles	
	G. W. Weaver	219
13.9	Product Class 9: 1,2,3-Thiadiazoles	
	D. J. Wilkins and P. A. Bradley	253
13.10	Product Class 10: 1,2,4-Thiadiazoles	
	D. J. Wilkins and P. A. Bradley	277
13.11	Product Class 11: 1,2,5-Thiadiazoles and Related Compounds	
	P. A. Koutentis	297
13.12	Product Class 12: 1,3,4-Thiadiazoles	
	S. J. Collier	349
13.13	Product Class 13: 1,2,3-Triazoles	
	A. C. Tomé	415

13.14	Product Class 14: 1,2,4-Triazoles A. D. M. Curtis	603
13.15	Product Class 15: Dithiophospholes and Their Analogues R. K. Bansal, N. Gupta, and S. J. Collier	641
13.16	Product Class 16: Oxazaphospholes and Thiazaphospholes R. K. Bansal and Neelima Gupta	647
13.17	Product Class 17: Oxadiphospholes and Their Analogues S. J. Collier	659
13.18	Product Class 18: Diazaphospholes and Diazarsoles R. K. Bansal and Neelima Gupta	689
13.19	Product Class 19: Azadiphospholes and Their Analogues S. J. Collier	717
13.20	Product Class 20: Triphospholes and Diphospharsoles R. K. Bansal and Neelima Gupta	729
13.21	Product Class 21: Thiadiazaphospholes S. J. Collier	739
13.22	Product Class 22: Triazaphospholes R. K. Bansal and Neelima Gupta	743
13.23	Product Class 23: Diazadiphospholes S. J. Collier	757
13.24	Product Class 24: Tetrphospholes S. J. Collier	763
13.25	Product Class 25: Tetraazaphospholes S. J. Collier	767
13.26	Product Class 26: Pentaphospholes and Pentarsoles R. K. Bansal and Neelima Gupta	771
13.27	Product Class 27: Selenazoles and Tellurazoles Containing One or More Other Heteroatoms R. A. Aitken	777
13.28	Product Class 28: Oxatriazoles M. Begtrup	823
13.29	Product Class 29: Thiatriazoles M. Begtrup	833

13.30	Product Class 30: Tetrazoles	
	A. F. Brigas	861
13.31	Product Class 31: Pentazoles	
	R. C. Storr	917
	Keyword Index	923
	Author Index	955
	Abbreviations	1005

Table of Contents

Introduction

R. C. Storr and T. L. Gilchrist

	Introduction	1
13.1	Product Class 1: 1,2,5-Oxathiazoles, 1,2,3-Dithiazoles, and Related Compounds N. G. Argyropoulos	
13.1	Product Class 1: 1,2,5-Oxathiazoles, 1,2,3-Dithiazoles, and Related Compounds	9
13.1.1	Product Subclass 1: Annulated 1,2,5-Oxathiazoles	9
13.1.1.1	Synthesis by Ring-Closure Reactions	10
13.1.1.1.1	By Formation of Two O—S Bonds and One S—C Bond, or One O—S, One S—S, and One S—C Bond	10
13.1.1.1.1.1	Method 1: 1,6-Dioxa-6 λ^4 -thia-2,5-diazapentalenes and 1-Oxa-6,6 λ^4 -dithia-2,5-diazapentalenes from 1,3-Dioximes ..	10
13.1.2	Product Subclass 2: Monocyclic 1,2,3-Dithiazoles	12
13.1.2.1	Synthesis by Ring-Closure Reactions	14
13.1.2.1.1	By Formation of One S—N and One S—C Bond	14
13.1.2.1.1.1	Method 1: Appel's Salt from Acetonitrile and Sulfur Monochloride	14
13.1.2.2	Synthesis by Substituent Modification	15
13.1.2.2.1	Method 1: From Appel's Salt and Substituted Phenols or Hydrazines	15
13.1.3	Product Subclass 3: Annulated 1,2,3-Dithiazoles	16
13.1.3.1	Synthesis by Ring-Closure Reactions	18
13.1.3.1.1	By Formation of One S—S and One S—N Bond	19
13.1.3.1.1.1	Method 1: 1,2,3-Benzodithiazolium Salts from 2-Aminobenzenethiols and Thionyl Chloride	19
13.1.3.1.2	By Formation of One S—N and One S—C Bond	20
13.1.3.1.2.1	Method 1: 1,2,3-Benzodithiazolium Salts (Herz Salts) from Arylamines and Sulfur Monochloride	20
13.1.3.1.2.2	Method 2: Heteroannulated Herz Salts from Heteroaromatic Amines and Sulfur Monochloride: Synthesis by Annulation to a Heterocyclic Ring	21
13.1.3.2	Aromatization	23
13.1.3.2.1	Method 1: 1,2,3-Benzodithiazolium Salts by Oxidation of Benzodithiazolyl Radicals	23

13.1.3.2.2	Method 2:	1,2,3-Benzodithiazolium Salts by Dehydration of 3 <i>H</i> -1,2,3-Benzodithiazole 2-Oxides	23
13.1.3.3	Synthesis by Substituent Modification		24
13.1.3.3.1	Method 1:	From Other 1,2,3-Benzodithiazolium Salts and Amines	24
13.2	Product Class 2: 1,2,4-Dioxazoles, 1,2,4-Oxathiazoles, and 1,2,4-Dithiazoles N. G. Argyropoulos		
13.2	Product Class 2: 1,2,4-Dioxazoles, 1,2,4-Oxathiazoles, and 1,2,4-Dithiazoles		29
13.2.1	Product Subclass 1: Monocyclic 1,2,4-Dithiazoles		29
13.2.1.1	Synthesis by Ring-Closure Reactions		34
13.2.1.1.1	By Formation of One S—S Bond, Two S—C Bonds, and One N—C Bond		34
13.2.1.1.1.1	Method 1:	1,2,4-Dithiazolium Salts from Nitriles and Phosphorus Pentasulfide	34
13.2.1.1.2	By Formation of One S—S and Two S—C Bonds		35
13.2.1.1.2.1	Method 1:	3,5-Diaryl-1,2,4-dithiazolium Salts from 1,3-Dichloro- 2-azoniaallene Salts and Hydrogen Sulfide	35
13.2.1.1.3	By Formation of One S—S and One S—N Bond		36
13.2.1.1.3.1	Method 1:	3,5-Diaryl-1,2,4-dithiazolium Salts by Oxidation of Aryl Thioamides	36
13.2.1.1.3.1.1	Variation 1:	Symmetrical 3,5-Diaryl-1,2,4-dithiazolium Salts	36
13.2.1.1.3.1.2	Variation 2:	3,5-Diaryl-1,2,4-Dithiazolium Salts by Oxidation of <i>N</i> -Thioaroyl Formamides and Formamidines	37
13.2.1.1.3.1.3	Variation 3:	Unsymmetrically Substituted 3,5-Diaryl-1,2,4-dithiazolium Salts from Aryl Thioamide <i>S</i> -Oxides and Thiobenzoic Acid Derivatives	38
13.2.1.1.3.1.4	Variation 4:	Unsymmetrically Substituted 3,5-Diaryl-1,2,4-dithiazolium Salts from the Oxidative Cyclization of Thiobenzamides	39
13.2.1.1.4	By Formation of One S—S and One S—C Bond		40
13.2.1.1.4.1	Method 1:	1,2,4-Dithiazolium Salts from <i>N</i> -Acylothiourea Derivatives	40
13.2.1.1.4.1.1	Variation 1:	3-Amino-5-aryl-1,2,4-dithiazolium Salts by Oxidation of <i>N</i> -Acylothiourea Derivatives	40
13.2.1.1.4.1.2	Variation 2:	3-Amino-5-aryl-1,2,4-dithiazolium Salts from Transition-Metal-Coordinated <i>N</i> -Acylothioureas and Thionyl Chloride	41
13.2.1.1.5	By Formation of One S—S Bond		42
13.2.1.1.5.1	Method 1:	1,2,4-Dithiazolium Salts by Oxidation of Dithiobiurets (Dithioimidodicarbonic Diamides)	42
13.2.1.1.5.1.1	Variation 1:	Oxidation of Preformed Dithiobiurets	42
13.2.1.1.5.1.2	Variation 2:	Synthesis by Oxidation of Dithiobiurets Formed In Situ	44
13.2.1.1.5.1.3	Variation 3:	Synthesis from 1,3-Dichloro-2-azaprop-2-eniminium Salts via a Dithiobiuret Intermediate	45
13.2.1.1.5.1.4	Variation 4:	Oxidative Dealkylation–Cyclization of Isodithiobiurets	46

13.2.1.1.5.2	Method 2:	1,2,4-Dithiazolium Salts by Oxidation of Aminocarbonothioyldithiocarbamate Esters	47
13.2.1.1.5.3	Method 3:	3-Amino-5-aryl-1,2,4-dithiazolium Salts by Oxidation of Transition-Metal Complexes of 1,1-Diethyl-3-thiobenzoylthiourea Derivatives	48
13.2.1.2	Synthesis by Ring Transformation		48
13.2.1.2.1	Method 1:	1,2,4-Dithiazolium Salts from Thiocarbonylimino-1,2,4-dithiazolidines and Alkylating Reagents	48
13.2.1.2.2	Method 2:	1,2,4-Dithiazolium Salts from 1,2,3,4-Thiatriazol-5-amine and <i>O</i> -Aryl Chlorothioformates	50
13.2.1.3	Aromatization		51
13.2.1.3.1	Method 1:	Hydride Abstraction from 5-Phenyl-3 <i>H</i> -1,2,4-dithiazole	51
13.2.1.3.2	Method 2:	Alkylation of 3 <i>H</i> -1,2,4-Dithiazole-3-thiones and 3 <i>H</i> -1,2,4-Dithiazol-3-imines	51
13.2.1.3.2.1	Variation 1:	Synthesis from 3 <i>H</i> -1,2,4-Dithiazole-3-thiones	51
13.2.1.3.2.2	Variation 2:	Synthesis by Alkylation of 3 <i>H</i> -1,2,4-Dithiazol-3-imines	52
13.2.1.4	Synthesis by Substituent Modification		53
13.2.1.4.1	Method 1:	1,2,4-Dithiazolium Salts by Nucleophilic Substitution of Substituents	53
13.2.2	Product Subclass 2: Annulated 1,2,4-Oxathiazoles and 1,2,4-Dithiazoles		54
13.2.2.1	Synthesis by Ring-Closure Reactions		55
13.2.2.1.1	Synthesis by Double-Cyclization Reactions		56
13.2.2.1.1.1	By Formation of Two S—S and Three S—C Bonds		56
13.2.2.1.1.1.1	Method 1:	2,5-Bis(dimethylamino)-1,6,6a λ^4 -trithia-3,4-diazapentalenes by Thiolysis of <i>N</i> -(Chloro[[(1 <i>Z</i>)-chloro[[(1 <i>Z</i>)-chloro(dimethylamino)methylene]amino]methylene]amino]methylene)- <i>N</i> -methylmethanaminium Chloride	56
13.2.2.1.1.2	By Formation of Two S—S and Two S—C Bonds		57
13.2.2.1.1.2.1	Method 1:	2,5-Diaryl-1,6,6a λ^4 -trithia-3,4-diazapentalenes from <i>S</i> -Methylisothiurea Derivatives and Phosphorus Pentasulfide	57
13.2.2.1.1.3	By Formation of Two O—S or Two S—S Bonds		57
13.2.2.1.1.3.1	Method 1:	1,6-Dioxa-6a λ^4 -thia-3,4-diazapentalenes by Oxidation of <i>N,N'</i> -Diacylthiourea Derivatives	57
13.2.2.1.1.3.2	Method 2:	1,6,6a λ^4 -Trithia-3,4-diazapentalenes from Dithiocyanatomethyl Disulfides	58
13.2.2.1.2	Synthesis by Annulation to a Heterocyclic Ring		59
13.2.2.1.2.1	By Formation of Two S—S Bonds and One N—C Bond		59
13.2.2.1.2.1.1	Method 1:	Heterapentalenes from 1,2,3,4-Thiatriazol-5-amines and Aryl Isothiocyanates	59
13.2.2.1.2.1.2	Method 2:	Heterapentalenes from 1,2,3,4-Thiatriazol-5-amine and <i>O</i> -Aryl Chlorothioformates	60
13.2.2.1.2.2	By Formation of One S—S and One S—C Bond		61

13.2.2.1.2.2.1	Method 1:	Trithiadiazapentalenes by Oxygen–Sulfur Exchange Reactions	61
13.2.2.1.2.2.1.1	Variation 1:	Diazapentalenes by Oxygen–Sulfur Exchange Reactions of 3-Acylimino-3 <i>H</i> -1,2,4-oxathiazoles and 3-Acylimino-3 <i>H</i> -1,2,4-Dithiazoles with Phosphorus Pentasulfide	61
13.2.2.1.2.2.1.2	Variation 2:	1,6,6aλ ⁴ -Trithia-3-azapentalenes by Oxygen–Sulfur Exchange Reactions of 3 <i>H</i> -1,2,4-Dithiazolylidene Derivatives	62
13.2.2.1.2.2.1.3	Variation 3:	1,6,6aλ ⁴ -Trithia-3-azapentalenes by Oxygen–Sulfur Exchange Reactions of (1,2-Dithiol-3-ylidene)benzamide Derivatives	62
13.2.2.1.2.3	By Formation of One S–S and One N–C Bond		63
13.2.2.1.2.3.1	Method 1:	Heterapentalenes from <i>N</i> -Aryl-3-imino-3 <i>H</i> -1,2,4-dithiazol-5-amines and Aryl Isothiocyanates	63
13.2.2.1.2.3.2	Method 2:	1,6,6aλ ⁴ -Trithia-3-azapentalenes from 3 <i>H</i> -1,2-Dithiol-3-imines and Isothiocyanates	65
13.2.2.2	Synthesis by Ring Transformation		66
13.2.2.2.1	Method 1:	5-Aryl-2-(methylsulfanyl)-1,6,6aλ ⁴ -trithia-3,4-diazapentalenes from 1,3,5-Triazinium Salts and Hydrogen Sulfide	66
13.2.2.3	Synthesis by Substituent Modification		67
13.2.2.3.1	Method 1:	Synthesis of Amino-Substituted 1,6,6aλ ⁴ -Trithia-3,4-diazapentalenes by Nucleophilic Substitution	67
13.3	Product Class 3: 1,3,2-Oxathiazoles, 1,3,2-Dithiazoles, and Related Compounds		
	N. G. Argyropoulos		
13.3	Product Class 3: 1,3,2-Oxathiazoles, 1,3,2-Dithiazoles, and Related Compounds		73
13.3.1	Product Subclass 1: Monocyclic 1,3,2-Oxathiazoles		73
13.3.1.1	Synthesis by Ring-Closure Reactions		75
13.3.1.1.1	By Formation of One S–N and One O–C Bond		75
13.3.1.1.1.1	Fragments C–C–S and N–O		75
13.3.1.1.1.1.1	Method 1:	Mesoionic 1,3,2-Oxathiazolium-5-olates from Aryl(sulfanyl)-acetic Acids by <i>S</i> -Nitrosation and Dehydration	75
13.3.2	Product Subclass 2: Monocyclic 1,3,2-Dithiazoles		76
13.3.2.1	Synthesis by Ring-Closure Reactions		79
13.3.2.1.1	By Formation of Two S–N Bonds		79
13.3.2.1.1.1	Fragments S–C–C–S and N		79
13.3.2.1.1.1.1	Method 1:	Syntheses of 1,3,2-Dithiazolium Chlorides from Ethane-1,2-disulfonyl Dichlorides	79
13.3.2.1.1.1.1.1	Variation 1:	From 1-Chloroethane-1,2-disulfonyl Dichloride and Bis(trimethylsilyl)sulfur Diimide	79
13.3.2.1.1.1.1.2	Variation 2:	From 1-Chloroethane-1,2-disulfonyl Chlorides and Trimethylsilyl Azide	80

13.3.2.1.2	By Formation of Two S—C Bonds	80
13.3.2.1.2.1	Fragments S—N—S and C—C	80
13.3.2.1.2.1.1	Method 1: 1,3,2-Dithiazolium Salts by Cycloaddition	80
13.3.2.1.2.1.1.1	Variation 1: 1,3-Dipolar Cycloaddition of the Dithionitronium Cation to Alkynes	80
13.3.2.1.2.1.1.2	Variation 2: Cycloadditions of Dichlorodithionitronium Hexafluoroarsenate to Alkynes	82
13.3.2.1.2.1.2	Method 2: Mesoionic 1,3,2-Dithiazol-4-imines from Phenylacetylene and Tetrasulfur Tetranitride	83
13.3.2.1.2.1.3	Method 3: Mesoionic 1,3,2-Dithiazole-4-thiones from Alkynes and 1,2,4,6-Tetrathia-3,5,7-triazepinium Chloride	83
13.3.2.2	Aromatization	84
13.3.2.2.1	Method 1: 1,3,2-Dithiazolium Salts by Oxidation of 1,3,2-Dithiazolyl Free Radicals	84
13.3.2.3	Synthesis by Substituent Modification	85
13.3.2.3.1	Method 1: Mesoionic 1,3,2-Dithiazole-4-thiones from 1,3,2-Dithiazolium Salts and Vice Versa	85
13.3.2.3.2	Method 2: 5-Amino-1,3,2-dithiazole-4-thiones from 1,3,2-Dithiazolium Salts	86
13.3.2.3.3	Method 3: Mesoionic 1,3,2-Dithiazol-4-ones by Oxidation of 1,3,2-Dithiazole-4-thiones	87
13.3.3	Product Subclass 3: Annulated 1,3,2-Dithiazoles	88
13.3.3.1	Synthesis by Ring-Closure Reactions	89
13.3.3.1.1	By Annulation to an Arene or a Hetarene	89
13.3.3.1.1.1	By Formation of Two S—N Bonds	89
13.3.3.1.1.1.1	Method 1: 1,3,2-Dithiazolium Salts from Sulfenyl Chlorides and Trimethylsilyl Azide	89
13.3.3.1.1.1.2	Method 2: 1,3,2-Benzodithiazolium Chloride from Benzene-1,2-disulfenyl Dichloride and Bis(trimethylsilyl)sulfur Diimide	91
13.3.3.2	Aromatization	92
13.3.3.2.1	Method 1: [1,3,2]Dithiazolo[4,5- <i>b</i>]quinoxalinium Salts by Oxidation of the [1,3,2]Dithiazolo[4,5- <i>b</i>]quinoxalin-2-yl Radical	92
13.4	Product Class 4: 1,4,2-Oxathiazoles and Related Compounds N. G. Argyropoulos	
<hr/>		
13.4	Product Class 4: 1,4,2-Oxathiazoles and Related Compounds	95
13.4.1	Product Subclass 1: 1,3,4-Oxathiazolium Salts	95
13.4.1.1	Synthesis by Ring-Closure Reactions	96
13.4.1.1.1	By Formation of One O—C Bond	96
13.4.1.1.1.1	Fragment C—N—S—C—O	96

