

Volume 41: Nitro, Nitroso, Azo, Azoxy, and Diazonium Compounds, Azides, Triazenes, and Tetrazenes

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
	Introduction	
	K. Banert	1
41.1	Product Class 1: Nitroalkanes	
	R. A. Aitken and K. M. Aitken	9
41.2	Product Class 2: Nitrosoalkanes and Nitroso Acetals (<i>N,N</i>-Dialkoxyamines)	
	H.-U. Reissig, B. Dugovič, and R. Zimmer	259
41.3	Product Class 3: <i>N</i>-Nitroamines	
	U. Jahn	371
41.4	Product Class 4: <i>N</i>-Nitrosoamines	
	M. M. K. Boysen	437
41.5	Product Class 5: Aliphatic Azoxy Compounds (Aliphatic Diazene Oxides)	
	M. M. K. Boysen	449
41.6	Product Class 6: Aliphatic Azo Compounds	
	S. Kempa, L. Wallach, and K. Rück-Braun	459
41.7	Product Class 7: Diazonium Compounds	
	S. Kubik	507
41.8	Product Class 8: Azidoalkanes	
	S. Bräse, B. Lesch, and V. Zimmermann	543
41.9	Product Class 9: Alkyltriazenes	
	N. Jung and S. Bräse	613
41.10	Product Class 10: Alkyltetrazenes	
	N. Jung and S. Bräse	641
41.11	Product Class 11: <i>N,N</i>-Dihaloamines	
	S. J. Collier and W. Xiang	651
	Keyword Index	681
	Author Index	721
	Abbreviations	765

Table of Contents

Introduction

K. Banert

Introduction	1
---------------------------	---

41.1 Product Class 1: Nitroalkanes

R. A. Aitken and K. M. Aitken

41.1 Product Class 1: Nitroalkanes	9
41.1.1 Synthesis of Product Class 1	9
41.1.1.1 Synthesis by Substitution	9
41.1.1.1.1 Method 1: Substitution of Hydrogen Using Nitric Acid	9
41.1.1.1.1.1 Variation 1: Using Dilute Nitric Acid	9
41.1.1.1.1.2 Variation 2: Using Concentrated or Fuming Nitric Acid	10
41.1.1.1.1.3 Variation 3: Using Nitric Acid with Sulfuric Acid	12
41.1.1.1.1.4 Variation 4: Using Nitric Acid with Acetic Acid	13
41.1.1.1.1.5 Variation 5: Using Nitric Acid in Ionic Liquids	13
41.1.1.1.1.6 Variation 6: Using Nitric Acid in the Gas Phase	13
41.1.1.1.1.7 Variation 7: Using Nitric Acid with Oxygen and Halogens in the Gas Phase	14
41.1.1.1.2 Method 2: Substitution of Hydrogen Using Metal Nitrates	15
41.1.1.1.2.1 Variation 1: Using Copper(II) or Manganese(II) Nitrates	15
41.1.1.1.2.2 Variation 2: Using Aluminum Trinitrate	15
41.1.1.1.3 Method 3: Substitution of Hydrogen Using Sulfuric Acid and Ammonium Nitrate	15
41.1.1.1.4 Method 4: Substitution of Hydrogen Using Nitrogen Dioxide	15
41.1.1.1.4.1 Variation 1: Without Additional Reagents	15
41.1.1.1.4.2 Variation 2: With Oxygen	16
41.1.1.1.4.3 Variation 3: With Hydrogen Peroxide	17
41.1.1.1.5 Method 5: Substitution of Hydrogen Using Sodium Nitrite and Silver(I) Nitrate	17
41.1.1.1.6 Method 6: Substitution of Hydrogen Using Alkyl Nitrites	17
41.1.1.1.6.1 Variation 1: Without Additional Reagents	17
41.1.1.1.6.2 Variation 2: With 3-Methylbutyl Nitrite and Butyllithium	18
41.1.1.1.7 Method 7: Substitution of Hydrogen Using Alkyl Nitrates with a Base	18
41.1.1.1.8 Method 8: Substitution of Hydrogen Using 2,4,6-Trichloro- <i>N</i> -nitroaniline	20
41.1.1.1.9 Method 9: Substitution of Lithium	20
41.1.1.1.10 Method 10: Substitution of Potassium	20
41.1.1.1.11 Method 11: Substitution of Magnesium	20
41.1.1.1.12 Method 12: Substitution of Mercury	21
41.1.1.1.13 Method 13: Substitution of a Carboxy Group	21

41.1.1.1.14	Method 14:	Substitution of a Cyano Group	22
41.1.1.1.15	Method 15:	Substitution of Chlorine Using Sodium Nitrite	22
41.1.1.1.15.1	Variation 1:	Without Additional Reagents	23
41.1.1.1.15.2	Variation 2:	With Urea	23
41.1.1.1.15.3	Variation 3:	With Benzene-1,3,5-triol	24
41.1.1.1.16	Method 16:	Substitution of Chlorine Using Potassium Nitrite	24
41.1.1.1.16.1	Variation 1:	In the Presence of a Base	24
41.1.1.1.16.2	Variation 2:	With Crown Ethers	25
41.1.1.1.17	Method 17:	Substitution of Chlorine Using Silver(I) Nitrite	25
41.1.1.1.17.1	Variation 1:	Without Additional Reagents	25
41.1.1.1.17.2	Variation 2:	With Urea	26
41.1.1.1.18	Method 18:	Substitution of Chlorine Using Mercury(I) Nitrite	27
41.1.1.1.19	Method 19:	Substitution of Chlorine Using Polymer-Supported Nitrite	27
41.1.1.1.20	Method 20:	Substitution of Bromine Using Sodium Nitrite	27
41.1.1.1.20.1	Variation 1:	Without Additional Reagents	27
41.1.1.1.20.2	Variation 2:	With Benzene-1,2-diol	29
41.1.1.1.20.3	Variation 3:	With Benzene-1,3,5-triol	29
41.1.1.1.20.4	Variation 4:	With Urea	31
41.1.1.1.20.5	Variation 5:	With Urea and Benzene-1,3,5-triol	32
41.1.1.1.20.6	Variation 6:	With a Phase-Transfer Catalyst	34
41.1.1.1.20.7	Variation 7:	With an Ionic Liquid	34
41.1.1.1.21	Method 21:	Substitution of Bromine Using Potassium Nitrite	34
41.1.1.1.22	Method 22:	Substitution of Bromine Using Silver(I) Nitrite	35
41.1.1.1.23	Method 23:	Substitution of Bromine Using Ammonium Nitrites	38
41.1.1.1.24	Method 24:	Substitution of Bromine Using Polymer-Supported Nitrite	39
41.1.1.1.25	Method 25:	Substitution of Iodine Using Sodium Nitrite	39
41.1.1.1.25.1	Variation 1:	Without Additional Reagents	40
41.1.1.1.25.2	Variation 2:	With Benzene-1,3,5-triol	41
41.1.1.1.25.3	Variation 3:	With Urea	41
41.1.1.1.25.4	Variation 4:	With Urea and Benzene-1,3,5-triol	42
41.1.1.1.26	Method 26:	Substitution of Iodine Using Silver(I) Nitrite	43
41.1.1.1.27	Method 27:	Substitution of Iodine Using Ammonium Nitrites	46
41.1.1.1.28	Method 28:	Substitution of Iodine Using Polymer-Supported Nitrite	46
41.1.1.1.29	Method 29:	Substitution of Sulfates	46
41.1.1.1.30	Method 30:	Substitution of Sulfonates	47
41.1.1.1.31	Method 31:	Substitution of Oxonium Tetrafluoroborates	48
41.1.1.1.32	Method 32:	Substitution of Nitrogen in Azo Compounds	48
41.1.1.2	Synthesis by Oxidation Reactions		49
41.1.1.2.1	Method 1:	Oxidation of a Primary Amino Group Using Caro's Acid	49
41.1.1.2.2	Method 2:	Oxidation of a Primary Amino Group Using Hypofluorous Acid	49
41.1.1.2.3	Method 3:	Oxidation of a Primary Amino Group Using Organic Peroxides	50
41.1.1.2.3.1	Variation 1:	Using Dimethyldioxirane	50
41.1.1.2.3.2	Variation 2:	Using <i>tert</i> -Butyl Hydroperoxide and Chromium Silicalite	52

