

Contents

1	Hybridization: The Shape Of Things To Come	15
A	Introduction	15
B	Electron Counting	16
	In Atoms	16
	In Molecules, and Valency	17
C	Mixing Atomic Orbitals To Maximize Overlap In Molecules	19
	Combining <i>s</i> - and <i>p</i> -Orbitals	19
	Geometric Shapes	19
	Shapes Of Molecules Based On Geometric Shapes	20
D	Multiple Bonds	23
2	Saturated Acyclic Hydrocarbons	28
A	Introduction	28
B	Conformations Of Acyclic Hydrocarbons	29
	Ethane	29
	Propane	31
	Butane	33
	Art In Organic Chemistry	35
	Three Dimensional Diagrams Of Organic Molecules	39
	Alkyl Fragments	40
C	Conclusion	43
3	Fragments And Functional Groups	44
A	Introduction	44
B	Fragments	45
C	Expanded Forms Of Functional Groups	48
D	Abbreviated Forms Of Functional Groups	50
4	Conformations Of Cyclic Hydrocarbons	55
A	Introduction	55
B	Angle Strain	56
C	Torsional Strain	56
D	Cyclohexanes	57
	Unsubstituted Cyclohexane	57
	Monosubstituted Cyclohexanes	62
	Disubstituted Cyclohexanes	64
	Cyclohexenes	66
E	Other Rings	67
5	Curly Arrows And Electron Flow	68
A	Introduction	68
B	Electron Flow	69
	Affecting Only One Bond	69
	Affecting Two Bonds	72
	Affecting Four Bonds	73
	Representations Of Charged Hydrocarbon Scaffolds	74
C	Heteroatoms, Lone Pairs, And Moving Electrons	76
6	Acids And Bases	80

A	Introduction	80
B	Log Scales To Measure Proton Dissociation From Organic Molecules	81
	Equilibria That Generate Protons	81
	Simplifying The Scale: pKa	84
C	Acid-Base Equilibria	85
D	Predicting Relative pK _a Values	89
E	Predicting Sites Of Protonation	90
F	Lewis Acids And Bases	92
7	Resonance: Practicing Curly Arrows	95
A	Introduction	95
B	Resonance	96
C	Resonance Stabilized Anions	96
	Hopping Across Atoms In Search Of Electronegativity	96
	How Resonance Stabilization Of Anions Influences Acidity	101
D	Resonance Stabilized Cations	105
E	Resonance In Neutral Molecules	108
F	Resonance Stabilizes Some Conformations	109
8	Stereochemistry	111
A	Introduction	111
B	Priority Rules	112
	Substituents Without Multiple Bonds	112
	Substituents Connected To Multiple Bonds	112
C	Classifying Alkene Geometries	115
D	Chiral Centers	115
E	Combinations Of Chiral Centers	118
F	Prochirality	120
9	S_N1 Displacement At sp³ Centers	124
A	Introduction	124
B	Types Of Nucleophilic Substitutions	125
	Negatively Charged Nucleophiles	125
	Neutral Nucleophiles	125
	Charges On Leaving Groups	126
C	S _N 1	127
	Introduction Into The Key Steps	127
	Kinetics Of S _N 1	133
	Stereochemistry And S _N 1	136

10	<u>S_N2 Displacement At sp³ Centers</u>	138
A	Introduction	138
B	Differentiating S _N 1 and S _N 2	139
	Stereochemical Inversion In S _N 2 Reactions	139
	Kinetics And S _N 2 Pathways	140
C	Interconversion Of Enantiomers And Diastereomers	141
	Conversion Of Alcohols Into Leaving Groups	141
	Stereoelectronic Effects	145
D	Making Amines Via S _N 2 Reactions	146
	Cyanide: A Useful C-Nucleophile	146
	Phthalimide: Useful N-Nucleophile For Syntheses Of Primary Amines	147
11	<u>Elimination Reactions To Form Alkenes</u>	149
A	Introduction	149
B	E1 Mechanisms	150
	Kinetics	150
C	E2 Mechanisms	152
	Kinetics	152
	Stereoselectivity	153
D	Factors That Favor E1, E2, S _N 1, or S _N 2	156
	Basicity vs Nucleophilicity	156
	Nucleophilicity	156
	Temperature (and Entropy)	157
E	E1cB	157
F	Eliminations To Give Allenes, Alkynes, Ketenes And Sulfenes	158
12	<u>Reactions Of Alkenes Via Protonation</u>	159
A	Introduction	159
B	Protonation Of Alkenes	160
	Generation Of Carbocations Via Protonation	160
	A Molecular Orbital Picture Of Alkene Protonation	161
C	Carbocation Stabilities	162
D	Alkenes Stabilities	163
	Heats Of Hydrogenation	164
E	Acid-mediated Alkene Isomerization	164
F	Carbocation Rearrangements	166
	Hydride Shifts	166
	Alkyl Shifts	168
G	Electrophilic Addition Mechanisms	169
H	Acid-mediated Hydration Of Alkenes	171
13	<u>Oxidation States, Hydrogenation, And Hydrogenolysis</u>	175
A	Introduction	175
B	Oxidation States In Organic Chemistry	176
C	Addition Of H ₂	177
	Hydrogenation And Hydrogenolysis	177
D	Hydrogenation	178
E	Hydrogenolysis	180
F	Double Bond Equivalents	183
G	Hydridic Reductions	184
14	<u>Halogenation Of Alkenes</u>	185