13.4.1.1.1.1	Method 1: Synthesis by Intramolecular Cyclization of <i>N</i> -(Acylsulfanyl)amides	96
13.4.2	Product Subclass 2: 1,4,2-Oxathiazolium Salts	97
13.4.2.1	Aromatization	97
13.4.2.1.1	Method 1: Synthesis by Solvolysis of 5 <i>H</i> -1,4,2-Oxathiazoles	97
13.4.3	Product Subclass 3: 1,4,2-Dithiazolium Salts	98
13.4.3.1	Synthesis by Ring-Closure Reactions	100
13.4.3.1.1	By Formation of One S—N Bond	100
13.4.3.1.1.1	Fragment N—C—S—C—S	100
13.4.3.1.1.1.1	Method 1: Intramolecular Cyclization of Iminomethyl Dithiocarbamates	100
13.4.3.1.1.1.1.1	Variation 1: From Aryl{[(methylsulfonyl)oxy]imino}methyl Dithiocarbamates	100
13.4.3.1.1.1.1.2	Variation 2: From Bromo(diethylamino)methaniminium Bromide and Sodium Pyrrolidinecarbothioate	101
13.4.3.1.2	By Formation of One S—C Bond	102
13.4.3.1.2.1	Fragment C—N—S—C—S	102
13.4.3.1.2.1.1	Method 1: Intramolecular Cyclization of <i>N</i> -(Thioacylsulfanyl)amides	102
13.4.3.2	Aromatization	103
13.4.3.2.1	Method 1: By Alkylation of 1,4,2-Dithiazole-5-thiones	103
13.4.3.2.2	Method 2: By Solvolysis of 5 <i>H</i> -1,4,2-Dithiazoles	104
13.4.3.3	Synthesis by Substituent Modification	106
13.4.3.3.1	Substitution of Existing Substituents	106
13.4.3.3.1.1	Method 1: Nucleophilic Substitution of 5-Methylsulfanyl Groups from 1,4,2-Dithiazolium Salts	106
13.5	Product Class 5: 1,2,3-Oxadiazoles T. L. Gilchrist	
13.5	Product Class 5: 1,2,3-Oxadiazoles	109
13.5.1	Synthesis by Ring-Closure Reactions	111
13.5.1.1	By Formation of One O—N Bond	111
13.5.1.1.1	Fragment O—C—C—N—N	111
13.5.1.1.1.1	Method 1: From α -Diazocarbonyl Compounds	111
13.5.1.2	By Formation of One O—C Bond	112
13.5.1.2.1	Fragment O—N—N—C—C	112
13.5.1.2.1.1	Method 1: Via <i>N</i> -Nitroso Compounds	112
13.5.1.2.1.1.1	Variation 1: Sydnones from <i>N</i> -Nitroso- α -amino Acids	112
13.5.1.2.1.1.2	Variation 2: Sydnone Imines from <i>N</i> -Nitroso- α -amino Nitriles	113
13.5.2	Synthesis by Substituent Modification	114
13.5.2.1	Substitution of Existing Substituents	114

13.5.2.1.1	Of Hydrogen	114
13.5.2.1.1.1	Method 1: By a Metal	114
13.5.2.1.1.2	Method 2: By a Carbon Functionality	115
13.5.2.1.1.3	Method 3: By a Heteroatom	116
13.5.2.1.2	Of Organometallic Groups	117
13.5.2.1.2.1	Method 1: By Another Metal	117
13.5.2.1.2.2	Method 2: By a Carbon Functionality	118
13.5.2.1.2.3	Method 3: By a Heteroatom	119
13.5.2.1.3	Of Carbon Functionalities	119
13.5.2.1.3.1	Method 1: By Hydrogen	119
13.5.2.1.4	Of Heteroatoms	120
13.5.2.1.4.1	Method 1: By Hydrogen	120
13.5.2.1.4.2	Method 2: By a Metal	120
13.5.2.1.4.3	Method 3: By a Carbon Functionality	121
13.5.2.1.4.4	Method 4: By Another Heteroatom	121
13.5.2.2	Modification of Substituents	122
13.5.2.2.1	Method 1: Of Side-Chain α -Carbon Substituents	122
13.5.2.2.2	Method 2: Of Side-Chain α -Heteroatom Substituents	123
13.6	Product Class 6: 1,2,4-Oxadiazoles	
	K. Hemming	
13.6	Product Class 6: 1,2,4-Oxadiazoles	127
13.6.1	Synthesis by Ring-Closure Reactions	128
13.6.1.1	By Formation of One O—C and One N—C Bond	128
13.6.1.1.1	Fragments O—N—C and N—C	128
13.6.1.1.1.1	Method 1: By the 1,3-Dipolar Cycloaddition Reactions of Nitrile Oxides with Nitriles	128
13.6.1.1.1.1.1	Variation 1: By Using an Aliphatic Nitrile Oxide Generated from a Nitroalkane and Phenyl Isocyanate	129
13.6.1.1.1.1.2	Variation 2: By Using Nitrile Oxides Generated from Imidoyl Halides (Halooximes)	130
13.6.1.1.1.2	Method 2: By 1,3-Dipolar Cycloaddition of Nitrile Oxides to Imines, Followed by Aromatization of the Intermediate 4,5-Dihydro-1,2,4-oxadiazole	130
13.6.1.1.2	Fragments C—N—C and N—O	131
13.6.1.1.2.1	Method 1: Via <i>N</i> -Acylamidoximes	131
13.6.1.1.2.1.1	Variation 1: Via <i>N</i> -Acylamidoximes Derived from the Reaction of Amide Precursors with <i>N,N</i> -Dialkylformamide Dialkyl Acetals	132
13.6.1.1.2.1.2	Variation 2: Via <i>N</i> -Acylamidoximes Derived from Nitriles	132
13.6.1.1.2.1.3	Variation 3: Via <i>N</i> -Acylamidoximes Derived from <i>N</i> -Acyl Isothiocyanates	133
13.6.1.1.2.1.4	Variation 4: Via <i>N</i> -Acylamidoximes Derived from <i>N</i> -Cyano Compounds	134

13.6.1.1.2.2	Method 2:	By Nitrosation of <i>N</i> -Acyl α -Amino Acid Derivatives Bearing Active Hydrogens on a Carbon Atom	135
13.6.1.1.3		Fragments O—N—C—N and C	136
13.6.1.1.3.1	Method 1:	From an Amidoxime and a Carbonic Acid Derivative	136
13.6.1.1.3.1.1	Variation 1:	From an Amidoxime and a Chloroformate	137
13.6.1.1.3.1.2	Variation 2:	From an Amidoxime and Phosgene	138
13.6.1.1.3.2	Method 2:	From an Amidoxime and a Carboxylic Acid or a Carboxylic Acid Derivative	138
13.6.1.1.3.2.1	Variation 1:	From an Amidoxime and a Carboxylic Acid	139
13.6.1.1.3.2.2	Variation 2:	From an Amidoxime and a Carboxylic Acid Ester	140
13.6.1.1.3.2.3	Variation 3:	From an Amidoxime and an Anhydride	141
13.6.1.1.3.2.4	Variation 4:	From an Amidoxime and an Acid Chloride	142
13.6.1.1.3.3	Method 3:	From an Amidoxime and a Nitrile Derivative	143
13.6.1.1.3.3.1	Variation 1:	From an Amidoxime and an Alkyl or Aryl Nitrile	145
13.6.1.1.3.3.2	Variation 2:	From an Amidoxime and a Cyanate	145
13.6.1.1.3.3.3	Variation 3:	From an Amidoxime and a Cyanogen Halide	145
13.6.1.1.3.4	Method 4:	From an Amidoxime and an Orthoformate	146
13.6.1.1.3.5	Method 5:	From an Amidoxime and a Cumulene or Heterocumulene ..	147
13.6.1.1.3.6	Method 6:	From an Amidoxime and an Iminium Compound	147
13.6.1.1.3.7	Method 7:	From an Amidoxime and an Imino Ether, Lactim Ether, Imidic Chloride, or Alkoxyimidoyl Compound	149
13.6.1.2		By Formation of One O—N Bond	150
13.6.1.2.1		Fragment O—C—N—C—N	150
13.6.1.2.1.1	Method 1:	From Nitrene Precursors	150
13.6.1.2.1.1.1	Variation 1:	By Using Nitrenes Derived from <i>N</i> -Acylamidrazones	151
13.6.1.2.1.1.2	Variation 2:	By Using Nitrenes Derived Ultimately from Trimethylsilyl Azide	151
13.6.1.3		By Formation of One O—C Bond	152
13.6.1.3.1		Fragment O—N—C—N—C	152
13.6.1.3.1.1	Method 1:	From <i>N</i> -Acylamidoximes	152
13.6.1.3.1.2	Method 2:	From <i>N</i> -(Dicyanovinyl)amidoximes	153
13.6.1.3.1.3	Method 3:	Cyclization of the Oxime Oxygen onto an Iminium Carbon ..	153
13.6.1.4		By Formation of One N—C Bond	154
13.6.1.4.1		Fragment N—C—O—N—C	154
13.6.1.4.1.1	Method 1:	From Imidates	154
13.6.1.4.2		Fragment N—C—N—O—C	154
13.6.1.4.2.1	Method 1:	From <i>O</i> -Acylamidoximes Derived from Amidoximes	154
13.6.1.4.2.2	Method 2:	Cyclization of <i>O</i> -Acylamidoximes Formed as Intermediates from Purine Precursors	155
13.6.1.4.2.3	Method 3:	Staudinger/Aza-Wittig Reaction of <i>O</i> -Acylazidooximes	156
13.6.2		Synthesis by Ring Transformation	157
13.6.2.1	Method 1:	From Tetrazoles	157
13.6.2.2	Method 2:	From 1,2,4-Oxadiazoles	158
13.6.2.3	Method 3:	From 1,2,5-Oxadiazoles	159

13.6.2.4	Method 4: From Imidazoles	159
13.6.3	Aromatization	161
13.6.3.1	Method 1: By Dehydrogenation	161
13.6.3.2	Method 2: By the Elimination of HX or YX	162
13.6.4	Synthesis by Substituent Modification	163
13.6.4.1	Substitution of Existing Substituents	163
13.6.4.1.1	Of Hydrogen	163
13.6.4.1.1.1	Method 1: By Metals	163
13.6.4.1.2	Of Metals	163
13.6.4.1.2.1	Method 1: By Heteroatoms	163
13.6.4.1.3	Of Carbon Functionalities	164
13.6.4.1.3.1	Method 1: By Heteroatoms	164
13.6.4.1.4	Of Heteroatoms	165
13.6.4.1.4.1	Method 1: By Carbon	165
13.6.4.1.4.2	Method 2: By Another Heteroatom	165
13.6.4.2	Addition Reactions	167
13.6.4.3	Modification of Existing Substituents	167
13.6.4.3.1	Method 1: Modification of Substituents with an α -CH	168
13.6.4.3.1.1	Variation 1: Deprotonation and Reaction of 5-Alkyl Groups	168
13.6.4.3.2	Method 2: Modification of a C3 or C5 Ester Functionality	169
13.6.4.3.2.1	Variation 1: Synthesis of 3-Carbonitrile Derivatives	170
13.6.4.3.2.2	Variation 2: Curtius Reaction	170
13.6.4.3.3	Method 3: Reactions of Halomethyl-Substituted Oxadiazoles	171
13.6.4.3.4	Method 4: Synthesis of 3- and 5-Carbaldehydes, Imines, and Related Derivatives	172
13.6.4.3.5	Method 5: Wittig Reactions at the α -Carbon	174
13.6.4.3.6	Method 6: Modification of Nitrogen Substituents	175
13.6.5	Solid-Phase Syntheses	176
13.6.5.1	Method 1: Synthesis from Solid-Supported Esters	177
13.6.5.2	Method 2: Synthesis Using Resin-Bound Amidoximes Derived from Resin-Bound Nitriles	178

13.7 Product Class 7: 1,2,5-Oxadiazoles

R. M. Paton

13.7	Product Class 7: 1,2,5-Oxadiazoles	185
13.7.1	Product Subclass 1: Monocyclic 1,2,5-Oxadiazoles (Furazans)	185
13.7.1.1	Synthesis by Ring-Closure Reactions	186
13.7.1.1.1	By Formation of One O—N Bond	186
13.7.1.1.1.1	Fragment O—N—C—C—N	186
13.7.1.1.1.1.1	Method 1: From 1,2-Dione Dioximes	186

13.7.1.2	Synthesis by Ring Transformation	188
13.7.1.2.1	Method 1: From 1,2,4-Oxadiazoles	188
13.7.1.2.2	Method 2: From Isoxazoles	189
13.7.1.3	Synthesis by Substituent Modification	189
13.7.1.3.1	Substitution of Existing Substituents	190
13.7.1.3.1.1	Method 1: Substitution of Halogens by Nucleophiles	190
13.7.1.3.1.2	Method 2: Deoxygenation of 1,2,5-Oxadiazole 2-Oxides	190
13.7.1.3.1.3	Method 3: Substitution of Nitrogen by Nucleophiles	191
13.7.1.3.2	Modification of Substituents	192
13.7.1.3.2.1	Of Oxygen	192
13.7.1.3.2.2	Of Sulfur	193
13.7.1.3.2.3	Of Nitrogen	193
13.7.1.3.2.4	Of Carbon	194
13.7.2	Product Subclass 2: 2,1,3-Benzoxadiazoles (Benzofurazans) and Other Annulated 1,2,5-Oxadiazoles	194
13.7.2.1	Synthesis by Ring-Closure Reactions	195
13.7.2.1.1	By Annulation to an Arene	195
13.7.2.1.1.1	By Formation of One O—N Bond	195
13.7.2.1.1.1.1	Fragment O—N—C—C—N	195
13.7.2.1.1.1.1.1	Method 1: From Benzo-1,2-quinone Dioximes	195
13.7.2.1.1.1.1.2	Method 2: From 2-Azidonitro- and 2-Azidonitrosoarenes, and 2-Azidoanilines	195
13.7.2.1.2	By Annulation to the Heterocyclic Ring	196
13.7.2.2	Synthesis by Ring Transformation	197
13.7.2.3	Synthesis by Substituent Modification	197
13.7.2.3.1	Substitution of Existing Substituents	197
13.7.2.3.1.1	Method 1: Substitution of Hydrogen	197
13.7.2.3.1.2	Method 2: Substitution of Halogens by Nucleophiles	197
13.7.2.3.2	Modification of Substituents	198
13.7.2.3.2.1	Method 1: Deoxygenation of 2,1,3-Benzoxadiazole 1-Oxides	198
13.7.3	Product Subclass 3: Monocyclic 1,2,5-Oxadiazole 2-Oxides (Furoxans)	199
13.7.3.1	Synthesis by Ring-Closure Reactions	200
13.7.3.1.1	By Formation of One O—N and One C—C Bond	200
13.7.3.1.1.1	Fragments O—N—C and N—C	200
13.7.3.1.1.1.1	Method 1: By Dimerization of Nitrile Oxides	200
13.7.3.1.1.1.1.1	Variation 1: From Nitrile Oxides Generated from Oximes and Hydroximoyl Halides	202
13.7.3.1.1.1.1.2	Variation 2: From Nitrile Oxides Generated from Nitrolic Acids and Their Precursors	202
13.7.3.1.1.1.1.3	Variation 3: From Nitrile Oxides Generated from Nitroalkyl Compounds	203

13.7.3.1.2	By Formation of One O—N Bond	203
13.7.3.1.2.1	Fragment O—N—C—N	203
13.7.3.1.2.1.1	Method 1: From 1,2-Dione Dioximes	203
13.7.3.1.2.1.2	Method 2: From α -Nitro Ketoximes	204
13.7.3.2	Synthesis by Substituent Modification	205
13.7.3.2.1	Substitution of Existing Substituents	205
13.7.3.2.1.1	Method 1: Substitution of Halogens by Nucleophiles	205
13.7.3.2.1.2	Method 2: Substitution of Sulfur by Nucleophiles	206
13.7.3.2.1.3	Method 3: Substitution of Nitrogen by Nucleophiles	206
13.7.3.2.2	Modification of Substituents	207
13.7.4	Product Subclass 4: 2,1,3-Benzoxadiazole 1-Oxides (Benzofuroxans) and Other Annulated Furoxans	207
13.7.4.1	Synthesis by Ring-Closure Reactions	208
13.7.4.1.1	By Annulation to an Arene	208
13.7.4.1.1.1	By Formation of One O—N Bond	208
13.7.4.1.1.1.1	Fragment O—N—C—N	208
13.7.4.1.1.1.1.1	Method 1: From 1,2-Quinone Dioximes	208
13.7.4.1.1.1.1.2	Method 2: From 2-Nitroanilines	209
13.7.4.1.1.1.1.3	Method 3: From 2-Nitroaryl Azides	209
13.7.4.1.2	By Annulation to the Heterocyclic Ring	210
13.7.4.2	Synthesis by Ring Transformation	211
13.7.4.3	Synthesis by Substituent Modification	211
13.7.4.3.1	Substitution of Existing Substituents	211
13.7.4.3.1.1	Method 1: Substitution of Hydrogen	211
13.7.4.3.1.2	Method 2: Substitution of Halogens by Nucleophiles	212
13.8	Product Class 8: 1,3,4-Oxadiazoles G. W. Weaver	
13.8	Product Class 8: 1,3,4-Oxadiazoles	219
13.8.1	Synthesis by Ring-Closure Reactions	220
13.8.1.1	By Formation of Two O—C Bonds	220
13.8.1.1.1	Fragments C—N—N—C and O	220
13.8.1.1.1.1	Method 1: Oxidation of Diazines with Lead(IV) Acetate	220
13.8.1.2	By Formation of One O—C and One N—C Bond	221
13.8.1.2.1	Fragments N—N—C and O—C	221
13.8.1.2.1.1	Method 1: Reaction of Diazo Compounds with Ketones	221
13.8.1.2.2	Fragments O—C—N—N and C	222
13.8.1.2.2.1	Method 1: Reaction of Acylhydrazines with Derivatives of Carbonic Acid	222

