

TABLE OF CONTENTS

Licensing

1: Structure and Bonding

- 1.1: The Periodic Table
- 1.2: Bonding
- 1.3: Lewis Structures
- 1.4: Lewis Structures Continued
- 1.5: Bond Length and Bond Strength
- 1.6: Electronegativity and Bond Polarity
- 1.7: Polarity of Molecules
- 1.8: L-Dopa—A Representative Organic Molecule
- 1.9: Resonance
- 1.10: Determining Molecular Shape
- 1.11: Drawing Organic Structures
- 1.12: Hybridization
- 1.13: Ethane, Ethylene, and Acetylene

2: Acids and Bases

- 2.1: Brønsted–Lowry Acids and Bases
- 2.2: Reactions of Brønsted–Lowry Acids and Bases
- 2.3: Acid Strength and pK_{a}
- 2.4: Predicting the Outcome of Acid–Base Reactions
- 2.5: Factors That Determine Acid Strength
- 2.6: Common Acids and Bases
- 2.7: Aspirin
- 2.8: Lewis Acids and Bases

3: Introduction to Organic Molecules and Functional Groups

- 3.1: Functional Groups
- 3.2: An Overview of Functional Groups
- 3.3: Intermolecular Forces
- 3.4: Physical Properties
- 3.5: Application - Vitamins
- 3.6: Application of Solubility- Soap
- 3.7: Application- The Cell Membrane
- 3.8: Functional Groups and Reactivity
- 3.9: Biomolecules

4: Alkanes

- 4.1: Alkanes—An Introduction
- 4.2: Cycloalkanes
- 4.3: An Introduction to Nomenclature
- 4.4: Naming Alkanes
- 4.5: Naming Cycloalkanes
- 4.6: Common Names
- 4.7: Fossil Fuels

- 4.8: Physical Properties of Alkanes
- 4.9: Conformations of Butane
- 4.10: An Introduction to Cycloalkanes
- 4.11: Cyclohexane
- 4.12: Substituted Cycloalkanes
- 4.13: Oxidation of Alkanes
- 4.14: Lipids—Part 1
- 4.15: Conformations of Acyclic Alkanes—Ethane

5: Stereochemistry

- 5.1: Starch and Cellulose
- 5.2: The Two Major Classes of Isomers
- 5.3: Looking Glass Chemistry—Chiral and Achiral Molecules
- 5.4: Stereogenic Centers
- 5.5: Stereogenic Centers in Cyclic Compounds
- 5.6: Labeling Stereogenic Centers with R or S
- 5.7: Diastereomers
- 5.8: Meso Compounds
- 5.9: R and S Assignments in Compounds with Two or More Stereogenic Centers
- 5.10: Disubstituted Cycloalkanes
- 5.11: Isomers—A Summary
- 5.12: Physical Properties of Stereoisomers
- 5.13: Chemical Properties of Enantiomers

6: Understanding Organic Reactions

- 6.1: Writing Equations for Organic Reactions
- 6.2: Kinds of Organic Reactions
- 6.3: Bond Breaking and Bond Making
- 6.4: Bond Dissociation Energy
- 6.5: Thermodynamics
- 6.6: Enthalpy and Entropy
- 6.7: Energy Diagrams
- 6.8: Energy Diagram for a Two-Step Reaction Mechanism
- 6.9: Kinetics
- 6.10: Catalysts
- 6.11: Enzymes
- 6.12: Kinds of Organic Reactions
- 6.13: Thermodynamics
- 6.14: Energy Diagrams
- 6.15: Energy Diagram for a Two-Step Reaction Mechanism
- 6.16: Kinetics

7: Alkyl Halides and Nucleophilic Substitution

- 7.1: Introduction to Alkyl Halides
- 7.2: Nomenclature
- 7.3: Physical Properties
- 7.4: Interesting Alkyl Halides
- 7.5: The Polar Carbon–Halogen Bond
- 7.6: General Features of Nucleophilic Substitution
- 7.7: The Leaving Group
- 7.8: The Nucleophile

- 7.9: Possible Mechanisms for Nucleophilic Substitution
- 7.10: Two Mechanisms for Nucleophilic Substitution
- 7.11: The $\text{S}_{\text{N}}2$ Mechanism
- 7.12: Application- Useful $\text{S}_{\text{N}}2$ Reactions
- 7.13: The $\text{S}_{\text{N}}1$ Mechanism
- 7.14: Carbocation Stability
- 7.15: The Hammond Postulate
- 7.16: Application- $\text{S}_{\text{N}}1$ Reactions, Nitrosamines, and Cancer
- 7.17: When Is the Mechanism $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$?
- 7.18: Vinyl Halides and Aryl Halides
- 7.19: Organic Synthesis

