

Table of Contents

Introduction

E. Schaumann

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

35.1 Product Class 1: One Saturated Carbon–Chlorine Bond

35.1.1 Product Subclass 1: Chloroalkanes

E. Schaumann

35.1.1 Product Subclass 1: Chloroalkanes	15
---	----

35.1.1.1 Synthesis by Substitution of Hydrogen

J. Hartung

35.1.1.1 Synthesis by Substitution of Hydrogen	19
35.1.1.1.1 Alkanes and Cycloalkanes	21
35.1.1.1.1.1 Method 1: Reactions with Molecular Chlorine	21
35.1.1.1.1.2 Method 2: Reactions with Sulfuryl Chloride	23
35.1.1.1.1.3 Method 3: Reactions with Trichloromethanesulfonyl Chloride	24
35.1.1.1.1.4 Method 4: Reactions with Trichloromethanesulfonyl Chloride	25
35.1.1.1.1.5 Method 5: Chlorination Reagents Containing an O–Cl Bond	26
35.1.1.1.1.5.1 Variation 1: <i>tert</i>-Butyl Hypochlorite as Chlorine-Atom Donor	26
35.1.1.1.1.5.2 Variation 2: Chlorination with Chlorine Monoxide	26
35.1.1.1.1.6 Method 6: Reactions with Chloroamines	27
35.1.1.1.1.7 Method 7: Chlorination with Phosphorus Pentachloride	28
35.1.1.1.1.8 Method 8: Chlorination Reagents Containing an I–Cl Bond	28
35.1.1.1.1.8.1 Variation 1: (Dichloroiodo)benzene as Chlorine-Atom Donor	28
35.1.1.1.1.8.2 Variation 2: Iodine Trichloride as Chlorine-Atom Donor	29
35.1.1.1.1.9 Method 9: Chlorination with Carbon Tetrachloride in the Presence of Transition-Metal Carbonyl Complexes	29
35.1.1.1.2 Haloalkanes and Halocycloalkanes	30
35.1.1.1.2.1 Method 1: Reactions with Molecular Chlorine	30
35.1.1.1.3 Alcohols	31
35.1.1.1.3.1 Method 1: Reactions with Molecular Chlorine	31
35.1.1.1.3.2 Method 2: Reactions with Chloroamines	32
35.1.1.1.4 Ethers	32
35.1.1.1.4.1 Method 1: Reactions with Molecular Chlorine	32
35.1.1.1.4.2 Method 2: Reactions with Hypohalites	34
35.1.1.1.4.3 Method 3: Chlorination with (Dichloroiodo)arenes	35

35.1.1.1.4.4	Method 4: Reactions with Phosphorus Pentachloride	36
35.1.1.1.5	Aldehydes	36
35.1.1.1.5.1	Method 1: Reactions with Sulfuryl Chloride	36
35.1.1.1.5.2	Method 2: Reactions with <i>N</i> -Chlorosuccinimide	37
35.1.1.1.6	Ketones	37
35.1.1.1.6.1	Method 1: Reactions with Molecular Chlorine	37
35.1.1.1.6.2	Method 2: Reactions with Manganese(III) Acetate and Lithium Chloride	38
35.1.1.1.6.3	Method 3: Chlorination with Sulfuryl Chloride	39
35.1.1.1.7	Carboxylic Acids and Derivatives	39
35.1.1.1.7.1	Method 1: Reactions with Molecular Chlorine	39
35.1.1.1.7.2	Method 2: Reactions with Sulfuryl Chloride	41
35.1.1.1.7.3	Method 3: Reactions with Chloroamines	42
35.1.1.1.8	Amines	43
35.1.1.1.8.1	Method 1: Reactions with Molecular Chlorine	43
35.1.1.2	Synthesis by Substitution of Metals P. Margaretha	
35.1.1.2	Synthesis by Substitution of Metals	47
35.1.1.2.1	Method 1: Synthesis from Organo-Group 15 Derivatives	47
35.1.1.2.2	Method 2: Synthesis from Trialkylboranes	47
35.1.1.3	Synthesis by Substitution of Carbon Functionalities P. Margaretha	
35.1.1.3	Synthesis by Substitution of Carbon Functionalities	49
35.1.1.3.1	Method 1: Decarbonylation of Acyl Chlorides	49
35.1.1.3.2	Method 2: Chlorodecarboxylation of the Heavy Metal Salts of Carboxylic Acids	49
35.1.1.3.3	Method 3: Chlorodecarboxylation of Carboxylic Acids by Lead(IV) Acetate	50
35.1.1.3.3.1	Variation 1: Chlorodecarboxylation in the Presence of Lithium Chloride ...	51
35.1.1.3.3.2	Variation 2: Chlorodecarboxylation in the Presence of <i>N</i> -Chlorosuccinimide	52
35.1.1.3.4	Method 4: Chlorodecarboxylation of 1-(Acyloxy)pyridine-2(1 <i>H</i>)-thiones ..	53
35.1.1.4	Synthesis by Substitution of Other Halogens P. Margaretha	
35.1.1.4	Synthesis by Substitution of Other Halogens	59
35.1.1.4.1	Method 1: Substitution of Bromine	59
35.1.1.4.2	Method 2: Substitution of Bromine or Iodine	60

35.1.1.5 Synthesis by Substitution of Oxygen Functionalities

P. Margaretha

35.1.1.5	Synthesis by Substitution of Oxygen Functionalities	63
35.1.1.5.1	Method 1: Decarboxylation of Chloroformates	63
35.1.1.5.2	Method 2: Synthesis from Alkanesulfonates and a Source of Chloride Ion	64
35.1.1.5.2.1	Variation 1: Using Lithium Chloride	64
35.1.1.5.2.2	Variation 2: Using Sodium or Potassium Chloride	65
35.1.1.5.2.3	Variation 3: Using Calcium Chloride	65
35.1.1.5.2.4	Variation 4: Using Pyridinium Hydrochloride	66
35.1.1.5.2.5	Variation 5: Using Tetraalkylammonium Chlorides	66
35.1.1.5.3	Method 3: Synthesis from Alkyl Xanthates (O-Alkyldithiocarbonates) or from Thionocarbonates (O,O-Dialkylthiocarbonates)	67
35.1.1.5.4	Method 4: Replacement of an Alcoholic Hydroxy Group with Hydrogen Chloride or a Metal Halide	68
35.1.1.5.4.1	Variation 1: Using Hydrochloric Acid or Hydrogen Chloride	68
35.1.1.5.4.2	Variation 2: Using Sodium Chloride	69
35.1.1.5.4.3	Variation 3: Using Tin(IV) Chloride	70
35.1.1.5.5	Method 5: Replacement of an Alcoholic Hydroxy Group with Thionyl Chloride	70
35.1.1.5.5.1	Variation 1: In an Inert Solvent in the Absence of a Base	71
35.1.1.5.5.2	Variation 2: In the Absence of a Solvent	72
35.1.1.5.5.3	Variation 3: In the Presence of an Equimolar Amount of Pyridine	72
35.1.1.5.5.4	Variation 4: In the Presence of an Equimolar Amount of 1 <i>H</i> -Benzotriazole	73
35.1.1.5.5.5	Variation 5: In the Presence of Excess Triethylamine	74
35.1.1.5.6	Method 6: Replacement of an Alcoholic Hydroxy Group with Selenium Tetrachloride	75
35.1.1.5.7	Method 7: Replacement of an Alcoholic Hydroxy Group with Chlorides of Phosphoric Acid and Related Compounds	76
35.1.1.5.7.1	Variation 1: Using Phosphorus Pentachloride	76
35.1.1.5.7.2	Variation 2: Using Phosphoryl Chloride	77
35.1.1.5.8	Method 8: Replacement of an Alcoholic Hydroxy Group via Oxyphosphonium Intermediates	78
35.1.1.5.8.1	Variation 1: Using Triphenylphosphine and Tetrachloromethane	79
35.1.1.5.8.2	Variation 2: Using Triphenylphosphine/2,3-Dichloro-5,6-dicyanobenzo-1,4-quinone and a Quaternary Ammonium Chloride	81
35.1.1.5.8.3	Variation 3: Using Triphenylphosphine and Cyclic <i>N</i> -Chloroimides	82
35.1.1.5.8.4	Variation 4: Using Triphenylphosphine and Dichloroselenuranes	83
35.1.1.5.8.5	Variation 5: Using Triphenylphosphine, Diethyl Azodicarboxylate, and Zinc(II) Chloride	84
35.1.1.5.9	Method 9: Replacement of an Alcoholic Hydroxy Group with Acetyl Chloride	84
35.1.1.5.10	Method 10: Replacement of an Alcoholic Hydroxy Group with Chloromethylenedimethyliminium Chloride and Related Reagents	85
35.1.1.5.11	Method 11: Replacement of an Alcoholic Hydroxy Group with <i>tert</i> -Butyl Chloride in an Ionic Liquid	90

