

Contents

Preface.....	xvii
Authors	xix
Chapter 1 General Concepts for Covalent Bonding and Constructing Lewis Structures for Organic Molecules.....	1
1.1 General Concepts	1
1.1.1 Covalent Bonding.....	1
1.1.2 Lewis Structures.....	2
1.2 Bonding Rules for Nonmetals in Covalent Molecules.....	3
1.2.1 General Concept of Normal Neutral Bond Numbers.....	3
1.2.2 Summary Table for Normal Neutral Bond Numbers in Covalent Molecules.....	4
1.2.2.1 For H, B, C, N, O, F (H Plus Row 2).....	4
1.2.2.2 Common Bond Numbers for Certain Elements in Rows 3–6 (Si, P, S, Cl, Br, I).....	4
1.3 Constructing Lewis Structures for Covalent Molecules: Molecules Which Do Not Require Exceptions to Normal Neutral Bonding Rules.....	5
1.3.1 Lewis Structure Concepts	5
1.3.2 Molecules Containing H, Be, B, C, N, O, F That Follow Normal Neutral Bonding Rules.....	5
1.3.3 Lewis Structures of Molecules Containing Atoms from Rows 3 to 6 (Si, P, S, Cl, Br, I)	9
1.4 Constructing Lewis Structures for Covalent Molecules: Molecules Which Require Exceptions to Normal Neutral Bonding Rules	10
1.4.1 Exceptions for Row-2 Elements: B, C, N, O.....	10
1.4.2 Lewis Structures for Polyatomic Ions: Use of Exception Rule #1	12
1.4.3 Use of Exception Rule #3	13
1.5 Additional Concepts and Techniques for Constructing Lewis Structures	14
1.5.1 Other Uses of Exception Rule #3.....	14
1.5.2 Resonance Structures.....	15
1.6 Guidelines for Constructing Lewis Structures of Larger Molecules.....	16
1.6.1 General Concept.....	16
1.6.2 Bonding Pattern Template Method; Process Listed in Step Sequence.....	17
Chapter 2 Guideline for Writing Organic Molecule Isomers and Determining Number of Rings Plus Pi-Bonds.....	25
2.1 General Concept.....	25
2.2 Use of the “Bonding-Pattern Template” Method to Find Sum of Rings Plus Pi-Bonds (Degree of Unsaturation)	26
2.3 Calculation of Sum of Rings Plus Pi-Bonds from the Molecular Formula.....	27

2.3.1	Process for Use of Formulas to Calculate Number of Rings Plus Pi-Bonds: Molecules Containing <u>Only</u> C, H, and O.....	27
2.3.2	Expanding the Calculation Method to Molecules Which Include F, Cl, Br, I.....	28
2.3.3	Expanding the Calculation Method to Molecules Which Include Nitrogen.....	28
Chapter 3	Guideline for Complete Analysis for Central Atoms and Molecules: Bonding/Hybridization/Geometry/Polarity.....	31
3.1	Process for Complete Hybridization/Geometry Analysis.....	31
3.2	General Summaries.....	37
3.2.1	Summary of Geometry/Hybridization for 2–4 Electron Regions.....	37
3.2.2	Summary for the Geometry/Hybridization for C, N, and O.....	37
3.3	Practice Exercises.....	38
3.4	Answers to Practice Exercises.....	38
Chapter 4	Notation in Organic Chemistry: Guide to Writing and Using Condensed Formulas and Line Drawings.....	41
4.1	Condensed Structural Formulas.....	41
4.1.1	Guidelines for Converting a Lewis Structure into a Condensed Structural Formula.....	41
4.1.2	Notes and Other Simplifications.....	42
4.1.3	Expanding Condensed Formulas: Reconstructing the Complete Molecule.....	43
4.2	Line Drawings.....	44
4.2.1	Rules for Producing Line Drawings.....	44
4.2.2	Converting Line Drawings into Structural Formulas.....	46
Chapter 5	Summary Guidelines for Organic Nomenclature.....	51
5.1	General Concepts.....	51
	Part 1: Description of General Process: Alkanes/Cycloalkanes/Alkyl Halides.....	52
5.2	Example for an Alkane/Alkyl Halide.....	57
	Part 2: Description of Complete General Process: Molecules with Higher-Priority Functional Groups.....	59
5.3	Examples for a Molecule with Higher-Priority Functional Groups.....	63
	Part 3: General Process for Esters and Amides.....	67
5.4	Adapted Process for Nomenclature of Esters.....	68
5.5	Adapted Process for Nomenclature of Amides.....	69
Chapter 6	Guidelines for Analysis of Intermolecular Forces for Organic Molecules.....	75
6.1	Interparticle and Intermolecular Forces for Individual Pure Compounds: Forces between Molecules of the Same Compound.....	75
6.1.1	Interparticle Forces for Nonmolecular Compounds.....	75
6.1.2	Intermolecular Forces for Molecular Compounds.....	76
6.1.3	Guideline for Comparing Total Strength of Intermolecular Forces in Individual Compounds.....	78
6.2	Interparticle and Intermolecular Forces for Combinations of Compounds: Solutions and Solubility.....	79

