

Asymmetric Phase Transfer Catalysis

Edited by
Keiji Maruoka



WILEY-VCH Verlag GmbH & Co. KGaA

Contents

Preface XI

List of Contributors XIII

1	The Basic Principle of Phase-Transfer Catalysis and Some Mechanistic Aspects	1
	<i>Takuya Hashimoto and Keiji Maruoka</i>	
1.1	Introduction	1
1.2	Inorganic Base-Promoted Activation of Acidic Organic Compounds	2
1.2.1	Generation of Reactive Onium Carbanion Species	2
1.2.2	Stability of the Onium Carbanion	3
1.2.3	Reactivity of the Onium Carbanion	3
1.2.4	Nuclueophilic Substitution Reaction	4
1.2.5	Nucleophilic Addition to Electrophilic C=X Double Bonds	5
1.3	Phase-Transfer-Catalyzed Addition of Anion Supplied as Metal Salt	6
1.4	Use of Crown Ether as Phase-Transfer Catalyst	7
	References	7
2	Cinchona-Derived Chiral Phase-Transfer Catalysts for Amino Acid Synthesis	9
	<i>Takashi Ooi</i>	
2.1	Introduction	9
2.2	α -Amino Acid Synthesis	9
2.2.1	Monoalkylation of Schiff Bases Derived from Glycine	9
2.2.2	Alkylation of Schiff Bases Derived from α -Alkyl- α -Amino Acids	19
2.2.3	Other Alkylations for α -Amino Acid Synthesis	21
2.2.4	Michael Reaction of Glycinate Benzophenone Schiff Bases	22

2.2.5	Aldol and Related Reactions	24
2.2.6	Aza-Henry Reaction	25
2.2.7	Strecker Reaction	27
2.2.8	Aziridination	27
2.2.9	Radical Reaction	28
2.3	β -Amino Acid Synthesis	29
2.3.1	Mannich Reaction	29
2.3.2	Cyclopropanation	29
2.4	Conclusions	30
	References	31
3	Cinchona-Derived Chiral Phase-Transfer Catalysts for Other Asymmetric Synthesis	35
	<i>Shigeru Arai</i>	
3.1	Introduction	35
3.2	Asymmetric Darzens Reaction	35
3.3	Asymmetric Conjugated Addition	36
3.4	Asymmetric Aldol Reaction	39
3.5	Asymmetric Oxygen-Functionalization	40
3.6	Asymmetric Alkylation	42
3.7	Asymmetric Alkenylation and Alkynylation	43
3.8	Asymmetric S_N Aromatic Reaction	45
3.9	Asymmetric Strecker Synthesis	46
3.10	Asymmetric Fluorination	46
	References	47
4	Cinchona-Derived Chiral Poly(Phase-Transfer Catalysts) for Asymmetric Synthesis	49
	<i>Sang-sup Jew and Hyeung-geun Park</i>	
4.1	Cinchona Alkaloids	49
4.1.1	Cinchona Alkaloids in Asymmetric Phase-Transfer Catalysis	49
4.1.2	The Origin of Stereoselectivity of Cinchona-PTCs	50
4.2	Development of Dimeric Cinchona-PTCs by the Park-Jew Group	51
4.2.1	Dimeric Cinchona-PTCs with Phenyl Linker	51
4.2.2	1,3-Dimeric Cinchona-PTCs with Electronically Modified Phenyl Linker	56
4.2.3	Polymeric Cinchona-PTCs with Other Linkers	56
4.2.4	1,3-Phenyl and 2,7-Naphthyl-Linked Dimeric Cinchona-PTCs	57
4.3	Polymeric PTCs Developed by the Najera Group	61
4.4	Polymeric PTCs Developed by the Siva Group	62
4.5	Polymeric PTCs Developed by the Wang Group	63
4.6	Asymmetric Epoxidation with Polymeric Cinchona-PTCs	63
4.7	Conclusions	68
	References	68