35.1.1.5.12	Method 12:	Replacement of an Alcoholic Hydroxy Group with Chlorotrimethylsilane	90
35.1.1.5.12.1	Variation 1:	In the Absence of Catalyst	90
35.1.1.5.12.2	Variation 2:	In the Presence of Selenium Dioxide	91
35.1.1.5.12.3	Variation 3:	In the Presence of Dimethyl Sulfoxide	91
35.1.1.5.12.4	Variation 4:	In the Presence of Bismuth(III) Chloride	92
35.1.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities P. Margaretha		
<hr/>			
35.1.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities		95
35.1.1.6.1	Method 1:	Chloroalkanes from Alkyl Phenyl Tellurides	95
35.1.1.7	Synthesis by Substitution of Nitrogen Functionalities P. Margaretha		
<hr/>			
35.1.1.7	Synthesis by Substitution of Nitrogen Functionalities		99
35.1.1.7.1	Method 1:	Synthesis from Primary Aliphatic Amines	99
35.1.1.7.2	Method 2:	Synthesis from Tertiary Aliphatic Amines	99
35.1.1.7.3	Method 3:	Synthesis from <i>N</i> -Alkyl-Substituted Amides	100
35.1.1.7.4	Method 4:	Synthesis from <i>N</i> -Alkyl- <i>N</i> -tosylhydrazines	100
35.1.1.8	Synthesis by Addition to π-Type C—C Bonds K.-M. Roy		
<hr/>			
35.1.1.8	Synthesis by Addition to π-Type C—C Bonds		103
35.1.1.8.1	Method 1:	Hydrochlorination of Alkynes or Allenes	103
35.1.1.8.1.1	Variation 1:	Preparation of 4-Chlorobuta-1,2-diene from But-1-en-3-yne	103
35.1.1.8.2	Method 2:	Hydrochlorination of Polyenes	104
35.1.1.8.2.1	Variation 1:	Conversion of Natural and Synthetic Rubbers	104
35.1.1.8.3	Method 3:	Hydrochlorination of 1,3-Dienes	104
35.1.1.8.3.1	Variation 1:	Using Hydrogen Chloride	104
35.1.1.8.3.2	Variation 2:	Synthesis of 1-Chloro-3-methylbut-2-ene Using Thionyl Chloride/Silica Gel	105
35.1.1.8.4	Method 4:	Hydrochlorination of Symmetrical Alkenes and Cycloalkenes	106
35.1.1.8.5	Method 5:	Hydrochlorination of Unsymmetrical Alkenes and Cycloalkenes (Markovnikov Addition)	106
35.1.1.8.5.1	Variation 1:	Synthesis with Aqueous Hydrogen Chloride	107
35.1.1.8.5.2	Variation 2:	Synthesis under Phase-Transfer Conditions	108
35.1.1.8.5.3	Variation 3:	Synthesis Using an Inorganic Support	108
35.1.1.8.6	Method 6:	Hydrochlorination of Unsymmetrical Alkenes and Cycloalkenes (anti-Markovnikov Addition)	108
35.1.1.8.6.1	Variation 1:	Synthesis via Hydroboration	109
35.1.1.8.6.2	Variation 2:	Synthesis via Hydroalumination	110
35.1.1.8.7	Method 7:	Enantioselective Hydrochlorination Reactions	110
35.1.1.8.8	Method 8:	Hydrochlorination of Methylenecyclopropanes	111

35.1.1.8.8.1	Variation 1: Synthesis with Hydrogen Chloride	111
35.1.1.8.8.2	Variation 2: Synthesis with Metal Chlorides	112
35.1.1.8.9	Method 9: Hydrochlorination of Cyclopropanes	112
35.1.1.8.10	Method 10: Carbochlorination	113
35.1.1.9	Synthesis from Other Chlorine Compounds H. Ulrich	
35.1.1.9	Synthesis from Other Chlorine Compounds	117
35.1.1.9.1	Method 1: Synthesis from Chloroalkynes by Hydrogenation	117
35.1.1.9.2	Method 2: Synthesis from Chloroalkenes	117
35.1.1.9.2.1	Variation 1: By Hydrogenation	117
35.1.1.9.2.2	Variation 2: By Polymerization	118
35.1.1.9.2.3	Variation 3: Coupling Reactions	120
35.1.1.9.2.4	Variation 4: [2 + 2]-Cycloaddition Reactions	120
35.1.1.9.2.5	Variation 5: [2 + 3]-Cycloaddition Reactions	125
35.1.1.9.2.6	Variation 6: [2 + 4]-Cycloaddition Reactions	126
35.1.1.9.3	Method 3: Synthesis from Chlorocarbenes	127
35.1.1.9.4	Method 4: Synthesis from Chloroalkanes	129
35.1.1.9.4.1	Variation 1: By Insertion of Methylene into C—Cl Bonds	129
35.1.1.9.4.2	Variation 2: Chloroalkylation Reactions	129
35.1.1.9.4.3	Variation 3: By Isomerization Reactions	130
35.1.1.9.4.4	Variation 4: Elimination of Benzeneseleninic Acid	130
35.1.2	Product Subclass 2: Propargylic Chlorides P. Margaretha	
35.1.2	Product Subclass 2: Propargylic Chlorides	133
35.1.2.1	Synthesis by Heteroatom Substitution	133
35.1.2.1.1	Synthesis by Deoxidative Halogenation of Ketones	133
35.1.2.1.1.1	Method 1: Addition of Chlorodimethylsilane to Ketones	133
35.1.2.1.2	Synthesis by Substitution of σ -Bonded Heteroatoms	134
35.1.2.1.2.1	Method 1: Synthesis from Propargylic Alcohols and Hydrochloric Acid	134
35.1.2.1.2.1.1	Variation 1: Chlorination Using Hydrochloric Acid, Calcium Chloride, Copper(I) Chloride, and Copper Metal	134
35.1.2.1.2.1.2	Variation 2: Chlorination Using Gaseous Hydrogen Chloride	135
35.1.2.1.2.2	Method 2: Synthesis from Propargylic Alcohols and Thionyl Chloride	136
35.1.2.1.2.3	Method 3: Synthesis from Propargylic Alcohols and 1-Chloro- <i>N,N</i> ,2-trimethylprop-1-en-1-amine	136

35.1.3 Product Subclass 3: Benzylic Chlorides

35.1.3.1 Synthesis by Substitution of Hydrogen

W. D. Pfeiffer

35.1.3.1	Synthesis by Substitution of Hydrogen	139
35.1.3.1.1	Method 1: Reaction with Chlorine under Irradiation	139
35.1.3.1.2	Method 2: Reaction with Chlorine and a Catalyst	141
35.1.3.1.3	Method 3: Reaction with Liquid Chlorine	142
35.1.3.1.4	Method 4: Reaction with Benzyltrimethylammonium Tetrachloroiodate	143
35.1.3.1.5	Method 5: Reaction with <i>tert</i> -Butyl Hypochlorite	144
35.1.3.1.6	Method 6: Reaction with Sulfuryl Chloride and a Catalyst	144
35.1.3.1.7	Method 7: Reaction with Benzenesulfonyl Chloride	146
35.1.3.1.8	Method 8: Reaction with Trichloromethanesulfonyl Chloride	147
35.1.3.1.9	Method 9: Reaction with <i>N</i> -Chlorosuccinimide	147
35.1.3.1.10	Method 10: Reaction with 1,3,5-Trichloro-1,3,5-triazine-2,4,6(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)-trione (Trichloroisocyanuric Acid)	149
35.1.3.1.11	Method 11: Reaction with Ammonium Cerium(IV) Nitrate–Lithium Chloride or Cobalt(III) Acetate–Lithium Chloride	149
35.1.3.1.12	Method 12: Reaction with Phosphorus Pentachloride	150
35.1.3.1.13	Method 13: Reaction with Phosphoryl Chloride	151
35.1.3.1.14	Method 14: Reaction with Trichloroacetyl Chloride, Chloroacetyl Chloride, Benzoyl Chloride, or Ethyl Chloroformate	151
35.1.3.1.15	Method 15: Reaction with Trichloromethyl Chloroformate or Bis(trichloromethyl) Carbonate	152

