

Structural Organic Chemistry
Timothy Eckert
Carthage College

Contents

- 1 Bonding, Structure, and Physical Properties
 - 1.1 Nature of Organic Chemistry 1
 - 1.2 Bonding 2
 - A. Ionic Bonds 2
 - B. Covalent Bonds 3
 - C. Multiple Bonds 3
 - 1.3 Structures of Organic Molecules 5
 - A. Types of Representations 5
 - B. Types of Organic Molecules 7
 - 1.4 Electron Accounting 10
 - A. Formal Charge 10
 - B. Octet Rule 11
 - 1.5 Resonance 14
 - 1.6 Molecular Geometry and Hybrid Orbitals 19
 - A. Molecular Geometry of Methane 20
 - B. Molecular Geometry of Methyl Carbocation 22
 - C. Molecular Geometry of Ethyne 23
 - D. General Rules of Molecular Geometry 25
 - E. Resonance and Hybridization 27
 - 1.7 Bond Lengths 28
 - A. Bond Lengths in 1-Butene 28
 - B. Bond Lengths in Propyne 30
 - C. Bond Lengths in Benzene 30
 - 1.8 Bond Energies 31
 - 1.9 Polarity 33
 - A. Bond Polarity 33
 - B. Molecular Polarity 35
 - 1.10 Intermolecular Forces 36
 - A. Ionic Bonds 37
 - B. Dipole-Dipole Forces 37
 - C. Hydrogen Bonds 38
 - D. Dispersion Forces 39
 - 1.11 Physical Properties 40
 - A. Boiling Points 40
 - B. Melting Points 41
 - C. Solubilities 42
- 2 Alkanes and Cycloalkanes
 - 2.1 Notable Alkanes 1
 - 2.2 Nomenclature 2

- A. Nomenclature of Alkanes 2
- B. Nomenclature of Alkyl Halides 6
- C. Nomenclature of Alcohols 6
- D. Nomenclature of Cycloalkanes 7
- E. Nomenclature of Benzene Compounds 7
- F. Classes of Carbon Atoms 8
- 2.3 Constitutional Isomers 9
- 2.4 Molecular Formulas 10
 - A. Mass Spectrometry 10
 - B. Structural Information from Molecular Formulas 12
- 2.5 Physical Properties of Alkanes and Cyclohexanes 15
- 2.6 Conformations of Alkanes 18
 - A. Conformations of Ethane 18
 - B. Conformations of Propane 20
 - C. Conformations of Butane 21
- 2.7 Reactions of Alkanes and Cycloalkanes 24
 - A. General Reactivity of Alkanes and Cycloalkanes 24
 - B. Combustion of Alkanes and Cycloalkanes 25
- 2.8 Ring Strain and Cycloalkane Conformations 27
 - A. Ring Strain in Cyclopropane 27
 - B. Ring Strain in Cyclobutane 28
 - C. Ring Strain in Cyclopentane 29
 - D. Ring Strain in Cyclohexane 29
 - E. Conformations of Substituted Cyclohexanes 31
- 3 Stereoisomers
 - 3.1 Nature of Enantiomers 1
 - A. Kinds of Isomers 1
 - B. Enantiomers 3
 - C. Physical Properties of Enantiomers 7
 - D. Chemical Properties of Enantiomers 9
 - 3.2 Chiral Atoms 11
 - A. Labeling Chiral atoms 11
 - B. Representations of Chiral Atoms 14
 - C. Chiral Atoms Other than Carbon 16
 - 3.3 Molecules with More than One Chiral Atom 17
 - A. Chiral Molecules with More than One Chiral Atom 17
 - B. Achiral Molecules with More than One Chiral Atom 19
 - 3.4 Stereoisomers of Disubstituted Cycloalkanes 22
 - 3.5 Stereoisomers of Alkenes 25
 - 3.6 Properties of Diastereomers 28
 - A. Physical Properties of Diastereomers 28
 - B. Chemical Properties of Diastereomers 31
- 4 Acids and Bases
 - 4.1 Brønsted-Lowry Theory of Acids and Bases 1