13.8.1.2.2.1.1	Variation 1:	Use of Carbonyldiimidazole To Effect Cyclization	222
13.8.1.2.2.1.2	Variation 2:	Synthesis of Mesoionic Isosydones Using Phosgene	223
13.8.1.2.2.1.3	Variation 3:	Cyclization Using Carbon Disulfide	223
13.8.1.2.2.1.4	Variation 4:	Reaction of Acylhydrazines with Cyanogen Bromide	224
13.8.1.2.2.2	Method 2:	Reaction of Acylhydrazines with Carboxylic Acid Derivatives	225
13.8.1.2.2.2.1	Variation 1:	Reaction with Ortho Esters	225
13.8.1.2.2.2.2	Variation 2:	Reaction with a Carboxylic Acid and 2-Chloro-1,3-dimethyl-4,5-dihydroimidazolium Chloride	226
13.8.1.2.2.2.3	Variation 3:	Reaction with Imidate Hydrochlorides	227
13.8.1.2.2.3	Method 3:	Reaction of Diacyl Diimides with Carbenes	228
13.8.1.3	By Formation of One O—C Bond		228
13.8.1.3.1	Fragment O—C—N—N—C		228
13.8.1.3.1.1	Method 1:	From Diacylhydrazine Compounds	228
13.8.1.3.1.1.1	Variation 1:	Dehydration Using Phosphoric Acid Derivatives	229
13.8.1.3.1.1.2	Variation 2:	Dehydration Using Polyphosphoric Acid	229
13.8.1.3.1.1.3	Variation 3:	Dehydration Using Thionyl Chloride	230
13.8.1.3.1.1.4	Variation 4:	Dehydration Using Carbodiimides	231
13.8.1.3.1.1.5	Variation 5:	Thermal Dehydration	232
13.8.1.3.1.1.6	Variation 6:	Dehydration Using Triphenylphosphine and Carbon Tetrachloride	232
13.8.1.3.1.1.7	Variation 7:	Dehydration Using Hexamethyldisilazane	233
13.8.1.3.1.1.8	Variation 8:	Dehydration Using Trifluoromethanesulfonic Anhydride	234
13.8.1.3.1.1.9	Variation 9:	Dehydration Using Tosyl Chloride	234
13.8.1.3.1.1.10	Variation 10:	Dehydration Using 2-Chloro-1,3-dimethyl-4,5-dihydroimidazolium Chloride	235
13.8.1.3.1.1.11	Variation 11:	Dehydration Using Burgess-Type Reagents	235
13.8.1.3.1.2	Method 2:	Synthesis of 1,3,4-Oxadiazolamines from Acyl Semicarbazides	236
13.8.1.3.1.2.1	Variation 1:	Cyclization Using Carbodiimides	236
13.8.1.3.1.2.2	Variation 2:	Desulfurization with Mercury(II) Acetate under Microwave Irradiation	237
13.8.1.3.1.3	Method 3:	Oxidation of Aldehyde Acyl Hydrazones	238
13.8.1.3.1.3.1	Variation 1:	Oxidation with Lead(IV) Oxide	238
13.8.1.3.1.3.2	Variation 2:	Oxidation with Lead(IV) Acetate	239
13.8.1.3.1.3.3	Variation 3:	Oxidation with Bromine	240
13.8.1.3.1.4	Method 5:	Ring Closure by Internal Alkylation	241
13.8.2	Synthesis by Ring Transformation		242
13.8.2.1	Method 1:	Reactions of Azirines with Acylhydrazines	242
13.8.2.2	Method 2:	By Photochemical Rearrangement of Substituted 1,2,4-Oxadiazoles	242
13.8.2.3	Method 3:	Reactions of Tetrazoles with Carboxylic Acid Derivatives	243
13.8.2.3.1	Variation 1:	Reaction with Acetic Anhydride	243
13.8.2.3.2	Variation 2:	Reaction with Carboxylic Acid Chlorides	244
13.8.2.4	Method 4:	Reactions of 1,2,4-Triazines with Bromine	245
13.8.3	Synthesis by Substituent Modification		245
13.8.3.1	Substitution of Existing Substituents		245

13.8.3.1.1	Of Hydrogen	245
13.8.3.1.1.1	Acylation Reactions	245
13.8.3.1.2	Of Heteroatoms	246
13.8.3.1.2.1	Method 1: Displacement of Chlorine by Nucleophiles	246
13.8.3.2	Addition Reactions	246
13.8.3.2.1	Protonation	247
13.8.3.2.2	N-Alkylation	247
13.8.3.2.3	N-Acylation	247
13.8.3.3	Modification of Existing Substituents	248
13.8.3.3.1	Reactions of Sulfur Substituents	248
13.8.3.3.2	Reactions of Nitrogen Substituents	248
13.8.3.3.3	Reactions of Carbon Substituents	249
13.8.3.3.3.1	Method 1: Lithiation of a Methyl Substituent, Silylation, and Peterson Alkenation with a Ketone	249

13.9 Product Class 9: 1,2,3-Thiadiazoles

D. J. Wilkins and P. A. Bradley

13.9	Product Class 9: 1,2,3-Thiadiazoles	253
13.9.1	Product Subclass 1: Monocyclic 1,2,3-Thiadiazoles	253
13.9.1.1	Synthesis by Ring-Closure Reactions	255
13.9.1.1.1	By Formation of One S—N and One S—C Bond	255
13.9.1.1.1.1	Method 1: Wolff's Synthesis	255
13.9.1.1.1.2	Method 2: Hurd–Mori Synthesis	256
13.9.1.1.1.2.1	Variation 1: Use of Thionyl Chloride in the Hurd–Mori Procedure	256
13.9.1.1.1.2.2	Variation 2: Use of Sulfur Dichloride or Sulfur Monochloride in the Hurd–Mori Procedure	257
13.9.1.1.2	By Formation of One S—N and One C—C Bond	258
13.9.1.1.2.1	Method 1: Pechmann and Nold Synthesis	258
13.9.1.1.2.1.1	Variation 1: Reaction of Isothiocyanates with Diazo Compounds	258
13.9.1.1.2.1.2	Variation 2: Modified Pechmann Synthesis	259
13.9.1.1.2.1.3	Variation 3: Use of Lithium (Trimethylsilyl)diazomethane	260
13.9.1.2	Synthesis by Ring Transformation	261
13.9.1.2.1	Method 1: Synthesis From 1,2,3-Triazolethiols	261
13.9.1.2.2	Method 2: Synthesis From 1,2,3-Oxadiazoles	262
13.9.1.2.3	Method 3: From Isothiazolones	262
13.9.1.3	Synthesis by Substituent Modification	263
13.9.1.3.1	Method 1: Transformations Involving Metalation and Subsequent Electrophilic Quench	263
13.9.1.3.2	Method 2: Removal of Carbonyl Substituents	264
13.9.1.3.3	Method 3: Transformations Involving Diazonium Intermediates	265

13.9.1.3.4	Method 4: Conversion of Substituents into Alkene Derivatives	266
13.9.2	Product Subclass 2: Annulated 1,2,3-Thiadiazoles	267
13.9.2.1	Synthesis by Ring-Closure Reactions	268
13.9.2.1.1	By Annulation to an Arene	268
13.9.2.1.1.1	Method 1: From 2-Aminobenzenethiols	268
13.9.2.1.1.2	Method 2: Reaction of Diazo Oxides with Phosphorus Pentasulfide	268
13.9.2.2	Synthesis by Ring Transformation	269
13.9.2.2.1	Method 1: Synthesis from Dithiazoles	269
13.9.2.2.2	Method 2: Synthesis from 1,2-Benzothiazol-7-amines	270
13.9.2.2.3	Method 3: Synthesis From 1,3-Benzothiazol-7-amines	271
13.9.2.2.4	Method 4: Synthesis From 1,2,3-Benzothiadiazol-7-amines	272
13.10	Product Class 10: 1,2,4-Thiadiazoles	
	D. J. Wilkins and P. A. Bradley	
13.10	Product Class 10: 1,2,4-Thiadiazoles	277
13.10.1	Synthesis by Ring-Closure Reactions	279
13.10.1.1	By Formation of One S–N, One S–C, and One N–C Bond	279
13.10.1.1.1	Fragments C–N, C–N, and S	279
13.10.1.1.1.1	Method 1: Reaction of Nitriles with Sulfur	279
13.10.1.1.1.2	Method 2: Reaction of Nitriles with Sulfur Dichloride	279
13.10.1.2	By Formation of One S–N and One N–C Bond	280
13.10.1.2.1	Fragments N–C–S and N–C	280
13.10.1.2.1.1	Method 1: Oxidation of Thioamides	280
13.10.1.2.2	Fragments N–C–N and C–S	281
13.10.1.2.2.1	Method 1: Oxidation of <i>N</i> -Arylthioureas and <i>N</i> -Alkylthioureas	281
13.10.1.2.2.2	Method 2: Reaction of Amidoximes and Related Derivatives	282
13.10.1.2.2.2.1	Variation 1: Amidoximes and Isothiocyanates	282
13.10.1.2.2.2.2	Variation 2: Reaction of Amidoximes with Carbon Disulfide	283
13.10.1.2.2.2.3	Variation 3: Reaction of <i>N</i> -Sulfonylamidines with Isothiocyanates	283
13.10.1.2.2.3	Method 3: Synthesis from Amidines	284
13.10.1.2.2.3.1	Variation 1: Reaction of Amidines with Carbon Disulfide	284
13.10.1.2.2.3.2	Variation 2: Reaction of Amidines with Trichloromethylsulfenyl Chloride	285
13.10.1.2.3	Fragments C–N–C–S and N	285
13.10.1.2.3.1	Method 1: From Thioimidates with Chloramine	285
13.10.1.2.3.1.1	Variation 1: Reaction of Cyanothioiminocarbonates with Chloramine	285
13.10.1.2.3.1.2	Variation 2: Reaction of Ethoxycarbonylimidothiocarbonates with Chloramine	286
13.10.1.3	By Formation of One S–C and One N–C Bond	286
13.10.1.3.1	Fragments C–N–S and C–N	286

13.10.1.3.1.1	Method 1: 1,3-Dipolar Cycloaddition Reactions of Nitrile Sulfides with Nitriles	286
13.10.1.4	By Formation of One S—N Bond	287
13.10.1.4.1	Fragments N—C—N—C—S	287
13.10.1.4.1.1	Method 1: Oxidation of Thioacylamidine Derivatives	287
13.10.1.4.1.1.1	Variation 1: Oxidation of Thioacylamidine Derivatives	288
13.10.1.4.1.1.2	Variation 2: Oxidation of Thioacylguanidines	288
13.10.1.4.1.1.3	Variation 3: Oxidation of Amidinothioureas	289
13.10.2	Synthesis by Ring Transformation	290
13.10.2.1	Method 1: Rearrangement of Oxadiazoles and Isoxazoles	290
13.10.2.1.1	Variation 1: 1,2,4-Oxadiazole Rearrangements	290
13.10.2.1.2	Variation 2: 1,2,5-Oxadiazole Rearrangements	291
13.10.2.1.3	Variation 3: Isoxazole Rearrangements	291
13.10.2.2	Method 2: Dithiazolidine Rearrangements	292
13.10.3	Synthesis by Substituent Modification	292
13.10.3.1	Method 1: Transformations Involving Diazonium Intermediates	292
13.10.3.2	Method 2: Nucleophilic Substitution of Halogen Substituents	293
13.11	Product Class 11: 1,2,5-Thiadiazoles and Related Compounds P. A. Koutentis	
13.11	Product Class 11: 1,2,5-Thiadiazoles and Related Compounds	297
13.11.1	Product Subclass 1: Monocyclic 1,2,5-Thiadiazoles	298
13.11.1.1	Synthesis by Ring-Closure Reactions	298
13.11.1.1.1	By Formation of Two S—N Bonds and One C—C Bond	298
13.11.1.1.1.1	Fragments N—C, N—C, and S	298
13.11.1.1.1.1.1	Method 1: Reaction of Potassium Cyanide and Sulfur Dioxide	298
13.11.1.1.2	By Formation of Two S—N Bonds	300
13.11.1.1.2.1	Fragments N—C—C—N and S	300
13.11.1.1.2.1.1	Method 1: From Aliphatic 1,2-Diamines	300
13.11.1.1.2.1.2	Method 2: From 2-Aminoacetamides	301
13.11.1.1.2.1.3	Method 3: From 2-Aminoacetamidine	303
13.11.1.1.2.1.4	Method 4: From Cyanoaminium Salts	304
13.11.1.1.2.1.5	Method 5: From Cyanoformamide and Its Esters	305
13.11.1.1.2.1.6	Method 6: From 1,2-Diimines and Related Compounds	307
13.11.1.1.3	By Formation of One S—N and One N—C Bond	308
13.11.1.1.3.1	Fragments S—N and C—C—N	308
13.11.1.1.3.1.1	Method 1: From Aliphatic Monoamines	308
13.11.1.1.3.1.2	Method 2: From Enamines	308
13.11.1.1.3.1.3	Method 3: From Alkyl Aryl Ketoximes	309
13.11.1.1.4	By Formation of Two N—C Bonds	310

13.11.1.1.4.1	Fragments C—C and N—S—N	310
13.11.1.1.4.1.1	Method 1: From Activated Methylene Compounds	310
13.11.1.1.4.1.2	Method 2: From Alkenes	312
13.11.1.1.4.1.3	Method 3: From Alkynes	312
13.11.1.1.5	By Formation of One S—N Bond	314
13.11.1.1.5.1	Fragment S—N—C—C—N	314
13.11.1.1.5.1.1	Method 1: From (1-Cyanocyclopentyl)imidodisulfurous Dichloride	314
13.11.1.2	Synthesis by Ring Transformation	314
13.11.1.2.1	Method 1: From <i>N</i> -Alkylpyrroles	314
13.11.1.2.2	Method 2: From Isoxazoles	315
13.11.1.2.3	Method 3: From 2-Alkyl-1,2,5-thiadiazolium Salts	316
13.11.1.2.4	Method 4: From 1,2,3-Triazoles	317
13.11.1.3	Aromatization	318
13.11.1.3.1	Method 1: Deoxygenation of 1,2,5-Thiadiazole 1-Oxides	318
13.11.1.4	Synthesis by Substituent Modification	318
13.11.1.4.1	Substitution of Existing Substituents	318
13.11.1.4.1.1	Of Hydrogen	318
13.11.1.4.1.1.1	Hydrogen–Deuterium Exchange	318
13.11.1.4.1.1.2	By Carbon	318
13.11.1.4.1.1.2.1	Method 1: Chloromethylation	318
13.11.1.4.1.1.2.2	Method 2: By Reaction with Organomagnesium Halides	319
13.11.1.4.1.1.3	By Heteroatoms	320
13.11.1.4.1.1.3.1	Method 1: Halogenation	320
13.11.1.4.1.2	Of Carbon Functionalities	320
13.11.1.4.1.2.1	Method 1: By Hydrogen	320
13.11.1.4.1.2.2	Method 2: By Halogen	320
13.11.1.4.1.3	Of Halogen	321
13.11.1.4.1.3.1	Method 1: By Hydrogen	321
13.11.1.4.1.3.2	Method 2: By Carbon	321
13.11.1.4.1.3.3	Method 3: By Fluorine	322
13.11.1.4.1.3.4	Method 4: By Oxygen	322
13.11.1.4.1.3.5	Method 5: By Sulfur	323
13.11.1.4.1.3.6	Method 6: By Nitrogen	324
13.11.1.4.1.4	Of Oxygen	325
13.11.1.4.1.4.1	Method 1: By Carbon (Palladium-Catalyzed Cross Coupling)	325
13.11.1.4.1.4.2	Method 2: By Halogens	325
13.11.1.4.1.4.3	Method 3: By Nitrogen	326
13.11.1.4.1.5	Of Sulfur	327
13.11.1.4.1.5.1	Method 1: Displacement of Alkylsulfonyl Groups by Oxygen and Sulfur Nucleophiles	327

13.11.1.4.2	Rearrangement of Substituents	328
13.11.1.4.2.1	Method 1: Curtius Rearrangement of Azidocarbonyl Compounds	328
13.11.1.4.2.2	Method 2: Rearrangement of Thionocarbamates	328
13.11.1.4.3	Modification of Substituents	329
13.11.1.4.3.1	Of Carbon	329
13.11.1.4.3.1.1	Method 1: Oxidative Degradation of 2,1,3-Benzothiadiazoles	329
13.11.1.4.3.1.2	Method 2: Beckmann Fragmentation of 2,1,3-Benzothiadiazole-4,5-dione Acetoximes	330
13.11.1.4.3.2	Of Heteroatoms	330
13.11.2	Product Subclass 2: Annulated 1,2,5-Thiadiazoles (2,1,3-Benzothiadiazoles and Related Systems)	331
13.11.2.1	Synthesis by Ring-Closure Reactions	331
13.11.2.1.1	By Annulation to an Arene	331
13.11.2.1.1.1	By Formation of Two S—N Bonds	331
13.11.2.1.1.1.1	Method 1: From Arene-1,2-diamines	331
13.11.2.1.1.1.2	Method 2: From Quinone 1,2-Dioximes	333
13.11.2.1.1.2	By Formation of One S—N and One N—C Bond	333
13.11.2.1.1.2.1	Method 1: From Anilines	333
13.11.2.1.1.3	By Formation of Two N—C Bonds	334
13.11.2.1.1.3.1	Method 1: From Active Hydrocarbons and Tetrasulfur Tetranitride	334
13.11.2.1.1.3.2	Method 2: From Phenols and Related Compounds and Tetrasulfur Tetranitride	335
13.11.2.1.1.3.3	Method 3: From Quinones or Hydroquinones	336
13.11.2.1.1.3.4	Method 4: From Indoles and Pyrroles with Trithiazyl Trichloride	337
13.11.2.1.1.3.5	Method 5: From Perfluoroarenes with Sulfur Diimides	338
13.11.2.1.1.4	By Formation of One S—N Bond	339
13.11.2.1.1.4.1	Method 1: From 1,2-Bis(sulfinylamino)benzene	339
13.11.2.1.1.5	By Formation of One N—C Bond	340
13.11.2.1.1.5.1	Method 1: From Arylsulfur Diimides	340
13.11.2.1.2	By Annulation to 1,2,5-Thiadiazole	341
13.11.2.1.2.1	Method 1: From 1,2,5-Thiadiazole-3,4-dicarbonitrile	341
13.11.2.1.2.2	Method 2: From 1,2,5-Thiadiazolamines	341
13.11.2.1.2.3	Method 3: From 1,2,5-Thiadiazole-3,4-diamine	342
13.11.2.1.2.4	Method 4: From 1,2,5-Thiadiazole-3,4-dicarbonyl Compounds	343
13.12	Product Class 12: 1,3,4-Thiadiazoles S. J. Collier	
13.12	Product Class 12: 1,3,4-Thiadiazoles	349
13.12.1	Synthesis by Ring-Closure Reactions	351
13.12.1.1	By Formation of Two S—C and Two N—C Bonds	352

