
**Volume 40a:
Amines and Ammonium Salts**

	Preface	V
	Volume Editors' Preface	VII
	Table of Contents	XI
	Introduction	
	E. Schaumann	1
40.1	Product Class 1: Amino Compounds	
40.1.1	Product Subclass 1: Alkyl- and Cycloalkylamines	
	E. Schaumann	7
40.1.1.1	Synthesis by Reduction	
40.1.1.1.1	Reduction of Carbonic and Carboxylic Acid Derivatives	
	B. Wünsch and C. Geiger	23
40.1.1.1.2	Reductive Amination of Carbonyl Compounds	
	P. Margaretha	65
40.1.1.1.3	Reaction of Acetals with Organometallic Reagents	
	G. K. Friestad	91
40.1.1.1.4	Hydroaminomethylation of Alkenes	
	A. Börner, M. Beller, and B. Wünsch	111
40.1.1.1.5	Reduction of Nitrogen-Based Functional Groups	
	P. Margaretha	119
40.1.1.2	Synthesis by Substitution	
40.1.1.2.1	Synthesis by Substitution of Hydrogen or Metals	
	H. Butenschön	157
40.1.1.2.2	Substitution of Carbon Functionalities via Solvolysis	
	F.-P. Montforts, M. Osmers, and V. A. Azov	203
40.1.1.2.3	Substitution of Sulfur or Phosphorus Functionalities	
	F.-P. Montforts and M. Osmers	233
40.1.1.3	Synthesis by Addition Reactions	
40.1.1.3.1	Hydroamination	
	S. Doye	241
40.1.1.3.2	Addition of Carbanions to Azomethines	
	G. K. Friestad	305

40.1.1.3.3	Pericyclic Reactions Involving C=N Units	
	W. Maison	343
40.1.1.4	Synthesis by Rearrangement	
	R. Purchase and M. Sainsbury	365
40.1.1.5	Synthesis from Other Amino Compounds	
40.1.1.5.1	Resolution of Chiral Amines	
	V. A. Azov	419
40.1.1.5.2	The Mannich Reaction	
	J. Ipaktschi and M. R. Saidi	435
40.1.1.5.3	Modification of Mannich Adducts	
	J. Ipaktschi and M. R. Saidi	479
40.1.1.5.4	Substitution on the Amine Nitrogen	
	S. A. Lawrence	501
40.1.2	Product Subclass 2: Propargylic Amines	
	J. Q. Feng and C.-J. Li	579
40.1.3	Product Subclass 3: Allylic Amines	
	J. Q. Feng and C.-J. Li	587
40.1.4	Product Subclass 4: n-Nitroge-n or n-Phosphorus-Functionalized Alkylamines (n ≥ 2)	
	K.-M. Roy	615
40.1.5	Product Subclass 5: Aziridines	
	J. B. Sweeney	643
40.1.6	Product Subclass 6: Azetidines	
	F. Couty	773
40.1.7	Product Subclass 7: Ammonium Compounds and Nitrogen Ylides	
	E. Kruiswijk and J. A. Deck	817
	Keyword Index	i
	Author Index	lix
	Abbreviations	cv

Table of Contents

	Introduction E. Schaumann	
	Introduction	1
40.1	Product Class 1: Amino Compounds	
40.1.1	Product Subclass 1: Alkyl- and Cycloalkylamines E. Schaumann	
40.1.1	Product Subclass 1: Alkyl- and Cycloalkylamines	7
40.1.1.1	Synthesis by Reduction	
40.1.1.1.1	Reduction of Carbonic and Carboxylic Acid Derivatives B. Wünsch and C. Geiger	
40.1.1.1.1	Reduction of Carbonic and Carboxylic Acid Derivatives	23
40.1.1.1.1.1	Method 1: Reduction of Carbon Monoxide Gas	23
40.1.1.1.1.2	Method 2: Reduction of Carbamates	23
40.1.1.1.1.2.1	Variation 1: Reduction with Aluminum Hydrides	24
40.1.1.1.1.2.2	Variation 2: Catalytic Hydrogenation	25
40.1.1.1.1.2.3	Variations 3: Miscellaneous Reductions	27
40.1.1.1.1.3	Method 3: Reduction of Isocyanates or Isothiocyanates	28
40.1.1.1.1.4	Method 4: Reduction of Nitriles	29
40.1.1.1.1.4.1	Variation 1: Catalytic Hydrogenation	29
40.1.1.1.1.4.2	Variation 2: Reduction with Aluminum Hydrides	34
40.1.1.1.1.4.3	Variation 3: Reduction with Boranes	38
40.1.1.1.1.4.4	Variation 4: Reduction with Borohydrides	41
40.1.1.1.1.4.5	Variation 5: The Kulinkovich–de Meijere Reaction	44
40.1.1.1.1.5	Method 5: Reduction of Amides or Thioamides	45
40.1.1.1.1.5.1	Variation 1: Reduction with Aluminum Hydrides	45
40.1.1.1.1.5.2	Variation 2: Reduction with Borane Derivatives	48
40.1.1.1.1.5.3	Variation 3: Reduction with Hydrosilanes	49
40.1.1.1.1.5.4	Variation 4: Reduction of Thioamides	50
40.1.1.1.1.5.5	Variation 5: The Kulinkovich–de Meijere Reaction	51
40.1.1.1.1.6	Method 6: Reduction of Imides	54
40.1.1.1.1.7	Method 7: Reduction of Imidates and Imidoyl Chlorides	55
40.1.1.1.2	Reductive Amination of Carbonyl Compounds P. Margaretha	
40.1.1.1.2	Reductive Amination of Carbonyl Compounds	65
40.1.1.1.2.1	Alkylamines from Carbonyl Compounds by Direct Reductive Amination	65

40.1.1.1.2.1.1	Method 1:	Direct Reductive Amination by Catalytic Hydrogenation	66
40.1.1.1.2.1.1.1	Variation 1:	Hydrogenation Using Heterogeneous Metal Catalysts	66
40.1.1.1.2.1.1.2	Variation 2:	Hydrogenation Using Homogeneous Metal Complex Catalysts	67
40.1.1.1.2.1.1.3	Variation 3:	Palladium-Catalyzed Transfer Hydrogenation	68
40.1.1.1.2.1.2	Method 2:	Direct Reductive Amination Using Silanes as a Hydrogen Source	69
40.1.1.1.2.1.2.1	Variation 1:	Using Polymethylhydrosiloxane	69
40.1.1.1.2.1.2.2	Variation 2:	Using Aminohydrosilanes	69
40.1.1.1.2.1.2.3	Variation 3:	Using Triethylsilane	70
40.1.1.1.2.1.3	Method 3:	Direct Reductive Amination with Borohydride or Borane Reducing Agents	70
40.1.1.1.2.1.3.1	Variation 1:	Using Sodium Cyanoborohydride	70
40.1.1.1.2.1.3.2	Variation 2:	Using Sodium Borohydride	72
40.1.1.1.2.1.3.3	Variation 3:	Using Zirconium(II) or Copper(I) Borohydrides	73
40.1.1.1.2.1.3.4	Variation 4:	Using Sodium Triacyloxyborohydrides	74
40.1.1.1.2.1.3.5	Variation 5:	Using Aminoboranes	74
40.1.1.1.2.2		Primary Alkylamines from Oximes and <i>O</i> -Alkyloximes	75
40.1.1.1.2.2.1		Primary Alkylamines from Oximes	76
40.1.1.1.2.2.1.1	Method 1:	Catalytic Hydrogenation	76
40.1.1.1.2.2.1.2	Method 2:	Catalytic Transfer Hydrogenation	77
40.1.1.1.2.2.1.3	Method 3:	Reduction with Metallic Zinc	77
40.1.1.1.2.2.1.3.1	Variation 1:	Using Zinc in the Presence of Ammonia	77
40.1.1.1.2.2.1.3.2	Variation 2:	Using Zinc in the Presence of a Carboxylic Acid	78
40.1.1.1.2.2.1.4	Method 4:	Reductions with Borane or Borohydrides	79
40.1.1.1.2.2.1.4.1	Variation 1:	Reduction with Borane	79
40.1.1.1.2.2.1.4.2	Variation 2:	Reduction with Borohydrides	79
40.1.1.1.2.2.1.5	Method 5:	Reductions with Aluminum Trihydride or Hydroaluminates	80
40.1.1.1.2.2.2		Primary Alkylamines from <i>O</i> -Alkyloximes	81
40.1.1.1.2.3		Secondary Alkylamines from <i>N</i> -Alkylidenealkylamines by Reduction	82
40.1.1.1.2.3.1	Method 1:	Stereorandom Reduction of <i>N</i> -Alkylidenealkylamines to Secondary Alkylamines	82
40.1.1.1.2.3.1.1	Variation 1:	Via Transfer Hydrogenation	82
40.1.1.1.2.3.1.2	Variation 2:	By Reduction with Hydrides	83
40.1.1.1.2.3.2	Method 2:	Enantioselective Reduction of <i>N</i> -Alkylidenealkylamines to Secondary Alkylamines	84
40.1.1.1.2.4		Tertiary Alkylamines from Enamines by Reduction	85
40.1.1.1.2.4.1	Method 1:	Amines from Enamines by Catalytic Hydrogenation	85
40.1.1.1.2.4.2	Method 2:	Amines from Enamines by Enantioselective (Asymmetric) Catalytic Hydrogenation	86
40.1.1.1.2.4.3	Method 3:	Amines from Enamines Using Other Reducing Agents	87
40.1.1.1.3		Reaction of Acetals with Organometallic Reagents G. K. Friestad	
40.1.1.1.3		Reaction of Acetals with Organometallic Reagents	91
40.1.1.1.3.1	Method 1:	Additions to <i>N,O</i> -Acetals	91