-
- A. Definitions of Brønsted Acids and Bases 2
 - B. Structures of Brønsted Acids and Bases 2
 - 4.2 Acidities 4
 - 4.3 Basicities 6
 - 4.4 Acid-Base Equilibria 7
 - 4.5 Successful Acid-Base Reactions 8
 - 4.6 Absolute Acid and Base Strengths 9
 - 4.7 Lewis Theory of Acids and Bases 11
 - 4.8 Comparison of Brønsted and Lewis Theories 12
 - 4.9 Hard and Soft Electrophiles and Nucleophiles 13
 - 4.10 Structural Influences on Acid and Base Strengths 15
 - A. Influence of Base Atom's Hardness 15
 - B. Influence of Base Atom's Electronegativity 16
 - C. Influence of Formal Charge 17
 - D. Influence of Partial Charge 18
 - E. Influence of Resonance 19
 - F. Influence of Base Atom's Hybridization 21
 - 4.11 Strengths of Electrophiles and Nucleophiles 22

 - 5 The Mechanics of Reactions
 - 5.1 Mechanisms and Electron Arrows 1
 - 5.2 Equilibrium and Free Energy 3
 - 5.3 Kinetics 6
 - A. Collision Theory 7
 - B. The Transition State and Energy-Reaction Diagrams 8
 - C. Effects of Temperature and Free Energy of Activation 9
 - D. Entropy of Activation 11
 - 5.4 Equilibrium versus Kinetics 13
 - A. Unfavorable Equilibrium and Favorable Kinetics 13
 - B. Favorable Equilibrium and Unfavorable Kinetics 14
 - 5.5 Reactions with Two-Step Mechanisms 15
 - A. The Energy-Reaction Diagram for Two-Step Mechanisms 15
 - B. The Rate-Limiting Step 17

 - 6 Substitution Reactions of Alkyl Halides
 - 6.1 Notable Alkyl Halides 1
 - 6.2 Physical Properties of Alkyl Halides 2
 - 6.3 Mechanism of S_N2 Reactions 3
 - A. Kinetics of S_N2 Reactions 3
 - B. Stereochemistry of S_N2 Reactions 4
 - 6.4 Effective Reactants for S_N2 Reactions 6
 - A. Leaving Groups of S_N2 Electrophiles 6
 - B. Carbon Skeletons of S_N2 Electrophiles 7
 - C. Nucleophiles for S_N2 Reactions 10
 - 6.5 Mechanism of S_N1 Reactions 12
 - A. General Characteristics of the S_N1 Mechanism 12

- B. The First Step of the S_N1 Mechanism 14
- C. The Second Step of the S_N1 Mechanism 16
- D. Carbocation Rearrangements in the S_N1 Mechanism 19
- 6.6 Preferred Solvents for S_N1 and S_N2 Reactions 21
- 6.7 Comparison of S_N1 and S_N2 Reactions 23
- 6.8 Synthetic Considerations 25
- 6.9 Grignard Reagents 27

- 7 Elimination Reactions of Alkyl Halides
 - 7.1 General Nature of Elimination Reactions 1
 - 7.2 Kinetic Studies and Mechanisms of Elimination Reactions 2
 - A. Mechanism of E2 Reactions 2
 - B. Mechanism of E1 Reactions 3
 - 7.3 Effects of Base Strength on Elimination Reactions 4
 - 7.4 Product Constitutional Isomers of Elimination Reactions 6
 - 7.5 Effective Electrophiles for Elimination Reactions 7
 - A. Leaving Groups of Effective Electrophiles 7
 - B. Carbon Skeletons of Effective Electrophiles 8
 - 7.6 Stereochemistry of Elimination Reactions 9
 - A. Product Stereoisomers 10
 - B. Steric Orientation 11
 - 7.7 Carbocation Rearrangements in Elimination Reactions 14
 - 7.8 Preferred Solvents for Elimination Reactions 15
 - 7.9 Comparisons of Elimination and Substitution Reactions 16
 - A. E2 versus E1 Reactions 17
 - B. E2 versus S_N2 Reactions 18
 - C. E1 versus S_N1 Reactions 20

- 8 Alkenes
 - 8.1 Notable Alkenes 1
 - 8.2 Nomenclature of Alkenes 2
 - 8.3 Structural Features of Alkenes 4
 - A. Geometry 4
 - B. Bond Strength 5
 - 8.4 Physical Properties of Alkenes 6
 - 8.5 Syntheses of Alkenes 7
 - 8.6 General Nature of Alkene Reactions 7
 - 8.7 Addition Reactions of Alkenes with Hydrogen 8
 - A. Catalytic Hydrogenation 8
 - B. Stabilities of Alkenes 11
 - 8.8 Addition Reactions of Alkenes with Acids 13
 - A. Reactions with Hydrogen Halides 13
 - B. Reaction with Aqueous Acid 15
 - C. Stereochemistry of Reactions with Acids 17
 - D. Carbocation Rearrangements in Reactions with Acids 18
 - 8.9 Addition Reaction of Alkenes with Mercuric Ethanoate 20