13.12.1.1.1	Fragments N–N, S, and Two C Fragments	352
13.12.1.1.1.1	Method 1: Reaction of Aldehydes with Hydrazine and Sulfur	352
13.12.1.2	By Formation of Two S–C Bonds and One N–C Bond	353
13.12.1.2.1	Fragments N–N–C, S, and C	353
13.12.1.2.1.1	Method 1: Reactions of Methylpyridines (or Methylquinolines) with Aroylhydrazines and Sulfur	353
13.12.1.3	By Formation of Two S–C Bonds	353
13.12.1.3.1	Fragments C–N–N–C and S	353
13.12.1.3.1.1	Method 1: From 2,3-Diazabuta-1,3-dienes and a Sulfur Source	353
13.12.1.3.1.2	Method 2: From Diformyl- or Diacylhydrazines and a Sulfur Source	356
13.12.1.4	By Formation of One S–C and One N–C Bond	356
13.12.1.4.1	Fragments S–C–N–N and C	356
13.12.1.4.1.1	Method 1: From Thiohydrazide Derivatives	356
13.12.1.4.1.1.1	Variation 1: By Reaction with Carboxylic Acid Derivatives	357
13.12.1.4.1.1.2	Variation 2: By Reaction with Ortho Esters or Trihalomethyl Compounds	358
13.12.1.4.1.1.3	Variation 3: By Reaction with Imines and Related Compounds	359
13.12.1.4.1.1.4	Variation 4: By Reaction with Isothiocyanates (and Isocyanates)	362
13.12.1.4.1.1.5	Variation 5: By Reaction with Nitriles and Related Compounds	363
13.12.1.4.1.1.6	Variation 6: By Reaction with Thiocarbonyl Compounds	365
13.12.1.4.1.1.7	Variation 7: By Reaction with Miscellaneous Reagents	366
13.12.1.4.2	Fragments N–N–C and S–C	367
13.12.1.4.2.1	Method 1: From Hydrazides and Thiocarbonyl Compounds	367
13.12.1.4.2.2	Method 2: From Amidrazones and Thiocarbonyl Compounds	368
13.12.1.4.2.3	Method 3: From Diazo Compounds and Thiocarbonyl Derivatives	369
13.12.1.5	By Formation of Two N–C Bonds	370
13.12.1.5.1	Fragments C–S–C and N–N	370
13.12.1.5.1.1	Method 1: From Hydrazine and Thiocarbonyl Compounds	370
13.12.1.6	By Formation of One S–C Bond	372
13.12.1.6.1	Fragment S–C–N–N–C	372
13.12.1.6.1.1	Method 1: By Cyclization of Monothiodiacylhydrazine Derivatives	372
13.12.1.6.1.2	Method 2: By Cyclization of Dithioacylhydrazine Derivatives	375
13.12.1.6.1.3	Method 3: By Cyclization of <i>N'</i> -Imidoylthiohydrazides	376
13.12.1.6.1.4	Method 4: By Cyclization of Thioacylhydrazones	377
13.12.2	Synthesis by Ring Transformation	380
13.12.3	Aromatization	381
13.12.4	Synthesis by Substituent Modification	383
13.12.4.1	Substitution of Existing Substituents	383
13.12.4.1.1	Of Hydrogen	383
13.12.4.1.1.1	Method 1: By Acylation (Through Rearrangement)	384
13.12.4.1.1.2	Method 2: By Halogen	384

13.12.4.1.1.3	Method 3: By Sulfur-Containing Groups	384
13.12.4.1.1.4	Method 4: By Nitrogen-Containing Groups	385
13.12.4.1.2	Of Carbon	385
13.12.4.1.2.1	Method 1: By Hydrogen	385
13.12.4.1.3	Of Heteroatoms	386
13.12.4.1.3.1	Substitution of Halogen	386
13.12.4.1.3.1.1	Method 1: By Hydrogen	386
13.12.4.1.3.1.2	Method 2: By Carbon	387
13.12.4.1.3.1.3	Method 3: By Oxygen	387
13.12.4.1.3.1.4	Method 4: By Sulfur	388
13.12.4.1.3.1.5	Method 5: By Nitrogen	388
13.12.4.1.3.2	Substitution of Oxygen	389
13.12.4.1.3.3	Substitution of Sulfur	389
13.12.4.1.3.3.1	Method 1: By Carbon	389
13.12.4.1.3.3.2	Method 2: By Oxygen	390
13.12.4.1.3.3.3	Method 3: By Nitrogen	391
13.12.4.1.3.4	Substitution of Nitrogen	391
13.12.4.1.3.4.1	Method 1: Reductive Deamination	391
13.12.4.1.3.4.2	Method 2: By Oxygen	392
13.12.4.1.3.4.3	Method 3: By Halogen	393
13.12.4.2	Addition Reactions	393
13.12.4.2.1	Of Organic and Heteroatom Groups	394
13.12.4.2.1.1	Method 1: N-Functionalization by Electrophiles	394
13.12.4.3	Modification of Substituents	396
13.12.4.3.1	Of Carbon	396
13.12.4.3.1.1	Method 1: Alkyl Groups	396
13.12.4.3.1.1.1	Variation 1: C-Metalation, Alkylation, and Acylation	396
13.12.4.3.1.1.2	Variation 2: C-Halogenation	398
13.12.4.3.2	Of Oxygen	399
13.12.4.3.2.1	Method 1: O-Acylation	399
13.12.4.3.2.2	Method 2: O-Dealkylation	400
13.12.4.3.3	Of Sulfur Groups	400
13.12.4.3.3.1	Method 1: S-Alkylation	401
13.12.4.3.3.2	Method 2: S-Dealkylation	402
13.12.4.3.4	Of Nitrogen	403
13.12.4.3.4.1	Method 1: N-Functionalization	403

13.13	Product Class 13: 1,2,3-Triazoles	
	A. C. Tomé	
<hr/>		
13.13	Product Class 13: 1,2,3-Triazoles	415
13.13.1	Product Subclass 1: Monocyclic N-Unsubstituted and 1-Substituted 1,2,3-Triazoles	418
13.13.1.1	Synthesis by Ring-Closure Reactions	418
13.13.1.1.1	By Formation of One N—N and One N—C Bond	418
13.13.1.1.1.1	Fragments C—C—N—N and N	418
13.13.1.1.1.1.1	Method 1: From 2-Diazo-1,3-dicarbonyl Compounds and Amine Derivatives	418
13.13.1.1.1.1.1.1	Variation 1: From 2-Diazo-3-oxopropanoates and Amine Derivatives	419
13.13.1.1.1.1.1.2	Variation 2: From 2-Diazo-3-oxoaldehydes and Amine Derivatives	420
13.13.1.1.1.1.1.3	Variation 3: From Dimethyl Diazomalonnate and Amines	421
13.13.1.1.1.1.2	Method 2: From Vinyl diazonium Salts and Amine Derivatives	422
13.13.1.1.1.1.3	Method 3: From Dichloro- or Trichloroacetaldehyde Sulfonylhydrazones and Primary Amines	423
13.13.1.1.1.2	Fragments C—C—N and N—N	424
13.13.1.1.1.2.1	Method 1: From Enaminones and Diazo Transfer Reagents	424
13.13.1.1.1.2.1.1	Variation 1: From Enaminones and 3-Diazo-1,3-dihydro-2 <i>H</i> -indol-2-one Derivatives	424
13.13.1.1.1.2.1.2	Variation 2: From Enaminones and Sulfonyl Azides	426
13.13.1.1.2	By Formation of One N—N and One C—C Bond	426
13.13.1.1.2.1	Fragments C—N—N and C—N	426
13.13.1.1.2.1.1	Method 1: From Diazoalkanes and Nitriles	426
13.13.1.1.2.1.1.1	Variation 1: From Diazoalkanes and Aryl Cyanates	428
13.13.1.1.2.1.1.2	Variation 2: From Diazoalkanes and Unactivated Nitriles	428
13.13.1.1.2.1.1.3	Variation 3: From [Diazo(trimethylsilyl)methyl]lithium and Nitriles	429
13.13.1.1.2.1.2	Method 2: From Diazoalkanes and Imines, Oximes, or Diarylazines	430
13.13.1.1.2.1.2.1	Variation 1: From Diazoalkanes and Imines	430
13.13.1.1.2.1.2.2	Variation 2: From Diazoalkanes and Oximes	431
13.13.1.1.2.1.2.3	Variation 3: From Diazoalkanes and Diarylazines	432
13.13.1.1.2.1.3	Method 3: From Diazoalkanes and Heterocumulenes	432
13.13.1.1.2.1.3.1	Variation 1: From Diazoalkanes and Ketanimines	433
13.13.1.1.2.1.3.2	Variation 2: From Diazoalkanes and Carbodiimides	434
13.13.1.1.2.1.3.3	Variation 3: From Diazoalkanes and Isocyanates	435
13.13.1.1.2.1.3.4	Variation 4: From Diazoalkanes and Isothiocyanates	436
13.13.1.1.2.1.4	Method 4: From <i>N</i> -Alkyl- <i>N</i> -nitrosoamines and Nitriles	437
13.13.1.1.3	By Formation of Two N—C Bonds	438
13.13.1.1.3.1	Fragments N—N—N and C—C	438
13.13.1.1.3.1.1	Addition of Azides to Alkynes	438
13.13.1.1.3.1.1.1	Method 1: Addition of Hydrazoic Acid to Alkynes	439
13.13.1.1.3.1.1.2	Method 2: Addition of the Azide Ion to Alkynes	440

13.13.1.1.3.1.1.3	Method 3:	Addition of Alkyl, Aryl, or Hetaryl Azides to Alkynes	441
13.13.1.1.3.1.1.3.1	Variation 1:	Addition of Azides to Acetylene and to Symmetrically Substituted Alkynes	442
13.13.1.1.3.1.1.3.2	Variation 2:	Addition of Azides to Alk-1-yne	443
13.13.1.1.3.1.1.3.3	Variation 3:	Addition of Azides to Unsymmetrical Disubstituted Alkynes	446
13.13.1.1.3.1.1.3.4	Variation 4:	Using Polymer-Supported Methods	448
13.13.1.1.3.1.1.3.5	Variation 5:	Intramolecular 1,3-Dipolar Cycloadditions	450
13.13.1.1.3.1.1.3.6	Variation 6:	Addition of Azides to Alkoxyalkynes	452
13.13.1.1.3.1.1.4	Method 4:	Addition of Ethyl Azidoformate and Cyanogen Azide to Alkynes	453
13.13.1.1.3.1.1.5	Method 5:	Addition of Sulfonyl Azides to Alkynes	454
13.13.1.1.3.1.1.6	Method 6:	Addition of Azidotrimethylsilane and Azidotributylstannane to Alkynes	456
13.13.1.1.3.1.1.7	Method 7:	Addition of Azides to Metal Acetylides	457
13.13.1.1.3.1.2	Addition of Azides to C=C Bonds		458
13.13.1.1.3.1.2.1	Method 1:	Addition of Sodium Azide to Activated Alkenes	458
13.13.1.1.3.1.2.2	Method 2:	Addition of Azides to Activated Alkenes	461
13.13.1.1.3.1.2.3	Method 3:	Addition of Azides to Strained Alkenes	462
13.13.1.1.3.1.2.4	Method 4:	Addition of Azides to Allenes	464
13.13.1.1.3.1.2.5	Method 5:	Addition of Azides to α -Acylphosphorus Ylides	466
13.13.1.1.3.1.2.6	Method 6:	Addition of Azides to Enamines or Enol Ethers	468
13.13.1.1.3.1.2.6.1	Variation 1:	Addition of Azides to Enamines	469
13.13.1.1.3.1.2.6.2	Variation 2:	Addition of Azides to Enol Ethers	473
13.13.1.1.3.1.2.7	Method 7:	Addition of Azides to Vinyl Acetate	474
13.13.1.1.3.1.2.8	Method 8:	Addition of Azides to Ketene Acetals	475
13.13.1.1.3.1.3	Reaction of Azides with Active Methylene Compounds		478
13.13.1.1.3.1.3.1	Method 1:	Reaction of Azides with 1,3-Diketones, 3-Oxo Esters, or 3-Oxoamides	478
13.13.1.1.3.1.3.2	Method 2:	Reaction of Azides with Malonic Esters, Malonamides, or Acetamides	481
13.13.1.1.3.1.3.3	Method 3:	Reaction of Azides with Acetonitrile Derivatives	483
13.13.1.1.3.1.3.4	Method 4:	Reaction of Aryl Azides with Alkoxides	486
13.13.1.1.4	By Formation of One N—N Bond		487
13.13.1.1.4.1	Fragment N—N—C—C—N		487
13.13.1.1.4.1.1	Method 1:	Cyclization of α -Diazoamides	487
13.13.1.1.4.1.2	Method 2:	Thermolysis of α -Azidoacetophenone (Phenylsulfonyl)hydrazones	487
13.13.1.1.4.1.3	Method 3:	Cyclization of α -Hydroxyimino Hydrazones	488
13.13.1.1.4.1.4	Method 4:	Cyclization of α -Hydroxyimino Aryl- or Arylsulfonylhydrazones	489
13.13.1.1.4.1.5	Method 5:	Cyclization of 1,2-Diketone Bis(hydrazone) Derivatives	490
13.13.1.1.4.1.5.1	Variation 1:	Cyclization of 1,2-Diketone Bis(hydrazones)	490
13.13.1.1.4.1.5.2	Variation 2:	Cyclization of 1,2-Diketone Bis(arylsulfonylhydrazones)	491
13.13.1.1.4.1.5.3	Variation 3:	Cyclization of 1,2-Diketone Bis(semicarbazones)	491
13.13.1.1.4.1.5.4	Variation 4:	Cyclization of 1,2-Diketone Bis(acylhydrazones)	492
13.13.1.1.4.1.6	Method 6:	Cyclization of (1,2-Diphenylethene-1,2-diyl)bis(trityldiazene)	493

13.13.1.1.5	By Formation of One N—C Bond	494
13.13.1.1.5.1	Fragment N—N—N—C—C	494
13.13.1.1.5.1.1	Method 1: Cyclization of Linear Triazenes and Tetrazenes	494
13.13.1.1.5.1.2	Method 2: Cyclization of Vinyl Azides	495
13.13.1.1.5.1.3	Method 3: Cyclization of 2-(Formyloxy)vinyl Azides	496
13.13.1.2	Synthesis by Ring Transformation	497
13.13.1.3	Aromatization	500
13.13.1.3.1	Method 1: By Oxidation Reactions	500
13.13.1.3.2	Method 2: By Elimination Reactions	502
13.13.1.4	Synthesis by Substituent Modification	503
13.13.1.4.1	Substitution of Existing Substituents	503
13.13.1.4.1.1	Of Hydrogen	503
13.13.1.4.1.1.1	Method 1: Lithiation	503
13.13.1.4.1.1.2	Method 2: N-Trimethylsilylation	505
13.13.1.4.1.1.3	Method 3: Carboxylation	505
13.13.1.4.1.1.4	Method 4: Acylation	506
13.13.1.4.1.1.5	Method 5: Formylation	507
13.13.1.4.1.1.6	Method 6: Arylation	507
13.13.1.4.1.1.7	Method 7: Alkylation	509
13.13.1.4.1.1.8	Method 8: Halogenation	511
13.13.1.4.1.1.9	Method 9: N-Amination	514
13.13.1.4.1.1.10	Method 10: N-Hydroxylation	514
13.13.1.4.1.1.11	Method 11: Nitration	515
13.13.1.4.1.2	Of Metals	516
13.13.1.4.1.2.1	Method 1: Desilylation	516
13.13.1.4.1.3	Of Carbon Functionalities	517
13.13.1.4.1.3.1	Method 1: Decarboxylation	517
13.13.1.4.1.3.2	Method 2: Deformylation	517
13.13.1.4.1.3.3	Method 3: Deacylation	518
13.13.1.4.1.3.4	Method 4: Dearylation	519
13.13.1.4.1.3.5	Method 5: Dealkylation	519
13.13.1.4.1.4	Of Heteroatoms	521
13.13.1.4.1.4.1	Method 1: Substitution of Halogens by Nucleophiles	521
13.13.1.4.1.4.2	Method 2: Substitution of Hydroxy Groups by Halogens	522
13.13.1.4.1.4.3	Method 3: Substitution of Diazonium Groups by Nucleophiles	522
13.13.1.4.1.4.4	Method 4: Deoxygenation	523
13.13.1.4.1.4.5	Method 5: Dehalogenation	524
13.13.1.4.2	Addition Reactions	524
13.13.1.4.2.1	Method 1: Conversion into N-Oxides	524
13.13.1.4.3	Rearrangement of Substituents	525
13.13.2	Product Subclass 2: Monocyclic 2-Substituted 1,2,3-Triazoles	528
13.13.2.1	Synthesis by Ring-Closure Reactions	528

