

5.12 Spring 2003
Outline: First Half of Semester

I. Review of Lewis Bonding Theory

- A. Ionic Bonding
- B. Covalent Bonding
 - 1. Multiple Bonding
 - 2. Formal Charge
- C. Short-Hand for Chemists
 - 1. Line-Angle Formulas
 - 2. Dashes and Wedges
 - 3. Curved Arrow Formalism

II. Resonance

- A. Drawing Resonance Structures
- B. Energy of Resonance Structures
- C. Structure and Reactivity from Resonance

III. Review of Molecular Orbital Theory

- A. Atomic Orbitals
- B. Sigma-Bonding
- C. Pi-Bonding
- D. VSEPR Theory

IV. Hybridization/LCAO

- A. sp Hybridization
- B. sp^2 Hybridization
- C. sp^3 Hybridization
 - 1. Rotation of Ethane versus Ethylene

V. Properties of Molecules

- A. Acidity of Organic Molecules
 - 1. Bronsted–Lowry Acidity
 - a) Review of Acid/Base Equations
 - b) Acidity Trends
 - i) Attached Atom: electronegativity, size and charge
 - ii) Inductive Effects
 - iii) Hybridization
 - iv) Resonance
 - 2. Lewis Acidity
- B. Bond Lengths

C. Bond Strengths

VI. Alkanes

A. Molecular Formulas

1. Degrees of Unsaturation
2. Constitutional Isomers

B. IUPAC Nomenclature

C. Conformational Analysis

1. Ethane
 - a) Newman Projections
2. Propane
3. Butane

VII. Cycloalkanes

A. Ring Size and Strain

B. Cyclopropane

C. Cyclobutane

D. Cyclopentane

E. Cyclohexane

1. Conformational Analysis
 - a) Drawing Chairs
 - b) Ring Flip
2. Mono-Substituted Cyclohexane
 - a) Axial versus Equatorial: A-Values
3. Di-Substituted Cyclohexane
 - a) Cis/Trans Isomerism
 - b) Preferred Conformers
4. Bicyclic Ring Systems

VIII. Stereochemistry

A. Stereoisomers

B. Chirality and Stereocenters

C. Enantiomers

1. Cahn–Ingold–Prelog Convention (R/S)
2. Optical Activity
3. Description of Samples (Optical Purity/Enantiomeric Excess)

D. Diastereomers

1. Cis/Trans Isomers (Geometric)
2. Molecules with >1 Stereocenter

E. Fischer Projections

IX. Free Radical Reactions

- A. Chlorination of Methane
 - 1. Mechanism
- B. Review of Thermodynamics
- C. Review of Kinetics
- D. Reaction-Energy Diagrams
 - 1. Thermodynamic Control
 - 2. Kinetic Control
 - 3. Hammond Postulate
 - 4. Multi-Step Reactions
 - 5. Chlorination of Methane
- E. Chlorination of Propane
 - 1. Inequivalent Hydrogens ($1^\circ, 2^\circ, 3^\circ$)
 - 2. Relative Reactivity
 - 3. Selectivity
- F. Bromination of Propane
 - 1. Selectivity (Hammond Postulate)
- G. Radical Stability
- H. General Selectivity of Radical Halogenations
- X. Substitution and Elimination Reactions of Alkyl Halides**
 - A. Alkyl Halides
 - 1. Nomenclature
 - 2. Structure
 - 3. Substitution/Elimination
 - B. S_N2 : Substitution Nucleophilic Bimolecular
 - 1. Mechanism
 - a) Arrow Pushing
 - b) Reaction-Energy Diagram
 - c) Stereochemistry
 - d) Molecular Orbitals
 - 2. Examples of S_N2
 - 3. Factors Affecting the Rate of S_N2
 - a) Substrate: Sterics
 - b) Nucleophile
 - c) Leaving Group
 - d) Solvent
 - C. S_N1 : Substitution Nucleophilic Unimolecular
 - 1. Mechanism
 - a) Arrow Pushing

- b) Reaction-Energy Diagram
 - c) Stereochemistry
 - 2. Factors Affecting the Rate of S_N1
 - a) Substrate: Carbocation Stability
 - b) Leaving Group
 - c) Solvent
 - 3. Carbocation Rearrangements
 - 4. S_N1 versus S_N2
- D. E1: Elimination Unimolecular
 - 1. Mechanism
 - a) Arrow Pushing
 - b) Reaction-Energy Diagram
 - 2. E1 versus S_N1
- E. E2: Elimination Bimolecular
 - 1. Mechanism
 - a) Arrow Pushing
 - b) Reaction-Energy Diagram
 - c) Transition State Geometry
 - d) Stereochemistry
 - 2. Positional Orientation (Saytzeff Rule)
 - a) Alkene Stability
 - b) Bulky Bases (Hofmann Products)
 - 3. E1 versus E2
 - 4. Substitution versus Elimination

XI. Structure and Synthesis of Alkenes

- A. IUPAC Nomenclature
- B. Structure
- C. Cycloalkanes
 - 1. Stability
 - 2. Bredt's Rule
- D. Synthesis of Alkenes
 - 1. Dehydrohalogenation (E1 and E2)
 - 2. Dehalogenation
 - 3. Dehydration of Alcohols