41.1.1.2.3.3	Variation 3:	Using <i>tert</i> -Butyl Hydroperoxide and Zirconium(IV) <i>tert</i> -Butoxide	52
41.1.1.2.3.4	Variation 4:	Using Oxaziridinium Salts	53
41.1.1.2.4	Method 4:	Oxidation of a Primary Amino Group Using Organic Peroxy Acids	53
41.1.1.2.4.1	Variation 1:	Using Peracetic Acid	53
41.1.1.2.4.2	Variation 2:	Using 3-Chloroperoxybenzoic Acid	54
41.1.1.2.5	Method 5:	Oxidation of a Primary Amino Group Using Ozone	55
41.1.1.2.6	Method 6:	Oxidation of an Azido Group Using Hypofluorous Acid	56
41.1.1.2.7	Method 7:	Oxidation of an Azido Group Using Ozone and a Phosphine	57
41.1.1.2.8	Method 8:	Oxidation of a Hydroxyamino Group Using Nitric Acid	57
41.1.1.2.8.1	Variation 1:	Without Additional Reagents	57
41.1.1.2.8.2	Variation 2:	With Ammonium Nitrate	58
41.1.1.2.9	Method 9:	Oxidation of a Hydroxyamino Group Using Potassium Permanganate in Sulfuric Acid	58
41.1.1.2.10	Method 10:	Oxidation of a Nitroso Group Using Nitric Acid	59
41.1.1.2.10.1	Variation 1:	With Ammonium Nitrate	59
41.1.1.2.10.2	Variation 2:	With Acetic Acid	59
41.1.1.2.11	Method 11:	Oxidation of a Nitroso Group Using Hydrogen Peroxide	59
41.1.1.2.11.1	Variation 1:	Without Additional Reagents	59
41.1.1.2.11.2	Variation 2:	With Sulfuric Acid	59
41.1.1.2.12	Method 12:	Oxidation of a Nitroso Group Using Manganese(VII)	60
41.1.1.2.12.1	Variation 1:	Using Potassium Permanganate in Acetone	60
41.1.1.2.12.2	Variation 2:	Using Manganese(VII) Oxide	60
41.1.1.2.13	Method 13:	Oxidation of a Nitroso Group Using Chromium(VI)	60
41.1.1.2.13.1	Variation 1:	Using Chromium(VI) Oxide Alone	60
41.1.1.2.13.2	Variation 2:	Using Chromium(VI) Oxide and Acetic Acid	60
41.1.1.2.13.3	Variation 3:	Using Chromium(VI) Oxide with Acetic and Sulfuric Acids	61
41.1.1.2.14	Method 14:	Oxidation of a Nitroso Group Using Lead(IV) Oxide	62
41.1.1.2.15	Method 15:	Oxidation of a Nitroso Group Using Oxidizing Gases	62
41.1.1.2.15.1	Variation 1:	Using Air	62
41.1.1.2.15.2	Variation 2:	Using Oxygen	62
41.1.1.2.15.3	Variation 3:	Using Nitrogen Dioxide/Dinitrogen Tetroxide	62
41.1.1.2.16	Method 16:	Oxidation of a Nitroso Group Using Organic Peroxy Acids	63
41.1.1.2.16.1	Variation 1:	Using Trifluoroperoxyacetic Acid	63
41.1.1.2.16.2	Variation 2:	Using 3-Chloroperoxybenzoic Acid	63
41.1.1.2.17	Method 17:	Photochemical Oxidation of a Nitroso Group	64
41.1.1.2.18	Method 18:	Oxidation of a Nitroso Group Using Iodosylbenzene	64
41.1.1.2.19	Method 19:	Oxidation of an Oxime Group Using Nitric Acid	64
41.1.1.2.19.1	Variation 1:	Without Other Reagents	64
41.1.1.2.19.2	Variation 2:	With Sulfuric Acid	64
41.1.1.2.20	Method 20:	Oxidation of an Oxime Group Using Peroxysulfates	65
41.1.1.2.20.1	Variation 1:	Using Caro's Acid	65
41.1.1.2.20.2	Variation 2:	Using Oxone	65

41.1.1.2.21	Method 21:	Oxidation of an Oxime Group Using Hydrogen Peroxide with Urea and Methyltrioxorhenium(VII) Catalyst	66
41.1.1.2.22	Method 22:	Oxidation of an Oxime Group Using Lead(IV) Acetate	66
41.1.1.2.23	Method 23:	Oxidation of an Oxime Group with Potassium Permanganate	66
41.1.1.2.24	Method 24:	Oxidation of an Oxime Group with Sodium Perborate	67
41.1.1.2.25	Method 25:	Oxidation of an Oxime Group Using Organic Peroxy Acids	67
41.1.1.2.25.1	Variation 1:	Using Trifluoroperoxyacetic Acid	67
41.1.1.2.25.2	Variation 2:	Using 3-Chloroperoxybenzoic Acid	70
41.1.1.2.26	Method 26:	Oxidation of an Oxime Group Using Dinitrogen Tetroxide	71
41.1.1.2.27	Method 27:	Enzymatic Oxidation of an Oxime Group	71
41.1.1.3	Synthesis by Addition Reactions		71
41.1.1.3.1	Method 1:	Oxidative Nitrosation of an Oxime Group	72
41.1.1.3.2	Method 2:	Oxidative Nitration of an Oxime Using Nitric Acid	72
41.1.1.3.2.1	Variation 1:	Without Additional Reagents	72
41.1.1.3.2.2	Variation 2:	Followed by Hydrogen Peroxide	73
41.1.1.3.2.3	Variation 3:	With Acetic Acid, Followed by Hydrogen Peroxide	73
41.1.1.3.3	Method 3:	Oxidative Nitration of an Oxime Using Nitrogen Oxides	74
41.1.1.3.3.1	Variation 1:	Using Nitrogen Dioxide/Dinitrogen Tetroxide	74
41.1.1.3.3.2	Variation 2:	Using Nitrogen Dioxide and Magnesium Sulfate	74
41.1.1.3.3.3	Variation 3:	Using Dinitrogen Pentoxide	75
41.1.1.3.4	Method 4:	Oxidative Chlorination of an Oxime Using Chlorine	76
41.1.1.3.4.1	Variation 1:	Using Chlorine Followed by Ozone	76
41.1.1.3.4.2	Variation 2:	Using Chlorine with Hydrochloric, Nitric, and Acetic Acids	77
41.1.1.3.5	Method 5:	Oxidative Chlorination of an Oxime Using Sodium Hypochlorite	77
41.1.1.3.6	Method 6:	Oxidative Chlorination of an Oxime Using Sodium Chloride, Oxone, and Alumina	77
41.1.1.3.7	Method 7:	Oxidative Chlorination of an Oxime Using Hydrochloric Acid and Hydrogen Peroxide	78
41.1.1.3.8	Method 8:	Oxidative Bromination of an Oxime Using Sodium Hypobromite Followed by Nitric Acid	78
41.1.1.3.9	Method 9:	Oxidative Bromination of an Oxime Using <i>N</i> -Bromoacetamide	79
41.1.1.3.10	Method 10:	Oxidative Bromination of an Oxime Using <i>N</i> -Bromosuccinimide and Potassium Carbonate	80
41.1.1.3.11	Method 11:	Oxidative Bromination of an Oxime Using Sodium Bromide, Oxone, and Alumina	81
41.1.1.3.12	Method 12:	Oxidative Acetoxylation of an Oxime Using Lead(IV) Acetate, Hydrogen Peroxide, and Sodium Nitrite	81
41.1.1.3.13	Method 13:	Addition of Nitrous Acid to an Alkene	82
41.1.1.3.13.1	Variation 1:	Using Sodium Nitrite and Acetic Acid	82
41.1.1.3.13.2	Variation 2:	Using Sodium Nitrite and Hydrochloric Acid	82
41.1.1.3.14	Method 14:	Addition of Tetranitromethane to an Alkene	83