6.2.1	Solubility and Solution Terms.....	79
6.2.2	Solubility Requirements.....	80
6.2.3	Interparticle (Intermolecular) Forces between Solute and Solvent.....	81
6.2.4	Analysis of Solubility for Possible Solute/Solvent Combinations.....	81
Chapter 7	Alkane and Cycloalkane Conformations.....	87
7.1	Conformers.....	87
7.2	Process for Recognition and Identification of Alkane Conformers through the Use of Torsion Angle.....	87
7.3	Drawing and Using Newman Projections.....	88
7.4	Potential Energies/Stabilities of Alkane Conformations.....	89
7.4.1	Potential Energy and Torsional Strain.....	89
7.4.2	Potential Energy and Van der Waal's Repulsion (Steric Repulsion).....	89
7.4.3	General Conclusions for Conformer Stability.....	90
7.4.4	Example.....	90
7.5	Cyclohexane Conformations.....	92
7.5.1	Description of the Chair Conformation of Cyclohexane.....	92
7.5.2	Drawing the Chair Conformation.....	93
7.5.3	Working with the Chair Conformation.....	94
7.5.4	Process for Solving Chair Conformation Problems.....	94
7.5.5	Additional Examples.....	95
Chapter 8	Summary Guide to Thermodynamic Concepts for Organic Chemistry.....	97
	Part 1: Bond Energy, Enthalpy, and Potential Energy Diagrams.....	97
8.1	Concept of Energy.....	97
8.2	Conservation of Energy: First Law of Thermodynamics.....	98
8.3	Chemical Bond Energetics.....	98
8.3.1	PE and Chemical Bonds.....	98
8.3.2	Bond Energies and Changes.....	99
8.4	Energy and Chemical Reactions.....	100
8.4.1	Reactions and Bond Changes.....	100
8.4.2	Calculating Reaction Enthalpy Values Using Bond Energies.....	101
8.4.3	Reaction Energy-Level Diagrams.....	103
8.4.4	PE, Enthalpy, and Reversible Reactions.....	105
8.4.5	Example Problem: Reading an Energy Diagram.....	106
	Part 2: Entropy, Free Energy, Spontaneity, and Equilibrium.....	107
8.5	Entropy.....	107
8.5.1	General Concepts.....	107
8.5.2	Predicting Entropy Changes for a Chemical Process.....	108
8.5.3	Entropy and the Second and Third Laws of Thermodynamics.....	110
8.6	Reaction Spontaneity.....	111
8.6.1	General Concepts.....	111
8.6.2	Enthalpy and Spontaneity.....	112
8.6.3	Entropy and Spontaneity.....	112
8.6.4	Reaction Spontaneity: Combining Enthalpy and Entropy.....	113
8.7	Free Energy (ΔG).....	114
8.7.1	General Concepts.....	114
8.7.2	Standard Free Energy: ΔG°_{298} and ΔG° at Variable Temperatures.....	115
8.7.3	Nonstandard Free Energy (ΔG) and Concentrations.....	118