A	Introduction	185
B	Mechanism	186
	Chlorination and Bromination	186
	Iodination	194
C	Kinetic And Thermodynamic Control	195
	Kinetic Control	195
	Thermodynamic Control	196
	Non-coincident Kinetic And Thermodynamic Control	197
D	Halogenations In Nucleophilic Solvents	199
15	<u>Epoxidation Of Alkenes, And Epoxides</u>	201
A	Introduction	201
B	Reagents And Mechanism	202
C	Rates Of Epoxidation	205
D	Stereospecificity	206
E	Regioselectivity Of Epoxide Ring Opening Reactions	209
	Under Neutral Or Basic Conditions	209
	Under Acidic Conditions	210
16	<u>Cycloadditions To Alkenes And Alkynes</u>	212
A	Introduction	212
B	Nomenclature Of Cycloadditions	213
C	Carbene Additions [2 + 1] (Cyclopropanations)	213
D	Ozonolysis [2 + 3]	215
E	Dihydroxylation [2 + 3]	220
F	Periodate Cleavage	224
G	Azide-Alkyne "Click Reactions" [2 + 3]	225
17	<u>Benzene And Aromaticity</u>	228
A	Introduction	228
B	Common Aromatic Compounds	229
C	Heats Of Hydrogenation And Aromaticity	232
D	Predicting Aromaticity	234
	Carbocycles	234
18	<u>Electrophilic Attack On Benzene</u>	237
A	Introduction	237
B	Electrophilic Bromination Of Alkenes And Benzene Compared	238
	First Step: Approach Of Electrophile	238
	Second Step: Loss Of Positive Charge	238
C	Halogenation Of Benzene	241
D	Sulfonation And Nitration Of Benzene	242
E	Acylation Of Benzene (Friedel-Crafts)	243
F	Alkylation (Friedel-Crafts)	245

19	Ultraviolet And Fluorescence Spectroscopy	248
A	Introduction	248
B	Fundamental Physics	249
C	Molecular Orbital Diagrams Of Alkenes, Dienes, and Polyenes	249
D	UV Spectroscopy	253
E	Fluorescence Spectroscopy	254
20	Infrared (IR) Spectroscopy	257
A	Introduction	257
B	Origin Of IR Absorbance	258
C	Functional Group Assignments	260
D	Assigning Structures From Spectra	262
21	¹³C NMR Spectroscopy	268
A	Introduction	268
B	Fundamental Physics Of NMR (Nuclear Magnetic Resonance)	269
C	Chemical Shifts In General	270
D	Chemical Shifts In ¹³ C Spectra	271
E	Coupling In ¹³ C NMR	274
F	Some Problems Involving Interpretation Of ¹³ C Spectra	278
22	¹H NMR Spectroscopy	281
A	Introduction	281
B	Chemical Shifts In ¹ H Spectra	282
C	Coupling In ¹ H NMR	287
	Heteronuclear Coupling To ¹³ C Is Unimportant	287
	Homonuclear ¹ H Coupling	287
	Spin Systems	288
D	Diastereotopic Protons	294
E	Some Problems Involving Spectral Interpretation	295
23	Mass Spectrometry (MS)	297
A	Introduction	297
B	Components Of Mass Spectrometers	298
C	Primary Ions Formed In Different Ionization Techniques	299
D	Isotopes In Mass Spectrometry	300
	Illustrative Interpretation Of Isotopes In MS	301
E	Fragmentation	303
	α -Cleavage	305
	The McLafferty Rearrangement	310