13.13.2.1.1	By Formation of One N—N and One N—C Bond	528
13.13.2.1.1.1	Fragments C—C—N—N and N	528
13.13.2.1.1.1.1	Method 1: From <i>N</i> -Aminophthalimide and Conjugated Azoalkenes	528
13.13.2.1.2	By Formation of Two N—C Bonds	528
13.13.2.1.2.1	Fragments N—N—N and C—C	528
13.13.2.1.2.1.1	Method 1: Addition of Azidotrimethylsilane and Azidotributylstannane to Alkynes	528
13.13.2.1.2.1.2	Method 2: Addition of Acyl or Alkoxy carbonyl Azides to α -Acylphosphorus Ylides	529
13.13.2.1.3	By Formation of One N—N Bond	529
13.13.2.1.3.1	Fragment N—N—C—C—N	529
13.13.2.1.3.1.1	Method 1: Cyclization of α -Hydroxyimino Hydrazones	529
13.13.2.1.3.1.2	Method 2: Cyclization of 1,2-Diketone Bis(arylhydrazones)	532
13.13.2.1.3.1.3	Method 3: Cyclization of α -Imino Hydrazones	534
13.13.2.1.3.1.4	Method 4: Cyclization of 1,2-Bis(<i>N</i> -alkoxy- <i>N</i> -nitrosoamines)	535
13.13.2.2	Synthesis by Ring Transformation	535
13.13.2.3	Synthesis by Substituent Modification	540
13.13.3	Product Subclass 3: N-Unsubstituted and 1-Substituted Benzotriazoles	540
13.13.3.1	Synthesis by Ring-Closure Reactions	540
13.13.3.1.1	By Formation of Two N—N Bonds	540
13.13.3.1.1.1	Fragments N—C—C—N and N	540
13.13.3.1.1.1.1	Method 1: From Benzene-1,2-diamines and Nitrous Acid	540
13.13.3.1.2	By Formation of One N—N and One N—C Bond	543
13.13.3.1.2.1	Fragments C—C—N and N—N	543
13.13.3.1.2.1.1	Method 1: From Arylamines and 2-Azido-3-ethyl-1,3-benzothiazolium Tetrafluoroborate	543
13.13.3.1.2.2	Fragments C—C—N—N and N	544
13.13.3.1.2.2.1	Method 1: From α -Diazo Ketones and Amines	544
13.13.3.1.3	By Formation of Two N—C Bonds	544
13.13.3.1.3.1	Fragments N—N—N and C—C	544
13.13.3.1.3.1.1	Method 1: From Azides and Dehydrobenzene	544
13.13.3.1.3.1.2	Method 2: From Azides and Quinones	546
13.13.3.1.4	By Formation of One N—N Bond	547
13.13.3.1.4.1	Fragment N—N—C—C—N	547
13.13.3.1.4.1.1	Method 1: Cyclization of 2-Nitrophenylhydrazines	547
13.13.3.1.4.1.1.1	Variation 1: Reaction of 1-Chloro-2-nitrobenzenes or 1,2-Dinitrobenzenes with Hydrazine	547
13.13.3.1.4.1.2	Method 2: Cyclization of (2-Aminophenyl)hydrazine Derivatives	549
13.13.3.1.4.1.3	Method 3: Cyclization of (2-Aminophenyl)triazene Derivatives	549

13.13.3.2	Synthesis by Ring Transformation	550
13.13.3.2.1	Method 1: From 4,5-Dimethylene-4,5-dihydro-1 <i>H</i> -triazoles	550
13.13.3.2.2	Method 2: Transformation of 1,3-Dihydro-2 <i>H</i> -benzimidazol-2-ones	550
13.13.3.2.3	Method 3: Transformation of 1,2,4-Benzotriazin-3(2 <i>H</i>)-ones	551
13.13.3.2.4	Method 4: Transformation of 1,2,3,4-Benzotetrazine 1,3-Dioxides	551
13.13.3.3	Synthesis by Substituent Modification	552
13.13.3.3.1	Substitution of Existing Substituents	552
13.13.3.3.1.1	Of Hydrogen	552
13.13.3.3.1.1.1	Method 1: N-Trimethylsilylation	552
13.13.3.3.1.1.2	Method 2: Carboxylation	552
13.13.3.3.1.1.3	Method 3: Acylation	553
13.13.3.3.1.1.4	Method 4: N-Formylation	553
13.13.3.3.1.1.5	Method 5: Arylation	554
13.13.3.3.1.1.6	Method 6: Alkynylation	556
13.13.3.3.1.1.7	Method 7: Alkenylation	556
13.13.3.3.1.1.8	Method 8: Alkylation	557
13.13.3.3.1.1.9	Method 9: Halogenation	561
13.13.3.3.1.1.10	Method 10: Sulfonylation	562
13.13.3.3.1.1.11	Method 11: N-Amination	563
13.13.3.3.1.1.12	Method 12: Nitration	564
13.13.3.3.1.1.13	Method 13: Azo Coupling	565
13.13.3.3.2	Of Carbon Functionalities	567
13.13.3.3.2.1	Method 1: Decarboxylation	567
13.13.3.3.2.2	Method 2: Deacylation	567
13.13.3.3.3	Of Heteroatoms	568
13.13.3.3.3.1	Method 1: Deoxygenation	568
13.13.3.3.3.2	Method 2: Dehalogenation	569
13.13.3.3.4	Addition Reactions	569
13.13.3.3.4.1	Method 1: Conversion into <i>N</i> -Oxides or Epoxides	569
13.13.4	Product Subclass 4: 2-Substituted Benzotriazoles	570
13.13.4.1	Synthesis by Ring-Closure Reactions	570
13.13.4.1.1	By Formation of Two N—N Bonds	570
13.13.4.1.1.1	Fragments N—C—C—N and N	570
13.13.4.1.1.1.1	Method 1: From Benzene-1,2-diamine and Nitrobenzenes	570
13.13.4.1.2	By Formation of One N—N Bond	571
13.13.4.1.2.1	Fragment N—N—C—C—N	571
13.13.4.1.2.1.1	Method 1: Cyclization of 2-Aminoazobenzenes	571
13.13.4.1.2.1.2	Method 2: Cyclization of 2-Azidoazobenzenes	572
13.13.4.1.2.1.3	Method 3: Cyclization of 2-Nitroazobenzenes	575
13.13.4.1.2.1.4	Method 4: Cyclization of 1-Substituted 2-(2-Nitroaryl)hydrazines	576
13.13.4.1.2.1.5	Method 5: Cyclization of Vicinal Diazides	577

13.13.4.2	Synthesis by Ring Transformation	578
13.13.4.2.1	Method 1: Isomerization of 4-(Arylazo)-2,1,3-benzoxadiazoles	578
13.13.4.2.2	Method 2: Transformation of 1,3,3-Trialkyl- 2-(2,4-dinitrophenyl)diaziridines	578
13.13.4.2.3	Method 3: Transformation of 1-(2-Nitrophenyl)-1 <i>H</i> -tetrazoles	579
13.13.4.3	Synthesis by Substituent Modification	580
13.13.5	Product Subclass 5: 1,2,3-Triazolium Salts	580
13.13.5.1	Synthesis by Ring-Closure Reactions	580
13.13.5.1.1	By Formation of One N—N and One N—C Bond	580
13.13.5.1.1.1	Fragments C—N—N and C—N	580
13.13.5.1.1.1.1	Method 1: From Diarylnitrimines and Alkyl Isocyanides	580
13.13.5.1.2	By Formation of One N—C Bond	581
13.13.5.1.2.1	Fragment N—N—N—C—C	581
13.13.5.1.2.1.1	Method 1: Cyclization of α -Imino Hydrazones	581
13.13.5.1.2.1.2	Method 2: Cyclization of (3-Aryl-1-methyltriaz-2-enyl)acetic Acid Derivatives	581
13.13.5.2	Synthesis by Introduction of Substituents	582
13.13.5.2.1	Method 1: Alkylation of <i>N</i> -Alkyl-1,2,3-triazoles	582
13.13.5.2.2	Method 2: Alkylation of <i>N</i> -Alkylbenzotriazoles	583
13.14	Product Class 14: 1,2,4-Triazoles A. D. M. Curtis	
13.14	Product Class 14: 1,2,4-Triazoles	603
13.14.1	Synthesis by Ring-Closure Reactions	604
13.14.1.1	By Formation of Four N—C Bonds	604
13.14.1.1.1	Fragments N—N, C, N, and C	604
13.14.1.1.1.1	Method 1: Reaction of Carboxylic Acids with Hydrazine	604
13.14.1.2	By Formation of Three N—C Bonds	605
13.14.1.2.1	Fragments C—N—N, C, and N	605
13.14.1.2.1.1	Method 1: From Acylhydrazines and Thioesters	605
13.14.1.2.2	Fragments N—C, N—N, and C	605
13.14.1.2.2.1	Method 1: From Amidines, Hydrazine, and Esters	605
13.14.1.3	By Formation of Two N—C Bonds	606
13.14.1.3.1	Fragments C—N—C and N—N	606
13.14.1.3.1.1	Method 1: From Iminoesters, Thioesters, Amidines, and Guanidines with Hydrazines	606
13.14.1.3.1.1.1	Variation 1: From <i>N</i> -Cyanoimines	606
13.14.1.3.1.1.2	Variation 2: From <i>N</i> -Acylimines	607
13.14.1.3.1.2	Method 2: From Diacylamines and Hydrazines	607

13.14.1.3.2	Fragments C—N—N and C—N	608
13.14.1.3.2.1	Method 1: From Acylhydrazines and Carboxylic Acid Derivatives	608
13.14.1.3.2.1.1	Variation 1: From Acylhydrazines and Carboxylic Ester Imides	608
13.14.1.3.2.1.2	Variation 2: From Aroylhydrazines and Thioamides	609
13.14.1.3.2.1.3	Variation 3: From Acylhydrazines and Aromatic Nitriles	609
13.14.1.3.2.2	Method 2: From Hydrazones of Carboxylic Acid Chlorides	610
13.14.1.3.3	Fragments C—N—N—C and N	610
13.14.1.3.3.1	Method 1: From Aroylsemicarbazides and Amines	610
13.14.1.3.3.2	Method 2: From Diacylhydrazines and Amines	611
13.14.1.3.3.3	Method 3: From Chlorinated Azines and Amines	612
13.14.1.3.4	Fragments N—C—N—N and C	612
13.14.1.3.4.1	Method 1: From Aminoguanidines	612
13.14.1.3.4.1.1	Variation 1: With Carboxylic Acids	613
13.14.1.3.4.1.2	Variation 2: With Carboxylic Ester Imides	614
13.14.1.3.4.2	Method 2: From Amidrazones	614
13.14.1.3.4.2.1	Variation 1: With Ortho Esters	614
13.14.1.3.4.2.2	Variation 2: With Carboxylic Acids	615
13.14.1.4	By Formation of One N—C Bond	615
13.14.1.4.1	Fragments N—C—N—N—C	615
13.14.1.4.1.1	Method 1: From Acylated Aminoguanidines	615
13.14.1.4.1.2	Method 2: From Acylated Amidrazones	616
13.14.1.4.1.3	Method 3: From Acylaminothioureas	616
13.14.1.4.2	Fragments C—N—C—N—N	617
13.14.1.4.2.1	Method 1: From Acylamidrazones	617
13.14.1.4.2.2	Method 2: By Oxidation of Amidrazones	617
13.14.2	Synthesis by Ring Transformation	618
13.14.2.1	Formal Exchange of Ring Members with Retention of the Ring Size	618
13.14.2.1.1	Method 1: From 1,3-Oxazolones	618
13.14.2.1.1.1	Variation 1: From 1,3-Oxazol-4(5 <i>H</i>)-ones	618
13.14.2.1.1.2	Variation 2: From 4-Hydrazono-1,3-oxazol-5(4 <i>H</i>)-ones	619
13.14.2.1.2	Method 2: From 1,2,4-Oxadiazoles	619
13.14.2.1.2.1	Variation 1: From 3-Arylazo-1,2,4-oxadiazoles	620
13.14.2.1.2.2	Variation 2: From <i>N</i> -(Anilinomethylene)-1,2,4-oxadiazol-3-amines	620
13.14.2.1.3	Method 3: From 1,3,4-Oxadiazoles	620
13.14.2.1.3.1	Variation 1: From 2,5-Bis(trifluoromethyl)-1,3,4-oxadiazole	620
13.14.2.1.3.2	Variation 2: From 1,3,4-Oxadiazol-2-amines	621
13.14.2.1.4	Method 4: From 1,3,4-Oxadiazolium Salts	621
13.14.2.1.5	Method 5: From Tetrazoles	622
13.14.2.1.5.1	Variation 1: From 2,5-Disubstituted Tetrazoles and Nitriles	622
13.14.2.1.5.2	Variation 2: From 2-Substituted Tetrazoles and Benzimidoyl Chlorides	623
13.14.2.2	By Ring Contraction	623
13.14.2.2.1	Method 1: From 4 <i>H</i> -1,3-Oxazin-4-ones and 4 <i>H</i> -1,3-Benzoxazin-4-ones	623
13.14.2.2.2	Method 2: From Pyrimidine and Quinazoline Derivatives	624

13.14.2.2.2.1	Variation 1: From 4-Imino-3,4-dihydropyrimidines	624
13.14.2.2.2.2	Variation 2: From 4,6-Diethoxypyrimidines	624
13.14.2.2.2.3	Variation 3: From 4-Chloroquinazolines	625
13.14.2.2.3	Method 3: From 1,3,5-Triazine	625
13.14.3	Aromatization	626
13.14.3.1	Method 1: By Dehydrogenation of Dihydro-1,2,4-triazoles	626
13.14.4	Synthesis by Substituent Modification	626
13.14.4.1	Substitution of Existing Substituents	626
13.14.4.1.1	Of Hydrogen	626
13.14.4.1.1.1	By Deuterium	626
13.14.4.1.1.2	By Metals	626
13.14.4.1.1.2.1	Method 1: Trimethylstannylation	626
13.14.4.1.1.3	By Carbon	627
13.14.4.1.1.3.1	Method 1: N-Alkylation	627
13.14.4.1.1.3.2	Method 2: C-Alkylation	628
13.14.4.1.1.3.2.1	Variation 1: By Lithiation	628
13.14.4.1.1.3.2.2	Variation 2: By Radical Substitution	628
13.14.4.1.1.3.3	Method 3: N-Arylation	629
13.14.4.1.1.3.4	Method 4: N-Acylation	629
13.14.4.1.1.3.5	Method 5: C-Acylation	630
13.14.4.1.1.4	By Halogens	631
13.14.4.1.1.5	By Other Heteroatoms	632
13.14.4.1.2	Of Metals	632
13.14.4.1.3	Of Carbon	633
13.14.4.1.4	Of Heteroatoms	633
13.14.4.1.4.1	Method 1: Of Halogens	633
13.14.4.1.4.2	Method 2: Of Sulfur	633
13.14.4.1.4.3	Method 3: Of Nitrogen	634
13.14.4.2	Addition Reactions	634
13.14.4.2.1	Method 1: N-Alkylation	634
13.14.4.3	Rearrangement	635
13.14.4.4	Modification of Substituents	635
13.14.4.4.1	Method 1: Modification of 1,2,4-Triazolones	636
13.14.4.4.2	Method 2: Modification of 1,2,4-Triazolethiones	636

13.15	Product Class 15: Dithiaphospholes and Their Analogues R. K. Bansal, N. Gupta, and S. J. Collier	
<hr/>		
13.15	Product Class 15: Dithiaphospholes and Their Analogues	641
13.15.1	Product Subclass 1: 1,3,2-Benzodithiaphospholium, 1,3,2-Benzodithiarsolium, and 1,3,2-Benzodithiastibolium Salts	641
13.15.1.1	Aromatization	643
13.15.1.1.1	Method 1: Synthesis by Chloride Abstraction	643
13.16	Product Class 16: Oxazaphospholes and Thiazaphospholes R. K. Bansal and Neelima Gupta	
<hr/>		
13.16	Product Class 16: Oxazaphospholes and Thiazaphospholes	647
13.16.1	Product Subclass 1: 1,2,4-Oxazaphospholes	647
13.16.1.1	Synthesis by Ring-Closure Reactions	648
13.16.1.1.1	By Formation of One O—C and One N—C Bond	648
13.16.1.1.1.1	Fragments C—P—C and O—N	648
13.16.1.1.1.1.1	Method 1: Cyclocondensation of a 2-Phosphaallylic Cation with Hydroxylamine	648
13.16.1.1.2	By Formation of One O—C and One P—C Bond	648
13.16.1.1.2.1	Fragments O—N—C and P—C	648
13.16.1.1.2.1.1	Method 1: [3 + 2] Cycloaddition of Nitrile Oxides	648
13.16.2	Product Subclass 2: 1,2,4-Thiazaphospholes	650
13.16.2.1	Synthesis by Ring-Closure Reactions	650
13.16.2.1.1	By Formation of One S—C and One P—C Bond	650
13.16.2.1.1.1	Fragments S—N—C and P—C	650
13.16.2.1.1.1.1	Method 1: Synthesis by [3 + 2] Cycloaddition	650
13.16.2.1.1.1.1.1	Variation 1: Using a Phosphaalkyne and 5-Phenyl-1,3,4-oxathiazol-2-one	650
13.16.2.1.1.1.1.2	Variation 2: Using a Phosphaalkyne and 4-Phenyl- 1,3,2-oxathiazolium-5-olate	650
13.16.2.1.1.1.1.3	Variation 3: Using a Phosphaalkene and 1,3,4-Oxathiazol-2-one	651
13.16.3	Product Subclass 3: 1,3,2-Oxazaphospholes	652
13.16.3.1	Synthesis by Ring-Closure Reactions	652
13.16.3.1.1	By Formation of One O—P and One N—P Bond	652
13.16.3.1.1.1	Fragments O—C—C—N and P	652
13.16.3.1.1.1.1	Method 1: Cyclocondensation of 2-Amino Ketones or 2-Aminophenols with Phosphorus(III) Compounds	652
13.16.4	Product Subclass 4: 1,3,2-Benzothiazaphospholes and -arsoles	653
13.16.4.1	Synthesis by Ring-Closure Reactions	653
13.16.4.1.1	By Formation of One S—P and One N—P Bond	653