8.8	Equilibrium	119
8.8.1	Concentrations and Equilibrium	119
8.8.2	Equilibrium Shifts	121
8.8.3	Comprehensive Example of All Concepts	123
Chapter 9	Guide to Kinetics and Reaction Mechanisms	135
9.1	General Concepts	135
9.1.1	Reaction Mechanisms	135
9.1.2	General Concept of Kinetics	136
9.1.3	Additional Variables Affecting Reaction Rates	137
9.1.4	Information Relationships for Kinetics and Mechanisms	137
9.2	Description of Reactions by Mechanisms	138
9.2.1	Reaction Steps and Complete Reactions	138
9.2.2	Variability of Mechanisms	138
9.3	Reactant Concentrations and Experimental Kinetics: Determining Reactant Orders and Rate Constants	139
9.3.1	Experimental Concepts	139
9.3.2	Zero-Order Reactants	140
9.3.3	First-Order Reactants	141
9.3.4	Second-Order Reactants	143
9.3.5	Experimental Determination of Reactant Orders in Multiple- Concentration Rate Expressions	145
9.4	Predicting Rate Expressions from Reaction Mechanisms	146
9.4.1	General Concepts for Rate Expression Comparison; Identification of the Rate-Determining Step	146
9.4.2	Predicting Rate Expressions from Mechanisms: Reaction Step Rate Rule and One-Step Reactions	147
9.4.3	Predicting Rate Expressions from Mechanisms: Multiple-Step Reaction Mechanisms	148
9.4.4	General Reaction Examples for Multistep Reactions	149
9.5	Energy and Chemical Reactions	155
9.5.1	Bonding Changes and Activation Energy	155
9.5.2	Energetics of Bond Making and Bond Breaking	155
9.5.3	Reaction Rates, Temperature, and E_a	156
9.5.4	Rates and Catalysis	157
9.6	Interpretation of Energy Level Diagrams	158
9.6.1	General Construction of Energy Diagrams	158
9.6.2	Energy Diagram Examples	159
9.6.3	Example Problem: Reading an Energy Diagram	160
9.6.4	Problem 1 Answer	161
9.7	Practice Problems	164
9.8	Answers to Practice Problems	166
Chapter 10	Review of Acid/Base Concepts for Organic Chemistry	173
10.1	Review of General Acid/Base Concepts	173
10.1.1	General Definitions	173
10.1.2	Review Process for Writing Acid/Base Reaction Equations	174
10.1.3	Concept of Conjugate Acid and Conjugate Base	175

10.1.4	Properties of Acids.....	176
10.1.5	Properties of Bases.....	177
10.2	Acid and Base Strength.....	178
10.2.1	Reference Reactions of Acids with Water.....	178
10.2.2	Reference Reactions of Bases with Water.....	178
10.2.3	Acid Strength.....	178
10.2.4	Base Strength.....	179
10.3	Relationship between Acid Strength (pK_a) and Conjugate Base Strength.....	180
10.4	Determining the Equilibrium Position for Acid/Base Reactions.....	181
10.5	Additional Examples.....	182
Chapter 11	Electrophiles and Nucleophiles in Organic Reaction Mechanisms.....	185
11.1	Overview of General Concepts.....	185
11.1.1	Electrophiles and Nucleophiles.....	185
11.1.2	Reaction Concepts.....	185
11.2	Species Identification and Characteristics.....	186
11.2.1	Electrophiles.....	186
11.2.2	Nucleophiles.....	187
11.3	Reaction Characteristics.....	189
11.3.1	Electrophiles and Nucleophiles in Mechanisms.....	189
11.3.2	Bond Formation with Electrophiles Having an Available Empty Orbital: Addition of the Electrophile to the Nucleophile.....	189
11.3.3	Bond Breaking between the Electrophile and Nucleophile by Elimination.....	190
11.3.4	Bond Formation with Electrophiles Having a Full Octet.....	191
11.4	Additional Concepts.....	192
11.4.1	Nucleophiles Using a Sigma-Bonding Electron Pair.....	192
11.4.2	Single Electron Transfer: Free Radical Reactions.....	192
11.5	Additional Problems.....	193
11.5.1	Practice Exercises.....	193
11.5.2	Answers to Practice Exercises.....	194
Chapter 12	Conceptual Guide to Mechanisms in Organic Chemistry.....	197
12.1	Overview for Understanding Reaction Mechanisms.....	197
12.1.1	Reaction Electron Changes.....	197
12.1.2	Substitution Patterns on Carbon: Mechanistic Effects.....	198
12.2	Free Radical Halogenation of Alkanes/Alkyl Groups.....	199
12.2.1	Reaction Concepts.....	199
12.2.2	Summary of General Mechanism.....	200
12.2.3	Conceptual Description of Mechanistic Steps.....	200
12.2.4	Summary: Determining the Correct Products for Free Radical Halogenation.....	201
12.3	Nucleophilic Substitution.....	202
12.3.1	Description of the General Reaction.....	202
12.3.2	Factors Influencing Rate and Mechanisms.....	203
12.3.3	Nucleophilic Substitution: General Mechanistic Concepts.....	204
12.3.4	General Summaries (Selected Formats): Notation R = Alkyl Group.....	205
12.3.5	Summary: Determination of the Correct Product for Nucleophilic Substitution.....	207