40.1.1.1.3.1.1	Variation 1:	Addition to <i>N,O</i> -Acetals Incorporating a Tertiary Amine Function	91
40.1.1.1.3.1.2	Variation 2:	Addition to <i>N,O</i> -Acetals Incorporating a Secondary Amine Function	95
40.1.1.1.3.1.3	Variation 3:	Development of Asymmetric Additions to <i>N,O</i> -Acetals	98
40.1.1.1.3.2	Method 2:	Additions to <i>N,N</i> -Acetals	99
40.1.1.1.3.3	Method 3:	Reductive Arylation of <i>N,O</i> -Acetals: The Tscherniac–Einhorn Reaction	100
40.1.1.1.3.3.1	Variation 1:	Asymmetric Equivalents of the Tscherniac–Einhorn Reaction	105
40.1.1.1.4	Hydroaminomethylation of Alkenes A. Börner, M. Beller, and B. Wunsch		
40.1.1.1.4	Hydroaminomethylation of Alkenes		111
40.1.1.1.4.1	Method 1:	Hydroaminomethylation	111
40.1.1.1.5	Reduction of Nitrogen-Based Functional Groups P. Margaretha		
40.1.1.1.5	Reduction of Nitrogen-Based Functional Groups		119
40.1.1.1.5.1	Reduction of Nitroalkanes		119
40.1.1.1.5.1.1	Method 1:	Cathodic Reduction	120
40.1.1.1.5.1.2	Method 2:	Catalytic Hydrogenation	120
40.1.1.1.5.1.3	Method 3:	Transfer Hydrogenation	122
40.1.1.1.5.1.4	Method 4:	Reduction Using Borohydrides and an Additional Catalyst	124
40.1.1.1.5.1.4.1	Variation 1:	Using Sodium Borohydride	124
40.1.1.1.5.1.4.2	Variation 2:	Using Borohydride Exchange Resin	125
40.1.1.1.5.1.4.3	Variation 3:	Using Zinc(II) Borohydride–Pyridine	125
40.1.1.1.5.1.5	Method 5:	Reduction Using Lithium Aluminum Hydride	125
40.1.1.1.5.1.6	Method 6:	Reduction Using Aluminum Amalgam Promoted by Ultrasound	127
40.1.1.1.5.1.7	Method 7:	Reduction Using Tin–Hydrochloric Acid	128
40.1.1.1.5.1.8	Method 8:	Reduction Using Samarium(II) Iodide	128
40.1.1.1.5.2	Reduction of Mesoionic 2-Alkyl-1,2,3-triazines		130
40.1.1.1.5.3	Reduction of Nitrosoalkanes		131
40.1.1.1.5.4	Reduction of Alkyl Azides		131
40.1.1.1.5.4.1	Method 1:	Catalytic Hydrogenation	131
40.1.1.1.5.4.2	Method 2:	Transfer Hydrogenation	133
40.1.1.1.5.4.3	Method 3:	Reduction Using Boranes or Boronates	135
40.1.1.1.5.4.3.1	Variation 1:	Using Dichloroborane–Dimethyl Sulfide	135
40.1.1.1.5.4.3.2	Variation 2:	Using Lithium Aminoborohydrides	136
40.1.1.1.5.4.3.3	Variation 3:	Using Sodium Borohydride	137
40.1.1.1.5.4.3.4	Variation 4:	Using Borohydride Exchange Resin–Nickel(II) Acetate	139
40.1.1.1.5.4.3.5	Variation 5:	Using Zinc(II) Borohydride	139
40.1.1.1.5.4.4	Method 4:	Reduction Using Lithium Aluminum Hydride	140
40.1.1.1.5.4.5	Method 5:	Reduction Using Tributyltin Hydride	141

40.1.1.5.4.6	Method 6:	Reduction Using Metals	141
40.1.1.5.4.7	Method 7:	Reduction Using Triphenylphosphine	143
40.1.1.5.4.8	Method 8:	Reduction Using Hydrogen Sulfide	144
40.1.1.5.4.9	Method 9:	Reduction Using Propane-1,3-dithiol	144
40.1.1.5.4.10	Method 10:	Reduction Using Low-Valent Metal Ion Salts	145
40.1.1.5.4.11	Methods 11:	Miscellaneous Methods	145
40.1.1.5.5		Reduction of 1,2-Diazenes	145
40.1.1.5.6		Reduction of Hydroxylamines	146
40.1.1.5.7		Reduction of Amine Oxides	147
40.1.1.5.8		Reduction of <i>N</i> -Nitro and <i>N</i> -Nitroso Compounds	149
40.1.1.5.9		Reduction of Alkylhydrazines	149
40.1.1.5.10		Reduction of Sulfonamides	153
40.1.1.2	Synthesis by Substitution		
40.1.1.2.1	Synthesis by Substitution of Hydrogen or Metals H. Butenschön		
40.1.1.2.1	Synthesis by Substitution of Hydrogen or Metals		
40.1.1.2.1.1	Method 1:	α -Amination of Carbonyl Compounds and Analogues	157
40.1.1.2.1.1.1	Variation 1:	Amination with Azodicarboxylates	157
40.1.1.2.1.1.2	Variation 2:	Amination with R_2NL Compounds (L = Leaving Group)	167
40.1.1.2.1.1.3	Variation 3:	Amination with Azides Followed by Reduction	170
40.1.1.2.1.1.4	Variation 4:	Amination with Oxaziridines	173
40.1.1.2.1.1.5	Variation 5:	Amination with 1-Chloro-1-nitroso Reagents	175
40.1.1.2.1.1.6	Variation 6:	Amination with Lithium <i>N</i> -(<i>tert</i> -Butoxycarbonyl)- <i>O</i> -tosylhydroxyamide	176
40.1.1.2.1.1.7	Variation 7:	Amination with Nitridomanganese(V) Complexes	176
40.1.1.2.1.1.8	Variations 8:	Other Variations	177
40.1.1.2.1.2	Method 2:	Substitution of Hydrogen Other Than the α -Hydrogen of Carbonyl Compounds	177
40.1.1.2.1.2.1	Variation 1:	Amination with Azidotrimethylsilane Followed by Reduction	178
40.1.1.2.1.2.2	Variation 2:	Amination of Unactivated C—H Groups with Haloamine	180
40.1.1.2.1.2.3	Variation 3:	Rhodium(II)-, Ruthenium(II)-, or Manganese(III)-Catalyzed Amination	181
40.1.1.2.1.2.4	Variations 4:	Miscellaneous Variations	184
40.1.1.2.1.3	Method 3:	Substitution of Metal Atoms	185
40.1.1.2.1.3.1	Variation 1:	Substitution of Boron	186
40.1.1.2.1.3.2	Variation 2:	Substitution of Zinc	187
40.1.1.2.1.3.3	Variation 3:	Substitution of Copper	190
40.1.1.2.1.3.4	Variation 4:	Substitution of Magnesium	191
40.1.1.2.1.3.5	Variation 5:	Substitution of Lithium	195
40.1.1.2.1.3.6	Variation 6:	Substitution of Other Metal Atoms	197