35.1.3.2 Synthesis by Substitution of Carbonyl Oxygen

W. D. Pfeiffer

35.1.3.2	Synthesis by Substitution of Carbonyl Oxygen	155
35.1.3.2.1	Method 1: Chloroalkylation with Aldehydes	155
35.1.3.2.1.1	Variation 1: Chloromethylation with Paraformaldehyde and Hydrogen Chloride	155
35.1.3.2.1.2	Variation 2: Chloromethylation with Formaldehyde and Hydrogen Chloride	158
35.1.3.2.1.3	Variation 3: Chloromethylation with 1,3,5-Trioxane	159
35.1.3.2.1.4	Variation 4: Chloroalkylation with Acetaldehyde	159
35.1.3.2.2	Method 2: Chloromethylation with Chloromethyl Methyl Ether or Bis(chloromethyl) Ether	160
35.1.3.2.3	Method 3: Chloromethylation with Methoxyacetyl Chloride and Aluminum Trichloride	161
35.1.3.2.4	Method 4: Chloromethylation with 1-Chloro-4-(chloromethoxy)butane or 1,4-Bis(chloromethoxy)butane	162
35.1.3.2.5	Method 5: Chloroalkylation of Arenecarbaldehydes Using Alkylboron Dichlorides in the Presence of Oxygen	162

35.1.3.3	Synthesis by Substitution of σ-Bonded Heteroatoms P. Margaretha	
<hr/>		
35.1.3.3	Synthesis by Substitution of σ-Bonded Heteroatoms	167
35.1.3.3.1	Benzylic Chlorides from Other Benzylic Halides	167
35.1.3.3.1.1	Method 1: Benzylic Chlorides from Benzylic Bromides Using Tin(IV) Chloride	167
35.1.3.3.2	Benzylic Chlorides from Benzylic Alcohols	167
35.1.3.3.2.1	Method 1: Synthesis Using Thionyl Chloride	168
35.1.3.3.2.2	Method 2: Synthesis Using 4-Toluenesulfonyl Chloride	168
35.1.3.3.2.3	Method 3: Synthesis Using Carbon Tetrachloride	169
35.1.3.3.2.4	Method 4: Synthesis Using Silica Chloride	169
35.1.3.3.2.5	Method 5: Synthesis Using Chlorotrimethylsilane	170
35.1.3.3.2.5.1	Variation 1: With Tellurium Dioxide	170
35.1.3.3.2.5.2	Variation 2: With Dimethyl Sulfoxide	171
35.1.3.3.3	Benzylic Chlorides from Benzylic Ethers	171
35.1.3.3.3.1	Method 1: Cleavage with Zinc and Acetyl Chloride	171
35.1.4	Product Subclass 4: Allylic Chlorides	
<hr/>		
35.1.4.1	Synthesis by Substitution of Hydrogen α to a C=C Bond W. D. Pfeiffer	
<hr/>		
35.1.4.1	Synthesis by Substitution of Hydrogen α to a C=C Bond	173
35.1.4.1.1	Method 1: Reaction with Chlorine	173
35.1.4.1.2	Method 2: Reaction with Hypochlorous Acid	174
35.1.4.1.3	Method 3: Reaction with Chlorine Monoxide	175
35.1.4.1.4	Method 4: Reaction with <i>tert</i> -Butyl Hypochlorite	176
35.1.4.1.5	Method 5: Reaction with <i>N</i> -Chloro- <i>N</i> -cyclohexylbenzenesulfonamide ..	177
35.1.4.1.6	Method 6: Reaction with <i>N</i> -Chlorosuccinimide	177
35.1.4.1.7	Method 7: Reaction with a Vilsmeier Reagent and Hydrogen Peroxide ..	178
35.1.4.1.8	Method 8: Synthesis by Electrochemical Chlorination	179
35.1.4.2	Synthesis by Substitution of σ-Bonded Heteroatoms P. Margaretha	
<hr/>		
35.1.4.2	Synthesis by Substitution of σ-Bonded Heteroatoms	181
35.1.4.2.1	Method 1: Allylic Chlorides from Other Allylic Halides	181
35.1.4.2.2	Method 2: Allylic Chlorides from Allylic Alcohols	181
35.1.4.2.2.1	Variation 1: With Thionyl Chloride	182
35.1.4.2.2.2	Variation 2: With Methanesulfonyl Chloride	182
35.1.4.2.2.3	Variation 3: With <i>N</i> -Chlorosuccinimide and Dimethyl Sulfide	183

35.1.4.2.2.4	Variation 4:	With Carbon Tetrachloride or Hexachloroacetone and Triphenylphosphine	183
35.1.4.2.2.5	Variation 5:	With 1-Chloro- <i>N,N</i> ,2-trimethylprop-1-enylamine	185
35.1.4.2.2.6	Variation 6:	With Chlorotrimethylsilane in the Presence of Bismuth(III) Chloride	186
35.1.4.2.2.7	Variation 7:	Allylic Chlorides from Allylic Phosphates	186
35.1.4.2.3	Method 3:	Allylic Chlorides from Allyloxybenzenes	187

35.1.5 **Product Subclass 5: 1-Chloro-*n*-Heteroatom-Functionalized Alkanes ($n \geq 2$) with Both Functions Formed Simultaneously**

35.1.5.1 **Synthesis by Addition across C=C Bonds**

R. Göttlich

35.1.5.1	Synthesis by Addition across C=C Bonds	189
35.1.5.1.1	Method 1: Chlorination of Arenes	189
35.1.5.1.2	Method 2: Chlorination of Alkenes	192
35.1.5.1.2.1	Variation 1: Using Chlorine	192
35.1.5.1.2.2	Variation 2: Using Sulfuryl Chloride	198
35.1.5.1.2.3	Variation 3: Using Other Reagents	200
35.1.5.1.3	Method 3: Bromochlorination of Alkenes	203
35.1.5.1.4	Method 4: Iodochlorination of Alkenes	206
35.1.5.1.5	Method 5: Fluorochlorination of Alkenes	208
35.1.5.1.6	Method 6: Oxychlorination of Alkenes	210
35.1.5.1.6.1	Variation 1: Intermolecular Addition	210
35.1.5.1.6.2	Variation 2: Intramolecular Cyclization	215
35.1.5.1.7	Method 7: Sulfochlorination of Alkenes	219
35.1.5.1.8	Method 8: Selenochlorination of Alkenes	223
35.1.5.1.9	Method 9: Tellurochlorination of Alkenes	227
35.1.5.1.10	Method 10: Aminochlorination of Alkenes	228
35.1.5.1.10.1	Variation 1: Intermolecular Additions	228
35.1.5.1.10.2	Variation 2: Intramolecular Cyclization	238
35.1.5.1.11	Method 11: Phosphochlorination of Alkenes	242

35.1.5.2 **Synthesis by Addition across C—O Bonds**

K. Rück-Braun and T. Freysoldt

35.1.5.2	Synthesis by Addition across C—O Bonds	251
35.1.5.2.1	Method 1: Hydrochlorination of Epoxides Using Hydrogen Chloride	251
35.1.5.2.2	Method 2: Hydrochlorination of Epoxides Using Elemental Chlorine	252
35.1.5.2.3	Method 3: Hydrochlorination of Epoxides Using Alkali Metal Chlorides	253
35.1.5.2.4	Method 4: Hydrochlorination of Epoxides Using Chloro(imido)metal Complexes	254
35.1.5.2.5	Method 5: Hydrochlorination of Epoxides Using Silicon Tetrachloride	254
35.1.5.2.5.1	Variation 1: Enantioselective Transformations and Desymmetrization	255

35.1.5.2.6	Method 6:	Hydrochlorination of Epoxides Using Trialkylchlorosilanes	256
35.1.5.2.7	Method 7:	Hydrochlorination of Epoxides Using Chloroorganostannanes	258
35.1.5.2.8	Method 8:	Hydrochlorination of Epoxides Using Organoaluminum Chlorides	259
35.1.5.2.9	Method 9:	Hydrochlorination of Epoxides Using Lithium Tetrachlorocuprate(II)	260
35.1.5.2.10	Method 10:	Hydrochlorination of Epoxides Using Niobium(V) Chloride	260
35.1.5.2.11	Method 11:	Hydrochlorination of Epoxides Using Titanium(IV) Chloride	261
35.1.5.2.12	Method 12:	Hydrochlorination of Epoxides Using Cerium(III) Chloride	262
35.1.5.2.13	Method 13:	Hydrochlorination of Epoxides Using Tetraalkylammonium Chlorides	262
35.1.5.2.14	Method 14:	Hydrochlorination of Epoxides Using Phosphorus Chlorides, Phosphonium Chlorides, Thionyl Chloride, and Related Compounds	263
35.1.5.2.15	Method 15:	Hydrochlorination of Epoxides Using Chlorocarbonylated Compounds	265
35.1.5.2.16	Method 16:	Hydrochlorination of Tetrahydrofurans and Other Cyclic Ethers	266
35.1.5.3	Synthesis by Addition across C—S Bonds		
	K. Rück-Braun and T. Freysoldt		
35.1.5.3	Synthesis by Addition across C—S Bonds		271
35.1.5.3.1	Method 1:	Hydrochlorination of Thiiranes Using Hydrogen Chloride	271
35.1.5.3.2	Method 2:	Hydrochlorination of Thiiranes by Reaction of Thiirane 1-Oxides with Chloro(organo)stannanes	271
35.1.5.3.3	Method 3:	Hydrochlorination of Thiiranes Using Chlorocarbonylated Compounds	272
35.1.5.3.4	Method 4:	Synthesis by Chlorination of Thiiranes	273
35.1.5.4	Synthesis by Addition across C—N Bonds		
	K. Rück-Braun and T. Freysoldt		
35.1.5.4	Synthesis by Addition across C—N Bonds		275
35.1.5.4.1	Method 1:	Hydrochlorination of Aziridines Using Hydrogen Chloride	275
35.1.5.4.2	Method 2:	Hydrochlorination of Aziridines Using Alkali Metal Chlorides	276
35.1.5.4.3	Method 3:	Hydrochlorination of Aziridines Using Other Metal Chlorides	277
35.1.5.4.4	Method 4:	Hydrochlorination of Aziridines Using Chlorotrimethylsilane	278
35.1.5.4.5	Method 5:	Hydrochlorination of Aziridines Using Activated Dimethylformamide Complexes	278
35.1.5.5	Synthesis by Addition across C—C Bonds		
	K. Rück-Braun and T. Freysoldt		
35.1.5.5	Synthesis by Addition across C—C Bonds		281
35.1.5.5.1	Method 1:	Chlorination of 1,1-Diacetylcyclopropane	281