12.4	Elimination Reactions of Alcohols and Alkyl Halides.....	208
12.4.1	General Reaction Concepts.....	208
12.4.2	Identification of Major Isomer Alkene Product in Eliminations (Non-Rearrangement).....	209
12.4.3	Summary: Determination of Major Alkene Product for Elimination (Non-Rearrangement).....	210
12.4.4	Mechanism Summary: E2 for Primary, Secondary, and Tertiary Alkyl Halides.....	211
12.4.5	Mechanism Summary: E1 for Tertiary Alkyl Halides.....	212
12.4.6	Mechanism Summary: E2 for Primary Alcohols.....	213
12.4.7	Mechanism Summary: E1 for Secondary and Tertiary Alcohols.....	214
12.5	Identification of Elimination versus Substitution Reactions.....	215
12.5.1	Reaction Analysis for Alcohols.....	215
12.5.2	Reaction Analysis for Alkyl Halides.....	216
12.6	Electrophilic Addition to Pi-Bonds of Alkenes and Alkynes.....	217
12.6.1	General Reaction Concepts.....	217
12.6.2	Mechanism Summary.....	218
12.6.3	Regiochemistry in Electrophilic Addition.....	220
12.6.4	Stereochemistry in Electrophilic Addition.....	221
12.6.5	Summary: Determination of the Correct Major Product for Electrophilic Addition to Alkenes (Excluding Rearrangements).....	222
12.6.6	Specific Examples.....	223
12.6.7	General Summary.....	224

Chapter 13 Guide to Stereochemistry Concepts and Analysis of Reaction

	Stereochemistry as Applied to Electrophilic Addition.....	227
	Part 1: Conceptual Guide to Stereochemistry.....	227
13.1	Concepts of Stereochemistry and Chirality.....	227
13.2	Absolute Configuration of Chiral Carbons.....	228
13.2.1	Priority System for Attached Atom Groups.....	228
13.2.2	Process to Apply the Priority System to the Four Different Groups Attached to Chiral Carbons.....	228
13.2.3	Process to Determine Absolute Configuration of Chiral Carbons.....	230
13.3	Molecular Relationships: Summary Example with Molecular Formula: C_8H_{16}	231
	Part 2: Analysis of Reaction Stereochemistry Applied to Electrophilic Addition.....	232
13.4	Stereochemistry Concepts for Electrophilic Addition.....	232
13.4.1	General Analysis for Reactions.....	232
13.4.2	Stereochemistry Concepts Applied to Alkene Electrophilic Addition.....	232
13.4.3	Analysis Requirements for Electrophilic Addition Possibilities.....	233
13.4.4	Stereospecificity.....	234
13.4.5	Stereospecific Reaction Summary.....	234
13.5	Stereospecificity and Reaction Analysis for Electrophilic Addition.....	235
13.5.1	Stereospecificity Options for Electrophilic Addition Mechanisms.....	235
13.5.2	Reaction Conditions That Require Analysis for Diastereomers.....	235
13.5.3	Example: All Requirements 1, 2, and 3 Are Met.....	236
13.6	Concepts of Ring Stereochemistry.....	236
13.6.1	Cycloalkene Diastereomers.....	236
13.6.2	Viewing Ring Diastereomers.....	236