8: Alkyl Halides and Elimination Reactions

- 8.1: General Features of Elimination
- 8.2: Alkenes—The Products of Elimination Reactions
- 8.3: The Mechanisms of Elimination
- 8.4: The E_2 Mechanism
- 8.5: The Zaitsev Rule
- 8.6: The E_1 Mechanism
- 8.7: $\text{S}_{\text{N}}1$ and E_1 Reactions
- 8.8: Stereochemistry of the E_2 Reaction
- 8.9: When is the Mechanism E_1 or E_2 ?
- 8.10: E_2 Reactions and Alkyne Synthesis
- 8.11: When Is the Reaction $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$, E_1 , or E_2 ?

9: Alcohols, Ethers, and Epoxides

- 9.1: Dehydration Using POCl_3 and Pyridine
- 9.2: Conversion of Alcohols to Alkyl Halides with HX
- 9.3: Conversion of Alcohols to Alkyl Halides with SOCl_2 and PBr_3
- 9.4: Tosylate—Another Good Leaving Group
- 9.5: Reaction of Ethers with Strong Acid
- 9.6: Reactions of Epoxides
- 9.7: Application- Epoxides, Leukotrienes, and Asthma
- 9.8: Application- Benzo[a]pyrene, Epoxides, and Cancer
- 9.9: Introduction
- 9.10: Structure and Bonding
- 9.11: Nomenclature
- 9.12: Physical Properties
- 9.13: Interesting Alcohols, Ethers, and Epoxides
- 9.14: Preparation of Alcohols, Ethers, and Epoxides
- 9.15: General Features—Reactions of Alcohols, Ethers, and Epoxides
- 9.16: Dehydration of Alcohols to Alkenes
- 9.17: Carbocation Rearrangements

10: Alkenes

- 10.1: Introduction
- 10.2: Calculating Degrees of Unsaturation
- 10.3: Nomenclature
- 10.4: Physical Properties
- 10.5: Interesting Alkenes
- 10.6: Lipids—Part 2

- 10.7: Preparation of Alkenes
- 10.8: Introduction to Addition Reactions
- 10.9: Hydrohalogenation—Electrophilic Addition of HX
- 10.10: Markovnikov's Rule
- 10.11: Stereochemistry of Electrophilic Addition of HX
- 10.12: Hydration—Electrophilic Addition of Water
- 10.13: Halogenation—Addition of Halogen
- 10.14: Stereochemistry of Halogenation
- 10.15: Halohydrin Formation
- 10.16: Hydroboration—Oxidation
- 10.17: Keeping Track of Reactions
- 10.18: Alkenes in Organic Synthesis

11: Alkynes

- 11.1: Introduction
- 11.2: Nomenclature
- 11.3: Physical Properties
- 11.4: Interesting Alkynes
- 11.5: Preparation of Alkynes
- 11.6: Introduction to Alkyne Reactions
- 11.7: Addition of Hydrogen Halides
- 11.8: Addition of Halogen
- 11.9: Addition of Water
- 11.10: Hydroboration—Oxidation
- 11.11: Reaction of Acetylide Anions
- 11.12: Synthesis

12: Oxidation and Reduction

- 12.1: Introduction
- 12.2: Reducing Agents
- 12.3: Reduction of Alkenes
- 12.4: Application- Hydrogenation of Oils
- 12.5: Reduction of Alkynes
- 12.6: The Reduction of Polar C–X σ Bonds
- 12.7: Oxidizing Agents
- 12.8: Epoxidation
- 12.9: Dihydroxylation
- 12.10: Oxidative Cleavage of Alkenes
- 12.11: Oxidative Cleavage of Alkynes
- 12.12: Oxidation of Alcohols
- 12.13: Green Chemistry
- 12.14: Application- The Oxidation of Ethanol
- 12.15: Sharpless Epoxidation

13: Radical Reactions

- 13.1: Introduction
- 13.2: General Features of Radical Reactions
- 13.3: Halogenation of Alkanes
- 13.4: The Mechanism of Halogenation
- 13.5: Chlorination of Other Alkanes
- 13.6: Chlorination versus Bromination