-
- 8.10 Addition Reactions of Alkenes with Halogens 22
 - A. Mechanism of Reactions with Halogens 22
 - B. Stereochemistry of Reactions with Halogens 23
 - C. Reactions with Halogens in Water 24
 - 8.11 Addition Reaction of Alkenes with Borane 25
 - A. A Different Kind of Hydration 26
 - B. Stereochemistry of Reaction with Borane 27
 - 8.12 Oxidation Reactions of Alkenes 28
 - A. Oxidation Reaction with Potassium Permanganate 30
 - B. Oxidation Reaction with Peroxyacids 31
 - C. Oxidation Reaction with Ozone 32
 - 9 Alkynes
 - 9.1 Notable Alkynes 1
 - 9.2 Nomenclature of Alkynes 2
 - 9.3 Structural Features of Alkynes 3
 - 9.4 Physical Properties of Alkynes 4
 - 9.5 Reactions of Alkynes 5
 - A. Addition Reactions with Hydrogen Halides 5
 - B. Addition Reaction with Aqueous Acid 8
 - C. Addition Reaction with Borane 10
 - D. Addition Reactions with Halogens 11
 - E. Addition Reactions with Hydrogen 13
 - F. Terminal Alkynes as Acids 15
 - 9.6 Syntheses of Alkynes 16
 - A. Alkynes from 1,2-Dihalides 16
 - B. Alkynes from Smaller Alkynes 18
 - C. Synthetic Strategies with Alkynes 20
 - 10 Alcohols and Ethers
 - 10.1 Notable Alcohols and Ethers 1
 - 10.2 Nomenclature of Ethers 2
 - 10.3 Physical Properties of Alcohols and Ethers 4
 - A. Boiling Points of Alcohols and Ethers 4
 - B. Solubilities of Alcohols and Ethers 5
 - 10.4 Syntheses of Alcohols 9
 - 10.5 Reactions of Alcohols 11
 - A. Reactions of Alcohols as Acids 11
 - B. Reactions of Alcohols as Bases 13
 - C. Reactions of Alcohols as Non-base Nucleophiles 14
 - D. Reactions Removing the Hydroxy Group from Alcohols 15
 - E. Oxidation Reactions of Alcohols 23
 - 10.6 Reactions of Alkoxide Ions 26
 - A. Reactions of Alkoxide Ions as Bases 26
 - B. Reactions of Alkoxide Ions as Non-base Nucleophiles 27
 - 10.7 Syntheses of Ethers 28

- 10.8 Reactions of Ethers 31
 - A. Reactions of Simple Ethers 32
 - B. Reactions of Oxiranes 34
- 11 Spectroscopy: Infrared and Nuclear Magnetic Resonance
 - 11.1 Theory of Spectroscopy 1
 - 11.2 Theory of Infrared Spectroscopy 4
 - 11.3 Characteristic Infrared Bands 6
 - A. General Patterns of Infrared Bands 6
 - B. Infrared Bands of Alkanes 9
 - C. Infrared Bands of Alkenes 10
 - D. Infrared Bands of Alkynes 11
 - E. Infrared Bands of Alcohols and Ethers 11
 - F. Infrared Bands of Alkyl Halides 13
 - 11.4 Theory of Nuclear Magnetic Resonance Spectroscopy 15
 - 11.5 Proton NMR Spectroscopy 17
 - A. Chemical Shifts 17
 - B. Peak Areas 26
 - C. Splitting of Signals 27
 - D. Hydrogens on Alcohol Oxygens and Amine Nitrogens 33
 - E. Complex Splitting Patterns 36
 - 11.6 ^{13}C NMR Spectroscopy 37
 - A. Chemical Shifts and Peak Areas 37
 - B. Splitting of Signals 41
- 12 Aldehydes and Ketones
 - 12.1 Notable Aldehydes and Ketones 1
 - 12.2 Nomenclature of Aldehydes and Ketones 2
 - 12.3 Structures and Physical Properties 4
 - 12.4 Syntheses of Aldehydes and Ketones 6
 - 12.5 Reactions as Non-acid Electrophiles 8
 - A. General Characteristics 8
 - B. Addition of Organometallic Reagents 11
 - C. Addition-Elimination Reactions of Amines 14
 - D. Additions of Water and Alcohols 18
 - E. Reductions 21
 - F. Oxidations 25
 - 12.6 Syntheses of Larger Carbon Structures 26
 - 12.7 Protecting Groups for Aldehydes and Ketones 30
 - 12.8 Spectroscopy of Aldehydes and Ketones 32
- 13 Carboxylic Acids
 - 13.1 Notable Carboxylic Acids 1
 - 13.2 Nomenclature of Carboxylic Acids 2
 - 13.3 Structures and Physical Properties of Carboxylic Acids 4
 - 13.4 Syntheses of Carboxylic Acids 6