41.1.1.3.15	Method 15:	Nitrofluorination of an Alkene	84
41.1.1.3.15.1	Variation 1:	Using Nitric and Hydrofluoric Acids	84
41.1.1.3.15.2	Variation 2:	Using Nitryl Fluoride	85
41.1.1.3.15.3	Variation 3:	Using Nitronium Tetrafluoroborate and Pyridinium Fluoride	85
41.1.1.3.16	Method 16:	Nitrochlorination of an Alkene	86
41.1.1.3.16.1	Variation 1:	Using Nitrosyl Chloride	86
41.1.1.3.16.2	Variation 2:	Using Nitrosyl Chloride, Nitrogen Dioxide, and Oxygen	87
41.1.1.3.16.3	Variation 3:	Using Nitryl Chloride	88
41.1.1.3.16.4	Variation 4:	Using Nitrogen Dioxide and Boron Trifluoride	89
41.1.1.3.16.5	Variation 5:	Using Nitrogen Dioxide and Chlorine	89
41.1.1.3.16.6	Variation 6:	Using Nitrogen Dioxide, Phosphorus Trichloride, and Oxygen	90
41.1.1.3.17	Method 17:	Nitrobromination of an Alkene	90
41.1.1.3.17.1	Variation 1:	Using Sodium Nitrite, Mercury(II) Chloride, and Bromine	90
41.1.1.3.17.2	Variation 2:	Using Nitrosyl Bromide	91
41.1.1.3.17.3	Variation 3:	Using Nitrogen Dioxide and Bromine	92
41.1.1.3.17.4	Variation 4:	Using Nitrogen Dioxide, Phosphorus Tribromide, and Oxygen	92
41.1.1.3.18	Method 18:	Nitroiodination of an Alkene	92
41.1.1.3.18.1	Variation 1:	Using Silver(I) Nitrite and Iodine	92
41.1.1.3.18.2	Variation 2:	Using Nitrogen Dioxide and Iodine	93
41.1.1.3.19	Method 19:	Nitroacetamidation of an Alkene	94
41.1.1.3.20	Method 20:	Nitronitrosation of an Alkene (Synthesis of ψ -Nitrosites)	94
41.1.1.3.20.1	Variation 1:	Using Sodium Nitrite and Sulfuric Acid	95
41.1.1.3.20.2	Variation 2:	Using Sodium Nitrite and Hydrochloric Acid	96
41.1.1.3.20.3	Variation 3:	Using Sodium Nitrite and Acetic Acid	96
41.1.1.3.20.4	Variation 4:	Using Sodium Nitrite and Phosphoric Acid	97
41.1.1.3.20.5	Variation 5:	Using Nitric Oxide with Catalysts	97
41.1.1.3.20.6	Variation 6:	Using Nitric Oxide with Air	98
41.1.1.3.21	Method 21:	1,2-Dinitration of an Alkene	99
41.1.1.3.21.1	Variation 1:	Using Pentyl Nitrite and Acetic Acid	99
41.1.1.3.21.2	Variation 2:	Using Nitrogen Dioxide	99
41.1.1.3.21.3	Variation 3:	Using Nitrogen Dioxide and Oxygen	101
41.1.1.3.22	Method 22:	Nitrohydroxylation of an Alkene	101
41.1.1.3.22.1	Variation 1:	Using Nitric Acid	101
41.1.1.3.22.2	Variation 2:	Using Nitric and Sulfuric Acids	102
41.1.1.3.22.3	Variation 3:	Using Sodium Nitrite and Ammonium Cerium(IV) Nitrate	102
41.1.1.3.22.4	Variation 4:	Using Dinitrogen Trioxide	103
41.1.1.3.22.5	Variation 5:	Using Nitrogen Dioxide	103
41.1.1.3.22.6	Variation 6:	Using Organic Nitrating Agents	104
41.1.1.3.23	Method 23:	Nitromethoxylation of an Alkene Using Tetranitromethane and Methanol	105
41.1.1.3.24	Method 24:	Addition of a Nitro Group and a Nitrate Group to an Alkene	105

41.1.1.3.24.1	Variation 1:	Using Nitric Acid	105
41.1.1.3.24.2	Variation 2:	Using Nitrogen Dioxide and Oxygen	105
41.1.1.3.24.3	Variation 3:	Using Dinitrogen Pentoxide	106
41.1.1.3.25	Method 25:	Nitroacetoxylation of an Alkene	108
41.1.1.3.25.1	Variation 1:	Using Acetyl Nitrate	108
41.1.1.3.25.2	Variation 2:	Using Nitric and Sulfuric Acids Followed by Acetic Anhydride	109
41.1.1.3.26	Method 26:	Addition of a Nitro Group and a Perchlorate Group to an Alkene	109
41.1.1.3.27	Method 27:	Addition of a Nitro Group and an Ethyl Sulfate Group to an Alkene	110
41.1.1.3.28	Method 28:	Conversion of Alkenes into α -Nitro Ketones	110
41.1.1.3.28.1	Variation 1:	Using Nitrogen Dioxide and Oxygen in Dimethyl Sulfoxide	110
41.1.1.3.28.2	Variation 2:	Using Chlorotrimethylsilane, Silver(I) Nitrate, and Chromium(VI) Oxide	111
41.1.1.3.28.3	Variation 3:	Using Chlorotrimethylsilane, Silver(I) Nitrate, and Dimethyl Sulfoxide	112
41.1.1.3.29	Method 29:	Nitration of Silyl Enol Ethers	112
41.1.1.3.29.1	Variation 1:	Using Tetranitromethane	112
41.1.1.3.29.2	Variation 2:	Using Nitronium Ethyl Sulfate	113
41.1.1.3.30	Method 30:	Destructive Nitration	113
41.1.1.4	Synthesis by Rearrangement or Disproportionation		115
41.1.1.4.1	Method 1:	Rearrangement of Alkyl Nitrates	115
41.1.1.4.2	Method 2:	Disproportionation Reactions	116
41.1.1.5	Synthesis with Retention of the Nitro Group		116
41.1.1.5.1	Method 1:	Alkylation of Nitroalkanes with Alkyl Halides	117
41.1.1.5.1.1	Variation 1:	With Fluoroalkanes	117
41.1.1.5.1.2	Variation 2:	With Chloroalkanes	117
41.1.1.5.1.3	Variation 3:	With Bromoalkanes	119
41.1.1.5.1.4	Variation 4:	With Iodoalkanes	121
41.1.1.5.2	Method 2:	Alkylation of Nitroalkanes with Alkylammonium Salts	122
41.1.1.5.3	Method 3:	Alkylation of Nitroalkanes with Alkyl(phenyl)iodonium Reagents	122
41.1.1.5.4	Method 4:	Alkylation of Nitroalkanes with Alkyl Arenesulfonates	123
41.1.1.5.5	Method 5:	Alkylation of Nitroalkanes with Alkyl Aryl Sulfones	124
41.1.1.5.6	Method 6:	Alkylation of Nitroalkanes with Hydrates or Hemiacetals of Aldehydes	125
41.1.1.5.7	Method 7:	Alkylation of Nitroalkanes with Alkyl Azides	126
41.1.1.5.8	Method 8:	Alkylation of Nitroalkanes with an Alkyl Difluoromethyl Nitrite	126
41.1.1.5.9	Method 9:	Vinylation of Nitroalkanes	126
41.1.1.5.10	Method 10:	Arylation of Nitroalkanes	127
41.1.1.5.11	Method 11:	Allylation of Nitroalkanes	129
41.1.1.5.11.1	Variation 1:	Nucleophilic Substitution	129
41.1.1.5.11.2	Variation 2:	Palladium-Catalyzed Allylation	131