- 13.7: Halogenation as a Tool in Organic Synthesis
- 13.8: The Stereochemistry of Halogenation Reactions
- 13.9: Application- The Ozone Layer and CFCs
- 13.10: Radical Halogenation at an Allylic Carbon
- 13.11: Application- Oxidation of Unsaturated Lipids
- 13.12: Application- Antioxidants
- 13.13: Radical Addition Reactions to Double Bonds
- 13.14: Polymers and Polymerization

14: Conjugation, Resonance, and Dienes

- 14.1: Conjugation
- 14.2: Resonance and Allylic Carbocations
- 14.3: Common Examples of Resonance
- 14.4: The Resonance Hybrid
- 14.5: Electron Delocalization, Hybridization, and Geometry
- 14.6: Conjugated Dienes
- 14.7: Interesting Dienes and Polyenes
- 14.8: The Carbon–Carbon σ Bond Length in 1,3-Butadiene
- 14.9: Stability of Conjugated Dienes
- 14.10: Electrophilic Addition- 1,2- Versus 1,4-Addition
- 14.11: Kinetic Versus Thermodynamic Products
- 14.12: The Diels–Alder Reaction
- 14.13: Specific Rules Governing the Diels–Alder Reaction
- 14.14: Other Facts About the Diels–Alder Reaction
- 14.15: Conjugated Dienes and Ultraviolet Light

15: Benzene and Aromatic Compounds

- 15.1: Background
- 15.2: The Structure of Benzene
- 15.3: Nomenclature of Benzene Derivatives
- 15.4: Spectroscopic Properties
- 15.5: Interesting Aromatic Compounds
- 15.6: Benzene's Unusual Stability
- 15.7: The Criteria for Aromaticity - Hückel's Rule
- 15.8: Examples of Aromatic Compounds
- 15.9: What Is the Basis of Hückel's Rule?
- 15.10: The Inscribed Polygon Method for Predicting Aromaticity
- 15.11: Buckminsterfullerene—Is It Aromatic?

16: Electrophilic Aromatic Substitution

- 16.1: Limitations on Electrophilic Substitution Reactions with Substituted Benzenes
- 16.2: Disubstituted Benzenes
- 16.3: Synthesis of Benzene Derivatives
- 16.4: Halogenation of Alkyl Benzenes
- 16.5: Oxidation and Reduction of Substituted Benzenes
- 16.6: Multistep Synthesis
- 16.7: Electrophilic Aromatic Substitution
- 16.8: The General Mechanism
- 16.9: Halogenation
- 16.10: Nitration and Sulfonation
- 16.11: Friedel–Crafts Alkylation and Friedel–Crafts Acylation

- 16.12: Substituted Benzenes
- 16.13: Electrophilic Aromatic Substitution of Substituted Benzenes
- 16.14: Why Substituents Activate or Deactivate a Benzene Ring
- 16.15: Orientation Effects in Substituted Benzenes

17: Carboxylic Acids and the Acidity of the O–H Bond

- 17.1: Inductive Effects in Aliphatic Carboxylic Acids
- 17.2: Substituted Benzoic Acids
- 17.3: Extraction
- 17.4: Sulfonic Acids
- 17.5: Amino Acids
- 17.6: Structure and Bonding
- 17.7: Nomenclature
- 17.8: Physical Properties
- 17.9: Spectroscopic Properties
- 17.10: Interesting Carboxylic Acids
- 17.11: Aspirin, Arachidonic Acid, and Prostaglandins
- 17.12: Preparation of Carboxylic Acids
- 17.13: Reactions of Carboxylic Acids—General Features
- 17.14: Carboxylic Acids—Strong Organic Brønsted–Lowry Acids

18: Introduction to Carbonyl Chemistry; Organometallic Reagents; Oxidation and Reduction

- 18.1: Introduction
- 18.2: General Reactions of Carbonyl Compounds
- 18.3: A Preview of Oxidation and Reduction
- 18.4: Reduction of Aldehydes and Ketones
- 18.5: The Stereochemistry of Carbonyl Reduction
- 18.6: Enantioselective Carbonyl Reductions
- 18.7: Reduction of Carboxylic Acids and Their Derivatives
- 18.8: Oxidation of Aldehydes
- 18.9: Organometallic Reagents
- 18.10: Reaction of Organometallic Reagents with Aldehydes and Ketones
- 18.11: Retrosynthetic Analysis of Grignard Products
- 18.12: Protecting Groups
- 18.13: Reaction of Organometallic Reagents with Carboxylic Acid Derivatives
- 18.14: Reaction of Organometallic Reagents with Other Compounds
- 18.15: α,β -Unsaturated Carbonyl Compounds
- 18.16: Summary—The Reactions of Organometallic Reagents
- 18.17: Synthesis