-
- A. Oxidations 7
 - B. Addition of Grignard Reagents to Carbon Dioxide 7
 - C. Hydrolysis of Nitriles 8
 - 13.5 Reactions of Carboxylic Acids 11
 - A. Reaction of Carboxylic Acids as Acids 11
 - B. Reduction of Carboxylic Acids 13
 - C. Formation of Acid Chlorides 15
 - 13.6 Spectroscopy of Carboxylic Acids 16

 - 14 Carboxylic Acid Derivatives
 - 14.1 Notable Carboxylic Acid Derivatives 1
 - 14.2 Structures of Carboxylic Acid Derivatives 2
 - 14.3 Nomenclature of Carboxylic Acid Derivatives 4
 - 14.4 Physical Properties of Carboxylic Acid Derivatives 6
 - A. Boiling Points of Carboxylic Acid Derivatives 6
 - B. Solubilities of Carboxylic Acid Derivatives 7
 - 14.5 Nucleophilic Addition-Elimination Reactions 8
 - A. General Nature of Addition-Elimination Reactions 8
 - B. Order of Reactivities 10
 - C. Comparison with S_N2 Reactions 12
 - D. Acid Catalysis in Addition-Elimination Reactions 14
 - 14.6 Interconversions of Carboxylic Acids and Derivatives 16
 - A. Reactions of Acid Chlorides 16
 - B. Hydrolyses of Carboxylic Acid Derivatives 18
 - C. Reactions of Acid Anhydrides 21
 - 14.7 Reduction Reactions of Carboxylic Acid Derivatives 24
 - A. Reduction Reactions with Lithium Aluminum Hydride 24
 - B. Reduction Reactions with Grignard Reagents 26
 - 14.8 Fats and Derivatives 27
 - A. Structures and Physical Properties of Fats 28
 - B. Soaps 30
 - C. Phosphoglycerides 32
 - 14.9 Spectroscopy of Carboxylic Acid Derivatives 33
 - A. Infrared Spectroscopy 33
 - B. Nuclear Magnetic Resonance Spectroscopy 36

 - 15 Amines
 - 15.1 Notable Amines 1
 - 15.2 Nomenclature of Amines 3
 - 15.3 Structure of Amines 5
 - 15.4 Physical Properties of Amines 6
 - 15.5 Syntheses of Amines 9
 - A. Alkylation of Ammonia or Amines 9
 - B. Phthalimide Synthesis 12
 - C. Reduction of Amides 14
 - D. Reduction of Nitro Compounds 15

- E. Reductions of Carbon-Nitrogen π Bonds 16
- 15.6 Reactions of Amines 18
 - A. Reaction of Amines as Acids 18
 - B. Reaction of Amines as Bases 21
 - C. Reactions of Amines as Non-Base Nucleophiles 23
 - D. Reactions of Amines with Nitrous Acid 25
- 15.7 Spectroscopy of Amines 27
 - A. Infrared Spectroscopy 27
 - B. Nuclear Magnetic Resonance Spectroscopy 28
- 16 Allylic and Conjugated Compounds
 - 16.1 Notable Conjugated and Allylic Compounds 1
 - 16.2 Allylic Electrophiles 2
 - A. S_N1 Reactions of Allylic Electrophiles 3
 - B. S_N2 Reactions of Allylic Electrophiles 5
 - C. Allylic versus Alkenyl Electrophiles 6
 - 16.3 Dienes 8
 - A. Types of Dienes 8
 - B. Synthesis of Conjugated Dienes 10
 - C. Reactions of Conjugated Dienes with Electrophiles 12
 - D. The Diels-Alder Reaction 14
 - 16.4 Reactions of α,β -Unsaturated Carbonyl Compounds 17
 - 16.5 Terpenes 21
 - A. The Isoprene Rule 21
 - B. Biosyntheses of Terpenes 24
 - 16.6 Ultraviolet-Visible Spectroscopy 27
 - A. Molecular Orbitals 27
 - B. Theory of UV-VIS Spectroscopy 29
 - C. Effects of Conjugation on UV-VIS Spectroscopy 30
 - D. Chemistry of Vision 34
 - 16.7 Infrared Spectroscopy of Conjugated Compounds 36
- 17 Aromatic Compounds and Electrophilic Substitutions
 - 17.1 Notable Benzene Compounds 1
 - 17.2 Nomenclature of Benzene Compounds 3
 - 17.3 Structures and Physical Properties of Benzene Compounds 4
 - 17.4 Aromaticity 6
 - A. Nature of Aromaticity 6
 - B. Ramifications of Aromaticity 10
 - C. Aromaticity in Heterocyclic Rings 12
 - 17.5 Electrophilic Aromatic Substitution Reactions 14
 - A. General Mechanism 14
 - B. Nitration 16
 - C. Sulfonation 18
 - D. Halogenations 20
 - E. Alkylations 22

