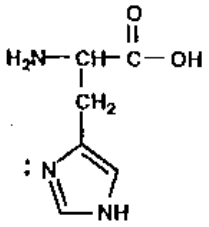
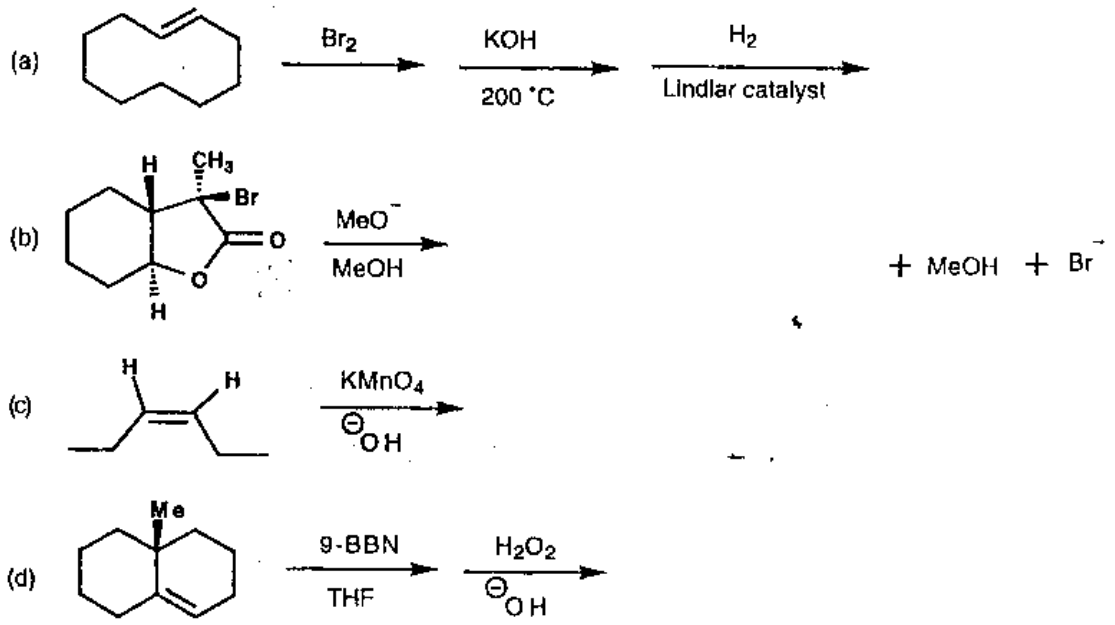
Total 100 points, 2 Pages

1. **Histidine** (**His**) is an important catalytic residue found at the active sites of many enzymes. In many cases, histidine appears to remove protons or to transfer protons from one location to another. (12 pts)

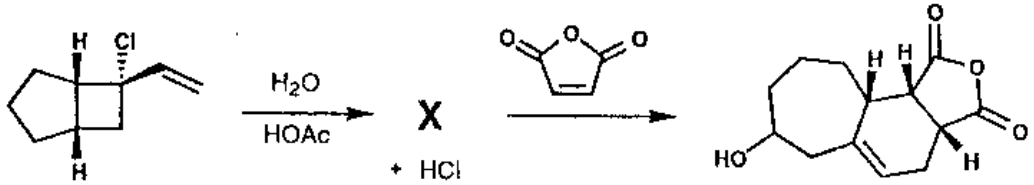


(a) Show which nitrogen atom of the histidine heterocycle is basic and which is not.
(b) Use resonance structures to show why the protonated form of a histidine residue is a particularly stable cation.
(c) Show the structure that results when the **His** residue accepts a proton on the basic nitrogen of the heterocycle and then is deprotonated on the other heterocyclic nitrogen. Explain how **His** might function as a pipeline to transfer protons between sites within an enzyme and its substrate.

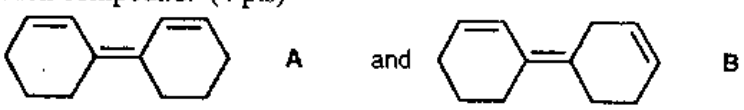
2. Predict the major product of the following reaction. (12 pts)



3. Use the structure of the Diels-Alder adduct to deduce the structure of the product X in the reaction below. (6 pts) Then give a mechanism for the formation of X. (4 pts)

