

Contents

Preface IX

1	Introduction	1
1.1	Reaction Mechanism and Reaction Arrows	4
1.2	Properties and Characteristics of a Reaction	5
1.2.1	Reactants and Reagents	6
1.2.2	Product Selectivity	6
1.2.3	Reaction Characteristics	7
1.2.4	Factors that Influence Reactions	7
1.3	Summary	16
	Further Reading	19
2	Carbocations	21
2.1	Introduction	21
2.2	History	22
2.2.1	Carbonium Ions and Carbenium Ions	23
2.3	Structures and Geometry of Carbocations	26
2.4	Generation of Carbocation	28
2.4.1	From a Halide	29
2.4.2	From an Alcohol	29
2.4.3	From an Amine	29
2.4.4	From an Alkene	30
2.4.5	From Carbonyl Compounds	30
2.4.6	Solvent Effects	30
2.5	Carbocation Stability	31
2.6	Detection of Carbocations	36
2.7	Fate of Carbocations	37
2.7.1	Reaction with a Nucleophile	38
2.7.2	Elimination of a Proton	38
2.7.3	Rearrangements of Carbocations	39
2.7.4	Cationic Polymerization	50
2.8	Nonclassical Carbocations	51
2.9	Radical Cations	55

2.10	Summary	60
	Further Reading	64
3	Carbanions	65
3.1	Structure and Geometry of Carbanions	65
3.2	Generation of Carbanions	69
3.2.1	Reduction of C–X Bond with Metal	69
3.2.2	Deprotonation from a C–H Bond	70
3.2.3	Reaction of a Metal with an Alkene	70
3.2.4	A Negative Ion Adds to a Carbon–Carbon Double or Triple Bond	71
3.3	Stability of Carbanions	72
3.4	Reactions of Carbanions	77
3.5	Enolate Reactions with Carbonyl Groups	78
3.5.1	Aldol Condensation	78
3.5.2	Enamine Additions	81
3.5.3	Robinson Ring-Forming Reaction	81
3.6	Rearrangements of Carbanions	86
3.6.1	Homoallylic Rearrangements	86
3.7	Chiral Carbanions	90
3.8	Carbanions and Tautomerism	91
3.8.1	Mechanism of Keto-Enol Interconversion	91
3.9	Summary	96
	Further Reading	100
4	Radicals	101
4.1	Introduction	101
4.2	Detection and Characterization of Radicals	103
4.3	Structure and Bonding of Radicals	107
4.4	Generation of Free Radicals	111
4.5	Stability of Radicals	114
4.6	Reactions of Free Radicals	116
4.7	Stereochemistry of Radical Reactions	131
4.7.1	Cyclization by Intramolecular Addition Reactions	136
4.8	Biradicals	142
4.9	Summary	146
	Further Reading	151
5	Carbenes	153
5.1	Structure and Geometry of Carbenes	153
5.2	Generation of Carbenes	160
5.2.1	Thermolysis or Photolysis of Diazo Compounds	160
5.2.2	Reaction of N-Nitrosoureas with Base	161
5.2.3	Reaction of Tosylhydrazone with Base	162
5.2.4	Carbene Formation by α -Elimination	163
5.2.5	Generation of Carbenoids (Simmons–Smith Reaction)	165

5.2.6	Formation of Carbenes under Neutral Conditions	165
5.2.7	Generation of Carbenes from Small Rings	166
5.3	Reactions of Carbenes	167
5.3.1	Addition Reactions	168
5.3.2	Cycloaddition to 1,2-Dienes (Allenes)	176
5.3.3	Cycloaddition to 1,3-Diene	176
5.3.4	Cycloaddition to Alkynes	177
5.3.5	Insertion Reactions	177
5.3.6	Rearrangement of Carbenes	181
5.3.6.1	Wolff Rearrangement	182
5.3.7	Reactions of Carbenes with Nucleophiles	187
5.4	Carbenes and Carbene Ligands in Organometallic Chemistry	188
5.5	Summary	192
	Further Reading	195
6	Nitrenes	197
6.1	Introduction	197
6.2	Structure and Reactivity	198
6.3	Generation of Nitrenes	202
6.3.1	Azides	203
6.3.2	Isocyanates	205
6.3.3	Ylides	205
6.3.4	Small Rings	206
6.3.5	Heterocycles	206
6.3.6	α -Elimination	207
6.3.7	Reduction of Nitro and Nitroso Compounds	207
6.3.8	Oxidation of Amines	208
6.3.9	From Sulfinylamines	208
6.4	Reactions of Nitrenes	209
6.4.1	Cycloaddition Reactions of Nitrenes	209
6.4.1.1	Cycloaddition to Alkenes	209
6.4.1.2	Cycloaddition to 1,3-Dienes	210
6.4.1.3	Cycloaddition to Alkynes	211
6.4.1.4	Cycloaddition to Arenes	212
6.4.2	Insertion Reactions of Nitrenes	212
6.4.3	Rearrangement of Nitrenes	216
6.4.4	Reactions of Nitrenes with Nucleophiles	218
6.5	Summary	220
	Further Reading	223
7	Miscellaneous Intermediates	225
7.1	Arynes	225
7.1.1	Introduction	225
7.1.2	Structure and Reactivity	226
7.1.3	Generation of Arynes	230

7.1.4	Reactions of Arynes	236
7.1.4.1	Nucleophilic Addition to Arynes	237
7.1.4.2	Regiochemistry of the Triple Bond Formation	239
7.1.4.3	Cycloaddition Reactions of Arynes (Diels–Alder Reaction)	240
7.1.4.4	1,3-Dipolar Cycloaddition	243
7.1.5	Uses of Arynes in Organic Synthesis	245
7.2	Ketenes and Cumulenes	246
7.2.1	Introduction	246
7.2.2	Generation of Ketenes	248
7.2.3	Photochemical Generation of Ketenes	250
7.2.4	Reactions of Ketenes	251
7.3	<i>ortho</i> -Quinone Methides	253
7.4	Zwitterions and Dipoles	258
7.5	Antiaromatic Systems	262
7.6	Tetrahedral Intermediates	264
7.6.1	Acetals and Hemiacetals	267
7.6.2	Weinreb Amides	269
7.6.3	Applications in Biomedicine	269
7.7	Summary	270
	Further Reading	273

Index 275