13.16.4.1.1.1	Fragments S—Arene—N and P	653
13.16.4.1.1.1.1	Method 1: Condensation of 2-Aminothiophenol with Phosphines	653
13.16.4.2	Aromatization	654
13.16.4.2.1	Method 1: By Halide Abstraction	654
13.16.5	Product Subclass 5: 1,3,4-Thiazaphospholes	655
13.16.5.1	Synthesis by Ring-Closure Reactions	655
13.16.5.1.1	By Formation of One N—P and One P—C Bond	655
13.16.5.1.1.1	Fragments C—S—C—N and P	655
13.16.5.1.1.1.1	Method 1: [4 + 1] Cyclocondensation	655
13.16.5.1.2	By Formation of One N—P and One S—C Bond	656
13.16.5.1.2.1	Fragments S—C—N and P—C	656
13.16.5.1.2.1.1	Method 1: [3 + 2] Cyclocondensation	656
13.17	Product Class 17: Oxadiphospholes and Their Analogues S. J. Collier	
13.17	Product Class 17: Oxadiphospholes and Their Analogues	659
13.17.1	Product Subclass 1: 1,2,4-Oxadiphospholes	660
13.17.1.1	Synthesis by Ring-Closure Reactions	661
13.17.1.1.1	By Formation of One O—P and One P—C Bond	661
13.17.1.1.1.1	Fragments P—C—O and P—C	661
13.17.1.1.1.1.1	Method 1: From Mesitylphosphaalkenes	661
13.17.2	Product Subclass 2: 1,2,4-Thiadiphospholes	662
13.17.2.1	Synthesis by Ring-Closure Reactions	665
13.17.2.1.1	By Formation of One S—P and Three P—C Bonds	665
13.17.2.1.1.1	Fragments S—C, C, and Two P Fragments	665
13.17.2.1.1.1.1	Method 1: From Lithium Phosphide and Carbon Disulfide	665
13.17.2.1.2	By Formation of One S—P, One S—C, and One P—C Bond	665
13.17.2.1.2.1	Fragments P—C, P—C, and S	665
13.17.2.1.2.1.1	Method 1: From Phosphaacetylenes and a Sulfur Source	665
13.17.2.1.2.1.1.1	Variation 1: Use of Stoichiometric Metal—Sulfur Complexes	666
13.17.2.1.2.1.1.2	Variation 2: Use of Elemental Sulfur with a Tantalum Catalyst	667
13.17.2.1.2.1.1.3	Variation 3: Use of Carbon Disulfide, Carbon Disulfide Ylides, and Other Sulfur Sources	669
13.17.2.2	Synthesis by Ring Transformation	670
13.17.2.3	Synthesis by Substituent Modification	671
13.17.2.3.1	Addition Reactions	671
13.17.2.3.1.1	Formation of Metal Complexes	671

13.17.3	Product Subclass 3: 1,2,4-Selenadiphospholes	673
13.17.3.1	Synthesis by Ring-Closure Reactions	675
13.17.3.1.1	By Formation of One Se—P, One Se—C, and One P—C Bond	675
13.17.3.1.1.1	Fragments P—C, P—C, and Se	675
13.17.3.1.1.1.1	Method 1: From Phosphaacetylenes and Elemental Selenium	675
13.17.3.2	Synthesis by Ring Transformation	676
13.17.3.3	Addition Reactions	677
13.17.3.3.1	Formation of Metal Complexes	677
13.17.4	Product Subclass 4: 1,2,4-Telluradiphospholes	678
13.17.4.1	Synthesis by Ring-Closure Reactions	679
13.17.4.1.1	By Formation of One Te—P, One Te—C, and One P—C Bond	679
13.17.4.1.1.1	Fragments P—C, P—C, and Te	679
13.17.4.1.1.1.1	Method 1: From Phosphaacetylenes and Elemental Tellurium	679
13.17.4.2	Synthesis by Ring Transformation	680
13.17.4.3	Synthesis by Substituent Modification	680
13.17.4.3.1	Addition Reactions	680
13.17.4.3.1.1	Formation of Metal Complexes	680
13.17.5	Product Subclass 5: 1,2,5-Thiadiphospholes	681
13.17.6	Product Subclass 6: 1,3,4-Thiadiphospholes	682
13.17.6.1	Synthesis by Ring-Closure Reactions	682
13.17.6.1.1	By Formation of One P—P, One S—C, and Two P—C Bonds	682
13.17.6.1.1.1	Fragments S—C, C, and Two P Fragments	682
13.17.6.1.1.1.1	Method 1: From Metallodisilylphosphanes and Carbon Disulfide	682
13.17.6.1.2	By Formation of One P—P and Two S—C Bonds	683
13.17.6.1.2.1	Fragments P—C, P—C, and S	683
13.17.6.1.2.1.1	Method 1: From Phosphaacetylenes and a Sulfur Source	683
13.17.6.2	Synthesis by Ring Transformation	684
13.17.6.3	Synthesis by Substituent Modification	684
13.17.6.3.1	Addition Reactions	684
13.17.6.3.1.1	Formation of Bis(η^1 -Complexes)	684
13.17.7	Product Subclass 7: 1,3,4-Selenadiphospholes	685
13.17.7.1	Synthesis by Ring-Closure Reactions	685
13.17.7.1.2	By Formation of One P—P and Two Se—C Bonds	685
13.17.7.1.2.1	Fragments P—C, P—C, and Se	685
13.17.7.1.2.1.1	Method 1: From Phosphaacetylenes and Elemental Selenium	685

13.18	Product Class 18: Diazaphospholes and Diazarsoles R. K. Bansal and Neelima Gupta	
<hr/>		
13.18	Product Class 18: Diazaphospholes and Diazarsoles	689
13.18.1	Product Subclass 1: Monocyclic 1,2,3-Diazaphospholes and 1,2,3-Diazarsoles	689
13.18.1.1	Synthesis by Ring-Closure Reactions	691
13.18.1.1.1	By Formation of One N–P/As and One P/As–C Bond	691
13.18.1.1.1.1	Fragments N–N–C–C and P/As	691
13.18.1.1.1.1.1	Method 1: Synthesis by [4 + 1] Cyclocondensation	691
13.18.1.2	Synthesis by Ring Transformation	692
13.18.1.2.1	Method 1: By Cycloaddition/Cycloreversion	692
13.18.2	Product Subclass 2: 1,2,3-Diazaphospholo[1,5-<i>a</i>]pyridines	693
13.18.2.1	Synthesis by Ring-Closure Reactions	693
13.18.2.1.1	By Formation of One N–P and One P–C Bond	693
13.18.2.1.1.1	Fragments N–N–C–C and P	693
13.18.2.1.1.1.1	Method 1: Synthesis by [4 + 1] Cyclocondensation	693
13.18.3	Product Subclass 3: Monocyclic 1,2,4-Diazaphospholes and 1,2,4-Diazarsoles	694
13.18.3.1	Synthesis by Ring-Closure Reactions	695
13.18.3.1.1	By Formation of Two N–C Bonds	695
13.18.3.1.1.1	Fragments C–P/As–C and N–N	695
13.18.3.1.1.1.1	Method 1: Cyclocondensation of 2-Heteroallylic Cations with Hydrazines	695
13.18.3.1.2	By Formation of One N–C and One P/As–C Bond	696
13.18.3.1.2.1	Fragments C–N–N and C–P/As	696
13.18.3.1.2.1.1	Method 1: [3 + 2] Cycloaddition	696
13.18.3.1.2.1.1.1	Variation 1: Of Phosphaalkynes and Diazoalkanes	696
13.18.3.1.2.1.1.2	Variation 2: Of Phosphaalkynes and Nitrilimines	697
13.18.3.1.2.1.1.3	Variation 3: Of Phosphaalkynes and SydnoneS	697
13.18.3.1.2.1.1.4	Variation 4: Of Phosphaalkenes or Arsaalkenes and Diazoalkanes	698
13.18.3.1.2.1.1.5	Variation 5: Of Phosphaalkenes and SydnoneS	699
13.18.3.2	Synthesis By Ring Transformation	699
13.18.3.2.1	Method 1: By O/P Exchange	699
13.18.4	Product Subclass 4: 1,2,4-Diazaphospholo[1,5-<i>a</i>]pyridines and 1,2,4-Diazarsole[1,5-<i>a</i>]pyridines	700
13.18.4.1	Synthesis by Ring Transformation	700
13.18.4.1.1	Method 1: By O/P or O/As Exchange	700
13.18.5	Product Subclass 5: Monocyclic 1,3,2-Diazaphospholes	701
13.18.5.1	Synthesis by Ring-Closure Reactions	702

13.18.5.1.1	By Formation of Two N—P Bonds	702
13.18.5.1.1.1	Fragments N—C—N and P	702
13.18.5.1.1.1.1	Method 1: [4 + 1] Cyclocondensation	702
13.18.5.1.1.1.1.1	Variation 1: Cyclocondensation with Phosphorus Trichloride	702
13.18.5.1.1.1.1.2	Variation 2: Cyclocondensation with Hexamethylphosphorous Triamide	703
13.18.6	Product Subclass 6: Pyrrolo[3,4-<i>d</i>][1,3,2]diazaphospholes	703
13.18.6.1	Synthesis by Ring-Closure Reactions	704
13.18.6.1.1	By Formation of Two N—P Bonds	704
13.18.6.1.1.1	Fragments N—C—N and P	704
13.18.6.1.1.1.1	Method 1: Cyclocondensation with Phosphorus Trichloride	704
13.18.7	Product Subclass 7: 1,3,2-Benzodiazaphospholes	705
13.18.7.1	Synthesis by Ring-Closure Reactions	705
13.18.7.1.1	By Formation of Two N—P Bonds	705
13.18.7.1.1.1	Fragments N—C—N and P	705
13.18.7.1.1.1.1	Method 1: Condensation of Benzene-1,2-diamines with Hexamethylphosphorous Triamide	706
13.18.7.2	Aromatization by Chloride Abstraction	706
13.18.8	Product Subclass 8: Monocyclic 1,4,2-Diazaphospholes	707
13.18.8.1	Synthesis by Ring-Closure Reactions	707
13.18.8.1.1	By Formation of One N—P and One N—C Bond	707
13.18.8.1.1.1	Fragments N—C—N and P	707
13.18.8.1.1.1.1	Method 1: By [3 + 2] Cyclocondensation	707
13.18.9	Product Subclass 9: Thiazolo[2,3-<i>e</i>][1,4,2]diazaphospholes, Thiazolo[3,2-<i>d</i>][1,4,2]diazaphospholes, and Related Systems	707
13.18.9.1	Synthesis by Ring-Closure Reactions	708
13.18.9.1.1	By Formation of One N—P and One N—C Bond	708
13.18.9.1.1.1	Fragments N—C—N and P—C	708
13.18.9.1.1.1.1	Method 1: By [3 + 2] Cyclocondensation with (Chloromethyl)dichlorophosphine	708
13.18.9.1.2	By Formation of One N—P and One P—C Bond	709
13.18.9.1.2.1	Fragments N—C—N—C and P	709
13.18.9.1.2.1.1	Method 1: By [4 + 1] Cyclocondensation with Phosphorus Trichloride	709
13.18.10	Product Subclass 10: 1,4,2-Diazaphospholo[4,5-<i>a</i>]pyridines and Related Systems	710
13.18.10.1	Synthesis by Ring-Closure Reactions	711
13.18.10.1.1	By Formation of One N—P and One N—C Bond	711
13.18.10.1.1.1	Fragments N—C—N and C—P	711

13.18.10.1.1.1.1	Method 1: [3 + 2] Cyclocondensation with (Chloromethyl)dichlorophosphine	711
13.18.10.1.2	By Formation of One N–P and One P–C Bond	712
13.18.10.1.2.1	Fragments N–C–N–C and P	712
13.18.10.1.2.1.1	Method 1: [4 + 1] Cyclocondensation with Phosphorus Trichloride	712
13.19	Product Class 19: Azadiphospholes and Their Analogues S. J. Collier	
13.19	Product Class 19: Azadiphospholes and Their Analogues	717
13.19.1	Product Subclass 1: Monocyclic 1,2,3-Azadiphospholes	717
13.19.1.1	Synthesis by Ring-Closure Reactions	719
13.19.1.1.1	By Formation of One P–P and One P–C Bond	719
13.19.1.1.1.1	Fragments C–C–N–P and P	719
13.19.1.1.1.1.1	Method 1: Flash Pyrolysis of Substituted Aminophosphines	719
13.19.1.2	Synthesis by Ring Transformation	720
13.19.2	Product Subclass 2: 1,2,3-Benzazadiphospholes and Analogues	721
13.19.2.1	Synthesis by Ring-Closure Reactions	721
13.19.2.1.1	By Formation of One N–P (As, Sb) and One P–P (As, Sb) Bond	721
13.19.2.1.1.1	Fragments P–C–C–N and P (As, Sb)	721
13.19.2.1.1.1.1	Method 1: Condensation of Phosphinoanilines with Hexamethylphosphorous Triamide, Hexamethylarsenous Triamide, or Tris(dimethylamino)stibine	721
13.19.3	Product Subclass 3: 1,2,4-Azadiphospholes	722
13.19.3.1	Synthesis by Ring-Closure Reactions	723
13.19.3.1.1	By Formation of One N–P, One N–C, and One P–C Bond	723
13.19.3.1.1.1	Fragments P–C, P–C, and N	723
13.19.3.1.1.1.1	Method 1: Synthesis from Alkylidynephosphines and Imidometal Complexes	723
13.19.3.1.2	By Formation of One N–P and One P–C Bond	724
13.19.3.1.2.1	Fragments N–C–P and C–P	724
13.19.3.1.2.1.1	Method 1: Dimerization of <i>N</i> -(<i>tert</i> -Butyl)- <i>N</i> -(phosphinidynemethyl)amine	724
13.19.4	Product Subclass 4: 1,2,5-Azadiphospholes	725
13.19.4.1	Synthesis by Ring-Closure Reactions	726
13.19.4.1.1	By Formation of Two N–P Bonds and One C–C Bond	726
13.19.4.1.1.1	Fragments P–C, P–C, and N	726
13.19.4.1.1.1.1	Method 1: Synthesis from Alkylidynephosphines and Imidovanadium Complexes	726

13.19.4.1.1.1.2	Method 2: Direct Synthesis of η^4 -1,2,5-Azadiphosphole Complexes from Alkylidynephosphines and Imidoiridium Complexes	726
13.19.5	Product Subclass 5: 1,3,4-Azadiphospholes	727
13.20	Product Class 20: Triphospholes and Diphospharsoles R. K. Bansal and Neelima Gupta	
13.20	Product Class 20: Triphospholes and Diphospharsoles	729
13.20.1	Product Subclass 1: 1,2,3-Triphospholides	729
13.20.1.1	Synthesis by Aromatization	730
13.20.1.1.1	Method 1: From 1,3-Dihydro-1,2,3-triphospholes	730
13.20.2	Product Subclass 2: 1,2,4-Triphospholides and 1,2,4-Triphospholes	731
13.20.2.1	Synthesis by Ring-Closure Reactions	732
13.20.2.1.1	By Formation of One P–P and Two P–C Bonds	732
13.20.2.1.1.1	Fragments P–C, P–C, and P	732
13.20.2.1.1.1.1	Method 1: Reductive Cyclocondensation of Phosphaalkynes or Phosphaalkenes	732
13.20.2.1.1.1.1.1	Variation 1: By the Use of Lithium Bis(trimethylsilyl)phosphide	732
13.20.2.1.1.1.1.2	Variation 2: By the Use of Potassium Menthoxide	732
13.20.2.1.2	By Formation of Two P–C Bonds	733
13.20.2.1.2.1	Fragments P–P–C and P–C	733
13.20.2.1.2.1.1	Method 1: Synthesis from a 2,3,4-Triphosphapentadienide Anion	733
13.20.2.2	Synthesis by Ring Transformation	734
13.20.2.2.1	Ring Contraction	734
13.20.2.2.1.1	Method 1: Of Tri- <i>tert</i> -butyl-1,3,5-triphosphabenzene	734
13.20.2.3	Aromatization	734
13.20.2.3.1	Method 1: Of a Triphospholane	734
13.20.2.4	Synthesis by Substituent Modification	735
13.20.2.4.1	Addition Reactions	735
13.20.2.4.1.1	Method 1: Reaction of 1,2,4-Triphospholides with Electrophiles	735
13.20.3	Product Subclass 3: Diphospharsoles	736
13.20.3.1	Synthesis by Ring-Closure Reactions	736
13.20.3.1.1	Method 1: Reductive Cyclization of a Phosphaalkyne with Lithium Bis(trimethylsilyl)arsenide	736

13.21	Product Class 21: Thiadiazaphospholes S. J. Collier	
<hr/>		
13.21	Product Class 21: Thiadiazaphospholes	739
13.21.1	Aromatization	740
13.21.1.1	Method 1: Synthesis by Chloride Abstraction	740
13.22	Product Class 22: Triazaphospholes R. K. Bansal and Neelima Gupta	
<hr/>		
13.22	Product Class 22: Triazaphospholes	743
13.22.1	Product Subclass 1: 1,2,3,4-Triazaphospholes	743
13.22.1.1	Synthesis by Ring-Closure Reactions	744
13.22.1.1.1	By Formation of One N–P and One N–C Bond	744
13.22.1.1.1.1	Fragments N–N–N and P–C	744
13.22.1.1.1.1.1	Method 1: [3 + 2] Cycloaddition of Azides	744
13.22.1.1.1.1.1.1	Variation 1: Use of Phosphaalkynes	744
13.22.1.1.1.1.1.2	Variation 2: Use of Phosphaalkenes	745
13.22.1.1.2	By Formation of One N–N and One P–C Bond	745
13.22.1.1.2.1	Fragments N–N–C and N–P	745
13.22.1.1.2.1.1	Method 1: [3 + 2] Cycloaddition of Halo(imino)phosphines	745
13.22.2	Product Subclass 2: Monocyclic 1,2,4,3-Triazaphospholes	746
13.22.2.1	Synthesis by Ring-Closure Reactions	747
13.22.2.1.1	By Formation of Two N–P Bonds	748
13.22.2.1.1.1	Fragments N–N–C–N and P	748
13.22.2.1.1.1.1	Method 1: [4 + 1] Cyclocondensation	748
13.22.2.1.1.1.1.1	Variation 1: From Amidrazone Hydrochlorides and Hexaalkylphosphorous Triamides	748
13.22.2.1.1.1.1.2	Variation 2: From Amidrazone Hydrochlorides and Phosphorus Pentachloride	749
13.22.2.1.2	By Formation of One N–P and One N–C Bond	749
13.22.2.1.2.1	Fragments P–N–C and N–N	749
13.22.2.1.2.1.1	Method 1: [3 + 2] Cyclocondensation of <i>N</i> -Phosphino Imidates and Hydrazines	749
13.22.2.2	Synthesis by Substituent Modification	751
13.22.2.2.1	Substitution of Hydrogen	751
13.22.3	Product Subclass 3: Thiazolo[2,3-<i>e</i>][1,2,4,3]triazaphospholes and [1,2,4,3]Triazaphospholo[1,5-<i>a</i>]pyridines	751
13.22.3.1	Synthesis by Ring-Closure Reactions	752
13.22.3.1.1	By Formation of Two N–P Bonds	752