40.1.1.2.2	Substitution of Carbon Functionalities via Solvolysis F.-P. Montforts, M. Osmer, and V. A. Azov	
<hr/>		
40.1.1.2.2	Substitution of Carbon Functionalities via Solvolysis	203
40.1.1.2.2.1	Method 1: Substitution of Carbamates	203
40.1.1.2.2.1.1	Variation 1: Cleavage by Nucleophilic Substitution	203
40.1.1.2.2.1.2	Variation 2: Cleavage by Protic or Lewis Acids	206
40.1.1.2.2.1.3	Variation 3: Cleavage by Base-Induced β -Elimination	210
40.1.1.2.2.1.4	Variation 4: Cleavage by Remote Attack of Bases or Nucleophiles at the Carbamate Group	213
40.1.1.2.2.2	Method 2: Substitution of Carboxylic Acid N-Derivatives	219
40.1.1.2.2.2.1	Variation 1: Acyclic Carboxylic Acid N-Derivatives	219
40.1.1.2.2.2.2	Variation 2: Cyclic Carboxylic Acid N-Derivatives (Cyclic Imide Derivatives)	226
40.1.1.2.2.2.3	Variation 3: Amidines	229
40.1.1.2.3	Substitution of Sulfur or Phosphorus Functionalities F.-P. Montforts and M. Osmer	
<hr/>		
40.1.1.2.3	Substitution of Sulfur or Phosphorus Functionalities	233
40.1.1.2.3.1	Method 1: Cleavage of Sulfonic, Sulfinic, and Sulfenic Acid N-Derivatives	233
40.1.1.2.3.2	Method 2: Cleavage of Phosphoric and Phosphinic Acid Amides	237
40.1.1.3	Synthesis by Addition Reactions	
<hr/>		
40.1.1.3.1	Hydroamination S. Doye	
<hr/>		
40.1.1.3.1	Hydroamination	241
40.1.1.3.1.1	Method 1: Hydroamination of Alkenes	241
40.1.1.3.1.1.1	Variation 1: Catalysis by Acids	241
40.1.1.3.1.1.2	Variation 2: Catalysis by Bases	243
40.1.1.3.1.1.3	Variation 3: Catalysis by Calcium Complexes	245
40.1.1.3.1.1.4	Variation 4: Catalysis by Rare Earth Metal Complexes	246
40.1.1.3.1.1.5	Variation 5: Catalysis by Actinide Complexes	256
40.1.1.3.1.1.6	Variation 6: Catalysis by Group 4 Metal Complexes	257
40.1.1.3.1.1.7	Variation 7: Catalysis by Group 8 Metal Complexes	259
40.1.1.3.1.1.8	Variation 8: Catalysis by Group 9 Metal Complexes	260
40.1.1.3.1.1.9	Variation 9: Catalysis by Group 10 Metal Complexes	261
40.1.1.3.1.1.10	Variation 10: Catalysis by Group 11 Metal Complexes	263
40.1.1.3.1.1.11	Variation 11: Catalysis by Group 12 Metal Complexes	264
40.1.1.3.1.2	Method 2: Hydroamination of Vinylarenes	264
40.1.1.3.1.2.1	Variation 1: Catalysis by Acids	264
40.1.1.3.1.2.2	Variation 2: Catalysis by Bases	265
40.1.1.3.1.2.3	Variation 3: Catalysis by Rare Earth Metal Complexes	266
40.1.1.3.1.2.4	Variation 4: Catalysis by Hafnium Complexes	268
40.1.1.3.1.2.5	Variation 5: Catalysis by Ruthenium Complexes	269
40.1.1.3.1.2.6	Variation 6: Catalysis by Rhodium Complexes	270

40.1.1.3.1.2.7	Variation 7:	Catalysis by Palladium or Platinum Complexes	272
40.1.1.3.1.2.8	Variation 8:	Catalysis by Copper Complexes	273
40.1.1.3.1.2.9	Variation 9:	Catalysis by Bismuth Complexes	274
40.1.1.3.1.2.10	Variation 10:	Catalysis by <i>N</i> -Bromosuccinimide	274
40.1.1.3.1.2.11	Variation 11:	Photoamination of Vinylarenes	275
40.1.1.3.1.3	Method 3:	Hydroamination of 1,3-Dienes	275
40.1.1.3.1.3.1	Variation 1:	Catalysis by Acids	276
40.1.1.3.1.3.2	Variation 2:	Catalysis by Bases	276
40.1.1.3.1.3.3	Variation 3:	Catalysis by Rare Earth Metal Complexes	277
40.1.1.3.1.3.4	Variation 4:	Catalysis by Group 10 Metal Complexes	278
40.1.1.3.1.3.5	Variation 5:	Catalysis by Gold Complexes	279
40.1.1.3.1.3.6	Variation 6:	Catalysis by Bismuth Complexes	279
40.1.1.3.1.3.7	Variation 7:	Photoamination of 1,3-Dienes	280
40.1.1.3.1.4	Method 4:	Hydroamination of Cyclohepta-1,3,5-triene	280
40.1.1.3.1.5	Method 5:	Hydroamination of Allenes	281
40.1.1.3.1.5.1	Variation 1:	Catalysis by Rare Earth Metal Complexes	281
40.1.1.3.1.5.2	Variation 2:	Catalysis by Titanium or Zirconium Complexes	282
40.1.1.3.1.5.3	Variation 3:	Catalysis by Ruthenium Complexes	283
40.1.1.3.1.5.4	Variation 4:	Catalysis by Palladium Complexes	284
40.1.1.3.1.5.5	Variation 5:	Catalysis by Gold or Silver Complexes	286
40.1.1.3.1.6	Method 6:	Hydroamination of Allenes and Subsequent Reduction	287
40.1.1.3.1.7	Method 7:	Hydroamination of Alkynes	288
40.1.1.3.1.8	Method 8:	Hydroamination of Alkynes and Subsequent Reduction	289
40.1.1.3.1.8.1	Variation 1:	Catalysis by Rare Earth Metal Complexes	289
40.1.1.3.1.8.2	Variation 2:	Catalysis by Group 4 Metal Complexes	290
40.1.1.3.1.8.3	Variation 3:	Catalysis by Iridium Complexes	292
40.1.1.3.1.8.4	Variation 4:	Catalysis by Silver Complexes	293
40.1.1.3.1.9	Method 9:	Hydroamination of Alkynes and Nucleophilic Addition	293
40.1.1.3.1.10	Method 10:	Hydroamination of Enynes	294
40.1.1.3.1.11	Method 11:	Hydroamination of Methylene-cyclopropanes	295
40.1.1.3.1.11.1	Variation 1:	Catalysis by Rare Earth Metal Complexes	295
40.1.1.3.1.11.2	Variation 2:	Catalysis by Palladium Complexes	296
40.1.1.3.1.11.3	Variation 3:	Catalysis by Gold Complexes	296
40.1.1.3.1.12	Method 12:	Hydroamination of Cyclopropenes	297
40.1.1.3.1.13	Method 13:	Hydroamination of Cyclopropanes	297
40.1.1.3.1.13.1	Variation 1:	Catalysis by Palladium Complexes	297
40.1.1.3.1.13.2	Variation 2:	Photoamination of Cyclopropanes	298
40.1.1.3.1.14	Method 14:	Hydroamination of Aromatic Compounds	298
40.1.1.3.2	Addition of Carbanions to Azomethines		
	G. K. Friestad		
40.1.1.3.2	Addition of Carbanions to Azomethines		305
40.1.1.3.2.1	Azomethines for Asymmetric Addition of Carbanions		305
40.1.1.3.2.1.1	Method 1:	Use of <i>N</i> -(1-Phenylethyl)imines	305
40.1.1.3.2.1.2	Method 2:	Use of <i>N</i> -Sulfinylimines	307
40.1.1.3.2.1.3	Method 3:	Use of SAMP and RAMP Hydrazones	308