13.6.3	Stereospecificity Options Viewed in Cycloalkenes	237
13.6.4	Notation for Product Identification	238
Chapter 14	A Process for Calculation of Product Distribution through Relative Rate Analysis: Examples for Free Radical Halogenation	239
14.1	Methods for Product Percent and Ratio Calculations.....	239
14.2	Additional Practice Problem.....	244
14.3	Practice Problem Answer (Following Steps Similar to Example 1).....	244
Chapter 15	Process to Identify and Solve the Reactions for Organic I.....	247
15.1	Reaction Flow Diagram.....	247
15.2	Summaries from Chapter 12.....	249
15.3	Reaction Examples.....	253
15.4	Additional Practice Problems	257
15.5	Additional Practice Problems: Answers.....	258
Chapter 16	Electrophilic Addition and Addition/Elimination to Conjugated Double Bond and Aromatic Systems.....	261
16.1	General Concepts of Pi-Bonding Systems	261
16.1.1	Properties of Nonaromatic Conjugated Systems	261
16.1.2	Properties of Aromatic Conjugated Systems	262
16.2	Electrophilic Addition to Conjugated Double Bonds in Polyenes.....	263
16.2.1	General Reaction.....	263
16.2.2	Regiochemistry for Electrophilic Addition to Conjugated Systems: Concept of Allylic Carbon Cations and Radicals	264
16.2.3	Techniques for Drawing Correct Resonance Structures for Conjugated Systems	265
16.2.4	Regiochemistry for Electrophilic Addition to Conjugated Systems: Constitutional Isomers Based on Resonance Structures	268
16.2.5	Regiochemistry for Electrophilic Addition to Conjugated Systems: Determination of Major and Minor Isomer Products.....	269
16.2.6	Summary: Determination of Products for Electrophilic Addition to Conjugated Systems.....	270
16.2.7	Reproduction of Summary Table: E-Z Reagents for Electrophilic Addition	271
16.2.8	Example: Electrophilic Addition to a Conjugated Diene	271
16.3	Electrophilic Aromatic Substitution by an Addition/Elimination Mechanism.....	273
16.3.1	General Reaction	273
16.3.2	Electrophilic Aromatic Substitution: General Mechanism	274
16.3.3	Determination of the Major Product for Reactions at Substituted Aromatic Rings: Analysis of Resonance Forms	275
16.3.4	Determination of the Major Product for Reactions at Substituted Aromatic Rings: General Results for Stabilizing and Destabilizing Substituents.....	277
16.3.5	General Summary: Determination of Correct Major Products for Electrophilic Aromatic Substitution	279