35.2	Product Class 2: One Saturated Carbon–Bromine Bond	
<hr/>		
35.2.1	Product Subclass 1: Bromoalkanes E. Schaumann	
<hr/>		
35.2.1	Product Subclass 1: Bromoalkanes	283
35.2.1.1	Synthesis by Substitution of Hydrogen J. Hartung	
<hr/>		
35.2.1.1	Synthesis by Substitution of Hydrogen	287
35.2.1.1.1	Alkanes and Cycloalkanes	288
35.2.1.1.1.1	Method 1: Bromination with Bromine	288
35.2.1.1.1.2	Method 2: Reaction with <i>tert</i> -Butyl Hypobromite	290
35.2.1.1.1.3	Method 3: Brominating Reagents Containing a C–Br Bond	291
35.2.1.1.1.3.1	Variation 1: Carbon Tetrabromide as Bromine-Atom Donor	291
35.2.1.1.1.3.2	Variation 2: Bromotrichloromethane as Bromine-Atom Donor	291
35.2.1.1.2	Haloalkanes and Halocycloalkanes	292
35.2.1.1.2.1	Method 1: Bromination with Bromine	292
35.2.1.1.3	Aldehydes and Ketones	293
35.2.1.1.3.1	Method 1: Bromination with Bromine	293
35.2.1.1.3.2	Method 2: Reaction with Bromomalonates	294
35.2.1.1.4	Carboxylic Acids and Carboxylic Acid Derivatives	294
35.2.1.1.4.1	Method 1: Bromination with Bromine	294
35.2.1.1.4.2	Method 2: Bromination with <i>N</i> -Bromosuccinimide	295
35.2.1.1.5	Isocyanates and Isothiocyanates	296
35.2.1.1.5.1	Method 1: Bromination with <i>N</i> -Bromosuccinimide	296
35.2.1.1.6	Alkylboranes and Alkylsilanes	297
35.2.1.1.6.1	Method 1: Bromination with Bromine	297
35.2.1.1.6.2	Method 2: Bromination with <i>N</i> -Bromosuccinimide	298
35.2.1.1.7	Carbohydrates	298
35.2.1.1.7.1	Method 1: Bromination with Bromine	298
35.2.1.1.7.2	Method 2: Bromination with <i>N</i> -Bromosuccinimide	299
35.2.1.2	Synthesis by Substitution of Metals P. Margaretha	
<hr/>		
35.2.1.2	Synthesis by Substitution of Metals	301
35.2.1.2.1	Method 1: Bromoalkanes from Organo-Group 15 Derivatives	301
35.2.1.2.2	Method 2: Bromoalkanes from Trialkylboranes	301

35.2.1.3	Substitution of Carbon Functionalities		
	P. Margaretha		
<hr/>			
35.2.1.3	Substitution of Carbon Functionalities		303
35.2.1.3.1	Method 1:	Decarbonylation of Acyl Bromides	303
35.2.1.3.2	Method 2:	Bromodecarboxylation of Heavy-Metal Salts of Carboxylic Acids	303
35.2.1.3.2.1	Variation 1:	Bromodecarboxylation of Silver(I) Carboxylates	303
35.2.1.3.2.2	Variation 2:	Bromodecarboxylation of Thallium(I) Carboxylates	304
35.2.1.3.3	Method 3:	Bromodecarboxylation of Carboxylic Acids	305
35.2.1.3.3.1	Variation 1:	Bromodecarboxylation of Carboxylic Acids in the Presence of Mercury(II) Oxide	306
35.2.1.3.3.2	Variation 2:	Bromodecarboxylation of Carboxylic Acids with (Diacetoxyiodo)benzene and Bromine	306
35.2.1.3.4	Method 4:	Bromodecarboxylation of <i>N</i> -(Acyloxy)pyridine-2(1 <i>H</i>)-thiones	307
35.2.1.4	Synthesis by Substitution of Other Halogens		
	M. Braun		
<hr/>			
35.2.1.4	Synthesis by Substitution of Other Halogens		313
35.2.1.4.1	Method 1:	Substitution of Fluorine	313
35.2.1.4.1.1	Variation 1:	Reaction with Aqueous Hydrogen Bromide	313
35.2.1.4.1.2	Variation 2:	Reactions with Lewis Acids	314
35.2.1.4.2	Method 2:	Substitution of Chlorine	314
35.2.1.4.2.1	Variation 1:	Reaction of Chloroalkanes with Aqueous Hydrogen Bromide	315
35.2.1.4.2.2	Variation 2:	Reactions of Chloroalkanes with Gaseous Hydrogen Bromide in the Presence of Iron(III) Bromide	315
35.2.1.4.2.3	Variation 3:	Reactions of Chloroalkanes with Metal Bromides and a Phase-Transfer Catalyst	317
35.2.1.4.2.4	Variation 4:	Reactions of Chloroalkanes with Bromoalkanes in the Presence of Alkali Metal Bromides	318
35.2.1.4.3	Method 3:	Substitution of Iodine	320
35.2.1.4.3.1	Variation 1:	Reactions of Iodoalkanes with Bromine	320
35.2.1.4.3.2	Variation 2:	Reactions of Iodoalkanes with Hypervalent Iodo Compounds	320
35.2.1.4.3.3	Variation 3:	Reactions of Iodoalkanes with Bismuth(III) Bromide	321
35.2.1.5	Synthesis by Substitution of Oxygen Functionalities		
	M. Braun		
<hr/>			
35.2.1.5	Synthesis by Substitution of Oxygen Functionalities		323
35.2.1.5.1	Method 1:	Substitution of Acyloxy Groups in Carboxylic Esters	323
35.2.1.5.1.1	Variation 1:	Reaction of Carboxylic Esters with Hydrogen Bromide	323
35.2.1.5.1.2	Variation 2:	Reaction of Carboxylic Esters with Bromotrimethylsilane	324
35.2.1.5.1.3	Variation 3:	Reaction of Carboxylic Esters with Bromine and Phosphorus	325
35.2.1.5.1.4	Variation 4:	Reaction of Carboxylic Esters with Triphenylphosphine–Bromine	326