40.1.1.3.2.1.4	Method 4:	Use of Chiral Acylhydrazones	309
40.1.1.3.2.1.5	Method 5:	Use of Chiral Oxime <i>O</i> -Ethers	310
40.1.1.3.2.1.6	Method 6:	Use of Chiral Reagents and Catalysts	311
40.1.1.3.2.2	Addition of Organometallic or Radical Reagents to Azomethines		313
40.1.1.3.2.2.1	Method 1:	Addition of Allylmetal Reagents	313
40.1.1.3.2.2.1.1	Variation 1:	Of Allyllithium and Allylmagnesium Reagents	314
40.1.1.3.2.2.1.2	Variation 2:	Of Allylboranes	317
40.1.1.3.2.2.1.3	Variation 3:	Of Allylstannanes	319
40.1.1.3.2.2.1.4	Variation 4:	Of Allylsilanes	322
40.1.1.3.2.2.1.5	Variation 5:	Of Other Allylic Reagents	325
40.1.1.3.2.2.2	Method 2:	Addition of Alkyl- and Arylmetal Reagents	326
40.1.1.3.2.2.2.1	Variation 1:	Of Organolithiums and Grignard Reagents	326
40.1.1.3.2.2.2.2	Variation 2:	Of Organozinc Reagents	327
40.1.1.3.2.2.2.3	Variation 3:	Of Organocerium Reagents	329
40.1.1.3.2.2.2.4	Variation 4:	Of Organotransition Metal Species	331
40.1.1.3.2.2.2.5	Variation 5:	Of Other Organometallic Reagents	333
40.1.1.3.2.2.3	Method 3:	Radical Alkyl Additions	333
40.1.1.3.3	Pericyclic Reactions Involving C=N Units		
	W. Maison		
40.1.1.3.3	Pericyclic Reactions Involving C=N Units		343
40.1.1.3.3.1	Method 1:	Cycloaddition Reactions of <i>N</i> -Acylimines	343
40.1.1.3.3.2	Method 2:	Cycloaddition Reactions of <i>N</i> -(Alkoxy carbonyl)imines	345
40.1.1.3.3.2.1	Variation 1:	Lewis Acid Mediated Cycloaddition of Biscarbamates	346
40.1.1.3.3.2.2	Variation 2:	Enantioselective Catalytic Cycloaddition	347
40.1.1.3.3.3	Method 3:	Cycloaddition Reactions of <i>N</i> -Sulfonylimines or <i>N</i> -Phosphorylimines	348
40.1.1.3.3.3.1	Variation 1:	Diastereoselective Cycloaddition Reactions of <i>N</i> -Tosylimines ·	349
40.1.1.3.3.3.2	Variation 2:	Enantioselective Catalytic Cycloaddition Reactions of <i>N</i> - Tosylimines	350
40.1.1.3.3.4	Method 4:	Cycloaddition Reactions of <i>N</i> -Alkylimines, <i>N</i> -Arylimines, or Their Salts	351
40.1.1.3.3.4.1	Variation 1:	Acid-Catalyzed Imino-Diels–Alder Reactions in Aqueous Media	352
40.1.1.3.3.4.2	Variation 2:	Diastereoselective Cycloaddition Reactions of <i>N</i> -Alkyl- or <i>N</i> -Arylimines	353
40.1.1.3.3.4.3	Variation 3:	Enantioselective Catalytic Cycloaddition Reactions of Alkylated and Arylated Imines	356
40.1.1.3.3.5	Method 5:	Cycloaddition Reactions of C-Heteroatom-Substituted Imines	357
40.1.1.4	Synthesis by Rearrangement		
	R. Purchase and M. Sainsbury		
40.1.1.4	Synthesis by Rearrangement		365
40.1.1.4.1	Rearrangements from Nitrogen to Carbon		365
40.1.1.4.1.1	Method 1:	Stevens and Sommelet–Hauser Rearrangements	365

40.1.1.4.1.2	Method 2:	[2,3]-Aza-Wittig and Related Sigmatropic Rearrangements ..	379
40.1.1.4.1.2.1	Variation 1:	[2,3]-Aza-Wittig Rearrangements	379
40.1.1.4.1.2.2	Variation 2:	Rearrangements Involving Compounds Containing Sulfur or Selenium	380
40.1.1.4.1.3	Method 3:	Rearrangements of Phenylhydrazines and Hydrazobenzenes ..	382
40.1.1.4.1.4	Method 4:	Overman Rearrangement (Aza-Oxa-Cope Rearrangement) ...	382
40.1.1.4.1.5	Method 5:	Rearrangements of N-Substituted Amines	388
40.1.1.4.1.5.1	Variation 1:	Fischer–Hepp Rearrangement	388
40.1.1.4.1.5.2	Variation 2:	Hofmann–Martius Rearrangement	389
40.1.1.4.1.5.3	Variation 3:	Reilly–Hickinbottom and Orton Rearrangements	391
40.1.1.4.1.5.4	Variation 4:	Bamberger Rearrangement	391
40.1.1.4.1.5.5	Variation 5:	Hofmann–Löffler–Freytag Rearrangement	392
40.1.1.4.2		Rearrangements from Carbon to Nitrogen	393
40.1.1.4.2.1	Method 1:	Stieglitz Rearrangements	393
40.1.1.4.2.2	Method 2:	Beckmann Rearrangement	393
40.1.1.4.2.3	Method 3:	Neber Rearrangement	394
40.1.1.4.2.4	Method 4:	Hofmann, Curtius, Schmidt, and Lossen Rearrangements ...	395
40.1.1.4.2.4.1	Variation 1:	Hofmann Rearrangement	396
40.1.1.4.2.4.2	Variation 2:	Lossen Rearrangement	401
40.1.1.4.2.4.3	Variation 3:	Curtius Rearrangement	404
40.1.1.4.2.4.4	Variation 4:	Schmidt Rearrangement	411
40.1.1.5		Synthesis from Other Amino Compounds	
40.1.1.5.1		Resolution of Chiral Amines	
		V. A. Azov	
40.1.1.5.1		Resolution of Chiral Amines	419
40.1.1.5.1.1	Method 1:	Resolution by Diastereomeric Crystallization	419
40.1.1.5.1.2	Method 2:	Kinetic Resolution	421
40.1.1.5.1.2.1	Variation 1:	Enzymatic Kinetic Resolution	421
40.1.1.5.1.2.2	Variation 2:	Dynamic Kinetic Resolution Using Enzymes	425
40.1.1.5.1.2.3	Variation 3:	Nonenzymatic Kinetic Resolution	427
40.1.1.5.1.3	Method 3:	Analytical and Preparative Chromatographic Separation	428
40.1.1.5.1.4	Method 4:	Analysis and Separation of Diastereomeric Amine Derivatives	429
40.1.1.5.1.4.1	Variation 1:	Using Chiral Solvating Agents	430
40.1.1.5.1.4.2	Variation 2:	Using Chiral Derivatizing Agents	431
40.1.1.5.2		The Mannich Reaction	
		J. Ipaktschi and M. R. Saidi	
40.1.1.5.2		The Mannich Reaction	435
40.1.1.5.2.1		Direct Organocatalytic Enantioselective Mannich Reaction	435
40.1.1.5.2.1.1	Method 1:	α -Aminoalkylation of Ketones	436
40.1.1.5.2.1.1.1	Variation 1:	Proline-Catalyzed Aminoalkylation of Aliphatic Ketones	436
40.1.1.5.2.1.1.2	Variation 2:	Chiral Brønsted Acid Catalyzed Aminoalkylation of Ketones ..	438