16.3.6	Summary Table: Electrophiles for Electrophilic Aromatic Substitution	279
16.4	Examples: Electrophilic Aromatic Substitution.....	280
16.5	Additional Practice Problems	283
Chapter 17	Oxidation/Reduction Relationships for Carbonyl Carbon.....	287
17.1	General Concept of Redox Reactions.....	287
17.2	Oxidation Numbers	289
17.3	Oxidation/Reduction for Carbon in Organic Molecules	290
17.4	Oxidation/Reduction Sequence for Alcohols, Aldehydes/Ketones, Carboxylic Acids, and Derivatives	291
17.5	Reagents and Results for <u>Oxidation</u> Reactions of Alcohols, Aldehydes/Ketones, Carboxylic Acids, and Derivatives.....	292
17.5.1	Complete Oxidation	292
17.5.2	Selective Oxidation of Primary Alcohols to Aldehydes.....	293
17.6	Reagents and Results for <u>Reduction</u> Reactions of Alcohols; Aldehydes/Ketones; Carboxylic Acids; and Derivatives.....	293
17.6.1	Hydrogenation: Reduction with Hydrogen	293
17.6.2	Metal Hydride Reduction of Aldehydes and Ketones Li ⁺ R ₃ Al—H; Na ⁺ R ₃ B—H	294
17.6.3	Lithium Aluminum Hydride Reduction of Carboxylic Acids and Esters Li ⁺ R ₃ Al—H	294
Chapter 18	A Complete System for Organizing, Identifying, and Solving Carbonyl Reactions: Nucleophilic Addition and Addition/Elimination	295
18.1	Mechanisms and Classification of Carbonyl Reactions.....	295
18.1.1	General Concepts	295
18.1.2	Nucleophilic Addition to the Carbonyl Carbon: c=O	296
18.1.3	General Mechanisms for Nucleophilic Addition to Carbonyl c=O	298
18.2	Classification of Nucleophilic Addition/Elimination Reactions through the Structure of the Tetrahedral Intermediate: Determining the Final Product for Carbonyl Reactions.....	300
18.3	Descriptions of Group Reaction Results and Mechanisms.....	302
18.3.1	Group [1].....	302
18.3.1.1	General Reactant Requirements	302
18.3.2	Group [2].....	304
18.3.2.1	General Group Reactant Requirements.....	304
18.3.3	Subgroup [2A] Reaction Results and Mechanism.....	304
18.3.4	Group [2A] Examples	306
18.3.5	Subgroup [2B]: Reaction Results and Mechanism	306
18.3.6	Group [2B] Examples.....	307
18.3.7	Group [3].....	308
18.3.7.1	General Reactant Requirements	308
18.3.8	Group [3] Examples.....	309
18.3.9	Group [4].....	310
18.3.9.1	General Reactant Requirements	315
18.3.10	General Addition Mechanisms for Group [5]	317
18.3.11	Group [5] Examples	319

18.3.12	Group [6].....	319
18.3.12.1	General Reactant Requirements	320
18.3.13	Group [6] Example.....	321
18.4	Process to Solve Nucleophilic Addition/Elimination Reactions at Carbonyl Additional Practice Examples for Groups [1] through [6]	321
18.5	Additional Practice Problems	324

Chapter 19	A Brief Guideline for Applying Fundamental Concepts in NMR Spectroscopy.....	327
19.1	General Concepts for ^1H NMR Interpretation: Number of Signals and Peak Ratios	327
19.1.1	Examples Demonstrating Principles #1 and #2	329
19.1.1.1	Example: Analysis for Molecules 1, 2, and 3.....	329
19.2	General Concepts for ^1H NMR Interpretation: Signal Position and Proton Coupling.....	330
19.3	Table of Approximate Positions for ^1H NMR Hydrogens	331
19.4	Examples: Predicting the ^1H NMR for Molecules Using Principles #1 through 4.....	333
19.4.1	Chemical Shift Estimation Method for Common C–H Protons	333
19.5	Examples: Predicting the ^1H NMR from Molecular Structure.....	333
19.6	Additional Practice Problems	337
19.7	Additional Practice Problems: Answers.....	338

SECTION I—Organic Practice Exams

Organic I: Practice Exam 1	343
Organic I: Practice Exam 2	347
Organic I: Practice Exam 3	351
Organic I: Practice Exam 4	363
Organic I: Practice Exam 5	371
Organic I: Practice Exam 6	377
Organic I: Practice Exam 7	381
Organic I: Practice Exam 8	387
Organic I: Practice Exam 9	391
Organic I: Practice Exam 10	403
Organic I: Practice Exam 11	415
Organic I: Practice Exam 12	421
Organic I: Practice Exam 13	425
Organic I: Practice Exam 14	429
Organic I: Practice Exam 15	433
Organic I: Practice Exam 16	445

Organic I: Practice Exam 17	457
Organic II: Practice Exam 18	467
Organic II: Practice Exam 19	477
Organic II: Practice Exam 20	495
Organic II: Practice Exam 21	509
Organic II: Practice Exam 22	523
Organic II: Practice Exam 23	533
Organic II: Practice Exam 24	551
Organic II: Practice Exam 25	567
Organic II: Practice Exam 26	579
Organic II: Practice Exam 27	593

SECTION II—Multiple-Choice Practice Exams

Organic I: Multiple-Choice Practice Exam 1	607
Organic I: Multiple-Choice Practice Exam 2	617
Organic II: Multiple-Choice Practice Exam 1	625
Organic II: Multiple-Choice Practice Exam 2	633
Index	649