**CONTENTS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>xiii</td>
</tr>
<tr>
<td>COMMON ABBREVIATIONS</td>
<td>xxi</td>
</tr>
<tr>
<td>BIOGRAPHICAL STATEMENT</td>
<td>xxv</td>
</tr>
<tr>
<td><strong>PART I  INTRODUCTION</strong></td>
<td></td>
</tr>
<tr>
<td>1. Localized Chemical Bonding</td>
<td></td>
</tr>
<tr>
<td>1.A. Covalent Bonding</td>
<td>3</td>
</tr>
<tr>
<td>1.B. Multiple Valence</td>
<td>6</td>
</tr>
<tr>
<td>1.C. Hybridization</td>
<td>7</td>
</tr>
<tr>
<td>1.D. Multiple Bonds</td>
<td>9</td>
</tr>
<tr>
<td>1.E. Photoelectron Spectroscopy</td>
<td>11</td>
</tr>
<tr>
<td>1.F. Electronic Structures of Molecules</td>
<td>14</td>
</tr>
<tr>
<td>1.G. Electronegativity</td>
<td>15</td>
</tr>
<tr>
<td>1.H. Dipole Moment</td>
<td>18</td>
</tr>
<tr>
<td>1.I. Inductive and Field Effects</td>
<td>19</td>
</tr>
<tr>
<td>1.J. Bond Distances</td>
<td>21</td>
</tr>
<tr>
<td>1.K. Bond Angles</td>
<td>25</td>
</tr>
<tr>
<td>1.L. Bond Energies</td>
<td>27</td>
</tr>
<tr>
<td>2. Delocalized Chemical Bonding</td>
<td>31</td>
</tr>
<tr>
<td>2.A. Molecular Orbitals</td>
<td>32</td>
</tr>
<tr>
<td>2.B. Bond Energies and Distances in Compounds Containing Delocalized Bonds</td>
<td>35</td>
</tr>
<tr>
<td>2.C. Molecules that have Delocalized Bonds</td>
<td>37</td>
</tr>
<tr>
<td>2.D. Cross-Conjugation</td>
<td>42</td>
</tr>
<tr>
<td>2.E. The Rules of Resonance</td>
<td>43</td>
</tr>
<tr>
<td>2.F. The Resonance Effect</td>
<td>45</td>
</tr>
<tr>
<td>2.G. Steric Inhibition of Resonance and the Influences of Strain</td>
<td>46</td>
</tr>
<tr>
<td>2.H. $\pi-\sigma$ Bonding. Ylids</td>
<td>49</td>
</tr>
<tr>
<td>2.I. Aromaticity</td>
<td>50</td>
</tr>
<tr>
<td>2.I.i. Six-Membered Rings</td>
<td>54</td>
</tr>
<tr>
<td>2.I.ii. Five, Seven, and Eight-Membered Rings</td>
<td>57</td>
</tr>
<tr>
<td>2.I.iii. Other Systems Containing Aromatic Sextets</td>
<td>62</td>
</tr>
<tr>
<td>2.J. Alternant and Nonalternant Hydrocarbons</td>
<td>63</td>
</tr>
</tbody>
</table>
4.N.ii. Conformation in Six-Membered Rings 180
4.N.iii. Conformation in Six-Membered Rings Containing Heteroatoms 186
4.N.iv. Conformation in Other Rings 188
4.O. Molecular Mechanics 190
4.P. STRAIN 192
4.P.i. Strain in Small Rings 193
4.P.ii. Strain in Other Rings 199
4.P.iii. Unsaturated Rings 201
4.P.iv. Strain Due to Unavoidable Crowding 204

5. Carbocations, Carbanions, Free Radicals, Carbenes, and Nitrenes 208

5.A. Carbocations 208
5.A.i. Nomenclature 208
5.A.ii. Stability and Structure of Carbocations 209
5.A.iii. The Generation and Fate of Carbocations 218

5.B. Carbanions 221
5.B.i. Stability and Structure 221
5.B.ii. The Structure of Organometallic Compounds 228
5.B.iii. The Generation and Fate of Carbanions 233