40.1.1.5.2.1.1.3	Variation 3:	Aminoalkylation under High Pressure	439
40.1.1.5.2.1.2	Method 2:	α -Aminomethylation of Ketones	440
40.1.1.5.2.1.2.1	Variation 1:	Proline-Catalyzed α -Aminomethylation	440
40.1.1.5.2.1.2.2	Variation 2:	α -Aminomethylation of Ketones under Microwave Irradiation	441
40.1.1.5.2.1.3	Method 3:	α -Aminoalkylation of Hydroxy and Protected Amino Ketones	442
40.1.1.5.2.1.3.1	Variation 1:	Synthesis of <i>syn</i> -1,2-Amino Alcohols	442
40.1.1.5.2.1.3.2	Variation 2:	Synthesis of Protected Amino Sugars by Direct Mannich Reaction	443
40.1.1.5.2.1.3.3	Variation 3:	Synthesis of Chiral <i>syn</i> -1,2-Diamines	445
40.1.1.5.2.1.3.4	Variation 4:	Synthesis of <i>anti</i> -1,2-Amino Alcohols	446
40.1.1.5.2.1.4	Method 4:	Asymmetric Cross-Mannich Reaction of Aldehydes	447
40.1.1.5.2.1.4.1	Variation 1:	Stereoselective Synthesis of β -Amino Alcohols	448
40.1.1.5.2.1.4.2	Variation 2:	Self-Mannich Reaction of Aliphatic and α -Hydroxy Aldehydes	449
40.1.1.5.2.1.4.3	Variation 3:	One-Pot Direct Synthesis of β -Formyl- α -amino Acids	449
40.1.1.5.2.2		Indirect Organocatalytic Enantioselective Mannich Reaction with Preformed Reagents	451
40.1.1.5.2.2.1	Method 1:	β -Amino Carbonyl Derivatives from Reactions of <i>N</i> -(<i>tert</i> -Butoxycarbonyl)-Protected Imines	451
40.1.1.5.2.2.1.1	Variation 1:	Proline-Catalyzed Addition of Aldehydes or Ketones	451
40.1.1.5.2.2.1.2	Variation 2:	Chiral Brønsted Acid Catalyzed Reaction of <i>N</i> -(<i>tert</i> -Butoxycarbonyl)-Protected Aldimines	452
40.1.1.5.2.2.2	Method 2:	α -Amino Acids by <i>syn</i> -Selective Synthesis	453
40.1.1.5.2.2.2.1	Variation 1:	Proline-Catalyzed Reaction of Ketones with <i>N</i> -(4-Methoxyphenyl)-Protected α -Imino Ethyl Glyoxylate	453
40.1.1.5.2.2.2.2	Variation 2:	5-(Pyrrolidin-2-yl)tetrazole-Catalyzed Reaction of Ketones with <i>N</i> -(4-Methoxyphenyl)-Protected Imines	454
40.1.1.5.2.2.2.3	Variation 3:	Reaction of Enolizable Aldehydes with <i>N</i> -(4-Methoxyphenyl)-Protected α -Imines	455
40.1.1.5.2.2.3	Method 3:	α -Amino Acids by <i>anti</i> -Selective Synthesis	456
40.1.1.5.2.2.3.1	Variation 1:	Reaction of Enolizable Aldehydes Catalyzed by a Chiral Amino Sulfonamide	456
40.1.1.5.2.2.3.2	Variation 2:	Reaction of Enolizable Aldehydes Catalyzed by a Chiral Pyrrolidine-Based Amino Sulfonamide	457
40.1.1.5.2.2.3.3	Variation 3:	Reaction of Enolizable Aldehydes Catalyzed by Amino Acid Derivatives	458
40.1.1.5.2.2.3.4	Variation 4:	<i>anti</i> -Mannich Reactions of Unmodified Ketones	459
40.1.1.5.2.2.3.5	Variation 5:	Synthesis of Optically Active Quaternary α -Amino Acid Derivatives	460
40.1.1.5.2.2.4	Method 4:	β -Amino Acids by Indirect Mannich Reaction of Ketene Silyl Acetals with Protected Imines	461
40.1.1.5.2.2.4.1	Variation 1:	Chiral-Thiourea-Catalyzed Addition of Ketene Silyl Acetals to <i>N</i> -(<i>tert</i> -Butoxycarbonyl)aldimines	461
40.1.1.5.2.2.4.2	Variation 2:	Chiral Brønsted Acid Catalyzed Reaction of Aldimines with Ketene Silyl Acetals	462
40.1.1.5.2.2.5	Method 5:	β -Amino Acids by Addition of CH-Acidic 1,3-Dicarbonyl Compounds to Protected Imines	464

40.1.1.5.2.2.5.1	Variation 1:	Enantioselective Addition of Malonate to <i>N</i> -(<i>tert</i> -Butoxy-carbonyl)-Protected Aromatic and Aliphatic Aldimines	464
40.1.1.5.2.2.5.2	Variation 2:	Addition of β -Oxo Esters to Protected Imines Catalyzed by Cinchona Alkaloids	464
40.1.1.5.2.2.5.3	Variation 3:	Stereoselective Synthesis of α,β -Diamino Acids Using a Chiral Phase-Transfer Catalyst	465
40.1.1.5.2.3		Metal-Catalyzed Asymmetric Mannich Reaction	467
40.1.1.5.2.3.1	Method 1:	Synthesis Using Silyl Enol Ethers and Ketene Silyl Acetals as Nucleophiles	467
40.1.1.5.2.3.1.1	Variation 1:	Enantio- and Diastereoselective Synthesis of β -Amino Carbonyl Compounds	468
40.1.1.5.2.3.1.2	Variation 2:	Enantio- and Diastereoselective Synthesis of β -Amino Ketones in Water	469
40.1.1.5.2.3.1.3	Variation 3:	Enantioselective Synthesis of β -Amino Esters	470
40.1.1.5.2.3.2	Method 2:	Synthesis of <i>anti</i> - or <i>syn</i> - β -Amino- α -hydroxy Ketones	472
40.1.1.5.2.3.2.1	Variation 1:	Metal-1,1'-Binaphthalene-2,2'-diol Complexes as Catalyst	472
40.1.1.5.2.3.2.2	Variation 2:	Dinuclear Zinc Complexes as Catalyst	473
40.1.1.5.3		Modification of Mannich Adducts J. Ipaktschi and M. R. Saidi	
40.1.1.5.3		Modification of Mannich Adducts	479
40.1.1.5.3.1		Modification of the Amino Group	479
40.1.1.5.3.1.1	Method 1:	Deprotection of the <i>N</i> -(<i>tert</i> -Butoxycarbonyl) Group	479
40.1.1.5.3.1.2	Method 2:	Deprotection of <i>N</i> -(4-Hydroxyphenyl), <i>N</i> -(4-Methoxyphenyl), and <i>N</i> -(2-Methoxyphenyl) Groups	480
40.1.1.5.3.1.3	Method 3:	Deprotection of <i>N</i> -(Diarylphosphoryl) Groups	481
40.1.1.5.3.1.4	Method 4:	Deprotection of <i>N</i> -(Arylsulfonyl) Groups	481
40.1.1.5.3.1.5	Method 5:	Deprotection of the <i>N</i> -[(<i>R</i>)-2-Hydroxy-1-phenylethyl] Group	482
40.1.1.5.3.1.6	Method 6:	Acylation Using Triphosgene	482
40.1.1.5.3.1.7	Method 7:	Guanidinylation and the Synthesis of Capreomycin	484
40.1.1.5.3.1.8	Method 8:	Synthesis of Enantioenriched Dihydropyrimidinones	485
40.1.1.5.3.2		Modification of the Carbonyl Group	486
40.1.1.5.3.2.1	Method 1:	Enantioselective Synthesis of β^2 -Amino Acid Derivatives	486
40.1.1.5.3.2.2	Method 2:	Enantioselective Synthesis of $\beta^{2,3}$ -Amino Acid Derivatives	488
40.1.1.5.3.2.3	Method 3:	Baeyer-Villiger Oxidation	489
40.1.1.5.3.2.4	Method 4:	Diastereoselective Reduction: Synthesis of (+)-Polyoxamic Acid	489
40.1.1.5.3.2.5	Method 5:	Synthesis of β -Lactams	491
40.1.1.5.3.2.6	Method 6:	Palladium-Catalyzed Carbonylation: Synthesis of (\pm)-Gelsemine	492
40.1.1.5.3.2.7	Method 7:	Synthesis of Peptides: Synthesis of Azumamide A	493
40.1.1.5.3.3		Reduction of the Carbonyl Group and Imines	494
40.1.1.5.3.3.1	Method 1:	Enantioselective Synthesis of 1,3-Amino Alcohols: Synthesis of HPA-12	495