41.1.1.5.12	Method 12:	Reaction of Nitroalkyl Anions with Aldehydes and Ketones (Henry Reaction)	133
41.1.1.5.13	Method 13:	Aza-Henry Reaction	137
41.1.1.5.14	Method 14:	Reaction of Nitroalkyl Anions with Carboxylic and Carbonic Acid Derivatives	139
41.1.1.5.14.1	Variation 1:	With Acid Halides	139
41.1.1.5.14.2	Variation 2:	With Esters	140
41.1.1.5.14.3	Variation 3:	With Anhydrides	140
41.1.1.5.14.4	Variation 4:	With Carbonates	141
41.1.1.5.14.5	Variation 5:	With Carbamoyl Chlorides	141
41.1.1.5.14.6	Variation 6:	With Isatoic Anhydride	142
41.1.1.5.14.7	Variation 7:	With Benzotriazole Derivatives	142
41.1.1.5.15	Method 15:	Reaction of Nitroalkyl Anions with Reactive Alkenes Not Conjugated to a Carbonyl Group	143
41.1.1.5.16	Method 16:	Reaction of Nitroalkyl Anions with Alkylmercury Compounds	144
41.1.1.5.17	Method 17:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a Ketone	144
41.1.1.5.18	Method 18:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a Nitroalkane	145
41.1.1.5.19	Method 19:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a Malonate	146
41.1.1.5.20	Method 20:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a 3-Oxo Ester	147
41.1.1.5.21	Method 21:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a 1,3-Diketone	148
41.1.1.5.22	Method 22:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from a Nitrile	149
41.1.1.5.23	Method 23:	Substitution of Chlorine in α -Chloronitroalkanes by a Carbanion Prepared from an (Alkoxy-carbonyl)methyl Aryl Sulfone	149
41.1.1.5.24	Method 24:	Substitution of Chlorine in α -Chloronitroalkanes by an Alkynyllithium Reagent	149
41.1.1.5.25	Method 25:	Substitution of Chlorine in α -Chloronitroalkanes by an Organotin(IV) Reagent	150
41.1.1.5.26	Method 26:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a Nitroalkane	150
41.1.1.5.27	Method 27:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a Malonate	151
41.1.1.5.28	Method 28:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a Nitrile	151
41.1.1.5.29	Method 29:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a 3-Oxo Nitrile	152
41.1.1.5.30	Method 30:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a 2-Cyano Ester	152
41.1.1.5.31	Method 31:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from an α -Cyanoalkyl Sulfone	153

41.1.1.5.32	Method 32:	Substitution of Bromine in α -Bromonitroalkanes by a Carbanion Prepared from a Malononitrile	153
41.1.1.5.33	Method 33:	Substitution of Bromine in α -Bromonitroalkanes by an Organotin(IV) Reagent	153
41.1.1.5.34	Method 34:	Substitution of Iodine in α -Iodonitroalkanes by a Carbanion Prepared from a Nitroalkane	154
41.1.1.5.35	Method 35:	Substitution of an Arylsulfonyl Group or Arylsulfonyl Group in Nitroalkanes by Carbon Nucleophiles	154
41.1.1.5.36	Method 36:	Substitution of a Nitro Group in Geminal Dinitroalkanes by Carbon Nucleophiles	155
41.1.1.5.37	Method 37:	Dimerization of Nitroalkanes	157
41.1.1.5.37.1	Variation 1:	Starting from Nitroalkanes	157
41.1.1.5.37.2	Variation 2:	Starting from Halonitroalkanes	158
41.1.1.5.38	Method 38:	Decarboxylation of 2-Nitro Acids	160
41.1.1.5.39	Method 39:	Dehalogenation of α -Halonitroalkanes	161
41.1.1.5.39.1	Variation 1:	Using Potassium Hydroxide	161
41.1.1.5.39.2	Variation 2:	Using Sodium Borohydride	162
41.1.1.5.39.3	Variation 3:	Using Catalytic Hydrogenation	162
41.1.1.5.39.4	Variation 4:	Using Tributyltin Hydride	163
41.1.1.5.40	Method 40:	Desulfonylation of Nitro Sulfones	164
41.1.1.5.41	Method 41:	Catalytic Reduction of Nitroalkenes	164
41.1.1.5.42	Method 42:	Borohydride Reduction of Nitroalkenes	166
41.1.1.5.42.1	Variation 1:	Using Sodium Borohydride	166
41.1.1.5.42.2	Variation 2:	Using Lithium Borohydride	167
41.1.1.5.42.3	Variation 3:	Using Zinc Borohydride	167
41.1.1.5.42.4	Variation 4:	Using Sodium Trimethoxyborohydride	168
41.1.1.5.43	Method 43:	Reduction of Nitroalkenes with Lithium Aluminum Hydride	168
41.1.1.5.44	Method 44:	Enantioselective Reduction of Nitroalkenes with Silanes	169
41.1.1.5.45	Method 45:	Reduction of Nitroalkenes Using Biological and Biomimetic Reducing Agents	169
41.1.1.5.46	Method 46:	Hydrocyanation of a Nitroalkene Using Hydrogen Cyanide	170
41.1.1.5.47	Method 47:	Hydrocyanation of a Nitroalkene Using Potassium Cyanide	171
41.1.1.5.48	Method 48:	Addition to a Nitroalkene by Electrophilic Aromatic Substitution	172
41.1.1.5.49	Method 49:	Addition to a Nitroalkene Using a Carbanion Prepared from an Aldehyde	174
41.1.1.5.50	Method 50:	Addition to a Nitroalkene Using a Carbanion Prepared from a Ketone	176
41.1.1.5.51	Method 51:	Addition to a Nitroalkene Using a Carbanion Prepared from an Ester	179
41.1.1.5.52	Method 52:	Addition to a Nitroalkene Using a Carbanion Prepared from a Nitrile	181

41.1.1.5.53	Method 53:	Addition to a Nitroalkene Using a Carbanion Prepared from an Amide	182
41.1.1.5.54	Method 54:	Addition to a Nitroalkene Using a Carbanion Prepared from a 1,3-Diester	184
41.1.1.5.55	Method 55:	Addition to a Nitroalkene Using a Carbanion Prepared from a 1,3-Diketone	189
41.1.1.5.56	Method 56:	Addition to a Nitroalkene Using a Carbanion Prepared from a 3-Oxo Ester	191
41.1.1.5.57	Method 57:	Addition to a Nitroalkene Using a Carbanion Prepared from a 2-Cyano Ester	194
41.1.1.5.58	Method 58:	Addition to a Nitroalkene Using a Carbanion Prepared from a Dinitrile	195
41.1.1.5.59	Method 59:	Addition to a Nitroalkene Using a Carbanion Prepared from a Thioester	195
41.1.1.5.60	Method 60:	Addition to a Nitroalkene Using a Carbanion Prepared from a (2,2,6,6-Tetramethylpiperidin-1-yloxy-carbonyl)alkane	196
41.1.1.5.61	Method 61:	Addition to a Nitroalkene Using a Carbanion Prepared from a 1,3-Oxazine	196
41.1.1.5.62	Method 62:	Addition to a Nitroalkene Using a Silyl Enol Ether	197
41.1.1.5.63	Method 63:	Addition to a Nitroalkene Using Enamino Compounds	199
41.1.1.5.63.1	Variation 1:	Using Enamines	199
41.1.1.5.63.2	Variation 2:	Using Enamino Esters	201
41.1.1.5.63.3	Variation 3:	Using Enamino Ketones	202
41.1.1.5.63.4	Variation 4:	Using Enaminonitriles	203
41.1.1.5.64	Method 64:	Addition to a Nitroalkene Using Organosulfur Reagents	203
41.1.1.5.64.1	Variation 1:	Using Sulfones	203
41.1.1.5.64.2	Variation 2:	Using 1,3-Dithianes	204
41.1.1.5.64.3	Variation 3:	Using Sulfur Ylides	205
41.1.1.5.65	Method 65:	Addition to a Nitroalkene Using a Carbanion Prepared from an Isocyanide	205
41.1.1.5.66	Method 66:	Addition to a Nitroalkene Using a Carbanion Prepared from a Nitroalkane	206
41.1.1.5.67	Method 67:	Addition to a Nitroalkene Using a Carbanion Prepared from a 2-Nitro Ester	207
41.1.1.5.68	Method 68:	Addition to a Nitroalkene Using a Carbanion Prepared from an α -Cyano- α -nitro Ester	208
41.1.1.5.69	Method 69:	Addition to a Nitroalkene Using Organophosphorus Reagents	208
41.1.1.5.69.1	Variation 1:	Using Phosphonoacetate Esters	208
41.1.1.5.69.2	Variation 2:	Using Phosphorus Ylides	209
41.1.1.5.70	Method 70:	Addition to a Nitroalkene Using an Organolithium Reagent	210
41.1.1.5.71	Method 71:	Addition to a Nitroalkene Using an Organomagnesium Reagent	211
41.1.1.5.71.1	Variation 1:	Using Alkylmagnesium Chlorides	211
41.1.1.5.71.2	Variation 2:	Using Alkylmagnesium Bromides	212
41.1.1.5.71.3	Variation 3:	Using Alkylmagnesium Iodides	213

