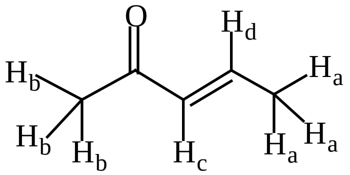
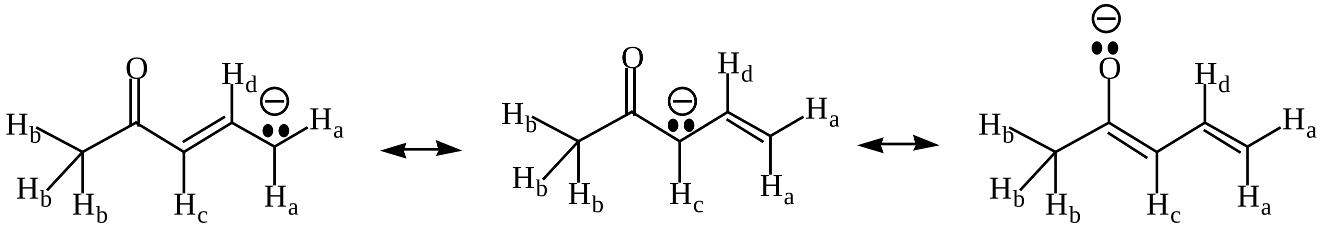
Chemistry 304B, Spring 1999 Problem Set 2 Due: in Lecture, Monday, 2/15/99

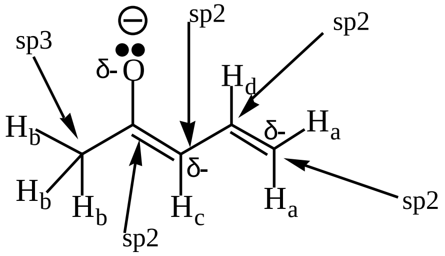
1. Consider the molecule drawn here.
The acidity of the protons in this compound are in the order:
pKa (H_a) < pKa (H_b) << pKa (H_c) and pKa (H_d).
This is presumably due to the usual collection of inductive, resonance, and hybridization effects.



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.
Ans:

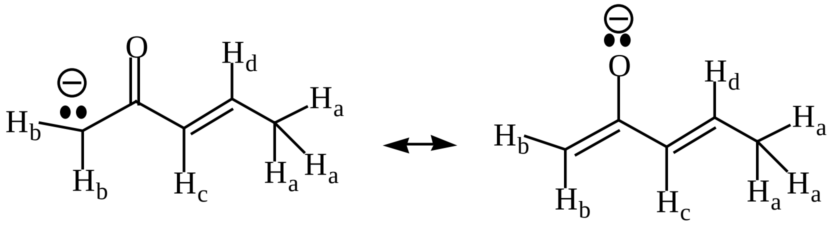


B. Draw the most stable resonance structure from part (a) on the figure here. Label each carbon atom with the most likely hybridization for that atom.
Also indicate carefully which atom(s) will have excess negative charge in the actual molecule.
Indicate the partial charge by writing δ- at each site.

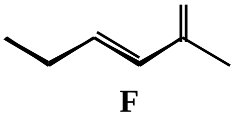


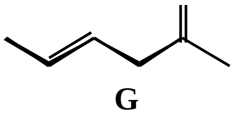
C. *Explain carefully the* ***single most important reason*** *why $pK_a(H_a) < pK_a(H_b)$.*
A complete answer will include drawings representing the conjugate bases.

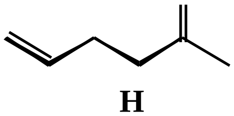
Ans: There are only two "good" resonance structures for the anion from removal of proton H_b, and therefore the other site of deprotonation is preferred. More resonance structures, more stable anion, more acidic conjugate acid.



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

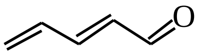

G


H

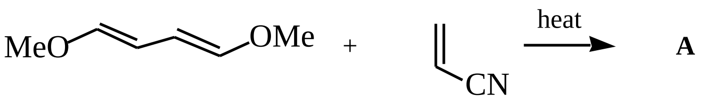
A. *Would UV allow you to differentiate* ***F*** *from* ***G****?* Ans: Yes. **F** would absorb at longer wavelength for both π−π* and n-π*.

B. *Would UV allow you to differentiate* ***G*** *from* ***H****?* Ans: NO. Both has the same extent of pi conjugation (none).

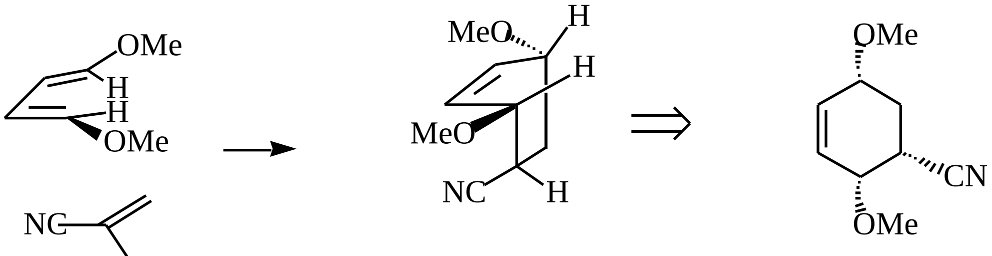
3. Suggest a structure with molecular formula C_5H_nO (n = any integer) which shows $\pi \rightarrow \pi$ absorption at longest wavelength.