35.2.1.5.2	Method 2:	Substitution of Alcoholic Hydroxy Groups	326
35.2.1.5.2.1	Variation 1:	Reaction of Alcohols with Aqueous Hydrobromic Acid	326
35.2.1.5.2.2	Variation 2:	Reaction of Alcohols with Hydrobromic Acid/Sulfuric Acid ...	328
35.2.1.5.2.3	Variation 3:	Reaction of Alcohols with Gaseous Hydrogen Bromide	328
35.2.1.5.2.4	Variation 4:	Reaction of Alcohols with Phosphorus Tribromide	329
35.2.1.5.2.5	Variation 5:	Reaction of Alcohols with Polymer-Bound Phosphorus Tribromide	330
35.2.1.5.2.6	Variation 6:	Reaction of Alcohols with Phosphorus Tribromide and Pyridine	331
35.2.1.5.2.7	Variation 7:	Reaction of Alcohols with Triphenylphosphine–Bromine	331
35.2.1.5.2.8	Variation 8:	Reaction of Alcohols with Triphenylphosphine–Carbon Tetrabromide and Related Reagents	333
35.2.1.5.2.9	Variation 9:	Reaction of Alcohols with Triphenylphosphine– N-Bromosuccinimide	334
35.2.1.5.2.10	Variation 10:	Reaction of Alcohols with Triphenyl Phosphite–Bromine	335
35.2.1.5.2.11	Variation 11:	Reaction of Alcohols with Bromotrimethylsilane	335
35.2.1.5.2.12	Variation 12:	Preparation of Bromoalkanes from Alcohols by a Modified Mitsunobu Procedure	336
35.2.1.5.2.13	Variations 13:	Miscellaneous Reactions	337
35.2.1.5.3	Method 3:	Substitution of Alcohols with Isomerization	337
35.2.1.5.3.1	Variation 1:	Reaction of 1-Cyclopropylalkan-1-ols with Hydrogen Bromide	338
35.2.1.5.3.2	Variation 2:	Reaction of 1-Cyclopropylalkan-1-ols with Magnesium Bromide	339
35.2.1.5.3.3	Variation 3:	Reaction of 1-Cyclopropylalkan-1-ols with Bromotrimethylsilane–Zinc(II) Bromide	340
35.2.1.5.3.4	Variations 4:	Miscellaneous Reactions	341
35.2.1.5.4	Method 4:	Cleavage of Alkyl Ethers	341
35.2.1.5.4.1	Variation 1:	Reaction of Ethers with Hydrobromic Acid	341
35.2.1.5.4.2	Variation 2:	Reaction of Ethers with 9-Bromo-9-borabicyclo[3.3.1]nonane	342
35.2.1.5.5	Method 5:	Cleavage of Silyl Ethers	343
35.2.1.5.5.1	Variation 1:	Reaction of Silyl Ethers with Triphenylphosphine–Bromine	343
35.2.1.5.5.2	Variation 2:	Reaction of Silyl Ethers with Triphenylphosphine/ 2,4,4,6-Tetrabromocyclohexa-2,5-dienone	344
35.2.1.5.5.3	Variation 3:	Reaction of Silyl Ethers with Triphenylphosphine–Carbon Tetrabromide	345
35.2.1.5.5.4	Variation 4:	Reaction of Silyl Ethers with Boron Tribromide	346
35.2.1.5.6	Method 6:	Substitution of Sulfonyloxy Groups	347
35.2.1.5.6.1	Variation 1:	Reaction of Arenesulfonates with Metal Bromides	347
35.2.1.5.6.2	Variation 2:	Reaction of Methanesulfonates with Metal Bromides	349
35.2.1.5.6.3	Variations 3:	Miscellaneous Reactions	350

35.2.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities M. Braun	
<hr/>		
35.2.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities	355
35.2.1.6.1	Method 1: Preparation from Sulfides and Cyanogen Bromide or from Selenides and Bromine	355
35.2.1.7	Synthesis by Substitution of Nitrogen Functionalities M. Braun	
<hr/>		
35.2.1.7	Synthesis by Substitution of Nitrogen Functionalities	357
35.2.1.7.1	Method 1: Synthesis from Amines by the von Braun Reaction	357
35.2.1.7.2	Method 2: Synthesis from Amines via Diazonium Salts	358
35.2.1.8	Synthesis by Addition to π-Type C–C Bonds K.-M. Roy	
<hr/>		
35.2.1.8	Synthesis by Addition to π-Type C–C Bonds	361
35.2.1.8.1	Method 1: Hydrobromination of Alkynes or Allenes	362
35.2.1.8.2	Method 2: Hydrobromination of 1,3-Dienes	362
35.2.1.8.2.1	Variation 1: Using Hydrogen Bromide	362
35.2.1.8.2.2	Variation 2: Using Phosphorus Tribromide on Silica Gel	363
35.2.1.8.2.3	Variation 3: Via Hydrozirconation	363
35.2.1.8.3	Method 3: Hydrobromination of Symmetrical Alkenes and Cycloalkenes	364
35.2.1.8.4	Method 4: Hydrobromination of Unsymmetrical Alkenes (Markovnikov Addition)	364
35.2.1.8.4.1	Variation 1: Using Hydrogen Bromide	364
35.2.1.8.4.2	Variation 2: Using Phase-Transfer Conditions	365
35.2.1.8.4.3	Variation 3: Using an Inorganic Support	366
35.2.1.8.5	Method 5: Hydrobromination of Unsymmetrical Alkenes (anti-Markovnikov Addition)	367
35.2.1.8.5.1	Variation 1: Using Hydrogen Bromide and a Radical Source	367
35.2.1.8.5.2	Variation 2: Using Benzeneselenenyl Bromide and Hydrogen Peroxide ..	368
35.2.1.8.5.3	Variation 3: Via Hydroboration	369
35.2.1.8.5.4	Variation 4: Via Hydroalumination	369
35.2.1.8.5.5	Variation 5: Via Hydrozirconation	370
35.2.1.8.6	Method 6: Asymmetric Hydrobromination of Functionalized Alkenes ..	370
35.2.1.8.7	Method 7: Hydrobromination of Methylene-cyclopropanes	371
35.2.1.8.7.1	Variation 1: Using Hydrogen Bromide	371
35.2.1.8.7.2	Variation 2: Using Titanium(IV) Bromide	371
35.2.1.8.8	Method 8: Hydrobromination of Cyclopropanes	372
35.2.1.8.9	Method 9: Carbobromination	373
35.2.1.8.9.1	Variation 1: Bromocyclization	374

35.2.1.9	Synthesis from Other Bromo Compounds	
	H. Ulrich	
<hr/>		
35.2.1.9	Synthesis from Other Bromo Compounds	379
35.2.1.9.1	Method 1: Synthesis from Bromoalkynes by Hydrogenation	379
35.2.1.9.2	Method 2: Synthesis from Bromoalkenes	379
35.2.1.9.2.1	Variation 1: By Hydrogenation	379
35.2.1.9.2.2	Variation 2: By Polymerization	380
35.2.1.9.2.3	Variation 3: By Cycloaddition Reactions	380
35.2.1.9.3	Method 3: Synthesis from Bromocarbenes	383
35.2.1.9.4	Method 4: Synthesis from Bromoalkanes	384
35.2.1.9.4.1	Variation 1: By Insertion of Methylene into Carbon–Halogen Bonds	384
35.2.1.9.4.2	Variation 2: By Bromoalkylation	384
35.2.1.9.4.3	Variation 3: By Isomerization Reactions	384
35.2.2	Product Subclass 2: Propargylic Bromides	
	M. Braun	
<hr/>		
35.2.2	Product Subclass 2: Propargylic Bromides	387
35.2.2.1	Synthesis by Heteroatom Substitution	387
35.2.2.1.1	Method 1: Substitution of Hydroxy Groups	387
35.2.2.1.2	Method 2: Substitution of Sulfonyloxy Groups	389
35.2.3	Product Subclass 3: Benzylic Bromides	
<hr/>		
35.2.3.1	Synthesis by Substitution of Hydrogen	
	W. D. Pfeiffer	
<hr/>		
35.2.3.1	Synthesis by Substitution of Hydrogen	391
35.2.3.1.1	Method 1: Reaction with Bromine	391
35.2.3.1.1.1	Variation 1: Reaction with Bromine in the Absence of a Catalyst	391
35.2.3.1.1.2	Variation 2: Reaction with Bromine in the Presence of a Catalyst	393
35.2.3.1.2	Method 2: Reaction with Copper(II) Bromide	395
35.2.3.1.3	Method 3: Reaction with Sodium Bromide and Hydrogen Peroxide	396
35.2.3.1.4	Method 4: Reaction with Ammonium Cerium(IV) Nitrate/Bromide or Cobalt(III) Acetate/Bromide	397
35.2.3.1.5	Method 5: Reaction with <i>N</i> -Bromosuccinimide	398
35.2.3.1.6	Method 6: Reaction with Ammonium-Type Bromides	402
35.2.3.1.6.1	Variation 1: Reaction with a Bromine Complex of Poly(styrene-co-4-vinylpyridine)	402
35.2.3.1.6.2	Variation 2: Reaction with Pyridinium Tribromide	403
35.2.3.1.6.3	Variation 3: Reaction with 3-Methylimidazolium Tribromide	404
35.2.3.1.7	Method 7: Reaction with Trichloromethanesulfonyl Bromide	405
35.2.3.1.8	Method 8: Reaction with Bromotrichloromethane	406

