CHAPTER OUTLINES/WORKSHEETS

CHAPTER 14

CONJUGATED DIENES AND ULTRAVIOLET SPECTROSCOPY

I. CONJUGATED DIENES

1. Preparation
   
   a. Dehydrobromination

2. Stability (14 kJ/mole)

3. Structure
   
   a. Molecular Orbital description (bonding/antibonding/HOMO/LUMO)
   
   b. Delocalization
   
   c. Bond lengths in butadiene (1.34-1.48-1.34 Å)

   Delocalization

   Orbital hybridization

4. Electrophilic additions
   
   a. Allylic Carbocation
   
   b. 1,2-addition — 1,4-addition
   
   c. Molecular orbital diagram
   
   d. Kinetic (irreversible) and thermodynamic (reversible) control of reaction

5. Diels-Alder reaction (pericyclic reaction)
   
   a. Dienophiles (diene "lover")
   
   b. Dienes (s-cis conformer)
   
   c. Stereocspecificity, "endo" rule

6. Other Conjugated systems (enamines, enol ethers, enolate anion)
II. STRUCTURE DETERMINATION

1. Ultraviolet spectroscopy (nature of the \( \pi \)-electron system — 200-400 nm)

2. Spectrum of 1,3-butadiene (\( \pi \rightarrow \pi^* \) [217 nm])
   a. HOMO-LUMO transition
   b. Absorbivity (extinction coefficient)

3. Spectra of other conjugated molecules
   a. Olefins, dienes, trienes, and tetraenes [170, 220, 258, 290 nm]
   b. Carbonyl n \( \rightarrow \pi^* \) [weak 272 nm]
   c. Benzene [254 nm]

4. Vision and conjugated molecules
   a. Carotene and Vitamin A

**Chapter 14 Worksheet**

What is a conjugated double bond?

Where do conjugated double bonds occur in nature?

What are two ways by which conjugated alkenes can be synthesized?

How much more stable is a conjugated diene than its non-conjugated counterpart?

How can molecular orbital theory account for this energy stabilization?

What is "delocalization"?

How does the C-C bond length in butadiene compare to the C=C in ethylene? To the C-C in ethane?

With what regiochemistry do electrophiles react with conjugated alkenes? What is the difference between 1,2 and 1,4-addition?

How does the special stability of the allylic cation contribute to formation of the 1,4 product?

What two explanations can be offered for the special stability of the allylic cation?
How does the addition of HBr to butadiene vary with temperature?

Explain the difference between kinetic and thermodynamic products.

Describe the process known as the Diels-Alder reaction.

What general type of process is the Diels-Alder reaction?

What is the most important mechanistic feature of a pericyclic reaction?

What is a dienophile?

What types of alkenes make good dienophiles?

What types of dienes react well in the Diels-Alder reaction?

What do the terms "exo" and "endo" mean?

What other types of conjugated systems exist? What is the feature common to all of these systems?

What can ultraviolet spectroscopy reveal concerning molecular structure?

How does the energy involved in an electronic transition compare to the energy involved in NMR transitions? in IR transitions?

The absorption of radiation in UV spectroscopy involves what change in orbital occupancy?

What is the definition of "extinction coefficient"?

How does the extent of conjugation in a molecule change the lambda max of its UV spectrum?

How does light absorption figure in the chemistry of vision?