41.1.1.5.72	Method 72:	Addition to a Nitroalkene Using an Alkylsamarium(II) Bromide	214
41.1.1.5.73	Method 73:	Addition to a Nitroalkene Using an Alkylmanganese(II) Chloride	214
41.1.1.5.74	Method 74:	Addition to a Nitroalkene Using an Alkylcopper Reagent	215
41.1.1.5.74.1	Variation 1:	Using Alkylcoppers	215
41.1.1.5.74.2	Variation 2:	Using Halozinc Alkylcyanocuprates	215
41.1.1.5.74.3	Variation 3:	Using Alkylzinc Alkylcyanocuprates	216
41.1.1.5.75	Method 75:	Addition to a Nitroalkene Using an Organozinc Reagent	217
41.1.1.5.75.1	Variation 1:	Using Alkylzinc Chlorides	217
41.1.1.5.75.2	Variation 2:	Using Alkylzinc Bromides	218
41.1.1.5.75.3	Variation 3:	Using Dialkylzincs	218
41.1.1.5.76	Method 76:	Addition to a Nitroalkene Using an Arylboronic Acid	221
41.1.1.5.77	Method 77:	Addition to a Nitroalkene Using an Alkylaluminum Reagent	222
41.1.1.5.77.1	Variation 1:	Using Trialkylaluminums	222
41.1.1.5.77.2	Variation 2:	Using Tetraalkylaluminates	224
41.1.1.5.78	Method 78:	Addition to a Nitroalkene Using a Lithium Tetraalkylgallate	225
41.1.1.5.79	Method 79:	Addition to a Nitroalkene Using Triethoxy(phenyl)silane	225
41.1.1.5.80	Method 80:	Addition to a Nitroalkene Using a Tetraalkylstannane	226
41.1.1.5.81	Method 81:	Addition to a Nitroalkene Using Dialkyl Phosphites	226
41.1.1.5.82	Method 82:	[2 + 2]-Cycloaddition Reactions of Nitroalkenes	227
41.1.1.5.82.1	Variation 1:	With Another Nitroalkene	227
41.1.1.5.82.2	Variation 2:	With Enamines	228
41.1.1.5.82.3	Variation 3:	With Tetramethoxyethene	229
41.1.1.5.83	Method 83:	[3 + 2]-Cycloaddition Reactions of Nitroalkenes	229
41.1.1.5.83.1	Variation 1:	With Diazo Compounds	229
41.1.1.5.83.2	Variation 2:	With Methylene cyclopropanes	230
41.1.1.5.83.3	Variation 3:	With Azides	231
41.1.1.5.83.4	Variation 4:	With Azomethine Ylides	231
41.1.1.5.83.5	Variation 5:	With Enamino Ketones	231
41.1.1.5.83.6	Variation 6:	With Nitrones	232
41.1.1.5.84	Method 84:	[2 + 4]-Cycloaddition Reactions of Nitroalkenes with Dienes	232
41.1.1.5.85	Method 85:	Rearrangements in the Synthesis of Nitroalkanes from Other Nitro Compounds	238
41.1.1.5.85.1	Variation 1:	Baylis–Hillman Reaction	238
41.1.1.5.85.2	Variation 2:	Disproportionation	238
41.1.1.5.85.3	Variation 3:	Thio-Claisen Rearrangement	239
41.1.1.5.85.4	Variation 4:	Cope Rearrangement	239

41.2	Product Class 2: Nitrosoalkanes and Nitroso Acetals (<i>N,N</i>-Dialkoxyamines)	
	H.-U. Reissig, B. Dugovič, and R. Zimmer	
<hr/>		
41.2	Product Class 2: Nitrosoalkanes and Nitroso Acetals (<i>N,N</i>-Dialkoxyamines)	259
41.2.1	Synthesis of Product Class 2	259
41.2.1.1	Method 1: Substitution Reactions	259
41.2.1.1.1	Variation 1: Substitution of a Hydrogen Atom in Nonactivated Compounds	260
41.2.1.1.2	Variation 2: Substitution of a Hydrogen Atom in Halogenated Compounds	260
41.2.1.1.3	Variation 3: Substitution of a Hydrogen Atom in Acceptor-Substituted Compounds	261
41.2.1.1.4	Variation 4: Substitution of Other Functional Groups	263
41.2.1.1.5	Variation 5: Substitution of Metals	264
41.2.1.2	Method 2: Addition Reactions	265
41.2.1.2.1	Variation 1: Addition to Alkenes	265
41.2.1.2.2	Variation 2: Addition to Electron-Rich Aromatic Compounds	269
41.2.1.3	Method 3: Elimination Reactions and Pyrolysis	269
41.2.1.4	Method 4: Oxidation Reactions	272
41.2.1.4.1	Variation 1: Oxidation of Amines	272
41.2.1.4.2	Variation 2: Oxidation of Hydroxylamines	275
41.2.1.4.3	Variation 3: Oxidation of Cyclic Nitrogen Compounds	276
41.2.1.5	Method 5: Reduction of Nitroalkanes	280
41.2.1.6	Method 6: Photochemical Reactions	280
41.2.1.7	Method 7: Rearrangements	284
41.2.1.8	Method 8: Conversions of Oximes	285
41.2.1.9	Method 9: Derivatization of Stable Nitrosoalkanes	296
41.2.1.10	Method 10: Synthesis of Metal-Coordinated Nitrosoalkanes	299
41.2.1.11	Method 11: Synthesis of Nitroso Acetals	302
41.2.2	Applications of Product Class 2 in Organic Synthesis	308
41.2.2.1	Method 1: Oxidation to Nitroalkanes	308
41.2.2.2	Method 2: Reduction to Amines	311
41.2.2.3	Method 3: Formation of Oximes and Derivatives	316
41.2.2.3.1	Variation 1: Formation of Oximes	316
41.2.2.3.2	Variation 2: Formation of Oxime Ethers and Phosphates	323
41.2.2.3.3	Variation 3: Formation of Hydroxamic Acid Derivatives	325
41.2.2.4	Method 4: Synthesis of Compounds with an N=X Functionality (X = C, N, P)	327
41.2.2.4.1	Variation 1: Synthesis of Nitrones	327
41.2.2.4.2	Variation 2: Synthesis of Azoxy Compounds	327
41.2.2.4.3	Variation 3: Synthesis of Other N=X Compounds (Imines and Azo Compounds)	329
41.2.2.4.4	Variation 4: Synthesis of N=P Compounds	330
41.2.2.5	Method 5: Conversion into Nitrosoalkenes	331