13.22.3.1.1.1	Fragments N—N—C—N and P	752
13.22.3.1.1.1.1	Method 1: [4 + 1] Cyclocondensation	752
13.23	Product Class 23: Diazadiphospholes S. J. Collier	
13.23	Product Class 23: Diazadiphospholes	757
13.23.1	Product Subclass 1: 1,2,3,4-Diazadiphospholes	757
13.23.1.1	Synthesis by Ring-Closure Reactions	758
13.23.1.1.1	By Formation of One N—P and One P—C Bond	758
13.23.1.1.1.1	Fragments N—N—C and P—P	758
13.23.1.1.1.1.1	Method 1: From Lithium Diazo(trimethylsilyl)methanide and White Phosphorus	758
13.23.1.2	Synthesis by Substituent Modification	758
13.23.1.2.1	Substitution of Existing Substituents	758
13.23.1.2.1.1	Of Hydrogen	758
13.23.1.2.1.1.1	Method 1: By a Metal	758
13.23.2	Product Subclass 2: 1,2,3,5-Diazadiphospholes	759
13.23.2.1	Synthesis by Ring-Closure Reactions	760
13.23.2.1.1	By Formation of Two N—P Bonds	760
13.23.2.1.1.1	Fragments P—C—P and N—N	760
13.23.2.1.1.1.1	Method 1: Condensation of Bis(dichlorophosphino)methane with Alkyl- and Arylhydrazines	760
13.24	Product Class 24: Tetraphospholes S. J. Collier	
13.24	Product Class 24: Tetraphospholes	763
13.24.1	Synthesis by Ring-Closure Reactions	764
13.24.1.1	Formation of Two P—C Bonds	764
13.24.1.1.1	Fragments P—P—P—P and C	764
13.24.1.1.1.1	Method 1: From White Phosphorus and Sodium Powder in Diglyme	764
13.25	Product Class 25: Tetraazaphospholes S. J. Collier	
13.25	Product Class 25: Tetraazaphospholes	767
13.25.1	Synthesis by Ring-Closure Reactions	767
13.25.1.1	By Formation of One N—N and One N—P Bond	767
13.25.1.1.1	Fragments N—N—N and N—P	767

13.25.1.1.1.1	Method 1: By 1,3-Dipolar Cycloaddition of Alkyl Azides with <i>N</i> -Aryl- <i>N</i> -phosphinidynammonium Ions	767
13.26	Product Class 26: Pentaphospholes and Pentarsoles R. K. Bansal and Neelima Gupta	
13.26	Product Class 26: Pentaphospholes and Pentarsoles	771
13.26.1	Product Subclass 1: Pentaphospholides	771
13.26.1.1	Synthesis by Ring-Closure Reactions	772
13.26.1.1.1	Method 1: Synthesis of Metal Pentaphospholides from Phosphorus and an Alkali Metal Phosphide	772
13.26.1.1.1.1	Variation 1: From White Phosphorus and Sodium Dihydrogenphosphide ·	772
13.26.1.1.1.2	Variation 2: From White Phosphorus and Lithium Dihydrogenphosphide ·	773
13.26.1.1.1.3	Variation 3: From Red Phosphorus and Potassium Dihydrogenphosphide	773
13.26.2	Product Subclass 2: Pentarsolides	774
13.26.2.1	Synthesis by Ring-Closure Reactions	775
13.26.2.1.1	Method 1: Synthesis of Pentarsolyl Complexes from Yellow Arsenic ···	775
13.27	Product Class 27: Selenazoles and Tellurazoles Containing One or More Other Heteroatoms R. A. Aitken	
13.27	Product Class 27: Selenazoles and Tellurazoles Containing One or More Other Heteroatoms	777
13.27.1	Product Subclass 1: 1,2,3,5-Diselenadiazolium Salts and 1,2,3,5-Diselenadiazolyl-Containing Compounds	777
13.27.1.1	Synthesis by Ring-Closure Reactions	778
13.27.1.1.1	By Formation of One Se—Se and Two Se—N Bonds	778
13.27.1.1.1.1	Method 1: Reaction of <i>N,N,N'</i> -Tris(trimethylsilyl)amidines with Selenium Dichloride	778
13.27.1.2	Synthesis by Ring Transformation	778
13.27.1.2.1	One-Electron Reduction	778
13.27.2	Product Subclass 2: 1,2,3-Benzoxaselenazoles	779
13.27.2.1	Synthesis by Ring-Closure Reactions	780
13.27.2.1.1	By Formation of One Se—O, One Se—N, and One O—C Bond	780
13.27.2.1.1.1	Method 1: Reaction of a Hindered Aniline with Selenium Oxychloride ··	780
13.27.3	Product Subclass 3: 2,1,3-Benzoxatellurazoles and Naphth[2,1-<i>c</i>][1,2,5]oxatellurazoles	780
13.27.3.1	Synthesis by Ring-Closure Reactions	781
13.27.3.1.1	By Formation of One Te—O, One Te—C, and One N—C Bond	781
13.27.3.1.1.1	Method 1: From α -Tetralone Oximes	781

13.27.3.1.2	By Formation of One Te—O and One N—C Bond	781
13.27.3.1.2.1	Method 1: Nitration and Reduction of an Aryltellurium Trichloride	781
13.27.4	Product Subclass 4: 1,2,3-Benzothiaselenazolium Salts and Benzobis(1,2,3-thiaselenazoles)	782
13.27.4.1	Synthesis by Ring-Closure Reactions	783
13.27.4.1.1	By Formation of One Se—S and One Se—N Bond	783
13.27.4.1.1.1	Method 1: Reaction of 2-Aminobenzenethiols with Selenious Acid	783
13.27.4.1.1.2	Method 2: Reaction of 1,2,3-Benzodithiazolium Salts with Selenious Acid	783
13.27.4.1.1.3	Method 3: Reaction of a Diaminobenzenedithiol with Selenium Tetrachloride	784
13.27.4.2	Synthesis by Substituent Modification	784
13.27.4.2.1	Substitution of Existing Substituents	784
13.27.4.2.1.1	Of Halogens	784
13.27.4.2.1.1.1	Method 1: Reaction with Anilines	784
13.27.4.2.1.2	Of Methoxy Groups	785
13.27.4.2.1.2.1	Method 1: Reaction with Dialkylammonium Acetates	785
13.27.5	Product Subclass 5: 2,1,3-Benzothiaselenazolium Salts	785
13.27.5.1	Synthesis by Ring-Closure Reactions	785
13.27.5.1.1	By Formation of One S—Se and One S—N Bond	785
13.27.5.1.1.1	Method 1: Reaction of 2-Aminobenzeneselenol Hydrochlorides with Thionyl Chloride	785
13.27.5.2	Synthesis by Substituent Modification	786
13.27.5.2.1	Substitution of Existing Substituents	786
13.27.5.2.1.1	Of Halogens	786
13.27.5.2.1.1.1	Method 1: Reaction with Anilines	786
13.27.5.2.1.2	Of Methoxy Groups	786
13.27.5.2.1.2.1	Method 1: Reaction with Dialkylammonium Acetates	786
13.27.6	Product Subclass 6: 1,2,4-Diselenazolium Salts	787
13.27.6.1	Synthesis by Ring-Closure Reactions	787
13.27.6.1.1	By Formation of One Se—Se and Two Se—C Bonds	787
13.27.6.1.1.1	Method 1: Reaction of a Chlorinated Iminium Salt with Sodium Hydrogen Selenide Followed by Oxidation	787
13.27.6.1.2	By Formation of One Se—Se and One Se—C Bond	787
13.27.6.1.2.1	Method 1: Reaction of an <i>N</i> -Benzoylselenourea Nickel Complex with Diphosgene	787
13.27.6.1.3	By Formation of One Se—Se and One N—C Bond	788
13.27.6.1.3.1	Method 1: Iodine Oxidation of Aromatic Selenoamides	788

13.27.7	Product Subclass 7: 1,2,3-Benzodiselenazolium Salts	788
13.27.7.1	Synthesis by Ring-Closure Reactions	789
13.27.7.1.1	By Formation of One Se—Se and One Se—N Bond	789
13.27.7.1.1.1	Method 1: Reaction of 2-Aminobenzeneselenol Hydrochlorides with Selenious Acid	789
13.27.7.2	Synthesis by Substituent Modification	789
13.27.7.2.1	Substitution of Existing Substituents	789
13.27.7.2.1.1	Of Halogens	789
13.27.7.2.1.1.1	Method 1: Reaction with Anilines	789
13.27.7.2.1.2	Of Methoxy Groups	790
13.27.7.2.1.2.1	Method 1: Reaction with Dialkylammonium Acetates	790
13.27.8	Product Subclass 8: 1,3,2-Benzodiselenazolium Salts	790
13.27.8.1	Synthesis by Ring-Closure Reactions	790
13.27.8.1.1	By Formation of Two Se—N Bonds	790
13.27.8.1.1.1	Method 1: Reaction of Benzene-1,2-diselenenyl Dichloride with Trimethylsilyl Azide	790
13.27.9	Product Subclass 9: 1,2,3-Selenadiazoles	791
13.27.9.1	Synthesis by Ring-Closure Reactions	791
13.27.9.1.1	By Formation of One Se—N and One Se—C Bond	791
13.27.9.1.1.1	Method 1: Reaction of Semicarbazones with Selenium Dioxide	791
13.27.9.1.1.1.1	Variation 1: In Acetic Acid	791
13.27.9.1.1.1.2	Variation 2: In Aqueous Dioxane	792
13.27.9.1.1.2	Method 2: Reaction of Tosylhydrazones with Diselenium Dichloride	793
13.27.9.1.1.3	Method 3: Reaction of Tosylhydrazones with Selenium Oxychloride	793
13.27.9.1.2	By Formation of One Se—N and One C—C Bond	794
13.27.9.1.2.1	Method 1: Reaction of an Aryl Isoselenocyanate with Diazomethane	794
13.27.9.2	Aromatization	795
13.27.9.2.1	Method 1: <i>N</i> -Debenzoylation of 2-Benzoyl-5-(benzoylimino)-2,5-dihydro-selenadiazoles	795
13.27.9.3	Synthesis by Substituent Modification	795
13.27.9.3.1	Rearrangement of Substituents	795
13.27.9.3.1.1	Method 1: Curtius Rearrangement of 5-(Azidocarbonyl)-1,2,3-selenadiazoles	795
13.27.10	Product Subclass 10: 1,2,3-Benzoselenadiazoles	796
13.27.10.1	Synthesis by Ring-Closure Reactions	796
13.27.10.1.1	By Formation of One Se—N and One N—N Bond	796
13.27.10.1.1.1	Method 1: Diazotization of 2-Aminobenzeneselenol	796
13.27.10.2	Aromatization	796

13.27.10.2.1	Method 1: Reaction of a 6,7-Dihydro-1,2,3-benzoselenadiazole with Selenium	796
13.27.11	Product Subclass 11: 1,2,4-Selenadiazoles	797
13.27.11.1	Synthesis by Ring-Closure Reactions	797
13.27.11.1.1	By Formation of One Se—N and One N—C Bond	797
13.27.11.1.1.1	Method 1: Oxidation of Selenoamides	797
13.27.11.1.1.1.1	Variation 1: Using Iodine	797
13.27.11.1.1.1.2	Variation 2: Using <i>N</i> -Bromosuccinimide	798
13.27.11.1.1.1.3	Variation 3: Using Hydrogen Peroxide	798
13.27.11.1.1.1.4	Variation 4: Using 3-Chloroperoxybenzoic Acid	799
13.27.11.1.1.2	Method 2: Reaction of <i>N</i> -Bromoamidines with Potassium Selenocyanate	799
13.27.12	Product Subclass 12: 1,2,5-Selenadiazoles	800
13.27.12.1	Synthesis by Ring-Closure Reactions	800
13.27.12.1.1	By Formation of Two Se—N Bonds	800
13.27.12.1.1.1	Method 1: Reaction of 1,2-Diamines with Selenium Compounds	800
13.27.12.1.1.1.1	Variation 1: Using Diselenium Dichloride	800
13.27.12.1.1.1.2	Variation 2: Using Selenium Dioxide	800
13.27.12.1.1.1.3	Variation 3: Using a Selenium Diimide	801
13.27.12.1.1.2	Method 2: Reaction of 1,2-Diimines with Selenium Compounds	801
13.27.12.1.1.2.1	Variation 1: Using Diselenium Dichloride	801
13.27.12.1.1.2.2	Variation 2: Using Selenium Oxychloride	802
13.27.12.1.1.3	Method 3: Reaction of 1,2-Dioximes with Selenium Compounds	802
13.27.12.1.1.3.1	Variation 1: Using Diselenium Dichloride	802
13.27.12.1.1.3.2	Variation 2: Using Selenium Dioxide	803
13.27.12.1.1.4	Method 4: Reaction of 1,2-Bis[(trimethylsilyl)imines] with Selenium Oxychloride	803
13.27.12.2	Synthesis by Ring Transformation	804
13.27.12.2.1	From 1,2,5-Thiadiazoles	804
13.27.12.2.1.1	Method 1: Reaction of 1,2,5-Thiadiazoles with Grignard Reagents and Diselenium Dichloride	804
13.27.12.2.2	From a Pyrimidin-4(3 <i>H</i>)-one	805
13.27.12.2.2.1	Method 1: Reaction of a 5-Aminopyrimidin-4(3 <i>H</i>)-one with Selenium Dioxide	805
13.27.13	Product Subclass 13: 2,1,3-Benzoselenadiazoles	805
13.27.13.1	Synthesis by Ring-Closure Reactions	806
13.27.13.1.1	By Formation of Two Se—N Bonds	806
13.27.13.1.1.1	Method 1: Reaction of 1,2-Diaminoarenes with Selenium Dioxide	806
13.27.13.1.1.2	Method 2: Reaction of 1,2-Diaminoarenes with Selenium Oxychloride ..	806
13.27.13.1.1.3	Method 3: Reaction of 1,2-Diaminoarenes with Selenium Tetrachloride ..	807
13.27.13.1.1.4	Method 4: Reaction of Spirocyclic Aminals with Selenium Dioxide	808
13.27.13.1.1.5	Method 5: Reaction of 1,2-Bis[(trimethylsilyl)imines] with Selenium Oxychloride or Selenium Tetrachloride	808

13.27.13.2	Synthesis by Substituent Modification	809
13.27.13.2.1	Substitution of Existing Substituents	809
13.27.13.2.1.1	Of Hydrogen	809
13.27.13.2.1.1.1	Method 1: Nitration	809
13.27.13.2.1.2	Of Bromine or Iodine	810
13.27.13.2.1.2.1	Method 1: Nucleophilic Substitution	810
13.27.13.2.2	Addition Reactions	811
13.27.13.2.2.1	Method 1: N-Alkylation	811
13.27.14	Product Subclass 14: 1,3,4-Selenadiazoles and 1,3,4-Selenadiazolium Salts	811
13.27.14.1	Synthesis by Ring-Closure Reactions	811
13.27.14.1.1	By Formation of One Se—C and Two N—C Bonds	811
13.27.14.1.1.1	Method 1: Reaction of Selenobenzamides with Hydrazine Hydrate	811
13.27.14.1.2	By Formation of Two Se—C Bonds	812
13.27.14.1.2.1	Method 1: Reaction of Dimethylformamide Azine with Hydrogen Selenide	812
13.27.14.1.2.2	Method 2: Reaction of 1,2-Diacetylhydrazine with Phosphorus Pentaselenide	812
13.27.14.1.3	By Formation of One Se—C and One N—C Bond	813
13.27.14.1.3.1	Method 1: Reaction of Isoselenocyanates with Selenosemicarbazides	813
13.27.14.1.3.2	Method 2: Reaction of Carboxylic Acids with Selenosemicarbazide and Phosphoryl Chloride	813
13.27.14.1.4	By Formation of One Se—C Bond	814
13.27.14.1.4.1	Method 1: Reaction of <i>N</i> -Acyl- <i>N'</i> -selenoacylhydrazines with Acetic Anhydride/Perchloric Acid	814
13.27.15	Product Subclass 15: 1,2,3-Benzotelluradiazolium Salts	815
13.27.15.1	Synthesis by Ring-Closure Reactions	815
13.27.15.1.1	By Formation of One Te—N Bond	815
13.27.15.1.1.1	Method 1: Reaction of a 2-(Arylazo)arenetellurenyl Chloride with Silver Perchlorate	815
13.27.16	Product Subclass 16: 1,2,5-Telluradiazoles	816
13.27.16.1	Synthesis by Ring Transformation	816
13.27.16.1.1	Method 1: Reaction of 1,2,5-Thiadiazoles or 1,2,5-Selenadiazoles with a Grignard Reagent Followed by Tellurium Tetrachloride	816
13.27.17	Product Subclass 17: 2,1,3-Benzotelluradiazoles	817
13.27.17.1	Synthesis by Ring-Closure Reactions	817
13.27.17.1.1	By Formation of Two Te—N Bonds	817
13.27.17.1.1.1	Method 1: Reaction of a 1,2-Bis[(trimethylsilyl)imine] with Tellurium Tetrachloride	817
13.27.17.1.1.2	Method 2: Reaction of a 1,2-Diamine with Tellurium Tetrachloride	817

