

Contents

Preface

1. Introduction

- 1.1 The olefin metathesis reaction
- 1.2 Brief history
- 1.3 The metal carbene mechanism
- 1.4 Equilibria and stereoselectivity
- 1.5 Reviews and papers containing useful summaries of the literature

2. Survey of catalyst systems

- 2.1 Introduction 13
- 2.2 Group IVA 17
- 2.3 Group VA 21
- 2.4 Group VIA 24
- 2.5 Group VIIA 32
- 2.6 Group VIII 34
- 2.7 Photochemically activated catalysts

3. The metal carbene mechanism

- 3.1 Introduction 43
- 3.2 Evidence from cross-metathesis reactions 44
- 3.3 Evidence from stereochemistry of metathesis of internal olefins 46
- 3.4 Evidence from ring-opening polymerizations 49
- 3.5 Reactions of isolable metal carbenes with olefins 54
- 3.6 Evidence from initial products 61
- 3.7 Metal carbene olefin complexes 69
- 3.8 Some properties of the metal carbene bond 71

4. Related reactions

- 4.1 Introduction 79
- 4.2 Cyclopropanation reactions 79
- 4.3 Generation of metal carbenes by reactions of cyclopropanes 81
- 4.4 Reactions of Mn^+ , MnO^+ , and $Mn=CH_2^+$ 86
- 4.5 Reactions involving metal-oxygen bonds 87
- 4.6 Reactions of tungstacyclobutanes 89
- 4.7 Homologation of n-alkanes on tungsten films 90
- 4.8 Metathesis between olefins and unsaturated phosphorus compounds 92
- 4.9 Ziegler-Natta polymerization 92

5. Ethene and terminal alkenes		
5.1	Introduction	98
5.2	Ethene	98
5.3	Propene	99
5.4	But-1-ene and its derivatives	111
5.5	Pent-1-ene and its derivatives	114
5.6	Hex-1-ene	115
5.7	Higher acyclic terminal olefins	116
6. Acyclic disubstituted ethenes		
6.1	Introduction	118
6.2	<i>Cis/trans</i> isomerization	118
6.3	Pent-2-ene and 4-substituted derivatives	120
6.4	Hex-2-ene and (<i>S</i>)-4-methylhex-2-ene	126
6.5	Hept-2-ene and hept-3-ene	126
6.6	Higher acyclic internal olefins	127
6.7	Stereoselectivity in the metathesis of acyclic olefins	128
6.8	1,1-Disubstituted olefins	139
7. Acyclic dienes		
7.1	Introduction	141
7.2	Two double bonds separated by a single bond	141
7.3	Two double bonds separated by two single bonds	142
7.4	Two double bonds separated by three single bonds	143
7.5	Two double bonds separated by four single bonds	144
7.6	Two double bonds separated by five single bonds	145
7.7	Two double bonds separated by seven single bonds	148
8. Acyclic unsaturated compounds containing functional groups		
8.1	Introduction	149
8.2	Esters	151
8.3	Other carbonyl-containing compounds	155
8.4	Ethers	156
8.5	Amines	156
8.6	Chlorides, bromides, and nitriles	159
8.7	Unsaturated organometallic compounds	159
9. Cross-metathesis between acyclic olefins		
9.1	Introduction	160
9.2	Ethene	162
9.3	Propene	162
9.4	Butenes	162
9.5	Pentenes	164
9.6	Hexenes	165
9.7	Higher olefins	166
9.8	Derivatives of oleic acid	

10. Acetylenes

10.1	Introduction	172
10.2	Metathesis reactions	173
10.3	Polymerization reactions	177
10.4	Cyclization reactions	188

11. Ring-opening polymerization: general aspects

11.1	Introduction	190
11.2	Effect of ring size and substitution on thermodynamic polymerizability	190
11.3	Formation of cyclic oligomers	194
11.4	Polymer microstructure	199

12. Monocyclic alkenes and polyenes

12.1	Introduction	224
12.2	C ₄ rings	224
12.3	C ₅ rings	227
12.4	C ₆ rings	235
12.5	C ₇ rings	236
12.6	C ₈ rings	236
12.7	C ₉ rings	242
12.8	C ₁₀ rings	243
12.9	C ₁₂ and higher rings	244

13. Bicyclic and tricyclic alkenes

13.1	Introduction	249
13.2	Unsubstituted bicycloalkenes	249
13.3	Monosubstituted bicyclo[2.2.1]hept-2-enes	256
13.4	5,5-Disubstituted bicyclo[2.2.1]hept-2-enes	258
13.5	5,6-Disubstituted bicyclo[2.2.1]hept-2-enes	259
13.6	Tetrasubstituted bicyclo[2.2.1]hept-2-enes	262
13.7	Derivatives of bicyclic dienes	263
13.8	6- and higher-membered unsaturated rings	264

14. Copolymers of cycloalkenes

14.1	Introduction	267
14.2	Direct copolymerization	267
14.3	Cyclic co-oligomers	278
14.4	Copolymers by successive addition of monomers	279
14.5	Copolymers by metathesis of unsaturated polymers with cycloalkenes	279
14.6	Copolymers by cross-metathesis of unsaturated homopolymers	281

15. Cross-metathesis between cyclic and acyclic olefins

15.1	Introduction	282
15.2	End groups and telomers	282

15.3	Dependence of molecular weight on $[M_2]/[M_1]$	289
15.4	Kinetic data	291
16. Degradation of unsaturated polymers by metathesis		
16.1	Introduction	299
16.2	Degradation by intramolecular metathesis	300
16.3	Degradation by intermolecular metathesis	305
17. Applications of the olefin metathesis reaction		
17.1	Introduction	323
17.2	The Phillips triolefin process	323
17.3	The neohexene process	324
17.4	Multistage processes involving metathesis	325
17.5	<i>trans</i> -Poly(1-pentenylene)	327
17.6	<i>trans</i> -Poly(1-octenylene)	331
17.7	Polymers of norbornene and derivatives	331
18. Appendix		
	Landmarks and summary of some recent work on olefin metathesis	333
	Bibliography	364
	Index	