41.2.2.6	Method 6:	Synthesis of Heterocycles	332
41.2.2.6.1	Variation 1:	Synthesis of Four-Membered Heterocycles	332
41.2.2.6.2	Variation 2:	Synthesis of Five-Membered Heterocycles	334
41.2.2.6.3	Variation 3:	Synthesis of Six-Membered Heterocycles	338
41.2.2.7	Method 7:	Synthesis of α -Carbonyl Hydroxylamines and <i>N</i> -Allyl Hydroxylamines	347
41.2.2.8	Method 8:	Reactions of Nitroso Acetals	352
41.3	Product Class 3: <i>N</i>-Nitroamines		
	U. Jahn		
41.3	Product Class 3: <i>N</i>-Nitroamines		371
41.3.1	Product Subclass 1: <i>N</i>-Alkyl-<i>N</i>-nitroamines		373
41.3.1.1	Synthesis of Product Subclass 1		373
41.3.1.1.1	Method 1:	Nitration of Amines with Cyanohydrin Nitrates	373
41.3.1.1.2	Method 2:	Nitration of Lithium Amides	374
41.3.1.1.3	Method 3:	Deacylation of <i>N</i> -Acyl- <i>N</i> -nitroamines and Related Reactions	374
41.3.1.1.3.1	Variation 1:	Of <i>N</i> -Nitrocarbamates	374
41.3.1.1.3.2	Variation 2:	Of <i>N</i> -Nitroureas	377
41.3.1.1.3.3	Variation 3:	Of <i>N</i> -Nitroguanidines	379
41.3.1.1.3.4	Variation 4:	Of <i>N</i> -Nitro Amides	381
41.3.1.1.3.5	Variation 5:	Of <i>N</i> -Nitro Sulfonamides	382
41.3.1.1.4	Method 4:	Substitution of <i>N,N</i> -Dichloroamines	383
41.3.1.1.5	Method 5:	Reduction of <i>N</i> -Nitroamines	384
41.3.1.1.6	Method 6:	Cleavage of Alkyl Groups in <i>N,N</i> -Dialkyl- <i>N</i> -nitroamines	386
41.3.2	Product Subclass 2: <i>N</i>-Aryl-<i>N</i>-nitroamines		387
41.3.2.1	Synthesis of Product Subclass 2		388
41.3.2.1.1	Method 1:	Nitration of Anilines	388
41.3.2.1.2	Method 2:	Nitration of Metal Anilides	395
41.3.2.1.3	Method 3:	Deacylation of <i>N</i> -Acyl- <i>N</i> -nitroanilines	395
41.3.2.1.4	Method 4:	Oxidation of (<i>E</i>)-Diazenolates	396
41.3.3	Product Subclass 3: <i>N</i>-Nitro-<i>N</i>-vinylamines		397
41.3.3.1	Synthesis of Product Subclass 3		397
41.3.3.1.1	Method 1:	Isomerization of <i>N</i> -Nitroamines	397
41.3.4	Product Subclass 4: <i>N,N</i>-Dialkyl-<i>N</i>-nitroamines		399
41.3.4.1	Synthesis of Product Subclass 4		399
41.3.4.1.1	Method 1:	Nitration of Amines	399
41.3.4.1.1.1	Variation 1:	Using Nitric Acid	399
41.3.4.1.1.2	Variation 2:	Using Dinitrogen Pentoxide or Dinitrogen Tetroxide	403
41.3.4.1.1.3	Variation 3:	Using Cyanohydrin Nitrates	404
41.3.4.1.1.4	Variation 4:	Using Mesitylcarbonyl Nitrate	405
41.3.4.1.1.5	Variation 5:	Using Nitronium Salts	405

41.3.4.1.1.6	Variation 6:	Using <i>N</i> -Methyl- <i>N,N</i> -dinitroamine	406
41.3.4.1.2	Method 2:	Nitrolysis of Amides	406
41.3.4.1.2.1	Variation 1:	Using Nitric Acid	406
41.3.4.1.2.2	Variation 2:	Using Dinitrogen Pentoxide	408
41.3.4.1.2.3	Variation 3:	Using Nitronium Salts	408
41.3.4.1.3	Method 3:	Nitration of Sulfamates	409
41.3.4.1.4	Method 4:	Substitution of <i>tert</i> -Butylamines	409
41.3.4.1.5	Method 5:	Nitroso Group Exchange by Nitration	410
41.3.4.1.6	Method 6:	Alkylation of <i>N</i> -Alkyl- <i>N</i> -nitroamines	411
41.3.4.1.6.1	Variation 1:	Using Alkyl, Allyl, and Benzyl Halides, Dimethyl Sulfate, Activated Alcohols, or Activated Amines	411
41.3.4.1.6.2	Variation 2:	Using Diazoalkanes	415
41.3.4.1.7	Method 7:	Radical Cyclizations of <i>N</i> -Alkyl- <i>N</i> -nitroamines	416
41.3.5	Product Subclass 5: <i>N</i>-Alkyl-<i>N</i>-aryl-<i>N</i>-nitroamines		417
41.3.5.1	Synthesis of Product Subclass 5		417
41.3.5.1.1	Method 1:	Nitration of <i>N</i> -Alkylanilines	417
41.3.5.1.2	Method 2:	Nitration of <i>N,N</i> -Dialkylanilines	422
41.4	Product Class 4: <i>N</i>-Nitrosoamines		
	M. M. K. Boysen		
41.4	Product Class 4: <i>N</i>-Nitrosoamines		437
41.4.1	Synthesis of Product Class 4		438
41.4.1.1	Formation of the N—N Bond		438
41.4.1.1.1	Method 1:	Nitrosation with Sodium Nitrite and Acids	438
41.4.1.1.1.1	Variation 1:	Nitrosation with Sodium Nitrite and Aqueous Acids	438
41.4.1.1.1.2	Variation 2:	Nitrosation with Sodium Nitrite and Solid Acids	439
41.4.1.1.2	Method 2:	Nitrosation with Nitrogen Oxides	439
41.4.1.1.3	Method 3:	Nitrosation with Nitrosyl Chloride	440
41.4.1.1.4	Method 4:	Nitrosation with Nitrosonium Tetrafluoroborate	441
41.4.1.1.5	Method 5:	Nitrosation with Alkyl Nitrites	442
41.4.1.1.6	Method 6:	Dealkylating Nitrosation of Tertiary Amines	443
41.4.1.2	Formation of C—C Bonds		443
41.4.1.2.1	Method 1:	α -Alkylation of <i>N</i> -Nitrosoamines	443
41.4.1.2.2	Method 2:	Alkylation of Diazenolates	445
41.4.1.3	Formation and Cleavage of N—O Bonds		446
41.4.1.3.1	Method 1:	Reduction of <i>N</i> -Nitroamines	446
41.4.1.3.2	Method 2:	Oxidation of 1,1-Disubstituted Hydrazines	446

