

## Contents

Preface *ix*

List of Abbreviations *xi*

<b>1</b>	<b>Asymmetric Cyclopropanation</b>	<b>1</b>
1.1	Introduction	1
1.2	Simmons–Smith Cyclopropanation	2
1.2.1	Chiral Substrates	3
1.2.1.1	Chiral Allylic Alcohols	3
1.2.1.2	Chiral Allylic Amines	7
1.2.1.3	Chiral Acetal-Directed Cyclopropanations	7
1.2.1.4	Simple Chiral Alkenes	9
1.2.2	Chiral Auxiliaries	11
1.2.3	Chiral Catalysts	15
1.2.3.1	Charette’s Ligand	15
1.2.3.2	Other Stoichiometric Ligands	20
1.2.3.3	Walsh’ Procedure	22
1.2.3.4	True Catalytic Procedures	24
1.3	Transition-Metal-Catalyzed Decomposition of Diazoalkanes	27
1.3.1	Intermolecular Cyclopropanation	28
1.3.1.1	Chiral Auxiliaries	28
1.3.1.2	Chiral Catalysts: Cobalt	32
1.3.1.3	Chiral Catalysts: Copper	38
1.3.1.4	Chiral Catalysts: Rhodium	56
1.3.1.5	Chiral Catalysts: Ruthenium	69
1.3.1.6	Chiral Catalyst: Other Metals	77
1.3.2	Intramolecular Cyclopropanation	80
1.3.2.1	Chiral Auxiliaries and Chiral Compounds	80
1.3.2.2	Chiral Catalysts	82
1.3.3	Chiral Stoichiometric Carbenes	93
1.4	Michael-Initiated and Other Ring Closures	94
1.4.1	Chiral Substrates	95
1.4.2	Chiral Auxiliaries	100
1.4.2.1	Chiral Michael Acceptors	100
1.4.2.2	Chiral Nucleophiles	106

1.4.3	Organocatalysis	115
1.4.3.1	Ylides	116
1.4.3.2	Nitrocyclopropanation	118
1.4.3.3	Halocarbonyl Compounds	128
1.4.4	Metal Catalysis	139
1.4.5	Other Ring Closures	140
1.5	Miscellaneous Reactions	148
1.5.1	Rearrangement of Chiral Oxiranes	148
1.5.2	Cycloisomerization of 1, <i>n</i> -Enynes	152
1.5.3	Denitrogenation of Chiral Pyrazolines	160
1.5.4	C–H Insertion	162
1.5.5	Addition to Cyclopropenes	164
1.5.6	Other Methods	167
1.6	Conclusions	172
	References	172
<b>2</b>	<b>Asymmetric Aziridination</b>	<b>205</b>
2.1	Introduction	205
2.2	Aziridination Based on the Use of Chiral Substrates	206
2.2.1	Addition to Alkenes	206
2.2.1.1	Aziridination via Nitrene Transfer to Alkenes	206
2.2.1.2	Aziridination via Addition–Elimination Processes	219
2.2.1.3	Miscellaneous Reactions	224
2.2.2	Addition to Imines	225
2.2.2.1	Methylation of Imines	226
2.2.2.2	Aza-Darzens and Analogous Reactions	248
2.2.2.3	Addition/Elimination Processes	255
2.2.2.4	Miscellaneous Reactions	266
2.2.3	Addition to Azirines	267
2.2.4	Aziridination via Intramolecular Substitution	270
2.2.4.1	From 1,2-Amino Alcohols	270
2.2.4.2	From 1,2-Amino Halides	278
2.2.4.3	From 1,2-Azido Alcohols	282
2.2.4.4	From 1,2-Amino Sulfides and 1,2-Amino Selenides	285
2.2.4.5	From Epoxides	286
2.2.5	Miscellaneous Reactions	287
2.3	Aziridination Based on the Use of Chiral Catalysts	296
2.3.1	Aziridination via Nitrene Transfer to Alkenes	296
2.3.1.1	Cu-Catalyzed Aziridination	296
2.3.1.2	Rh-Catalyzed Aziridination	310
2.3.1.3	Ru-Catalyzed Aziridination	312
2.3.1.4	Catalysis by Other Metals	314
2.3.1.5	Organocatalyzed Aziridination	318
2.3.2	Aziridination via Carbene Transfer to Imines	332
2.3.2.1	Carbene Methodology	332
2.3.2.2	Sulfur-Ylide-Mediated Aziridination	350

2.3.3	Miscellaneous Reactions	353
2.3.4	Kinetic Resolutions of Aziridines	357
2.4	Conclusions	363
	References	364
<b>3</b>	<b>Asymmetric Epoxidation</b>	<b>379</b>
3.1	Introduction	379
3.2	Asymmetric Epoxidations Based on the Use of Chiral Auxiliaries	380
3.3	Asymmetric Metal-Catalyzed Epoxidations	381
3.3.1	Ti-, Zr-, Hf-Catalyzed Epoxidations	381
3.3.2	V-, Nb-, Ta-Catalyzed Epoxidations	391
3.3.3	Cr-, Mo-, W-Catalyzed Epoxidations	397
3.3.4	Mn-, Re-, Fe-, Ru-Catalyzed Epoxidations	400
3.3.5	Pt-, Zn-, Lanthanoid-Catalyzed Epoxidations	412
3.4	Asymmetric Organocatalyzed Epoxidations	419
3.4.1	Phase-Transfer Catalyst	419
3.4.2	Polyamino Acids and Aspartate-Derived Peracids	423
3.4.3	Chiral Dioxiranes, Iminium Salts, and Alkyl Hydroperoxides	431
3.4.4	Chiral Amines	447
3.5	Kinetic Resolution of Racemic Epoxides	468
3.6	Asymmetric Sulfur-Ylide-Mediated Epoxidations	480
3.7	Asymmetric Darzens-Type Epoxidations	489
3.7.1	Chiral Auxiliary- and Reagent-Mediated Darzens Reactions	489
3.7.2	Catalytic Asymmetric Darzens Reactions	492
3.8	Other Ylide-Mediated Epoxidations	503
3.9	Asymmetric Biocatalyzed Synthesis of Epoxides	505
3.10	Conclusions	512
	References	514
<b>4</b>	<b>Asymmetric Oxaziridination</b>	<b>539</b>
4.1	Introduction	539
4.2	Oxaziridination Using Chiral Substrates	540
4.3	Oxaziridination Using Chiral Catalysts	544
4.4	Kinetic Resolutions	551
4.5	Conclusions	554
	References	555
<b>5</b>	<b>Asymmetric Azirination and Thiirination</b>	<b>559</b>
5.1	Introduction	559
5.2	Asymmetric Azirination	559
5.2.1	Neber Approaches	560
5.2.2	Elimination Approaches	565
5.2.3	Other Approaches	569
5.3	Asymmetric Thiirination	570
5.3.1	Conversion of Epoxides	571

5.3.2	Condensation of Sulfur-Stabilized Carbanions to Carbonyl Compounds	572
5.3.3	Intramolecular Nucleophilic Substitution	574
5.3.4	Miscellaneous Reactions	576
5.4	Conclusions	577
	References	579

<b>Index</b>	583
--------------	-----