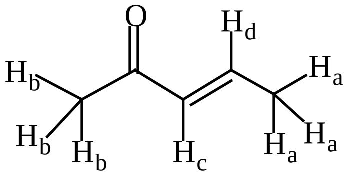
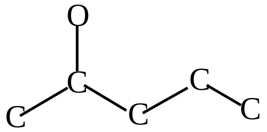
Chemistry 304B, Spring 1999 Problem Set 2 Due: in Lecture, Monday, 2/15/99

1. Consider the molecule drawn here.
The acidity of the protons in this compound are in the order:
$pKa (H_a) < pKa (H_b) << pKa (H_c)$ and $pKa (H_d)$.
This is presumably due to the usual collection of inductive, resonance, and hybridization effects.



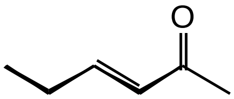
A. Consider the conjugate base obtained by removal of proton $\mathbf{H_a}$.
Draw carefully the three most important resonance structures, showing carefully the location of all non-bonding electron pairs and formal charges in each structure.

B. Draw the most stable resonance structure from part (a) on the figure here. Label each carbon atom with the most likely hybridization for that atom.
Also indicate carefully which atom(s) will have excess negative charge in the actual molecule.
Indicate the partial charge by writing δ- at each site.

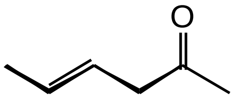


C. *Explain carefully the* ***single most important reason*** *why $pK_a (H_a) < pK_a (H_b)$.*
A complete answer will include drawings representing the conjugate bases.

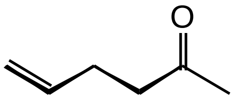
2. Consider the isomers, **F, G, H**. Think about how UV could differentiate them. Respond to the questions below, and give the single most clear-cut feature for each differentiation.



F



G

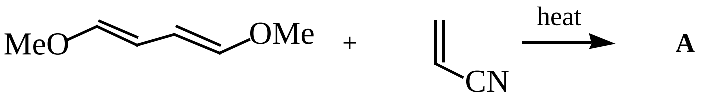


H

A. *Would UV allow you to differentiate* ***F*** *from* ***G****?*
B. *Would UV allow you to differentiate* ***G*** *from* ***H****?*

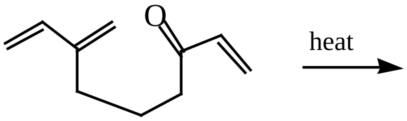
3. Suggest a structure with molecular formula C_5H_nO (n = any integer) which shows $\pi \rightarrow \pi$ absorption at longest wavelength.

4. Write the most likely product from the following reaction. Note that three stereogenic (chiral) centers are created in this process. Show the exact stereorelationship among these new centers, and justify your choice by writing the mechanism carefully.



5. Explain the fact that 2,3-dimethyl-1,3-butadiene and maleic anhydride readily react to give a Diels-Alder adduct, but 2,3-di-t-butyl-1,3-butadiene and maleic anhydride do not react under the same conditions.

6. Write the most likely major product from the following reaction and write a mechanism to justify your choice. Be sure to draw carefully all the details of the structure.



an isomer strong IR absorption at 1715 cm^{-1}

7. In an effort to carry out catalytic hydrogenation of just one double bond in isoprene, an optimistic allowed a solution of isoprene (75 mg) in dichloromethane over a Pd catalyst react under a hydrogen atmosphere until he calculated that one mole-equivalent of hydrogen had been absorbed. When he diluted the solution to exactly 1 L with methanol and recorded the UV spectrum, he found significant absorption with a maximum at 222.5 nm. The magnitude of the absorption with a 1-cm cell was 0.356. Given that the extinction coefficient of pure isoprene is 10,750 at this wavelength, what can he conclude (quantitatively) about his plan to convert the isoprene completely to one of the isopentene?

8. Give the most likely major product expected when *trans*-1,3-hexadiene reacts with each of the following reagents:

- a. bromine
- b. HBr
- c. H_2O, H^+

If the decision as to which is the major product is ambiguous, please discuss, with a mechanism.