40.1.1.5.3.3.2	Method 2:	Enantioselective Synthesis of 1,3-Amino Alcohols: Synthesis of (–)-Sedamine	495
40.1.1.5.3.3.3	Method 3:	Enantioselective Synthesis of 1,3-Diamines	497
40.1.1.5.4	Substitution on the Amine Nitrogen S. A. Lawrence		
40.1.1.5.4	Substitution on the Amine Nitrogen		501
40.1.1.5.4.1	Dealkylation Reactions of Amines		501
40.1.1.5.4.1.1	Method 1:	The von Braun Reaction with Cyanogen Bromide	501
40.1.1.5.4.1.2	Method 2:	Dealkylation by Acylation	504
40.1.1.5.4.1.3	Method 3:	Nitrosative Dealkylation Reactions	509
40.1.1.5.4.1.4	Method 4:	Dealkylation by Transamination	509
40.1.1.5.4.1.5	Method 5:	Acid-Mediated Dealkylation	511
40.1.1.5.4.1.6	Method 6:	Photolytic Dealkylation	512
40.1.1.5.4.1.7	Method 7:	Cleavage of the C–N Bond Using Selenols	512
40.1.1.5.4.1.8	Method 8:	Cleavage of the C–N Bond Using Wilkinson’s Catalyst	513
40.1.1.5.4.1.9	Method 9:	Reductive Cleavage of the C–N Bond	514
40.1.1.5.4.2	Dealkylation Reactions of Ammonium Salts		515
40.1.1.5.4.2.1	Method 1:	Thermolytic Dealkylation	515
40.1.1.5.4.2.2	Method 2:	The Hofmann Elimination Reaction	515
40.1.1.5.4.2.3	Method 3:	Dealkylation with Ammonia, Amines, 2-Aminoethanol, or Other Bases	518
40.1.1.5.4.2.4	Method 4:	Dealkylation Reactions with Alkali Metals or Metal Hydrides ·	519
40.1.1.5.4.2.5	Method 5:	Dealkylation Reactions Using Sulfur Nucleophiles	520
40.1.1.5.4.2.6	Method 6:	Electrolytic Methods of Cleavage	523
40.1.1.5.4.3	Replacement of Halogen Functionalities		523
40.1.1.5.4.3.1	Method 1:	Reaction of Ammonia with Alkyl Halides	523
40.1.1.5.4.3.2	Method 2:	Reactions of Primary, Secondary, or Tertiary Amines with Alkyl Halides	526
40.1.1.5.4.3.3	Method 3:	Reactions of Alkali Metal Amide Salts	531
40.1.1.5.4.3.4	Method 4:	The Gabriel Synthesis and Related Reactions of Carboxylic Acid Derivatives	531
40.1.1.5.4.3.5	Method 5:	Reactions of Nitrogen-Containing Derivatives of Carbonic Acid	534
40.1.1.5.4.3.6	Method 6:	Reactions with Hexamethylenetetramine	536
40.1.1.5.4.3.7	Method 7:	Reaction with Sulfonamides	538
40.1.1.5.4.3.8	Method 8:	Reaction with Amides of Phosphorus Acids	539
40.1.1.5.4.3.9	Method 9:	Reactions of Alkyl Halides with Silylamines and Silylamides ·	542
40.1.1.5.4.3.10	Method 10:	Intra- and Intermolecular Cyclization Reactions	543
40.1.1.5.4.3.11	Method 11:	Reactions of Haloamines	547
40.1.1.5.4.4	Replacement of Oxygen Functionalities		548
40.1.1.5.4.4.1	Method 1:	Reactions of Ammonia with Alcoholic Hydroxy Groups	548
40.1.1.5.4.4.2	Method 2:	Reactions of Primary or Secondary Amines with Alcoholic Hydroxy Groups	550

40.1.1.5.4.4.3	Method 3:	The Mitsunobu and Related Reactions	552
40.1.1.5.4.4.4	Method 4:	Intermolecular Schmidt Reaction	559
40.1.1.5.4.4.5	Method 5:	Reactions of Ammonia and Amines with Ethers	560
40.1.1.5.4.4.6	Method 6:	Alkylation with Sulfates	565
40.1.1.5.4.4.7	Method 7:	Alkylation with Sulfonates	566
40.1.1.5.4.4.8	Method 8:	Alkylation with Nitrates	569
40.1.1.5.4.4.9	Method 9:	Reactions with O–P Groups	569
40.1.1.5.4.4.10	Method 10:	Reactions with O–Si Groups	569
40.1.2	Product Subclass 2: Propargylic Amines		
	J. Q. Feng and C.-J. Li		
40.1.2	Product Subclass 2: Propargylic Amines		
	J. Q. Feng and C.-J. Li		
40.1.2	Product Subclass 2: Propargylic Amines		
40.1.2.1	Synthesis of Product Subclass 2		
40.1.2.1.1	Method 1:	Ethynylations of Azomethines	579
40.1.2.1.1.1	Variation 1:	Catalyzed by Iridium(I) Complexes	579
40.1.2.1.1.2	Variation 2:	Catalyzed by a Copper(I)–pybox Complex	580
40.1.2.1.2	Method 2:	Three-Component Coupling of an Aldehyde, an Alkyne, and an Amine	580
40.1.2.1.2.1	Variation 1:	Catalyzed by Copper(I) Salts	580
40.1.2.1.2.2	Variation 2:	Catalyzed by Copper(I) Bromide/Ruthenium(III) Chloride	582
40.1.2.1.2.3	Variation 3:	Catalyzed by Gold(III) Bromide	582
40.1.2.1.2.4	Variation 4:	Catalyzed by Silver(I) Salts	583
40.1.2.1.3	Method 3:	Copper-Catalyzed Cross-Dehydrogenative Coupling	584
40.1.3	Product Subclass 3: Allylic Amines		
	J. Q. Feng and C.-J. Li		
40.1.3	Product Subclass 3: Allylic Amines		
	J. Q. Feng and C.-J. Li		
40.1.3	Product Subclass 3: Allylic Amines		
40.1.3.1	Synthesis of Product Subclass 3		
40.1.3.1.1	Method 1:	Synthesis by Substitution of Hydrogen	587
40.1.3.1.1.1	Variation 1:	By Ene-Type Reaction	587
40.1.3.1.1.2	Variation 2:	Allylic Amination via the Insertion of Nitrenes	590
40.1.3.1.2	Method 2:	Synthesis by the Substitution of a Halogen or a Leaving Group	591
40.1.3.1.2.1	Variation 1:	By Palladium-Catalyzed Allylic Substitution	591
40.1.3.1.3	Method 3:	Synthesis by Addition	594
40.1.3.1.3.1	Variation 1:	Of Nitrogen Reagents to Vinylphosphonium Salts	594
40.1.3.1.3.2	Variation 2:	By Aza-Baylis–Hillman Reaction	597
40.1.3.1.3.3	Variation 3:	By Aza-Diels–Alder Reaction	601
40.1.3.1.4	Method 4:	Synthesis by Rearrangement	606
40.1.3.1.4.1	Variation 1:	Of Aziridines	606
40.1.3.1.4.2	Variation 2:	By Aza-Oxa-Cope Rearrangement	606
40.1.3.1.4.3	Variation 3:	By [2,3]-Sigmatropic Rearrangement	609