13.27.17.1.2	By Formation of One Te—N and One N—C Bond	818
13.27.17.1.2.1	Method 1: Reaction of a Lithiated Arylamine with a Silylated Tellurium Imide	818
13.27.17.2	Synthesis by Ring Transformation	818
13.27.17.2.1	Method 1: Reaction of an Aromatic-Fused 1,2,5-Selenadiazole with a Grignard Reagent, Followed by Tellurium Tetrachloride	818
13.28	Product Class 28: Oxatriazoles M. Begtrup	
13.28	Product Class 28: Oxatriazoles	823
13.28.1	Product Subclass 1: 1,2,3,4-Oxatriazoles	823
13.28.1.1	Synthesis by Ring-Closure Reactions	824
13.28.1.1.1	By Formation of One N—N, One O—C, and One N—C Bond	824
13.28.1.1.1.1	Method 1: 1,2,3,4-Oxatriazol-3-ium-5-olates from Nitromethide Anions and Arenediazonium Ions	824
13.28.1.1.2	By Formation of One N—N and One O—C Bond	825
13.28.1.1.2.1	Fragments C—N—N and N—O	825
13.28.1.1.2.1.1	Method 1: 1,2,3,4-Oxatriazol-3-ium-5-thiolates from Hydrazinium Dithiocarbazates and Nitrous Acid	825
13.28.1.1.2.1.2	Method 2: 1,2,3,4-Oxatriazolium-5-aminides from Thiosemicarbazides and Nitrous Acid or Alkyl Nitrites	825
13.28.1.1.3	By Formation of One O—C and One N—C Bond	826
13.28.1.1.3.1	Fragments O—N—N—N and C	826
13.28.1.1.3.1.1	Method 1: 1,2,3,4-Oxatriazolium-5-olates from <i>N</i> -Nitrosohydrazines and Phosgene	826
13.28.1.1.4	By Formation of One O—C Bond	827
13.28.1.1.4.1	Fragment C—N—N—N—O	827
13.28.1.1.4.1.1	Method 1: 1,2,3,4-Oxatriazolium-5-aminide Hydrochlorides from 1-Nitroso-2-guanidinohydrazines	827
13.28.1.1.4.1.2	Method 2: 1,2,3,4-Oxatriazol-3-ium-5-olates from (Arylhydrazono)-methanedisulfonates and Nitrous Acid	827
13.28.1.1.4.1.3	Method 3: 1,2,3,4-Oxatriazolium-5-olates from Semicarbazides and Nitrous Acid	828
13.28.1.2	Synthesis by Ring Transformation	828
13.28.1.2.1	Method 1: 1,2,3,4-Oxatriazolium-5-aminides from 1,2,3,4-Oxatriazolium-5-anilides and Aryl Isocyanates	828
13.28.1.3	Synthesis by Substituent Modification	829
13.28.1.3.1	Method 1: 1,2,3,4-Oxatriazolium Salts by Alkylation of 1,2,3,4-Oxatriazolium-5-thiolates	829

13.28.1.3.2	Method 2: N-Acylation and Sulfonation of 1,2,3,4-Oxatriazolium-5-aminides	829
13.28.1.3.3	Method 3: 1,2,3,4-Oxatriazolium-5-olates from 1,2,3,4-Oxatriazolium-5-aminides and Nitrous Acid	830
13.28.2	Product Subclass 2: 1,2,3,5-Oxatriazoles	830
13.28.2.1	Synthesis by Ring-Closure Reactions	830
13.28.2.1.1	By Formation of One O—N and One N—C Bond	830
13.28.2.1.1.1	Fragments C—N—O and N—N	830
13.28.2.1.1.1.1	Method 1: 2,3-Dihydro-1,2,3,5-oxatriazoles from Nitrile Oxides and Azo Compounds	830
13.29	Product Class 29: Thiatriazoles M. Begtrup	
13.29	Product Class 29: Thiatriazoles	833
13.29.1	Product Subclass 1: 1,2,3,4-Thiatriazoles	833
13.29.1.1	Synthesis by Ring-Closure Reactions	834
13.29.1.1.1	By Formation of One S—N and One N—N Bond	834
13.29.1.1.1.1	Method 1: From Thiohydrazides and Nitrous Acid	834
13.29.1.1.1.1.1	Variation 1: 5-Substituted 1,2,3,4-Thiatriazoles from Thiohydrazides and Nitrous Acid	834
13.29.1.1.1.1.2	Variation 2: Alkoxy- and Aryloxy-1,2,3,4-thiatriazoles from O-Substituted Hydrazinecarbothioates and Nitrous Acid	834
13.29.1.1.1.1.3	Variation 3: 5-(Alkylsulfanyl)-1,2,3,4-thiatriazoles from Hydrazinecarbodithioates and Nitrous Acid	835
13.29.1.1.1.1.4	Variation 4: 1,2,3,4-Thiatriazol-5-amines from Thiosemicarbazides and Nitrous Acid	835
13.29.1.1.1.1.5	Variation 5: 1,2,3,4-Thiatriazol-5-amines from Thiosemicarbazides and Diazonium Salts	836
13.29.1.1.1.1.6	Variation 6: 5-Hydrazino-1,2,3,4-thiatriazole from Thiocarbazide and Nitrous Acid	836
13.29.1.1.2	By Formation of One S—N and One N—C Bond	837
13.29.1.1.2.1	Method 1: 1,2,3,4-Thiatriazoles from Dithiocarboxylates and Sodium Azide	837
13.29.1.1.2.2	Method 2: 5-Chloro-1,2,3,4-thiatriazole from Thiophosgene and Sodium Azide	837
13.29.1.1.2.3	Method 3: 5-Alkyl- and 5-Aryl-1,2,3,4-thiatriazoles from 1-Methyl- 2-[(thioacyl)sulfanyl]pyridinium Iodides and Sodium Azide ..	838
13.29.1.1.2.4	Method 4: 5-Alkoxy- and 5-Aryloxy-1,2,3,4-thiatriazoles from O-Alkyl or O-Aryl Chloridithiocarbonates and Sodium Azide	839
13.29.1.1.2.5	Method 5: From Thioketenes and Hydrazoic Acid	839
13.29.1.1.2.6	Method 6: 1,2,3,4-Thiatriazol-5-amines from Isothiocyanates and Hydrazoic Acid or Trimethylsilyl Azide	840

13.29.1.1.2.6.1	Variation 1:	1,2,3,4-Thiatriazol-5-amines from Isothiocyanates and Hydrazoic Acid	840
13.29.1.1.2.6.2	Variation 2:	1,2,3,4-Thiatriazol-5-amines from Isothiocyanates and Trimethylsilyl Azide	841
13.29.1.1.2.7	Method 7:	1,2,3,4-Thiatriazole-5-thiol from Carbon Disulfide and Azide Salts	841
13.29.1.1.2.7.1	Variation 1:	1,2,3,4-Thiatriazole-5-thiol from Carbon Disulfide and Diazidobis(triphenylphosphine)palladium	842
13.29.1.2	Synthesis by Ring Transformation		842
13.29.1.2.1	Method 1:	1,2,3,4-Thiatriazol-3-ium-5-olates from 1,2,3,4-Oxatriazol-3-ium-5-thiolates	842
13.29.1.2.2	Method 2:	N-Substituted 1,2,3,4-Thiatriazol-5-amines from Substituted Tetrazole-5-thiols	843
13.29.1.2.3	Method 3:	5-Diazoalkyl-1,2,3,4-thiatriazoles from 5-Chloro-1,2,3-thiadiazoles and Sodium Azide	843
13.29.1.2.4	Method 4:	Sulfonylamino-1,2,3,4-thiatriazoles from 1,3-Thiazetidine-2,4-diimines and Sodium Azide	844
13.29.1.3	Synthesis by Substituent Modification		844
13.29.1.3.1	Method 1:	5-Substituted 1,2,3,4-Thiatriazoles by Reaction of 5-Chloro-1,2,3,4-thiatriazole with Nucleophiles	844
13.29.1.3.2	Method 2:	5-Substituted 3-Alkyl-1,2,3,4-thiatriazolium Salts by Reaction of 5-Alkoxy-3-alkyl-1,2,3,4-thiatriazolium Salts with Nucleophiles	845
13.29.1.3.3	Method 3:	5-Substituted 1,2,3,4-Thiatriazolium Salts by Alkylation of 1,2,3,4-Thiatriazoles, 1,2,3,4-Thiatriazol-3-ium-5-olates, and 1,2,3,4-Thiatriazol-3-ium-5-aminides	845
13.29.1.3.4	Method 4:	Oxidation of 5-Phenyl-1,2,3,4-thiatriazole	846
13.29.1.3.5	Method 5:	Alkylation and Acylation of 1,2,3,4-Thiatriazole-5-thiol	847
13.29.1.3.6	Method 6:	Alkylation and Acylation of 1,2,3,4-Thiatriazol-5-amines	847
13.29.2	Product Subclass 2: 1,2,3,5-Thiatriazoles		848
13.29.2.1	Synthesis by Ring-Closure Reactions		849
13.29.2.1.1	By Formation of Two S—N Bonds		849
13.29.2.1.1.1	Method 1:	1,2,3,5-Thiatriazol-3-ium-4-aminides from 1-Aminoguanidines and Thionyl Chloride	849
13.29.2.1.1.2	Method 2:	From Amidrazones and Thionyl Chloride	850
13.29.2.1.1.3	Method 3:	From Amidrazones and Sulfuryl Fluoride	850
13.29.2.1.1.4	Method 4:	1,2,3,5-Thiatriazolidin-4-one 1-Oxides from Semicarbazides and Thionyl Chloride	851
13.29.2.1.1.5	Method 5:	1,2,3,5-Thiatriazolidine-4-thiones from 1,2,4-Triaza-3-silacyclopentane-5-thiones and Sulfur Dichloride	851
13.29.2.1.2	By Formation of One S—N and One N—C Bond		852
13.29.2.1.2.1	Method 1:	2,5-Dihydro-1,2,3,5-thiatriazoles from Nitrilimines and N-Thionylaniline	852
13.29.2.1.2.2	Method 2:	From Nitrilimines and N-Sulfonylamines	852

13.29.2.1.2.3	Method 3: From <i>N'</i> -(Chlorosulfonyl)carbamimidic Chlorides and Hydrazines	852
13.29.2.1.2.4	Method 4: From Sulfonylcarbamoyl Chlorides and Hydrazines	853
13.29.2.1.3	By Formation of One N—C Bond	853
13.29.2.1.3.1	Method 1: From Hydrazinesulfonamides and Base	853
13.29.2.2	Synthesis by Ring Transformation	854
13.29.2.2.1	Method 1: From 1,2,5-Thiadiazol-3(2 <i>H</i>)-one 1-Oxides and Hydrazines ..	854
13.29.2.3	Synthesis by Substituent Modification	855
13.29.2.3.1	Method 1: N-Alkylation of 2,5-Dihydro-1,2,3,5-thiatriazole 1-Oxides ...	855
13.29.2.3.2	Method 2: N-Alkylation of 2,5-Dihydro-1,2,3,5-thiatriazole 1,1-Dioxides	855
13.29.2.3.3	Method 3: N-Alkylation of 1,2,3,5-Thiatriazolidin-4-one 1,1-Dioxides ...	856
13.29.2.3.4	Method 4: Treatment of 2,5-Dihydro-1,2,3,5-thiatriazole 1-Oxides with Phosphorus Pentachloride	856

13.30 Product Class 30: Tetrazoles

A. F. Brigas

13.30	Product Class 30: Tetrazoles	861
13.30.1	Synthesis by Ring-Closure Reactions	864
13.30.1.1	By Formation of One N—N and Two N—C Bonds	864
13.30.1.1.1	Fragments N—N—N, N, and C	864
13.30.1.1.1.1	Method 1: From Carbon Disulfide or Carboxylic Acid Derivatives with Amine and Azide	864
13.30.1.1.1.1.1	Variation 1: From Ortho Esters	864
13.30.1.1.1.1.2	Variation 2: From Acid Chlorides	864
13.30.1.1.1.1.3	Variation 3: From Amidines	865
13.30.1.1.1.1.4	Variation 4: From Chloroalkaniminium Salts	865
13.30.1.1.1.2	Method 2: Via Ketone and Azide (Schmidt Reaction)	866
13.30.1.2	By Formation of Two N—N Bonds	867
13.30.1.2.1	Fragments N—C—N—N and N	867
13.30.1.2.1.1	Method 1: From Amidrazones and Sodium Nitrite	867
13.30.1.3	By Formation of One N—N and One N—C Bond	868
13.30.1.3.1	Fragments C—N—N—N and N	868
13.30.1.3.1.1	Method 1: Via Azidochloroalkaniminium Chlorides and Amines	868
13.30.1.3.1.2	Method 2: Via 1,1-Diazido-1-ethoxyalkanes and Amines	868
13.30.1.3.2	Fragments N—N—N and C—N	868
13.30.1.3.2.1	Method 1: From Carbonic Acid Derivatives	869
13.30.1.3.2.1.1	Variation 1: From Carbonimidic Dichlorides	869
13.30.1.3.2.1.2	Variation 2: From Isocyanates, Isothiocyanates, or Carbodiimides	869
13.30.1.3.2.1.3	Variation 3: From Other Carbonic Acid Derivatives	871
13.30.1.3.2.1.4	Variation 4: From Cyanates, Thiocyanates, and Their Derivatives	872
13.30.1.3.2.2	Method 2: From Carboxylic Acid Derivatives	874

13.30.1.3.2.2.1	Variation 1:	From Amides	874
13.30.1.3.2.2.2	Variation 2:	From Acid Chlorides	875
13.30.1.3.2.2.3	Variation 3:	From Imidoyl Chlorides	876
13.30.1.3.2.2.4	Variation 4:	From Other Carboxylic Acid Derivatives (Imidates, Thioimidates, and Amidines)	877
13.30.1.3.2.2.5	Variation 5:	From Nitriles	877
13.30.1.3.2.2.6	Variation 6:	From Nitrilium Salts	878
13.30.1.3.2.2.7	Variation 7:	From Isocyanides	880
13.30.1.3.2.2.8	Variation 8:	From Ketene <i>S,N</i> -Acetals	881
13.30.1.3.2.3	Method 3:	From Oximes	882
13.30.1.3.3	Fragments C—N—N and N—N		882
13.30.1.3.3.1	Method 1:	From Acylhydrazines and Aryldiazonium Salts	882
13.30.1.3.3.2	Method 2:	From Aldehyde Hydrazones and Azides	883
13.30.1.4	By Formation of One N—N Bond		884
13.30.1.4.1	Fragment N—N—C—N—N		884
13.30.1.4.1.1	Method 1:	From Formazanes	884
13.30.1.4.2	Fragment N—C—N—N—N		885
13.30.1.4.2.1	Method 1:	From α -Azidooximes	885
13.30.1.4.2.2	Method 2:	From <i>gem</i> -Diazides	885
13.30.1.4.2.3	Method 3:	From Hetaryltriazenes	886
13.30.1.5	By Formation of One N—C Bond		887
13.30.1.5.1	Fragment C—N—N—N—N		887
13.30.1.5.1.1	Method 1:	From Tetrazenes	887
13.30.2	Synthesis by Ring Transformation		887
13.30.2.1	Method 1:	From Azidoaziridines	887
13.30.2.2	Method 2:	From Isoxazoles and Isoxazolium Salts	888
13.30.2.3	Method 3:	From Oxazolones	888
13.30.2.4	Method 4:	From Triazoles and from Thiazotriazolamines	889
13.30.2.5	Method 5:	From 1,3,5-Triazines	890
13.30.3	Aromatization		890
13.30.4	Synthesis by Substituent Modification		891
13.30.4.1	Substitution of Existing Substituents		891
13.30.4.1.1	Of Hydrogen		891
13.30.4.1.1.1	Method 1:	Hydrogen–Deuterium Exchange	891
13.30.4.1.1.2	Method 2:	Metalation	891
13.30.4.1.1.3	Method 3:	Of Hydrogen at Nitrogen	891
13.30.4.1.1.4	Method 4:	By Carbon	892
13.30.4.1.1.5	Method 5:	By a Heteroatom (X, O, S, Se, N, and P)	894
13.30.4.1.2	Of Metals		894
13.30.4.1.2.1	Method 1:	By Deuterium	894
13.30.4.1.2.2	Method 2:	By Hydrogen	894
13.30.4.1.2.3	Method 3:	By Another Metal	895

13.30.4.1.2.4	Method 4: By Carbon	895
13.30.4.1.2.5	Method 5: By a Heteroatom	897
13.30.4.1.3	Of Carbon Functionalities	897
13.30.4.1.3.1	Nitrogen and Carbon Decarboxylation, Deacylation, and Dealkylation	897
13.30.4.1.4	Of Heteroatoms	898
13.30.4.1.4.1	Of Halogen	898
13.30.4.1.4.1.1	Method 1: By Hydrogen	898
13.30.4.1.4.1.2	Method 2: By Palladium at Carbon	899
13.30.4.1.4.1.3	Method 3: By Carbon at Carbon	899
13.30.4.1.4.1.4	Method 4: By Nitrogen	900
13.30.4.1.4.1.5	Method 5: By Fluorine at Carbon	901
13.30.4.1.4.1.6	Method 6: By Oxygen at Carbon	901
13.30.4.1.4.1.6.1	Variation 1: By Reaction with Phenols	901
13.30.4.1.4.1.6.2	Variation 2: By Reaction with Alcohols	902
13.30.4.1.4.1.7	Method 7: Of Chlorine by Sulfur or Selenium at Carbon	903
13.30.4.1.4.2	Of Other Functions	903
13.30.4.1.4.2.1	Method 1: Of Oxygen Functions	903
13.30.4.1.4.2.2	Method 2: Of Sulfur Functions	904
13.30.4.2	Addition Reactions	904
13.30.4.3	Rearrangements	905
13.30.4.3.1	Method 1: Dimroth Rearrangement	905
13.30.4.3.2	Method 2: N1 to N2 Isomerization	906
13.30.4.3.3	Method 3: Smiles Rearrangement	906
13.30.4.3.4	Method 4: Claisen-Type Rearrangement	907
13.30.4.3.5	Method 5: N1-Alkyl Group Rearrangement	908
13.31	Product Class 31: Pentazoles R. C. Storr	
13.31	Product Class 31: Pentazoles	917
13.31.1	Synthesis by Ring-Closure Reactions	919
13.31.1.1	By Formation of Two N–N Bonds	919
13.31.1.1.1	Method 1: From a Diazonium Salt and an Azide Ion	919
13.31.2	Synthesis by Substituent Modification	920
13.31.2.1	Method 1: Dearylation of <i>N</i> -Arylpentazoles	920
	Keyword Index	923
	Author Index	955
	Abbreviations	1005