-
- F. Acylations 24
 - 17.6 Regioselectivity in Electrophilic Aromatic Substitutions 26
 - A. Meta-Directing Substituents 26
 - B. Ortho,Para-Directing Substituents 28
 - C. Steric Effects 29
 - D. Preferred Order of Substitution 30
 - E. Effect of Multiple Substituents 31
 - 17.7 Rates of Electrophilic Aromatic Substitutions 32
 - A. Meta-Directing Substituents 32
 - B. Ortho,Para-Directing Substituents 33
 - C. Limitations on Alkylation and Acylation Reactions 36
 - 18 Further Chemistry of Benzene Compounds
 - 18.1 Syntheses of Carbon Substituents on Benzene Rings 1
 - 18.2 Reactions of Carbon Substituents on Benzene Rings 4
 - A. Oxidation of Carbon Substituents 4
 - B. S_N1 Reactions with Benzylic Electrophiles 6
 - C. S_N2 Reactions with Benzylic Electrophiles 9
 - D. Benzylic versus Phenyl Electrophiles 11
 - E. Elimination Reactions 13
 - F. Addition Reactions with Styrenes 15
 - 18.3 Reactions of Phenyl Diazonium Ions 17
 - 18.4 Phenols 20
 - 18.5 Nucleophilic Aromatic Substitution Reactions 22
 - 18.6 Spectroscopy of Benzene Compounds 26
 - 19 Enolate Ions and Related Compounds
 - 19.1 Structures of Enolate Ions and Enols 1
 - 19.2 Reactions of Enols with Halogens 6
 - 19.3 Reactions of Simple Enolate Ions 8
 - A. General Characteristics of Enolate Reactions 8
 - B. Reactions of Simple Enolate Ions with Halogens 10
 - C. Reactions of Simple Enolate Ions with Alkyl Halides 11
 - D. Reactions of Simple Enolate Ions with Aldehydes 13
 - E. Reactions of Simple Enolate Ions with Esters 18
 - 19.4 Reactions of 1,3-Dicarbonyl Enolate Ions 22
 - 19.5 Biosynthesis of Fatty Acids 26
 - 19.6 The Wittig Reaction 28
 - 19.7 Reactions of Enamines 31
 - 20 Carbohydrates
 - 20.1 Structures and Classes of Monosaccharides 1
 - 20.2 Cyclization of Monosaccharides 4
 - 20.3 Stereochemistry of Monosaccharides 7
 - A. Fischer Projections and Haworth Projections 7
 - B. D and L Monosaccharides 9

- C. Anomers 12
- 20.4 Reactions of Monosaccharides 15
 - A. Interconversion of Anomers 15
 - B. Formation of Acetal Glycosides 17
 - C. Oxidation of Reducing Sugars 20
 - D. Esterification of Alcohol Groups 22
- 20.5 Oligosaccharides and Polysaccharides 26
 - A. Structures of Notable Oligosaccharides 26
 - B. Structures of Notable Polysaccharides 28
 - C. Syntheses of Oligosaccharides and Polysaccharides 30
 - D. Hydrolyses of Oligosaccharides and Polysaccharides 33
- 21 Amino Acids and Proteins
 - 21.1 Structures of Amino Acids 1
 - 21.2 Amino Acids as Acids and Bases 6
 - A. Amino Acids as Dipolar Ions 6
 - B. Neutral Amino Acids 7
 - C. Acidic and Basic Amino Acids 10
 - 21.3 Peptides 12
 - A. Peptide Structures 12
 - B. Determination of Peptide and Protein Structures 15
 - 21.4 Syntheses of Peptides and Proteins 17
 - A. General Synthetic Principles 18
 - B. Laboratory Syntheses of Peptides and Proteins 19
 - C. Biosyntheses of Proteins 24
 - 21.5 Structures of Proteins 26
 - 21.6 Catalysis by an Enzyme 31