Ans: Maximum pi bonds in a line:  is as good as any.

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.



Ans:



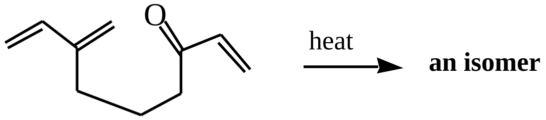
A

See Prob 12.28 in Jones, p. 542.

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.

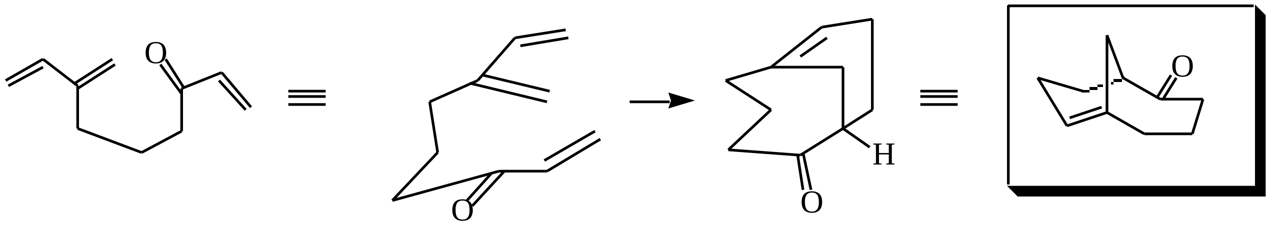
Ans: It is prohibitive for 2,3-di-t-butyl-1,3-butadiene to assume the required cisoid geometry; the t-butyl groups bump into one another and prevent a planar cisoid structure.

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.



strong IR absorption at 1715 cm^{-1}

Ans: IR suggests a "normal", noon-conjugated ketone group.



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 isopentenes?

75 mg of isoprene, MW 68.12, equals 1.10 mmol. This amount of H_2 was allowed to react.
With a 1-cm path length, and A=0.356, ε = 10,750, one can calculate the amount of isoprene left after the attempted selective hydrogenation, assuming that no other dienes are present and that any mono-enes or simple hydrocarbons will not show up in the UV at 222.5 nm.
$c = A/\varepsilon b = 0.356/10{,}750 \times 1 = 0.331\ \text{mM} = 0.33$ mmol of isoprene left

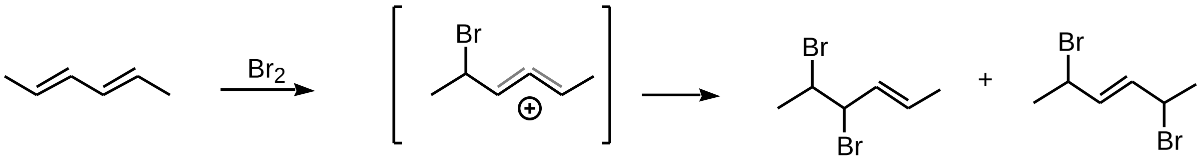
Therefore, 0.331/1.10 = 30% of the isoprene left.

Conclusion: Of the 1.10 mmol of H_2, 0.77 mmol converted 0.77 mmol of the isoprene to an isopentene, and, simultaneously, the isopentene was being further hydrogenated to the hydrocarbon, isopentane, using the remaining 0.33 mmol of H_2. The mixture should then consist of:

0.33 mmol of isoprene
0.43 mmol of an isopentene
0.33 mmol of isopentane.

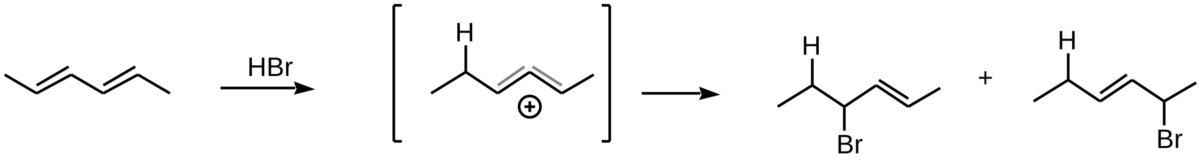
8. Give the most likely major product expected when *trans*-1,3-hexadiene reacts with each of the following reagents:

a. bromine



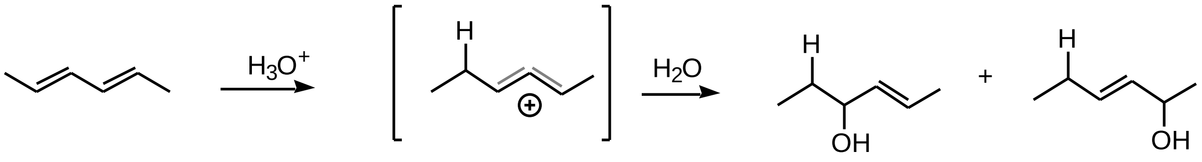
Ambiguous: kinetic or thermodynamic control? Both are possibly major.

b. HBr



Ambiguous: kinetic or thermodynamic control? Both are possibly major.

c. H_2O, H^+



Ambiguous: Probably kinetic control, but products (and therefore the transition states) are very similar in stabilization. Probably 50:50