35.2.3.1.9	Method 9:	Reaction with Carbon Tetrabromide	406
35.2.3.1.10	Method 10:	Reaction with 4-Bromo-2,4,6-tri- <i>tert</i> -butylhexa-2,5-dienone	407
35.2.3.2	Synthesis by Substitution of Carbonyl Oxygen		
	W. D. Pfeiffer		
<hr/>			
35.2.3.2	Synthesis by Substitution of Carbonyl Oxygen		409
35.2.3.2.1	Method 1:	Bromomethylation of Arenes	409
35.2.3.2.1.1	Variation 1:	Using Paraformaldehyde and Hydrogen Bromide	409
35.2.3.2.1.2	Variation 2:	Using Paraformaldehyde, Hydrogen Bromide, and Ultrasound	411
35.2.3.2.1.3	Variation 3:	Using 1,3,5-Trioxane and Hydrogen Bromide	412
35.2.3.2.2	Method 2:	Alkylation of Arenes with 1,2-Dibromo-1-ethoxyethane	413
35.2.3.2.3	Method 3:	Alkylation of Arenes with 1-(Bromomethoxy)-4-chlorobutane or 1,4-Bis(bromomethoxy)butane	413
35.2.3.2.4	Method 4:	Bromoalkylation of Arenealdehydes Using Alkylboron Dibromides	414
35.2.3.3	Synthesis by Substitution of σ-Bonded Heteroatoms		
	M. Braun		
<hr/>			
35.2.3.3	Synthesis by Substitution of σ-Bonded Heteroatoms		417
35.2.3.3.1	Method 1:	Substitution of Other Halogens	417
35.2.3.3.2	Method 2:	Substitution of Oxygen Functionalities	418
35.2.4	Product Subclass 4: Allylic Bromides		
<hr/>			
35.2.4.1	Synthesis by Substitution of Hydrogen α to a C=C Bond		
	W. D. Pfeiffer		
<hr/>			
35.2.4.1	Synthesis by Substitution of Hydrogen α to a C=C Bond		423
35.2.4.1.1	Method 1:	Allylic Bromination Using Bromine	423
35.2.4.1.2	Method 2:	Allylic Bromination Using <i>N</i> -Bromosuccinimide	424
35.2.4.1.2.1	Variation 1:	Reactions with Aliphatic and Alicyclic Alkenes	424
35.2.4.1.2.2	Variation 2:	Reactions with Unsaturated Esters, Nitriles, and Heterocycles	427
35.2.4.1.2.3	Variation 3:	Reaction with Allyl(trimethyl)silane	429
35.2.4.1.2.4	Variation 4:	Reactions with Isoprenoids	430
35.2.4.1.2.5	Variation 5:	Reactions with Steroids	431
35.2.4.1.3	Method 3:	Reactions with Halogenated <i>N</i> -Bromoacetamides	432

35.2.4.2	Synthesis by Substitution of σ-Bonded Heteroatoms		
	M. Braun		
<hr/>			
35.2.4.2	Synthesis by Substitution of σ-Bonded Heteroatoms		435
35.2.4.2.1	Method 1:	Substitution of Other Halogens	435
35.2.4.2.2	Method 2:	Substitution of Oxygen Functionalities	435
35.2.5	Product Subclass 5: 1-Bromo-n-Heteroatom-Functionalized Alkanes (n \geq 2) with Both Functions Formed Simultaneously		
<hr/>			
35.2.5.1	Synthesis by Addition across C=C Bonds		
	T. Troll		
<hr/>			
35.2.5.1	Synthesis by Addition across C=C Bonds		439
35.2.5.1.1	Method 1:	Bromination of Aromatic Compounds	440
35.2.5.1.2	Method 2:	Bromination of 1,3-Dienes	441
35.2.5.1.3	Method 3:	Bromination of Alkenes	445
35.2.5.1.3.1	Variation 1:	Bromination with Bromine–Amine Complexes	464
35.2.5.1.3.2	Variation 2:	Generation of Electrophilic Bromine by In Situ Oxidation of Bromide	465
35.2.5.1.4	Method 4:	Hydroxy- and Alkoxybromination of Alkenes	471
35.2.5.1.5	Method 5:	Sulfobromination of Alkenes	484
35.2.5.1.6	Method 6:	Aminobromination of Alkenes	485
35.2.5.1.7	Method 7:	Azidobromination of Alkenes	492
35.2.5.1.8	Method 8:	Phosphobromination of Alkenes	493
35.2.5.2	Synthesis by Addition across C–O Bonds		
	K. Rück-Braun and T. Freysoldt		
<hr/>			
35.2.5.2	Synthesis by Addition across C–O Bonds		503
35.2.5.2.1	Method 1:	Hydrobromination of Epoxides Using Hydrogen Bromide	504
35.2.5.2.2	Method 2:	Hydrobromination of Epoxides Using Elemental Bromine	505
35.2.5.2.3	Method 3:	Hydrobromination of Epoxides Using Alkali Metal Bromides	506
35.2.5.2.3.1	Variation 1:	Catalyzed by Lewis Acids	508
35.2.5.2.4	Method 4:	Hydrobromination of Epoxides Using Magnesium Bromide	508
35.2.5.2.5	Method 5:	Hydrobromination of Epoxides Using Tin(II) Bromide	510
35.2.5.2.6	Method 6:	Hydrobromination of Epoxides Using Bromo(imido)metal Complexes	510
35.2.5.2.7	Method 7:	Enantioselective Hydrobromination of Epoxides Using Azidotrialkylsilanes and Allyl Bromide	511
35.2.5.2.8	Method 8:	Hydrobromination of Epoxides Using Boron Bromides	512
35.2.5.2.8.1	Variation 1:	Enantioselective Transformations	513
35.2.5.2.9	Method 9:	Hydrobromination of Epoxides Using Lithium Tetrabromocuprate(II)	513

35.2.5.2.10	Method 10:	Hydrobromination of Epoxides Using Lithium Tetrabromonickelate(II)	514
35.2.5.2.11	Method 11:	Hydrobromination of Epoxides Using Ammonium Bromides	514
35.2.5.2.12	Method 12:	Hydrobromination of Epoxides Using Phosphorus Tribromide or Phosphonium Bromides	515
35.2.5.2.13	Method 13:	Hydrobromination of Tetrahydrofurans and Oxetanes	518
35.2.5.3	Synthesis by Addition across C–S Bonds		
	K. Rück-Braun and T. Freysoldt		
35.2.5.3	Synthesis by Addition across C–S Bonds		523
35.2.5.3.1	Method 1:	Hydrobromination of Thiiranes Using Methanesulfonyl Bromide	523
35.2.5.3.2	Method 2:	Hydrobromination of Thiiranes Using Bromo(organo)stannanes	523
35.2.5.3.3	Method 3:	Synthesis by Bromination of Thiiranes	524
35.2.5.4	Synthesis by Addition across C–N Bonds		
	K. Rück-Braun and T. Freysoldt		
35.2.5.4	Synthesis by Addition across C–N Bonds		527
35.2.5.4.1	Method 1:	Hydrobromination of Aziridines Using Hydrogen Bromide ...	527
35.2.5.4.2	Method 2:	Hydrobromination of Aziridines Using Alkali Metal Bromides	528
35.2.5.4.3	Method 3:	Hydrobromination of Aziridines Using Other Metal Bromides	529
35.2.5.4.4	Method 4:	Hydrobromination of Aziridines Using Tetraalkylammonium Bromides	531
35.2.5.4.5	Method 5:	Hydrobromination of Aziridines with Bromotrimethylsilane	532
35.2.5.4.6	Method 6:	Hydrobromination of Aziridines Using Activated Dimethylformamide Complexes	532
35.2.5.4.7	Method 7:	Hydrobromination of Aziridines Using Benzyl Bromides	533
35.2.5.5	Synthesis by Addition across C–C Bonds		
	K. Rück-Braun and T. Freysoldt		
35.2.5.5	Synthesis by Addition across C–C Bonds		535
35.2.5.5.1	Method 1:	Bromination of Pentafluoro(vinyl)cyclopropanes	535
35.3	Product Class 3: One Saturated Carbon–Iodine Bond		
35.3.1	Product Subclass 1: Iodoalkanes		
	E. Schaumann		
35.3.1	Product Subclass 1: Iodoalkanes		537

