12: Conjugated and Aromatic Molecules

12.1 Conjugated Molecules
1,3-Butadiene (12.1A)
   Atomic Orbital Overlap in 1,3-Butadiene
   Molecular Orbitals
   The Bonding M.O.'s
   Conformations
   Other Alternating Multiple Bonds

Pentadienes (12.1B)
   1,3-Pentadiene
   1,4-Pentadiene
   1,2-Pentadiene

Stability of Conjugated Systems (12.1C)
   Heats of Hydrogenation of Pentadienes
   Heats of Hydrogenation of Butadienes

Aromatic Molecules (12.1D)

12.2 Reactivity of Conjugated Systems
Addition of H-Cl to 1,3-Butadiene (12.2A)
   Products
   Mechanism
   Delocalized Carbocation

Resonance Structures (12.2C)
   Carbocation Resonance Structures
   Meaning of Resonance Structures
   Meaning of The Double Headed Arrow

Other Reactions with Delocalized Intermediates (12.2D)
   Acid Catalyzed Hydration
   Electrophilic Halogenation
   Free Radical Addition of H-Br.

12.3 Writing Resonance Structures
   A General Procedure (12.3A)
   Carbocations (C⁺) (12.3B)
   Carbanions (C⁻) (12.3C)
   Radicals (C-) (12.3D)

12.4 More on Delocalized Systems
   Localized vs. Delocalized Intermediates (12.4A)
   Reactions other than Addition (12.4B)
      Radical Halogenation
      Resonance Forms with Heteroatom
      Relative Importance of Resonance Forms

12.5 Benzenoid Aromatic Molecules
   Benzene (12.5A)
      Reactivity
      Stability
      ¹H NMR Spectra

(continued)
The Real Structure of Benzene (12.5B)
- Benzene Geometry
- Benzene Resonance Structures
- Benzene Molecular Orbitals
Benzene MO's, Resonance, and Unusual Properties (12.5C)
- Chemical Reactivity
- Stability
- $^{1}H$ NMR Chemical Shifts
Substituted Benzenes (12.5D)

12.6 Nomenclature of Benzenoid Aromatic Molecules
- Monocyclic Arenes (12.6A)
  - Systematic Nomenclature
  - Common Nomenclature
- ortho, meta, and para (12.6B)
  - The Phenyl Group
  - The Benzyl Group
- Polycyclic Arenes (12.6C)

12.7 Aromatic Systems without Benzene Rings
- Annulenes (12.7A)
  - Aromatic and Nonaromatic Annulenes
  - Cyclobutadiene and Cyclooctatetraene
  - Resonance Structures Do Not Tell the Story
- MO Diagrams for $C_4H_4$, $C_6H_6$ and $C_8H_8$ (12.7B)
  - Cyclooctatetraene
  - Cyclobutadiene
- Aromatic Annulenes Besides Benzene (12.7C)
  - Hückel's Rule
  - Other Annulenes
- Heteroaromatic Systems (12.7D)
  - Pyridine
  - Pyrrole
  - Furan and Thiophene
  - Purine and Pyrimidine
- Aromatic Ions (12.7E)
  - Cycloheptatrienyl Cation
  - Cyclopentadienyl Anion
  - Cyclopropenyl Cation
  - Cyclooctadienyl Dianion

12.8 Making Substituted Benzenes
- Electrophilic Aromatic Substitution Mechanism (12.8A)
  - Electrophiles
  - Arenium Ion Formation
  - Deprotonation of the Arenium Ion
  - Reactions with Substituted Benzenes

(continued)
Formation of the Electrophile (12.8B)
  Halogenation
  Sulfonation
  Nitration.
  Alkylation

NH₂ and OH Groups on Arenes (12.8C)
  Synthesis of Aniline (Ph-NH₂)
  Synthesis of Phenol (Ph-OH)
  Acidity of Arene OH Groups
  Basicity of Arene NH₂ Groups

12.9 Spectrometry of Conjugated and Aromatic Molecules
  NMR Spectral Data (12.9A)
    ¹H Chemical Shifts
    ¹³C Chemical Shifts
  UV-Visible Spectral Data (12.9B)
    Conjugated Polyenes
    The Electron Excitation Process
    Arenes
    The Use of UV-Visible Data
  Infrared Spectrometry (12.9C)