40.1.4	Product Subclass 4: n-Nitrogen- or n-Phosphorus-Functionalized Alkylamines (n ≥ 2) K.-M. Roy	
40.1.4	Product Subclass 4: n-Nitrogen- or n-Phosphorus-Functionalized Alkylamines (n ≥ 2)	615
40.1.4.1	Synthesis of Product Subclass 4	615
40.1.4.1.1	Synthesis by Addition across C=C Bonds	615
40.1.4.1.1.1	Method 1: Amination of 1,3-Dienes	615
40.1.4.1.1.1.1	Variation 1: 1,2-Diamination	615
40.1.4.1.1.1.2	Variation 2: 1,4-Diamination	615
40.1.4.1.1.2	Method 2: Amination of Alkenes	616
40.1.4.1.1.2.1	Variation 1: Direct Addition of Nitrogen Compounds	616
40.1.4.1.1.2.2	Variation 2: α,ω-Diamines by Carbonylative Bis(hydroaminomethylation) of α,ω-Dialkenes	619
40.1.4.1.1.2.3	Variation 3: 1,2-Diamines via 4,5-Dihydroimidazoles	620
40.1.4.1.2	Synthesis by Addition across C–N Bonds	621
40.1.4.1.2.1	Method 1: Ring Opening of Aziridines	621
40.1.4.1.2.1.1	Variation 1: Addition of Amines	621
40.1.4.1.2.1.2	Variation 2: Addition of Azides	622
40.1.4.1.2.2	Method 2: Ring Opening of Azetidines	625
40.1.4.1.2.3	Method 3: Synthesis by Coupling of Nitrogen Compounds	625
40.1.4.1.2.3.1	Variation 1: Coupling of Imines	625
40.1.4.1.2.3.2	Variation 2: Coupling of Amines	629
40.1.4.1.2.3.3	Variation 3: Coupling of Nitriles	630
40.1.4.1.3	Synthesis by Addition across C–C Bonds	630
40.1.4.1.3.1	Method 1: Amine Addition to Epoxides	630
40.1.4.1.4	Synthesis by Rearrangement	631
40.1.4.1.4.1	Method 1: 1,2-Diamines via [2,3]-Sigmatropic Rearrangement	631
40.1.4.1.4.1.1	Variation 1: Rearrangement of Sulfur Imides	631
40.1.4.1.4.1.2	Variation 2: Rearrangement of Selenium Imides	632
40.1.4.1.4.2	Method 2: 1,2-Diamines via [3,3]-Sigmatropic Rearrangement	633
40.1.4.1.5	Synthesis by Reduction of α-Amino Amides	633
40.1.4.1.6	Synthesis of 2-Nitroamines	634
40.1.4.1.6.1	Method 1: Synthesis by Nitro-Mannich Reaction	634
40.1.4.1.6.2	Method 2: Synthesis by Addition of Nitrogen Compounds to Alkenes ..	636
40.1.4.1.7	Synthesis of (Aminoalkyl)phosphines	637
40.1.4.1.7.1	Method 1: Synthesis by Amination of Unsaturated Phosphines	637
40.1.4.1.7.2	Method 2: Synthesis by Addition of Phosphines to Unsaturated Amines ·	637
40.1.4.2	Applications of Product Subclass 4 in Organic Synthesis	638

40.1.5	Product Subclass 5: Aziridines J. B. Sweeney	
40.1.5	Product Subclass 5: Aziridines	643
40.1.5.1	Synthesis of Product Subclass 5	643
40.1.5.1.1	Method 1: Addition to Alkenes	643
40.1.5.1.1.1	Variation 1: Addition of Nitrenes	643
40.1.5.1.1.2	Variation 2: Addition of Metal Nitrenoids	648
40.1.5.1.1.3	Variation 3: Addition of Azides	658
40.1.5.1.1.4	Variation 4: Addition of Hydrazine Derivatives	659
40.1.5.1.1.5	Variation 5: Addition of Hydroxylamine Derivatives	660
40.1.5.1.2	Method 2: Addition to Imines	662
40.1.5.1.2.1	Variation 1: Addition of Carbenes	662
40.1.5.1.2.2	Variation 2: Addition of Metal Carbenoids	663
40.1.5.1.2.3	Variation 3: Via Nucleophilic Attack of Anions of 2-Halo and 2-Pseudohalo Esters	667
40.1.5.1.2.4	Variation 4: Cyclization of Azomethine Ylides	675
40.1.5.1.2.5	Variation 5: Addition of Nucleophiles to Azirines	676
40.1.5.1.2.6	Variation 6: Cycloaddition of Azirines	683
40.1.5.1.3	Method 3: Addition to Aldehydes Using Guanidinium Ylides	685
40.1.5.1.4	Method 4: Cyclization Reactions	686
40.1.5.1.4.1	Variation 1: Cyclization of 2-Haloalkanamines	686
40.1.5.1.4.2	Variation 2: Cyclization of 2-Aminoalkanols	691
40.1.5.1.4.3	Variation 3: Cyclization of 2-Azidoalkanols	698
40.1.5.1.4.4	Variation 4: Via Cyclic Sulfates	700
40.1.5.1.4.5	Variation 5: Cyclization of 1-Azido-2-haloalkanes	701
40.1.5.1.4.6	Variation 6: Cyclization of Allenyl-Substituted Amines	702
40.1.5.1.4.7	Variation 7: Cyclization of (2-Bromoallyl)amines	703
40.1.5.1.5	Method 5: Ring Contraction of 4,5-Dihydro-1 <i>H</i> -1,2,3-triazoles	703
40.1.5.1.6	Method 6: Substituent Modification	705
40.1.5.1.6.1	Variation 1: Substitution of Existing Substituents	705
40.1.5.1.6.2	Variation 2: Of Hydrogen: Deprotonation	707
40.1.5.2	Applications of Product Subclass 5 in Organic Synthesis	712
40.1.5.2.1	Ring Opening of Saturated Aziridines	712
40.1.5.2.1.1	Method 1: Ring Opening with Hydrogen	713
40.1.5.2.1.1.1	Variation 1: Hydrogenolysis	713
40.1.5.2.1.1.2	Variation 2: By Complex Hydrides	715
40.1.5.2.1.1.3	Variation 3: By Metal Reducing Agents	716
40.1.5.2.1.2	Method 2: Ring Opening Using Oxygen Nucleophiles	717
40.1.5.2.1.2.1	Variation 1: By Water	717
40.1.5.2.1.2.2	Variation 2: By Alcohols	719
40.1.5.2.1.2.3	Variation 3: By Carboxylates	720
40.1.5.2.1.2.4	Variation 4: Intramolecular Ring Opening by Oxygen Nucleophiles	721
40.1.5.2.1.3	Method 3: Ring Opening Using Nitrogen Nucleophiles	724
40.1.5.2.1.3.1	Variation 1: By Aliphatic Amines	724
40.1.5.2.1.3.2	Variation 2: By Aromatic Amines	725