5.C. Free Radicals 234
5.C.i. Stability and Structure 234
5.C.ii. The Generation and Fate of Free Radicals 245
5.C.iii. Radical Ions 248

5.D. Carbenes 249
5.D.i. Stability and Structure 249
5.D.ii. The Generation and Fate of Carbenes 253

5.E. Nitrenes 257

6. Mechanisms and Methods of Determining them 261

6.A. Types of Mechanism 261
6.B. Types of Reaction 262
6.C. Thermodynamic Requirements for Reaction 264
6.D. Kinetic Requirements for Reaction 266
6.E. The Baldwin Rules for Ring Closure 270
6.F. Kinetic and Thermodynamic Control 271
6.G. The Hammond Postulate 272
6.H. Microscopic Reversibility 273
6.I. Marcus Theory 273
6.J. Methods of Determining Mechanisms 275
6.J.i. Identification of Products 275
6.J.iii. The Study of Catalysis 277
6.J.iv. Isotopic Labeling 277
6.J.v. Sterechemical Evidence 278
6.J.vi. Kinetic Evidence 278
7. Irradiation Processes in Organic Chemistry 289
7.A. Photochemistry 289
7.A.i. Excited States and the Ground State 289
7.A.iii. Types of Excitation 292
7.A.iv. Nomenclature and Properties of Excited States 294
7.A.v. Photolytic Cleavage 295
7.A.vi. The Fate of the Excited Molecule: Physical Processes 296
7.A.vii. The Fate of the Excited Molecule: Chemical Processes 301
7.A.viii. The Determination of Photochemical Mechanisms 306
7.B. Sonochemistry 307
7.C. Microwave Chemistry 309

8. Acids and Bases 312
8.A. Brønsted Theory 312
8.A.i. Brønsted Acids 313
8.A.ii. Brønsted Bases 320
8.B. The Mechanism of Proton-Transfer Reactions 323
8.C. Measurements of Solvent Acidity 324
8.D. Acid and Base Catalysis 327
8.E. Lewis Acids and Bases 330
8.F. The Effects of Structure on the Strengths of Acids and Bases 334
8.G. The Effects of the Medium on Acid and Base Strength 343

9. Effects of Structure and Medium on Reactivity 347
9.A. Resonance and Field Effects 347
9.B. Steric Effects 349
9.C. Quantitative Treatments of the Effect of Structure on Reactivity 352
9.D. Effect of Medium on Reactivity and Rate 361
9.D.i. High Pressure 362
9.D.iii. Ionic Solvents 364

PART II INTRODUCTION 367

10. Aliphatic Substitution, Nucleophilic and Organometallic 373
10.A. Mechanisms 373
10.A.i. The S_N2 Mechanism 374
10.A.ii. The S_N1 Mechanism 379
10.A.iii. Ion Pairs in the S_N1 Mechanism 383
10.A.iv. Mixed S_N1 and S_N2 Mechanisms 387
10.B. SET Mechanisms 389
11. Aromatic Substitution, Electrophilic 569

11.A. Mechanisms 569
11.A.i. The Arenium Ion Mechanism 570
11.A.ii. The $S_{E1}$ Mechanism 576

11.B. Orientation and Reactivity 576
11.B.i. Orientation and Reactivity in Monosubstituted Benzene Rings 576
11.B.ii. The Ortho/Para Ratio 580
11.B.iii. Ipso Attack 581
11.B.iv. Orientation in Benzene Rings with More Than One Substituent 583
11.B.v. Orientation in Other Ring Systems 584

11.C. Quantitative Treatments of Reactivity in the Substrate 586


11.E. The Effect of the Leaving Group 591

11.F. Reactions 591
11.F.i. Hydrogen as the Leaving Group in Simple Substitution Reactions 592
11.F.ii. Hydrogen as the Leaving Group in Rearrangement Reactions 635
11.F.iii. Other Leaving Groups 641
**CONTENTS**