5	Binaphthyl- and Biphenyl-Modified Chiral Phase-Transfer Catalysts for Asymmetric Synthesis	71
	<i>Keiji Maruoka</i>	
5.1	Introduction	71
5.2	Alkylation	71
5.2.1	Asymmetric Synthesis of α -Alkyl α -Amino Acids and Their Derivatives	71
5.2.1.1	Asymmetric Monoalkylation of Glycine Ester Schiff Bases	71
5.2.1.2	Asymmetric Monoalkylation of Glycine Amide Schiff Bases	85
5.2.1.3	Diastereoselective Alkylation of Glycine Schiff Base with Optically Enriched Alkyl Halides	87
5.2.1.4	Recyclable Catalysts and Reagents and Solid-Phase Synthesis	87
5.2.1.5	Application of Asymmetric Synthesis of α -Amino Acids	87
5.2.2	Asymmetric Synthesis of α,α -Dialkyl- α -Amino Acids	90
5.2.3	Alkylation of Schiff Base-Activated Peptides	94
5.2.4	Other Alkylations	97
5.3	Michael Addition	99
5.4	Aldol Reaction	105
5.5	Mannich Reaction	106
5.6	Neber Rearrangement	106
5.7	Epoxidation	108
5.8	Strecker Reaction	109
5.9	Conclusions	110
	References	111
6	Two-Center Chiral Phase-Transfer Catalysts for Asymmetric Synthesis	115
	<i>Masakatsu Shibasaki and Takashi Ohshima</i>	
6.1	Introduction	115
6.2	Design and Synthesis of Two-Center Chiral Phase-Transfer Catalyst	115
6.3	Catalytic Asymmetric Phase-Transfer Alkylation	118
6.4	Catalytic Asymmetric Phase-Transfer Michael Addition to α,β -Unsaturated Esters	119
6.5	Catalytic Asymmetric Phase-Transfer Michael Addition to Enones	120
6.6	Catalytic Asymmetric Phase-Transfer Mannich-Type Reaction	122
6.7	Synthetic Applications	123
6.7.1	Enantioselective Syntheses of Aeruginosin 298-A and its Analogues	123
6.7.2	Short Syntheses of (+)-Cylindricine and Formal Synthesis of (-)-Lepadiformine	124
6.7.3	Formal Synthesis of (+)-CP-99,994 and Total Synthesis of (+)-Nemonapride	125
6.8	Catalyst Recovery and Reuse	126
6.9	Role of Two Ammonium Cations	127
6.10	Other Two-Center Chiral Phase-Transfer Catalysts	128
6.10.1	Two-Center Chiral Phase-Transfer Catalyst Derived from BINOL (1)	128

6.10.2	Two-Center Chiral Phase-Transfer Catalyst Derived from BINOL (2)	129
6.10.3	Two-Center Chiral Phase-Transfer Catalyst Derived from BINOL (3)	129
6.10.4	Two-Center Chiral Phase-Transfer Catalyst Derived from Tartrate (1)	130
6.10.5	Two-Center Chiral Phase-Transfer Catalyst Derived from Tartrate (2)	132
6.11	Conclusions	132
	References	133
7	Other Chiral Phase-Transfer Catalysts for Asymmetric Synthesis	135
	<i>Hiroaki Sasai and Mahesh L. Patil</i>	
7.1	Introduction	135
7.2	Other Chiral Phase-Transfer-Catalyzed Reactions	136
7.2.1	Alkylation	136
7.2.1.1	Substrate Scope	147
7.2.1.2	Mechanistic Investigations	149
7.2.2	Michael Reaction	150
7.2.3	Epoxidation	152
7.2.4	Hydroxylation	156
7.3	Conclusions	157
	References	157
8	Crown Ethers, Taddol, Nobin and Metal(salen) Complexes as Chiral Phase-Transfer Catalysts for Asymmetric Synthesis	161
	<i>Michael North</i>	
8.1	Introduction	161
8.2	Crown Ethers as Chiral Phase-Transfer Catalysts	163
8.2.1	Use of Crown Ethers in Asymmetric Michael Additions	163
8.2.2	Use of Crown Ethers in Darzens Condensations	165
8.2.3	Use of Crown Ethers in Asymmetric Epoxidations	166
8.3	Use of Taddolates as Chiral Phase-Transfer Catalysts	166
8.4	Use of Nobin and Related Species as Asymmetric Phase-Transfer Catalysts	170
8.5	Use of Metal(salen) Complexes as Chiral Phase-Transfer Catalysts	173
8.5.1	Nickel(salen) Complexes	173
8.5.2	Copper(salen) Complexes	175
8.5.3	Use of Other Metal(salen) Complexes as Catalysts for Enolate Alkylation	182
8.5.4	Metal(salen) Complexes as Catalysts for Darzens Condensations	183
8.6	Conclusions	184
	References	185

9	Chiral Quaternary Ammonium Fluorides for Asymmetric Synthesis	189
	<i>Seiji Shirakawa, Takashi Ooi, and Keiji Maruoka</i>	
9.1	Introduction	189
9.2	<i>In-Situ</i> Generation of Chiral Quaternary Ammonium Fluorides	189
9.3	Chiral Quaternary Ammonium Fluorides: Preparation and Application to Organocatalytic Asymmetric Reactions	193
9.4	Chiral Quaternary Ammonium Bifluorides: Preparation and Use as Organocatalysts for Asymmetric Carbon–Carbon Bond-Forming Reactions	197
9.5	Conclusions	205
	References	205
	Index	207