

Contents

<i>Preface to the first edition</i>	<i>page</i> vii
<i>Preface to the fourth edition</i>	ix
1 Formation of carbon–carbon single bonds	1
1.1 Main-group chemistry	1
1.1.1 Alkylation of enolates and enamines	1
1.1.2 Conjugate addition reactions of enolates and enamines	19
1.1.3 The aldol reaction	27
1.1.4 Asymmetric methodology with enolates and enamines	36
1.1.5 Organolithium reagents	45
1.1.6 Organomagnesium reagents	63
1.1.7 Organozinc reagents	67
1.1.8 Allylic organometallics of boron, silicon and tin	71
1.2 Transition-metal chemistry	75
Problems	101
1.2.1 Organocopper reagents	75
1.2.2 Organochromium chemistry	81
1.2.3 Organocobalt chemistry	85
1.2.4 Organopalladium chemistry	89
2 Formation of carbon–carbon double bonds	105
2.1 β -Elimination reactions	105
2.2 Pyrolytic <i>syn</i> eliminations	111
2.3 Fragmentation reactions	118
2.4 Alkenes from hydrazones	120
2.5 Alkenes from 1,2-diols	123
2.6 Alkenes from alkynes	125
2.7 The Wittig and related reactions	132

vi	<i>Contents</i>	
2.8	Alkenes from sulfones	144
2.9	Alkenes using titanium or chromium reagents	148
2.10	Alkene metathesis reactions	151
	Problems	155
3	Pericyclic reactions	159
3.1	The Diels–Alder cycloaddition reaction	159
3.1.1	The dienophile	162
3.1.2	The diene	174
3.1.3	Regiochemistry of the Diels–Alder reaction	185
3.1.4	Stereochemistry of the Diels–Alder reaction	188
3.1.5	Intramolecular Diels–Alder reactions	193
3.1.6	The retro Diels–Alder reaction	199
3.1.7	Asymmetric Diels–Alder reactions	202
3.2	[2+2] Cycloaddition reactions	211
3.3	Cycloaddition reactions with allyl cations and allyl anions	219
3.4	1,3-Dipolar cycloaddition reactions	222
3.5	The ene reaction	231
3.6	[3,3]-Sigmatropic rearrangements	238
3.6.1	The Cope rearrangement	239
3.6.2	The Claisen rearrangement	244
3.7	[2,3]-Sigmatropic rearrangements	253
3.8	Electrocyclic reactions	259
	Problems	264
4	Radical and carbene chemistry	268
4.1	Radicals	268
4.1.1	Radical abstraction reactions	269
4.1.2	Radical addition reactions	280
4.2	Carbenes	299
	Problems	312
5	Functionalization of alkenes	315
5.1	Hydroboration	315
5.1.1	Reactions of organoboranes	322
5.2	Epoxidation and aziridination	331
5.2.1	Epoxidation	331
5.2.2	Asymmetric epoxidation	337
5.2.3	Aziridination	346

<i>Contents</i>		vii
5.3	Dihydroxylation	349
5.3.1	Dihydroxylation with osmium tetroxide	349
5.3.2	Other methods of dihydroxylation	355
5.3.3	Amino-hydroxylation	358
5.4	Oxidative cleavage	360
5.5	Palladium-catalysed oxidation of alkenes	365
	Problems	367
6	Oxidation	370
6.1	Oxidation of hydrocarbons	370
6.1.1	Alkanes	370
6.1.2	Aromatic hydrocarbons	371
6.1.3	Alkenes	374
6.2	Oxidation of alcohols	378
6.2.1	Chromium reagents	378
6.2.2	Oxidation via alkoxysulfonium salts	381
6.2.3	Manganese reagents	384
6.2.4	Other metal-based oxidants	386
6.2.5	Other non-metal-based oxidants	389
6.2.6	Oxidation to carboxylic acids or esters	392
6.3	Oxidation of ketones	394
6.3.1	α,β -Unsaturated ketones	394
6.3.2	α -Hydroxy-ketones	396
6.3.3	Baeyer–Villiger oxidation of ketones	398
	Problems	402
7	Reduction	405
7.1	Catalytic hydrogenation	405
7.2	Reduction by dissolving metals	422
7.3	Reduction by hydride-transfer reagents	434
7.3.3	Derivatives of lithium aluminium hydride and sodium borohydride	443
7.3.4	Mixed lithium aluminium hydride–aluminium chloride reagents	444
7.3.5	Diisobutylaluminium hydride (DIBAL-H)	445
7.3.6	Sodium cyanoborohydride and sodium triacetoxyborohydride	446
7.3.7	Borane and derivatives	449

viii	<i>Contents</i>	
7.4	Other methods of reduction	454
7.4.1	Enzyme catalysed	454
7.4.2	Wolff–Kishner reduction	457
7.4.3	Reductions with diimide	459
7.4.4	Reductions with trialkylsilanes	460
	Problems	462
	<i>Answers to problems</i>	466
	<i>Index</i>	487