35.3.1.1	Synthesis by Substitution of Hydrogen J. Hartung	
<hr/>		
35.3.1.1	Synthesis by Substitution of Hydrogen	541
35.3.1.1.1	Method 1: Alkane Functionalization in the Presence of Polyiodomethanes and Sodium Hydroxide	542
35.3.1.1.2	Method 2: Alkane Functionalization in the Presence of Nonafluoro-1-iodobutane	543
35.3.1.1.3	Method 3: Alkane Functionalization in the Presence of <i>tert</i> -Butyl Hypoiodite	544
35.3.1.1.4	Method 4: Alkane Functionalization in the Presence of Iodine and (Diacetoxyiodo)benzene in Alcohols	545
35.3.1.1.5	Method 5: Alkane Functionalization with Iodine in the Presence of Aluminum Triiodide and Tetrahalomethanes	546
35.3.1.2	Synthesis by Substitution of Metals S. Härtinger and M. Härtinger	
<hr/>		
35.3.1.2	Synthesis by Substitution of Metals	549
35.3.1.2.1	Method 1: Synthesis from Compounds of the Alkali or Alkaline Earth Metals	549
35.3.1.2.2	Method 2: Synthesis from Organomercury Compounds	553
35.3.1.2.3	Method 3: Synthesis from Organozinc Reagents	555
35.3.1.2.4	Method 4: Synthesis from Organostannane Compounds	557
35.3.1.2.5	Method 5: Synthesis from Organosilicon Compounds	558
35.3.1.2.6	Method 6: Synthesis from Organoboranes or Organoaluminum Compounds	560
35.3.1.3	Synthesis by Substitution of Carbon Functionalities S. Härtinger and M. Härtinger	
<hr/>		
35.3.1.3	Synthesis by Substitution of Carbon Functionalities	565
35.3.1.3.1	Method 1: Synthesis from Aliphatic Acids by Decarboxylation with Hypervalent Iodine Compounds	565
35.3.1.3.2	Method 2: Synthesis from Aliphatic Acids by Decarboxylation with <i>tert</i> -Butyl Hypoiodite	567
35.3.1.3.3	Method 3: Synthesis from Aliphatic Acids by Decarboxylation with Organic Peroxides	568
35.3.1.3.4	Method 4: Synthesis from <i>N</i> -(Acyloxy)pyridine-2(1 <i>H</i>)-thiones by Degradation	569
35.3.1.3.5	Method 5: Synthesis from Salts of Aliphatic Acids by Degradation (Hunsdiecker Reaction)	571
35.3.1.3.5.1	Variation 1: Synthesis from Mercury(II) Carboxylates of Aliphatic Acids ..	572
35.3.1.3.5.2	Variation 2: Synthesis from Lead(IV) Salts of Aliphatic Acids	573
35.3.1.3.6	Method 6: Synthesis from Aliphatic Esters or Acid Chlorides by O-Silylation	574

35.3.1.3.7	Method 7: Synthesis from Aliphatic Peroxyacids and Hydroperoxides by Degradation	575
35.3.1.4	Synthesis by Substitution of Other Halogens S. Härtinger and M. Härtinger	
35.3.1.4	Synthesis by Substitution of Other Halogens	579
35.3.1.4.1	Method 1: Synthesis from Chloro- or Bromoalkanes with Alkali Metal Iodides	579
35.3.1.4.2	Method 2: Synthesis from Chloro- and Bromoalkanes under Phase-Transfer Catalysis	581
35.3.1.4.3	Method 3: Synthesis from Haloalkanes by Iodide-Catalyzed Exchange Reactions	582
35.3.1.4.4	Method 4: Synthesis from Haloalkanes with Hydriodic Acid	583
35.3.1.4.5	Method 5: Synthesis from Haloalkanes with Iodosilanes	584
35.3.1.5	Synthesis by Substitution of Oxygen Functionalities S. Härtinger	
35.3.1.5	Synthesis by Substitution of Oxygen Functionalities	589
35.3.1.5.1	Method 1: Synthesis from Aliphatic Carbonyl Compounds or Acetals	589
35.3.1.5.1.1	Variation 1: Reductive Iodination with an Amine–Borane Complex	590
35.3.1.5.1.2	Variation 2: Reductive Iodination with Diiodosilane	591
35.3.1.5.1.3	Variation 3: Direct Iodination of the Tetrahydropyran-2-yloxy Group	592
35.3.1.5.2	Method 2: Synthesis from Aliphatic Carboxylic Acid Esters	593
35.3.1.5.2.1	Variation 1: Cleavage with Hydriodic Acid	594
35.3.1.5.2.2	Variation 2: Metal-Catalyzed Iodinolysis	595
35.3.1.5.2.3	Variation 3: Cleavage of an Acyloxy or α -Chloroalkyl Carbonate Group with Metal Iodides	596
35.3.1.5.2.4	Variation 4: Cleavage of an Acyloxy, Formyloxy, or Carbamate Group with Iodotrimethylsilane	598
35.3.1.5.2.5	Variation 5: Reaction with Iodomethane	599
35.3.1.5.2.6	Variation 6: Decarboxylation of a Chloroformate Group	600
35.3.1.5.3	Method 3: Synthesis from Cyclic Alcohols or Ketones, Lactols, or Hydroxymethyl-Substituted Cycloalkanes by Isomerization and Fragmentation	601
35.3.1.5.3.1	Variation 1: Alkoxy-Radical-Mediated Reactions	601
35.3.1.5.3.2	Variation 2: Ring-Expanded Iodides by Wagner–Meerwein Rearrangement	609
35.3.1.5.3.3	Variation 3: Ring Opening and Fragmentation Reactions of Cyclopropyl Alcohols	610
35.3.1.5.3.4	Variation 4: Ring-Opening Reactions of Cyclobutanones	612
35.3.1.5.4	Method 4: Synthesis from Ethers	613
35.3.1.5.4.1	Variation 1: Cleavage with Hydriodic Acid	613
35.3.1.5.4.2	Variation 2: Cleavage with Alkali Metal Iodides and Acids	615
35.3.1.5.4.3	Variation 3: Iodinolysis with Borohydride Reagents	616
35.3.1.5.4.4	Variation 4: Cleavage with Iodosilane Reagents	617

35.3.1.5.4.5	Variation 5:	Cleavage of a Trimethylsiloxy Group	619
35.3.1.5.4.6	Variation 6:	Cleavage with Carboxylic Acid Iodides	620
35.3.1.5.4.7	Variation 7:	Activation with Metal-Containing Lewis Acids	622
35.3.1.5.5	Method 5:	Synthesis from Esters of Sulfur, Nitrogen, or Phosphorus Oxyacids	623
35.3.1.5.5.1	Variation 1:	Cleavage of a Sulfonyloxy Group with Metal Iodides	623
35.3.1.5.5.2	Variation 2:	Phase-Transfer-Catalyzed Cleavage of a Sulfonyloxy Group ..	628
35.3.1.5.5.3	Variation 3:	Nucleophilic Substitution in Ionic Liquids	631
35.3.1.5.5.4	Variation 4:	Cleavage of Ammonioalkanesulfonate Esters	632
35.3.1.5.5.5	Variation 5:	Cleavage of Dialkyl Sulfates	633
35.3.1.5.5.6	Variation 6:	Cleavage of Esters or Amides of Mononuclear Oxyacids of Phosphorus	633
35.3.1.5.6	Method 6:	Synthesis from Alcohols	635
35.3.1.5.6.1	Variation 1:	Direct Iodinolysis	635
35.3.1.5.6.2	Variation 2:	Iodination with Hydriodic Acid	636
35.3.1.5.6.3	Variation 3:	Iodination with Metal Iodides and Acid as a Source of Hydriodic Acid	638
35.3.1.5.6.4	Variation 4:	Iodination with Metal Iodides and 70% Hydrogen Fluoride/Pyridine	639
35.3.1.5.6.5	Variation 5:	Iodination with Metal Iodides	640
35.3.1.5.6.6	Variation 6:	Iodine Transfer from Organic or Organometallic Iodides	642
35.3.1.5.6.7	Variation 7:	Activation with Diazolides	643
35.3.1.5.6.8	Variation 8:	Activation with <i>O</i> -Alkylisoureas	644
35.3.1.5.6.9	Variation 9:	Activation with Alkoxyformamidineium Salts	646
35.3.1.5.6.10	Variation 10:	Activation with Onium Salts of 2-Fluoroazaarenes	647
35.3.1.5.6.11	Variation 11:	Iodination with Phosphorus and Iodine or with Phosphorus Triiodide	648
35.3.1.5.6.12	Variation 12:	Activation with Phosphite Esters or Phosphorus Amides	649
35.3.1.5.6.13	Variation 13:	Activation with Phosphine Reagents	652
35.3.1.5.6.14	Variation 14:	Iodination with Iodosilane Reagents	656
35.3.1.5.6.15	Variation 15:	Iodinolysis with Borane or Boronate Reagents	657
35.3.1.5.6.16	Variation 16:	Iodination in Ionic Liquids	659
35.3.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities S. Härtinger and M. Härtinger		
35.3.1.6	Synthesis by Substitution of Sulfur, Selenium, or Tellurium Functionalities		673
35.3.1.6.1	Method 1:	Reaction of Aliphatic Sulfur or Selenium Compounds with Phosphine Reagents and Iodine	673
35.3.1.6.2	Method 2:	Synthesis from Alkyl Sulfides via Formation of Sulfonium Salts	675

