Bilirubin, the principal conjugated pigment of bile responsible for the yellowing of skin and sclera observed in jaundice
Note: Problems with italicized numbers are more challenging.
You may want to try them last.
Concepts for Chapter 17: Conjugated Dienes and Ultraviolet-Visible Spectroscopy

I. Dienes can be
   A. Isolated
      1. alkene units are separated by $\geq 1\ sp^3$ atom
      2. undergo chemical reactions like alkenes
   B. Cumulated
      1. alkene units share a carbon
      2. the shared carbon is $sp$-hybridized
   C. Conjugated
      1. alkene units are separated by no atoms
      2. have 4 $p$-orbitals all in a row
      4. are more stable than isolated (by about 4 kcal/mol) or cumulated dienes
         a. consider the MO configuration which delocalizes electrons over all 4
            of the constituent $p$-orbitals
   3. preparations
      a. same as making alkenes, but twice
      b. examples: dehydrohalogenations of allyl halides, dehydrations of allyl
         alcohols, double dehydration of vicinal diols
   4. stereochemistry
      a. Can be $(E,E)$, $(E,Z)$, or $(Z,Z)$
         i. exhibit $s$-cis and $s$-trans conformations; usually $s$-trans is about
            3 kcal/mol more stable
   5. reactions
      a. electrophilic addition of HX
         i. 1,2 addition: favored by low temperatures, major product forms
            from kinetic control of the reaction (fastest-forming product
            predominates)
         ii. 1,4 addition: favored by warmer temperatures, major product
            forms from thermodynamic control of the reaction (more
            stable product predominates)
      b. electrophilic addition of $X_2$
         i. 1,4 addition products usually are major products
            I. reaction control can be explained by considering steric
               approach control of $X$ when it attacks halonium ion
      c. thermal [4+2] cycloadditions
         i. called the Diels-Alder reaction
         ii. diene that is electron rich + dienophile that is electron poor add
            to make two new C—C bonds of a six-membered ring
            I. diene reacts from $s$-cis conformation only
            II. $trans$-dienophiles give $trans$-cyclohexenes
            III. $cis$-dienophiles give $cis$-cyclohexenes
            IV. dienophile can be alkene or alkyne
         iii. reaction follows the Alder rule: more sterically crowded
              product usually predominates
d. sigmatropic rearrangements
   i. Cope rearrangement
      I. [3.3] sigmatropic rearrangement of 1,5-alkadienes
      II. equilibrium favors formation of more substituted alkenes
   ii. Claisen rearrangement
      I. also called an oxy-Cope rearrangement
      II. [3.3] sigmatropic rearrangement of allyl vinyl ethers
      III. forms 3-alkeneones

II. UV/VIS
   A. When light energy is absorbed by a molecule having conjugated multiple bonds, the electrons in either the $\pi$ or $n$ molecular orbitals are promoted to antibonding orbitals.
      1. This process follows Beer’s law
      2. Most common transitions:
         a. $n \rightarrow \pi^*$
         b. $\pi \rightarrow \pi^*$
      3. Increasing conjugation increases the wavelength of the absorption. The conjugated system responsible for the absorption is called a chromophore
         a. Sample common chromophores:
            i. a 1,3 diene $\lambda_{max} = 217 \text{ nm}$
            ii. a phenyl group $\lambda_{max} = 254 \text{ nm}$
      4. the Woodward-Fieser rules can be used to predict $\lambda_{max}$
1. Like the addition of HBr to 1,3-butadiene, the addition of HCN to 2,3-dimethyl-1,3-cyclopentadiene proceeds to give a mixture of products at 0°C.

   a. Draw the two products that can be obtained from addition of HCN to 2,3-dimethyl-1,3-cyclopentadiene. Label the kinetic and thermodynamic product; label the 1,2 addition and 1,4 addition product.

   b. Draw an energy versus reaction coordinate diagram of the reaction, including starting materials, intermediates, and products.

   c. Which product will increase in chemical yield if the reaction temperature is increased to 50°C?
2. Write the structure(s) of the major product(s) expected in each of the following reactions. If no reaction is expected, write "NR":

a.  
\[
\text{\begin{tikzpicture}
  \tikzstyle{every node}=[font=\scriptsize]
  \node[shape=circle,draw,inner sep=1pt] (a) at (0,0) {\ce{Cl}};
  \node[shape=circle,draw,inner sep=1pt] (b) at (0,1) {\ce{O}};
  \node[shape=circle,draw,inner sep=1pt] (c) at (1,0) {\ce{O}};
  \node[shape=circle,draw,inner sep=1pt] (d) at (1,1) {\ce{O}};
  \node[shape=circle,draw,inner sep=1pt] (e) at (0,2) {\ce{\Delta}};
  \node[shape=circle,draw,inner sep=1pt] (f) at (2,0) {\ce{\Delta}};
\end{tikzpicture}}
\]

b.  
\[
\text{\begin{tikzpicture}
  \tikzstyle{every node}=[font=\scriptsize]
  \node[shape=circle,draw,inner sep=1pt] (a) at (0,0) {\ce{CO_2CH_3}};
  \node[shape=circle,draw,inner sep=1pt] (b) at (0,1) {\ce{CO_2CH_3}};
  \node[shape=circle,draw,inner sep=1pt] (c) at (1,0) {\ce{\Delta}};
  \node[shape=circle,draw,inner sep=1pt] (d) at (2,0) {\ce{ether}};
\end{tikzpicture}}
\]

3. Write a synthetic route for a reasonable laboratory preparation of the following compounds, starting with the reactant shown and any other needed organic or inorganic reagents:

a. 3-iodo-1-cyclohexene from 1-bromocyclohexane
b. *cis*-1,4-dibromo-2-butene from 1-butanol (this is a tough problem!)

4. A rare but interesting class of cumulated alkenes are the cumulatrienes. Two examples are:

![Two cumulatrienes](image)

a. Even though neither compound possesses a chiral carbon, one of these compounds is optically active. Circle which one.

b. Explain your choice.
5. Conjugated dienes react with free radicals by both 1,2- and 1,4-addition routes. Account for this fact by providing a mechanism for the reaction of 1,3-butadiene with HBr in the presence of light to yield both 1-bromo-2-butene and 4-bromo-1-butene.

6. Dehydrohalogenation of 1,2-dihaloalkanes normally provides an alkyne instead of a conjugated diene as the major product. However, when trans-1,2-dibromocyclohexane is dehydrobrominated, 1,3-cyclohexadiene is produced in good yield. Why?
7. Heptachlor (shown below) is a good insecticide, but persists in the environment and has possible harmful side effects. These reasons, it is no longer used. The commercial synthesis of Heptachlor begins with 1,3-cyclopentadiene and 1,2,3,4,5,5-hexachloro-1,3-cyclopentadiene. Provide a clear sequence of chemical reactions that will provide Heptachlor from these starting materials.

![Chemical structure of Heptachlor](image)