40.1.5.2.1.3.3	Variation 3:	By Azide	726
40.1.5.2.1.3.4	Variation 4:	By Hydroxylamine	729
40.1.5.2.1.3.5	Variation 5:	Intramolecular Ring Opening by Nitrogen Nucleophiles	730
40.1.5.2.1.4	Method 4:	Ring Opening Using Sulfur Nucleophiles	730
40.1.5.2.1.5	Method 5:	Ring Opening Using Halogen Nucleophiles	732
40.1.5.2.1.6	Method 6:	Ring Opening Using Carbon Nucleophiles	735
40.1.5.2.1.6.1	Variation 1:	By Carbanions	735
40.1.5.2.1.6.2	Variation 2:	By Enolates	741
40.1.5.2.1.6.3	Variation 3:	By Arenes	742
40.1.5.2.1.6.4	Variation 4:	By Cyanide	744
40.1.5.2.1.7	Method 7:	Ring Opening by Deprotonation	745
40.1.5.2.1.7.1	Variation 1:	Elimination Reactions	745
40.1.5.2.1.7.2	Variation 2:	Rearrangement Reactions	746
40.1.5.2.1.8	Method 8:	Ring Opening Using Lewis Acids	747
40.1.5.2.1.9	Method 9:	Ring Opening by Thermolysis	749
40.1.5.2.1.10	Method 10:	Carbonylative Ring Expansion	750
40.1.5.2.2		Ring Opening of Alkenyl- and Alkynylaziridines	751
40.1.5.2.2.1	Method 1:	Ring Opening by Hydride	751
40.1.5.2.2.2	Method 2:	Ring Opening by Oxygen Nucleophiles	752
40.1.5.2.2.2.1	Variation 1:	By Water	752
40.1.5.2.2.2.2	Variation 2:	By Carboxylates	753
40.1.5.2.2.2.3	Variation 3:	Intramolecular Ring Opening by Oxygen Nucleophiles	753
40.1.5.2.2.3	Method 3:	Ring Opening Using Amino Nucleophiles	754
40.1.5.2.2.4	Method 4:	Ring Opening Using Halogen Nucleophiles	755
40.1.5.2.2.5	Method 5:	Ring Opening Using Carbon Nucleophiles	755
40.1.5.2.2.5.1	Variation 1:	By Carbanions	755
40.1.5.2.2.5.2	Variation 2:	With Palladium Catalysis	758
40.1.5.2.2.6	Method 6:	Ring Opening via Rearrangement	759
40.1.6	Product Subclass 6: Azetidines		
	F. Couty		
40.1.6	Product Subclass 6: Azetidines		773
40.1.6.1	Synthesis of Product Subclass 6		773
40.1.6.1.1	Ring-Closure Reactions		773
40.1.6.1.1.1	Method 1:	Ring Closure of Amines and 1,3-Functionalized Hydrocarbons	773
40.1.6.1.1.1.1	Variation 1:	From Amines and 1,3-Dihalo Compounds	773
40.1.6.1.1.1.2	Variation 2:	From Amines and 1,3-Diol Derivatives	774
40.1.6.1.1.2	Method 2:	Thermal [2 + 2] Cycloaddition of Imines and Alkenes	775
40.1.6.1.1.3	Method 3:	Ring Closure of Acyclic Amines	776
40.1.6.1.1.3.1	Variation 1:	Of γ -Haloamines	776
40.1.6.1.1.3.2	Variation 2:	Of γ -Amino Alcohols and Derivatives	777
40.1.6.1.1.3.3	Variation 3:	Of Alkenyl- or Allenylamines	782
40.1.6.1.1.3.4	Variation 4:	Of γ,δ -Epoxyamines	784
40.1.6.1.1.3.5	Variation 5:	Of γ -Azidoamines	785
40.1.6.1.1.4	Method 4:	Ring Closure of Acyclic Imine Derivatives	785

40.1.6.1.1.5	Method 5:	Ring Closure of Stabilized Carbanions (C—C Bond Formation).	788
40.1.6.1.1.5.1	Variation 1:	Intramolecular Alkylation of β -Amino Halides	789
40.1.6.1.1.5.2	Variation 2:	Intramolecular Michael Addition	792
40.1.6.1.1.6	Method 6:	Photochemical Cyclizations	793
40.1.6.1.1.6.1	Variation 1:	Intermolecular Photochemical Cyclizations	793
40.1.6.1.1.6.2	Variation 2:	Intramolecular Photochemical Cyclizations	794
40.1.6.1.1.7	Method 7:	Cyclizations through Insertion of Carbenoids into N—H Bonds	796
40.1.6.1.1.8	Method 8:	Cyclizations through Copper-Catalyzed Intramolecular N-Vinylation	798
40.1.6.1.1.9	Method 9:	Cyclization of Amines with Alkenes via Azazircona- cyclopentanes	799
40.1.6.1.2		Reduction of Four-Membered Ring Compounds	800
40.1.6.1.2.1	Method 1:	Reduction of Azetidin-2-ones (β -Lactams)	800
40.1.6.1.2.2	Method 2:	Alkenation of Azetidin-2-ones (β -Lactams)	804
40.1.6.1.2.3	Method 3:	Reduction of Azetidinium Ions	806
40.1.6.1.3		Ring-Transformation Reactions	807
40.1.6.1.3.1	Method 1:	Ring Expansion of Three-Membered Rings	807
40.1.6.1.3.2	Method 2:	Ring Contraction of Five- or Six-Membered Rings	810
40.1.6.1.3.3	Method 3:	Ring Transformation of 3-(Chloromethyl)azetidin-2-ones	812
40.1.7		Product Subclass 7: Ammonium Compounds and Nitrogen Ylides	
		E. Kruiswijk and J. A. Deck	
40.1.7		Product Subclass 7: Ammonium Compounds and Nitrogen Ylides	817
40.1.7.1		Synthesis of Product Subclass 7	817
40.1.7.1.1	Method 1:	Synthesis of Quaternary Ammonium Compounds from Primary and Secondary Amines	817
40.1.7.1.2	Method 2:	Synthesis from Amines and Diazomethane	818
40.1.7.1.2.1	Variation 1:	From Amines and Activated Diazomethane	818
40.1.7.1.2.2	Variation 2:	From Amino Acids	819
40.1.7.1.3	Method 3:	Alkylation of Tertiary Amines	820
40.1.7.1.3.1	Variation 1:	With Haloalkanes under Pressure	821
40.1.7.1.3.2	Variation 2:	With Tertiary Oxonium Salts	821
40.1.7.1.3.3	Variation 3:	With Dialkoxycarbenium Salts	822
40.1.7.1.3.4	Variation 4:	With Methyl Trifluoromethanesulfonate	823
40.1.7.1.3.5	Variation 5:	With Methyl Chloroformate	824
40.1.7.1.3.6	Variation 6:	With <i>O</i> -Alkylisoureas	825
40.1.7.1.3.7	Variation 7:	With Dimethyl Sulfate	826
40.1.7.1.3.8	Variation 8:	With Electron-Poor Alkenes and Alkynes	827
40.1.7.1.3.9	Variation 9:	With Alkylideneammonium Halides	829
40.1.7.1.3.10	Variation 10:	Synthesis of Polymer-Bound Ammonium Compounds	830
40.1.7.1.4	Method 4:	Synthesis of Compounds Containing Several Quaternary Ammonium Centers	830
40.1.7.1.4.1	Variation 1:	Derivatives of Diamines	830
40.1.7.1.4.2	Variation 2:	Derivatives of Bis(aminomethyl)arenes	832
40.1.7.1.4.3	Variation 3:	Derivatives of <i>N</i> -Alkylated Macrocycles	834

40.1.7.1.5	Method 5: Synthesis of Nitrogen Ylides	835
40.1.7.1.5.1	Variation 1: From Quaternary Ammonium Compounds	835
40.1.7.1.5.2	Variation 2: Addition of a Tertiary Amine to a Metal Carbene	836
40.1.7.1.5.3	Variation 3: Addition of a Tertiary Amine to the Simmons–Smith Reagent	837
40.1.7.2	Applications of Product Subclass 7 in Organic Synthesis	838
	Keyword Index	i
	Author Index	lix
	Abbreviations	cv