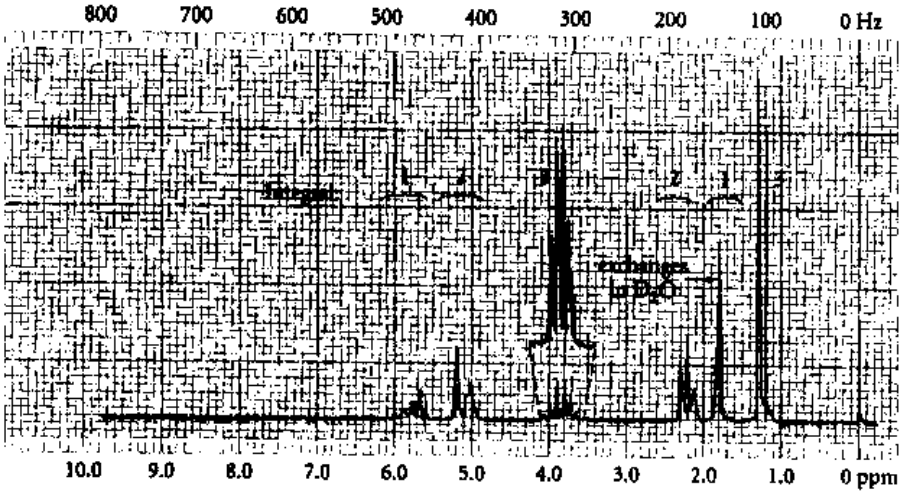


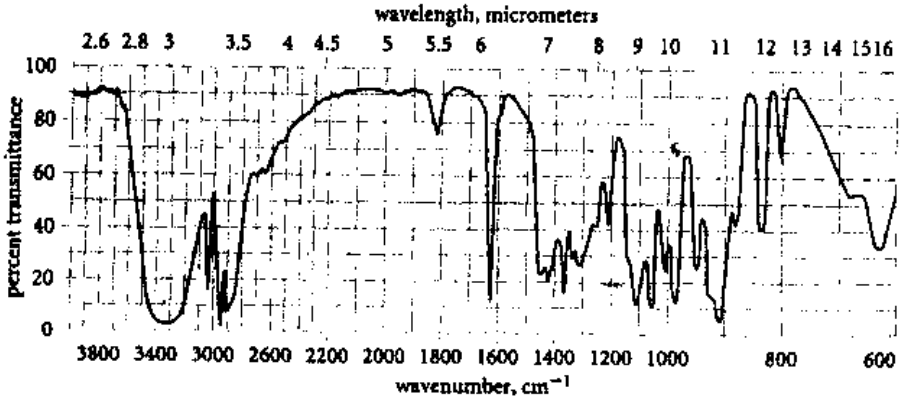
4. Assume you have the following unlabeled compounds. Explain how UV spectroscopy could be used to identify each compound. (4 pts)



5. When Br_2 is added to 1,3-butadiene at **-15 °C**, the product mixture contains 60 percent of product **A** and 40 percent of product **B**. When the same reaction takes place at **60 °C**, the product ratio is 10 percent **A** and 90 percent **B**.
   (a) Propose structures for products **A** and **B**. (4 pts)
   (b) Give a mechanism to account for formation of both **A** and **B**. (4 pts)
   (c) Explain why A predominates at **-15 °C**, yet B predominates at **60 °C**. Draw a potential-energy diagram to show your explanation. (4 pts)
   (d) If you had a solution of pure **A**, and its temperature were raised to 60°C, what would you expect to happen? Give a mechanism to support your prediction. (4 pts)

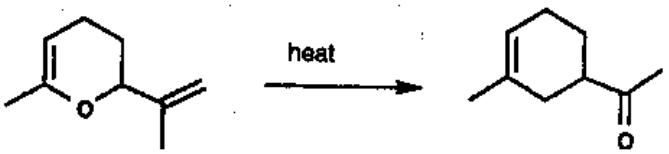
6. (a) Propose a structure for a compound $C_5H_{10}O$ that can be resolved into enantiomers and has the NMR and IR spectra as shown. (10 pts)
(b) Rationalize the base peak at m/z = 45 in the mass spectrum of this compound. (4 pts)



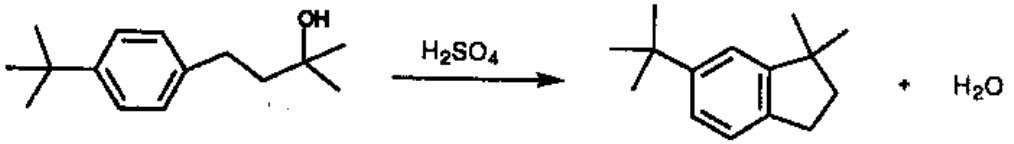


7. Using the curved-arrow formalism, suggest a mechanism for each of the following reactions. (16 pts)

(a)



(b)



8. Outline a synthesis for each of the following compounds from the indicated starting material and any other reagents. (16pts)

(a)

(b)