41.5	Product Class 5: Aliphatic Azoxy Compounds (Aliphatic Diazene Oxides) M. M. K. Boysen	
41.5	Product Class 5: Aliphatic Azoxy Compounds (Aliphatic Diazene Oxides)	449
41.5.1	Synthesis of Product Class 5	450
41.5.1.1	Formation or Cleavage of N—O Bonds	450
41.5.1.1.1	Method 1: Oxidation of Diazenes	450
41.5.1.1.2	Method 2: Oxidation of Hydrazones	451
41.5.1.1.3	Method 3: Oxidation of Hydrazines	452
41.5.1.1.4	Method 4: Reduction of Dimeric Nitroso Compounds	452
41.5.1.2	Formation of the N=N Bond	452
41.5.1.2.1	Method 1: Condensation of Hydroxylamines with Dimeric Nitroso Compounds	452
41.5.1.2.2	Method 2: Condensation of <i>N,N</i> -Dihaloamines with Nitroso Compounds	454
41.5.1.2.3	Method 3: Oxidation of Hydroxylamines	455
41.5.1.3	Formation of the C—N Bond	455
41.5.1.3.1	Method 1: Alkylation of Diazenolates	455
41.6	Product Class 6: Aliphatic Azo Compounds S. Kempa, L. Wallach, and K. Rück-Braun	
41.6	Product Class 6: Aliphatic Azo Compounds	459
41.6.1	Synthesis by Formation of the N=N Bond	460
41.6.1.1	Method 1: Oxidative Coupling of Primary Amines	460
41.6.1.2	Method 2: Condensation of Nitrosoalkanes with Alkylamines	462
41.6.1.3	Method 3: Rearrangement of <i>N,N'</i> -Dialkylsulfamides	464
41.6.1.3.1	Variation 1: Rearrangement of <i>N,N'</i> -Dialkylureas	468
41.6.2	Synthesis from Compounds Containing an N—N Bond	469
41.6.2.1	Method 1: Oxidation of 1,2-Dialkylhydrazines	469
41.6.2.1.1	Variation 1: From Corresponding Ketazines	477
41.6.2.2	Method 2: 1,4-Elimination of α -Substituted Alkylhydrazones	478
41.6.2.3	Method 3: Reduction of Azoxy Compounds	481
41.6.2.4	Method 4: Oxidation of Alkylhydrazones	483
41.6.2.4.1	Variation 1: Oxidation with Lead(IV) Acetate	483
41.6.2.4.2	Variation 2: Oxidation with Peracetic Acid	484
41.6.2.4.3	Variation 3: Oxidation with (Diacetoxyiodo)benzene	485
41.6.2.4.4	Variation 4: Oxidation of Ketazines with Lead(IV) Acetate	486
41.6.2.5	Method 5: Alkylation of Alkylhydrazones	487
41.6.2.6	Method 6: Isomerization of Alkylhydrazones	491
41.6.2.7	Method 7: Hydrogenation of Ketazines	492
41.6.2.8	Method 8: Chlorination of Ketazines	492

41.6.2.9	Method 9: Ring Opening of Heterocycles	497
41.6.2.10	Method 10: [2,3]-Sigmatropic Rearrangement of 1-Alkyl-1-allyldiazenes and 1-Alkyl-1-propargyldiazenes	500
41.6.2.11	Method 11: Reactions of 2-Diazo 1,3-Diketones with CH-Acidic Compounds	501
41.6.3	Synthesis by Other Methods	502
41.7	Product Class 7: Diazonium Compounds S. Kubik	
41.7	Product Class 7: Diazonium Compounds	507
41.7.1	Product Subclass 1: Alkanediazonium Compounds	507
41.7.1.1	Synthesis of Product Subclass 1	509
41.7.1.1.1	Method 1: Synthesis from Primary Amines	509
41.7.1.1.1.1	Variation 1: With Nitrous Acid	509
41.7.1.1.1.2	Variation 2: With Disodium Pentacyanonitrosylferrate(III)	510
41.7.1.1.1.3	Variation 3: With Alkyl Nitrites	510
41.7.1.1.1.4	Variation 4: With Nitrosyl Chloride	511
41.7.1.1.1.5	Variation 5: With Dinitrogen Tetroxide	511
41.7.1.1.2	Method 2: Synthesis from Triazenes	511
41.7.1.1.3	Method 3: Synthesis from <i>N</i> -Nitrosoamides	512
41.7.1.1.3.1	Variation 1: By Thermolysis	512
41.7.1.1.3.2	Variation 2: By Alkali Cleavage	513
41.7.1.1.4	Method 4: Synthesis from Diazoalkanes	514
41.7.1.1.5	Method 5: Miscellaneous Methods	514
41.7.2	Product Subclass 2: Alkenediazonium Compounds	514
41.7.2.1	Synthesis of Product Subclass 2	517
41.7.2.1.1	Method 1: Synthesis from Diazoalkanes	517
41.7.2.1.2	Method 2: Synthesis from 2-Diazoacarbonyl Compounds	517
41.7.2.1.2.1	Variation 1: By O-Alkylation	518
41.7.2.1.2.2	Variation 2: By O-Sulfonylation or O-Benzoylation	520
41.7.2.1.3	Method 3: Synthesis from Hydrazones	521
41.7.2.1.3.1	Variation 1: From Aldehyde Hydrazones	522
41.7.2.1.3.2	Variation 2: From Ketone Hydrazones	524
41.7.2.1.4	Method 4: Synthesis from Alk-1-enyl Derivatives	525
41.7.2.1.4.1	Variation 1: From Enamines	525
41.7.2.1.4.2	Variation 2: From Alk-1-enyl Isocyanates	527
41.7.2.1.4.3	Variation 3: From Alk-1-enyltriazenes	528
41.7.2.1.4.4	Variation 4: From 1-(Tosylazo)alk-1-enes	529
41.7.2.1.5	Method 5: Synthesis from <i>N</i> -Nitrosooxazolidin-2-ones	529
41.7.2.1.6	Method 6: Synthesis from Other Alkenediazonium Compounds	531
41.7.2.2	Applications of Product Subclass 2 in Organic Synthesis	534
41.7.2.2.1	Method 1: Synthesis of Pyrazoles	534
41.7.2.2.2	Method 2: Synthesis of 1 <i>H</i> -1,2,3-Triazoles	535

41.7.2.2.3	Method 3:	Synthesis of 6 <i>H</i> -1,3,4-Oxadiazines and 1,3,4-Oxadiazoles	536
41.7.2.2.4	Method 4:	Synthesis of 2-Diazoimines	536
41.8	Product Class 8: Azidoalkanes		
	S. Bräse, B. Lesch, and V. Zimmermann		
41.8	Product Class 8: Azidoalkanes		
41.8.1	Synthesis of Product Class 8		
41.8.1.1	Method 1:	Synthesis from Benzyl Ethers or Related Compounds by Radical Substitution (C–H Activation)	543
41.8.1.2	Method 2:	Synthesis from Carboxylic Acids by Azidative Decarboxylation	544
41.8.1.3	Method 3:	Synthesis from Alkyl Halides by Radical Substitution	545
41.8.1.4	Method 4:	Synthesis by Nucleophilic Substitution of Alkyl Halides	545
41.8.1.4.1	Variation 1:	Classical Synthesis	545
41.8.1.4.2	Variation 2:	Asymmetric Synthesis	548
41.8.1.4.3	Variation 3:	1,3-Substitution in Allyl Halides	550
41.8.1.5	Method 5:	Synthesis by Nucleophilic Substitution of Alkyl Esters and Related Compounds	551
41.8.1.5.1	Variation 1:	Classical Synthesis	551
41.8.1.5.2	Variation 2:	Asymmetric Synthesis	554
41.8.1.6	Method 6:	Synthesis by Nucleophilic Substitution of Alkanols and Related Compounds	556
41.8.1.6.1	Variation 1:	Classical Synthesis	556
41.8.1.6.2	Variation 2:	Asymmetric Synthesis	560
41.8.1.7	Method 7:	Synthesis from Acetals	566
41.8.1.8	Method 8:	Synthesis by Ring Opening of Epoxides, Aziridines, and Related Compounds	567
41.8.1.8.1	Variation 1:	Classical Synthesis	567
41.8.1.8.2	Variation 2:	Asymmetric Synthesis	577
41.8.1.9	Method 9:	Electrophilic Azidation	578
41.8.1.10	Method 10:	Synthesis by Addition to C=C Bonds	580
41.8.1.10.1	Variation 1:	Nucleophilic Hydroazidation of C=C Bonds	580
41.8.1.10.2	Variation 2:	Electrophilic Hydroazidation of C=C Bonds	581
41.8.1.10.3	Variation 3:	Radical Hydroazidation of C=C Bonds	584
41.8.1.10.4	Variation 4:	Carboazidation of C=C Bonds	585
41.8.1.10.5	Variation 5:	Haloazidation of C=C Bonds	585
41.8.1.10.6	Variation 6:	Azidoselanylation of C=C Bonds	590
41.8.1.11	Method 11:	Synthesis by Addition to C=X Bonds	590
41.8.1.12	Method 12:	Synthesis from Amines by Nitrogen Transfer	590
41.8.1.13	Method 13:	Synthesis with Retention of Azide Functionality	591
41.8.2	Applications of Product Class 8 in Organic Synthesis		
41.8.2.1	Method 1:	Reactions with All-Carbon Functional Groups	594
41.8.2.1.1	Variation 1:	[3 + 2]-Cycloaddition Reactions	594