19: Aldehydes and Ketones—Nucleophilic Addition

- 19.1: The Wittig Reaction
- 19.2: Addition of 1° Amines
- 19.3: Addition of 2° Amines
- 19.4: Addition of H_2O —Hydration
- 19.5: Addition of Alcohols—Acetal Formation
- 19.6: Acetals as Protecting Groups
- 19.7: Cyclic Hemiacetals
- 19.8: An Introduction to Carbohydrates

- 19.9: Introduction
- 19.10: Nomenclature
- 19.11: Physical Properties
- 19.12: Spectroscopic Properties
- 19.13: Interesting Aldehydes and Ketones
- 19.14: Preparation of Aldehydes and Ketones
- 19.15: Reactions of Aldehydes and Ketones—General Considerations
- 19.16: Nucleophilic Addition of H[−] and R[−]—A Review
- 19.17: Nucleophilic Addition of [−]CN

20: Carboxylic Acids and Their Derivatives— Nucleophilic Acyl Substitution

- 20.1: Reactions of Carboxylic Acids
- 20.2: Reactions of Esters
- 20.3: Application- Lipid Hydrolysis
- 20.4: Reactions of Amides
- 20.5: Application- The Mechanism of Action of β -Lactam Antibiotics
- 20.6: Summary of Nucleophilic Acyl Substitution Reactions
- 20.7: Natural and Synthetic Fibers
- 20.8: Biological Acylation Reactions
- 20.9: Nitriles
- 20.10: Introduction
- 20.11: Structure and Bonding
- 20.12: Nomenclature
- 20.13: Physical Properties
- 20.14: Spectroscopic Properties
- 20.15: Interesting Esters and Amides
- 20.16: Introduction to Nucleophilic Acyl Substitution
 - 20.16.1: 22.8 Reactions of Acid Chlorides
- 20.17: Reactions of Acid Chlorides
- 20.18: Reactions of Anhydrides

21: Substitution Reactions of Carbonyl Compounds at the Alpha Carbon

- 21.1: Acetoacetic Ester Synthesis
- 21.2: Introduction
- 21.3: Enols
- 21.4: Enolates
- 21.5: Enolates of Unsymmetrical Carbonyl Compounds
- 21.6: Racemization at the α Carbon
- 21.7: A Preview of Reactions at the α Carbon
- 21.8: Halogenation at the α Carbon
- 21.9: Direct Enolate Alkylation
- 21.10: Malonic Ester Synthesis

22: Carbonyl Condensation Reactions

- 22.1: The Aldol Reaction
- 22.2: Crossed Aldol Reactions
- 22.3: Directed Aldol Reactions
- 22.4: Intramolecular Aldol Reactions
- 22.5: The Claisen Reaction

- 22.6: The Crossed Claisen and Related Reactions
- 22.7: The Dieckmann Reaction
- 22.8: The Michael Reaction
- 22.9: The Robinson Annulation

23: Amines

- 23.1: Relative Basicity of Amines and Other Compounds
- 23.2: Amines as Nucleophiles
- 23.3: Hofmann Elimination
- 23.4: Reaction of Amines with Nitrous Acid
- 23.5: Substitution Reactions of Aryl Diazonium Salts
- 23.6: Coupling Reactions of Aryl Diazonium Salts
- 23.7: Application- Synthetic Dyes
- 23.8: Application- Sulfa Drugs
- 23.9: Introduction
 - 23.9.1: 25.2 Structure and Bonding
- 23.10: Structure and Bonding
- 23.11: Nomenclature
- 23.12: Physical Properties
- 23.13: Spectroscopic Properties
- 23.14: Interesting and Useful Amines
- 23.15: Preparation of Amines
- 23.16: Reactions of Amines—General Features
- 23.17: Amines as Bases

24: Synthetic Polymers

- 24.1: Introduction
- 24.2: Chain-Growth Polymers—Addition Polymers
- 24.3: Anionic Polymerization of Epoxides
- 24.4: Ziegler–Natta Catalysts and Polymer Stereochemistry
- 24.5: Natural and Synthetic Rubbers
- 24.6: Step-Growth Polymers—Condensation Polymers
- 24.7: Polymer Structure and Properties
- 24.8: Green Polymer Synthesis
- 24.9: Polymer Recycling and Disposal

[Index](#)

[Glossary](#)

[Detailed Licensing](#)