35.3.1.7	Synthesis by Substitution of Nitrogen Functionalities S. Härtinger and M. Härtinger	
<hr/>		
35.3.1.7	Synthesis by Substitution of Nitrogen Functionalities	679
35.3.1.7.1	Method 1: Synthesis from Alkylamines via Formation of Trialkylammonium Salts	679
35.3.1.7.2	Method 2: Synthesis from Alkylamines via Pyrolysis of 1-Alkylpyridinium Salts	680
35.3.1.7.3	Method 3: Synthesis from Alkylamines via Formation of <i>N</i> -Alkyl- <i>N,N</i> -disulfonylamines	681
35.3.1.7.4	Method 4: Synthesis from Hydrazines by Iodolysis	682
35.3.1.7.5	Method 5: Synthesis from Nitroalkanes by Substitution	683
35.3.1.8	Synthesis by Addition to π-Type C—C Bonds K.-M. Roy	
<hr/>		
35.3.1.8	Synthesis by Addition to π-Type C—C Bonds	685
35.3.1.8.1	Method 1: Hydroiodination of 1,3-Dienes	685
35.3.1.8.1.1	Variation 1: Synthesis of 1-Iodo-3-methylbut-2-ene with Phosphorus Triiodide/Silica Gel	685
35.3.1.8.2	Method 2: Hydroiodination of Alkenes and Cycloalkenes (Markovnikov Addition)	686
35.3.1.8.2.1	Variation 1: Synthesis Using Hydrogen Iodide	686
35.3.1.8.2.2	Variation 2: Surface-Mediated Synthesis	687
35.3.1.8.3	Method 3: Hydroiodination of Alkenes and Cycloalkenes (anti-Markovnikov Addition)	688
35.3.1.8.3.1	Variation 1: Synthesis via Hydroboration	688
35.3.1.8.3.2	Variation 2: Synthesis via Hydroalumination	689
35.3.1.8.3.3	Variation 3: Synthesis via Hydrozirconation	690
35.3.1.8.4	Method 4: Hydroiodination of Methylene-cyclopropanes	691
35.3.1.8.5	Method 5: Hydroiodination of Cyclopropanes	691
35.3.1.8.6	Method 6: Carboiodination	692
35.3.1.8.6.1	Variation 1: Iodocyclization	693
35.3.1.9	Synthesis from Other Iodo Compounds H. Ulrich	
<hr/>		
35.3.1.9	Synthesis from Other Iodo Compounds	697
35.3.1.9.1	Method 1: Synthesis from Iodoalkynes	697
35.3.1.9.1.1	Variation 1: By Cycloaddition Reactions	697
35.3.1.9.2	Method 2: Synthesis from Iodoalkenes	697
35.3.1.9.2.1	Variation 1: By Hydrogenation	697
35.3.1.9.2.2	Variation 2: By Polymerization	697
35.3.1.9.2.3	Variation 3: By Cycloaddition Reactions	698
35.3.1.9.3	Method 3: Synthesis from Iodocarbenes	698
35.3.1.9.4	Method 4: Synthesis from Iodoalkanes	699

35.3.1.9.4.1	Variation 1: By Iodoalkylation Reactions	699
35.3.1.9.4.2	Variation 2: By Isomerization Reactions	699
35.3.2	Product Subclass 2: Propargylic Iodides	
	S. Härtinger	
<hr/>		
35.3.2	Product Subclass 2: Propargylic Iodides	701
35.3.2.1	Synthesis of Product Subclass 2	701
35.3.2.1.1	Method 1: Chemoselective Substitution of Heteroatoms	701
35.3.2.1.2	Method 2: Modification of the Carbon Skeleton	702
35.3.3	Product Subclass 3: Benzylic Iodides	
<hr/>		
35.3.3.1	Synthesis by Substitution of Carbonyl Oxygen	
	W. D. Pfeiffer	
<hr/>		
35.3.3.1	Synthesis by Substitution of Carbonyl Oxygen	705
35.3.3.1.1	Method 1: Photochemical Iodination at the Benzylic Position	705
35.3.3.1.2	Method 2: Iodomethylation of an Arene Using Chloromethyl Methyl Ether and Hydrogen Iodide	705
35.3.3.2	Substitution of σ-Bonded Heteroatoms	
	S. Härtinger and M. Härtinger	
<hr/>		
35.3.3.2	Substitution of σ-Bonded Heteroatoms	707
35.3.3.2.1	Method 1: Synthesis by Substitution of σ -Bonded Heteroatoms	707
35.3.4	Product Subclass 4: Allylic Iodides	
	S. Härtinger	
<hr/>		
35.3.4	Product Subclass 4: Allylic Iodides	711
35.3.4.1	Synthesis of Product Subclass 4	711
35.3.4.1.1	Method 1: Synthesis by Regioselective Substitution of Heteroatoms	711
35.3.4.1.2	Method 2: Synthesis by Regioselective Addition to the Carbon Skeleton	712

35.3.5	Product Subclass 5: 1-Iodo-<i>n</i>-Heteroatom-Functionalized Alkanes (<i>n</i> ≥ 2) with Both Functions Formed Simultaneously		
<hr/>			
35.3.5.1	Synthesis by Addition across C=C Bonds		
	T. Troll		
<hr/>			
35.3.5.1	Synthesis by Addition across C=C Bonds		717
35.3.5.1.1	Method 1:	Iodination of Alkenes	717
35.3.5.1.2	Method 2:	Hydroxy- or Alkoxyiodination of Alkenes	718
35.3.5.1.2.1	Variation 1:	Oxidation of Iodide by Hydrogen Peroxide	718
35.3.5.1.2.2	Variation 2:	Iodocyclization of Enols	719
35.3.5.1.2.3	Variation 3:	Iodination To Form Iodo Acetates	720
35.3.5.1.2.4	Variation 4:	Iodohydrins Using Hypoiodous Acid	720
35.3.5.1.2.5	Variation 5:	Iodohydrins Using Hypervalent Iodine Compounds	722
35.3.5.1.2.6	Variation 6:	Iodohydrins Using <i>N</i> -Iodosuccinimide	725
35.3.5.1.3	Method 3:	Iodosulfonation of Alkenes	729
35.3.5.1.4	Method 4:	Azido- and Aminoiodination of Alkenes	731
35.3.5.2	Synthesis by Addition across C—O Bonds		
	K. Rück-Braun and T. Freysoldt		
<hr/>			
35.3.5.2	Synthesis by Addition across C—O Bonds		741
35.3.5.2.1	Method 1:	Hydroiodination of Epoxides Using Hydrogen Iodide	741
35.3.5.2.2	Method 2:	Hydroiodination of Epoxides Using Elemental Iodine	742
35.3.5.2.3	Method 3:	Hydroiodination of Epoxides Using Alkali Metal Iodides	743
35.3.5.2.3.1	Variation 1:	Catalyzed by Lewis Acids	745
35.3.5.2.4	Method 4:	Hydroiodination of Epoxides Using Magnesium Iodide	746
35.3.5.2.5	Method 5:	Enantioselective Hydroiodination of Epoxides Using Trialkylazidosilanes and Allyl Iodide	747
35.3.5.2.6	Method 6:	Hydroiodination of Epoxides Using Samarium(II) Iodide	748
35.3.5.2.7	Method 7:	Hydroiodination of Epoxides Using Phosphorus Iodides and Phosphonium Iodides	749
35.3.5.2.8	Method 8:	Iodination of Epoxides and Other Cyclic Ethers	750
35.3.5.3	Synthesis by Addition across C—S Bonds		
	K. Rück-Braun and T. Freysoldt		
<hr/>			
35.3.5.3	Synthesis by Addition across C—S Bonds		753
35.3.5.3.1	Method 1:	Synthesis by Iodination of Thiiranes	753

35.3.5.4	Synthesis by Addition across C–N Bonds K. Rück-Braun and T. Freysoldt	
<hr/>		
35.3.5.4	Synthesis by Addition across C–N Bonds	757
35.3.5.4.1	Method 1: Hydroiodination of Aziridines Using Hydrogen Iodide	757
35.3.5.4.2	Method 2: Hydroiodination of Aziridines Using Alkali Metal Iodides	757
35.3.5.4.3	Method 3: Hydroiodination of Aziridines Using Other Metal Iodides	759
35.3.5.4.4	Method 4: Hydroiodination of Aziridines Using Indium(III) or Zinc(II) Iodide	759
35.3.5.4.5	Method 5: Hydroiodination of Aziridines Using Samarium(II) Iodide	760
35.3.5.4.6	Method 6: Hydroiodination of Aziridines Using Iodotrimethylsilane	761
35.3.5.5	Synthesis by Addition across C–C Bonds K. Rück-Braun and T. Freysoldt	
<hr/>		
35.3.5.5	Synthesis by Addition across C–C Bonds	763
35.3.5.5.1	Method 1: Ring Opening of Cyclopropanes Using Mercury(II) Salts and Iodine	763
35.3.5.5.2	Method 2: Ring Opening of Vinylcyclopropanes	764
35.3.5.5.3	Method 3: Iodination of 1,1-Diacetylcyclopropane	765
	Keyword Index	767
	Author Index	805
	Abbreviations	845