12. Aliphatic, Alkenyl, and Alkynyl Substitution, Electrophilic and Organometallic  

12.A. Mechanisms  
12.A.i. Bimolecular Mechanisms: $S_{E2}$ and $S_{E1}$  
12.A.ii. The $S_{E1}$ Mechanism  
12.A.iii. Electrophilic Substitution Accompanied by Double-Bond Shifts  
12.A.iv. Other Mechanisms  

12.B. Reactivity  
12.C. Reactions  
12.C.i. Hydrogen as Leaving Group  
12.C.ii. Metals as Leaving Groups  
12.C.iii. Halogen as Leaving Group  
12.C.iv. Carbon Leaving Groups  
12.C.v. Electrophilic Substitution at Nitrogen  

13. Aromatic Substitution: Nucleophilic and Organometallic  

13.A. Mechanisms  
13.A.i. The $S_{NAr}$ Mechanism  
13.A.ii. The $S_{N1}$ Mechanism  
13.A.iii. The Benzyne Mechanism  
13.A.iv. The $S_{RN1}$ Mechanism  
13.A.v. Other Mechanisms  

13.B. Reactivity  
13.B.i. The Effect of Substrate Structure  
13.B.ii. The Effect of the Leaving Group  
13.B.iii. The Effect of the Attacking Nucleophile  

13.C. Reactions  
13.C.i. All Leaving Groups Except Hydrogen and $N_2^+$  
13.C.ii. Hydrogen as Leaving Group  
13.C.iii. Nitrogen as Leaving Group  
13.C.iv. Rearrangements  

14. Substitution Reactions: Radical  

14.A. Mechanisms  
14.A.i. Radical Mechanisms in General  
14.A.iii. Mechanisms at an Aromatic Substrate  

14.B. Reactivity  
14.B.i. Reactivity for Aliphatic Substrates  
14.B.ii. Reactivity at a Bridgehead  
14.B.iii. Reactivity in Aromatic Substrates  
14.B.iv. Reactivity in the Attacking Radical  
14.B.v. The Effect of Solvent on Reactivity
14.C. Reactions
14.C.i. Hydrogen as a Leaving Group
14.C.ii. N₂ as Leaving Group
14.C.iii. Metals as Leaving Groups
14.C.iv. Halogen as Leaving Group
14.C.v. Sulfur as Leaving Group
14.C.vi. Carbon as Leaving Group

15. Addition to Carbon–Carbon Multiple Bonds

15.A. Mechanisms
15.A.i. Electrophilic Addition
15.A.ii. Nucleophilic Addition
15.A.iii. Free Radical Addition
15.A.iv. Cyclic Mechanisms
15.A.v. Addition to Conjugated Systems

15.B. Orientation and Reactivity
15.B.i. Reactivity
15.B.ii. Orientation
15.B.iii. Stereochemical Orientation
15.B.iv. Addition to Cyclopropane Rings

15.C. Reactions
15.C.i. Isomerization of Double and Triple Bonds
15.C.ii. Reactions in which Hydrogen Adds to One Side
15.C.iii. Reactions in which Hydrogen Adds to Neither Side
15.C.iv. Cycloaddition Reactions

16. Addition to Carbon–Hetero Multiple Bonds

16.A. Mechanism and Reactivity
16.A.i. Nucleophilic Substitution at an Aliphatic Trigonal Carbon: The Tetrahedral Mechanism

16.B. Reactions
16.B.i. Reactions in which Hydrogen or a Metallic Ion Adds to the Heteroatom
16.B.ii. Acyl Substitution Reactions
16.B.iii. Reactions in which Carbon Adds to the Heteroatom
16.B.iv. Addition to Isocyanides
16.B.v. Nucleophilic Substitution at a Sulfonyl Sulfur Atom

17. Eliminations

17.A. Mechanisms and Orientation
17.A.i. The E2 Mechanism
17.A.ii. The E1 Mechanism
17.A.iii. The E1cB Mechanism
17.A.iv. The E1–E2–E1cB Spectrum
17.A.v. The E2C Mechanism

17.B. Regiochemistry of the Double Bond