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°,2°,3°)
    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