41.8.2.2	Method 2:	Hydrogenation and Reactions with Heteroatom-Containing Groups	595
41.8.2.2.1	Variation 1:	Reduction to Amines	595
41.8.2.2.2	Variation 2:	Schmidt and Boyer Reactions	598
41.8.2.2.3	Variation 3:	Staudinger Reductions	600
41.8.2.2.4	Variation 4:	Staudinger Ligations	602
41.8.2.2.5	Variation 5:	Aza-Wittig Reactions	603
41.8.2.2.6	Variation 6:	Miscellaneous Reactions	605

41.9 Product Class 9: Alkyltriazenes

N. Jung and S. Bräse

41.9	Product Class 9: Alkyltriazenes	613	
41.9.1	Synthesis of Product Class 9	614	
41.9.1.1	Method 1:	Alkylation of Alkyl Azides	614
41.9.1.1.1	Variation 1:	By Grignard Reagents	614
41.9.1.1.2	Variation 2:	By Lithium Reagents	615
41.9.1.2	Method 2:	Alkylation or Acylation of Aryl- or Alkyltriazenes	616
41.9.1.2.1	Variation 1:	Alkylation	616
41.9.1.2.2	Variation 2:	Acylation	616
41.9.1.3	Method 3:	Reaction of Arenediazonium Salts with Primary Amines	617
41.9.1.4	Method 4:	Reaction of Diazonium Salts with Secondary Amines	619
41.9.1.4.1	Variation 1:	Diazotization of Arylamines and Reaction with Secondary Amines	619
41.9.1.4.2	Variation 2:	Preparation of Bistriazenes of Secondary Amines	623
41.9.1.4.3	Variation 3:	Formation on Solid Supports	624
41.9.1.4.4	Variation 4:	Preparation of Imidazolyltriazenes	625
41.9.1.4.5	Variation 5:	Preparation of Indol-3-yltriazenes	625
41.9.1.4.6	Variation 6:	Preparation of Pyrrol-3-yltriazenes	626
41.9.1.4.7	Variation 7:	Preparation of Pyridyltriazenes	627
41.9.1.4.8	Variation 8:	Preparation of Pyrazolyltriazenes/Indazolyltriazenes	627
41.9.1.4.9	Variation 9:	Preparation of Acyl(alkyl)triazenes	628
41.9.1.5	Method 5:	Synthesis from <i>N'</i> -Alkyl- <i>N</i> -aryl- <i>N</i> -nitrosoareas	629
41.9.1.5.1	Variation 1:	With Primary Amines/Secondary Amines	629
41.9.1.5.2	Variation 2:	By Decomposition	629
41.9.1.6	Method 6:	Synthesis from Nitroso-Containing Compounds with Alkylhydrazines	630
41.9.1.7	Method 7:	Reaction of Arenediazonium Salts with Primary Amines and Formaldehyde	631
41.9.1.8	Method 8:	Reaction of Arenediazonium Salts with Diamines and Formaldehyde	632
41.9.1.9	Method 9:	Synthesis by Ring Opening of Cyclic Compounds	633
41.9.1.9.1	Variation 1:	Ring Opening of Triaziridines	633
41.9.1.9.2	Variation 2:	Ring Opening to 3-Alkyl-1-aryltriazenes	633
41.9.1.9.3	Variation 3:	Ring Opening of Spirocyclic Triazoles	634

41.9.1.9.4	Variation 4: Ring Opening of Benzotriazoles	634
41.9.2	Applications of Product Class 9 in Organic Synthesis	635
41.10	Product Class 10: Alkyltetrazenes N. Jung and S. Bräse	
<hr/>		
41.10	Product Class 10: Alkyltetrazenes	641
41.10.1	Product Subclass 1: Tetraz-1-enes	641
41.10.1.1	Synthesis of Product Subclass 1	641
41.10.1.1.1	Method 1: Reaction of 1,1-Dialkylhydrazines with Diazonium Chlorides	641
41.10.2	Product Subclass 2: Tetraz-2-enes	642
41.10.2.1	Synthesis of Product Subclass 2	642
41.10.2.1.1	Method 1: Symmetrical Oxidative Dimerization of Hydrazines	642
41.10.2.1.2	Method 2: Tetrazenes from <i>N</i> -Nitrosoamines	645
41.10.2.1.3	Method 3: Dimerization of Diazenes Generated from Amines	645
41.10.2.1.4	Method 4: Dimerization of Diazenes Generated from Hydrazones	646
41.10.2.1.5	Method 5: Synthesis of Unsymmetrical Tetrazenes	646
41.10.2.1.6	Method 6: Synthesis of Tetrazenes from Cyclic Precursors	647
41.10.2.1.7	Method 7: Synthesis of Vinyltetrazenes	648
41.11	Product Class 11: <i>N,N</i>-Dihaloamines S. J. Collier and W. Xiang	
<hr/>		
41.11	Product Class 11: <i>N,N</i>-Dihaloamines	651
41.11.1	Product Subclass 1: <i>N,N</i>-Difluoroamines	651
41.11.1.1	Synthesis of Product Subclass 1	653
41.11.1.1.1	Method 1: Direct Fluorination of Amines and Related Reactions	653
41.11.1.1.2	Method 2: Difluoroamination of Carbon Skeletons	655
41.11.1.1.2.1	Variation 1: With Tetrafluorohydrazine	655
41.11.1.1.2.2	Variation 2: With Difluoroamine and Related Reagents	659
41.11.1.1.3	Method 3: Other Methods	662
41.11.2	Product Subclass 2: <i>N,N</i>-Dichloroamines	663
41.11.2.1	Synthesis of Product Subclass 2	665
41.11.2.1.1	Method 1: Direct Chlorination of Amines	665
41.11.2.1.2	Method 2: Chlorination of Nitriles and Related Reactions	666
41.11.2.1.3	Method 3: Dichloroamination of Carbon Skeletons	668
41.11.2.1.4	Method 4: Other Methods	669
41.11.3	Product Subclass 3: <i>N,N</i>-Dibromoamines	669
41.11.3.1	Synthesis of Product Subclass 3	670
41.11.3.1.1	Method 1: Direct Bromination of Amines	670

41.11.3.1.2	Method 2: Halide Metathesis of <i>N,N</i> -Dichloroamines	670
41.11.3.1.3	Method 3: Other Methods	672
41.11.4	Product Subclass 4: <i>N,N</i>-Diiodoamines	672
41.11.4.1	Synthesis of Product Subclass 4	672
41.11.5	Product Subclass 5: <i>N</i>-Chloro-<i>N</i>-fluoroamines	673
41.11.5.1	Synthesis of Product Subclass 5	673
41.11.5.1.1	Method 1: Chlorofluorination of Nitriles	673
41.11.5.1.2	Method 2: Chlorofluorination of <i>N</i> -Fluoroimines	674
41.11.5.1.3	Method 3: Fluorination of <i>N</i> -Chloroaziridines	675
41.11.6	Product Subclass 6: <i>N</i>-Bromo-<i>N</i>-fluoroamines	675
41.11.6.1	Synthesis of Product Subclass 6	675
41.11.7	Product Subclass 7: <i>N</i>-Bromo-<i>N</i>-chloroamines	675
41.11.7.1	Synthesis of Product Subclass 7	676
	Keyword Index	681
	Author Index	721
	Abbreviations	765

