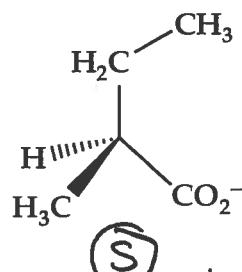
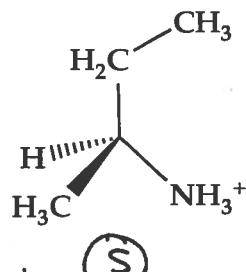


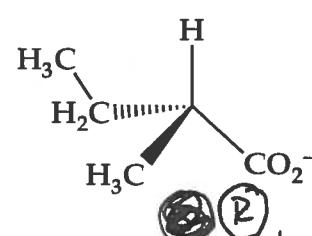
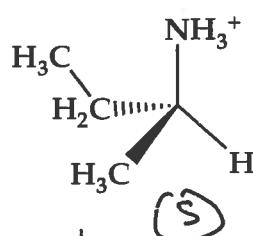
Chemistry 3311-100  
Organic Chemistry / Dr. Barney Ellison  
Final Exam: Tuesday 8, 2012 @ 4:30 pm → 7:00 pm (RAMY C250)

Name: Kreg (please print)

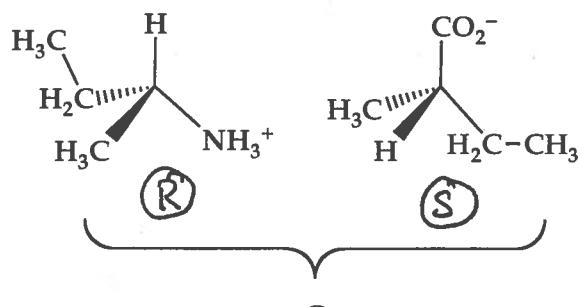
1. (10 pts) Which of the salts below should have identical solubilities in methanol?  
Why? (hint: work out the stereochemistry of each salt)



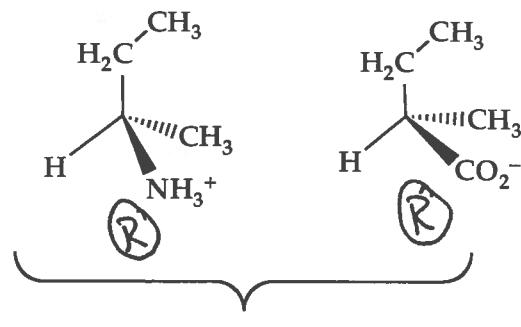
A



B



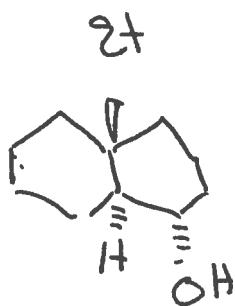
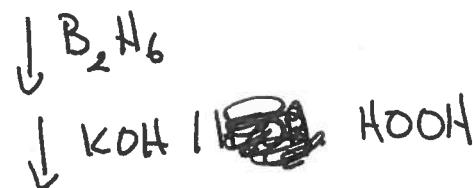
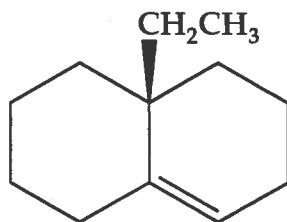
C



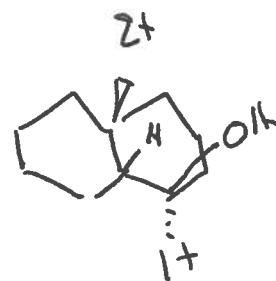
D

Salt A is mirror image of D  $\Rightarrow$  A & D are enantiomers, have same solubility  
Salt B is mirror image of C  $\Rightarrow$  B & C have same solubility. They are enantiomers.  
But solubility of (A, D) will be different than that of (B, C)

2. (10 pts) What two diastereomeric products could be formed in the hydroboration-oxidation of this alkene? Which compound would be the major product?



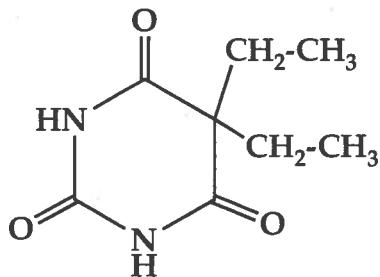
or



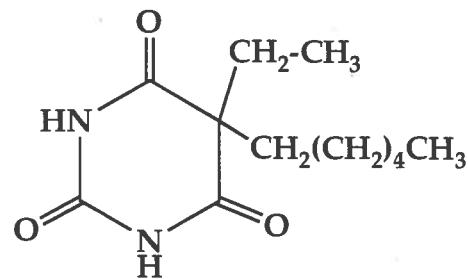
trans  
in favored

cis

3. (10 pts) The effectiveness of barbiturates is directly related to their solubility in lipid bilayers of membranes. Which of the following two barbiturates would be the most potent sedative? Why?



barbital

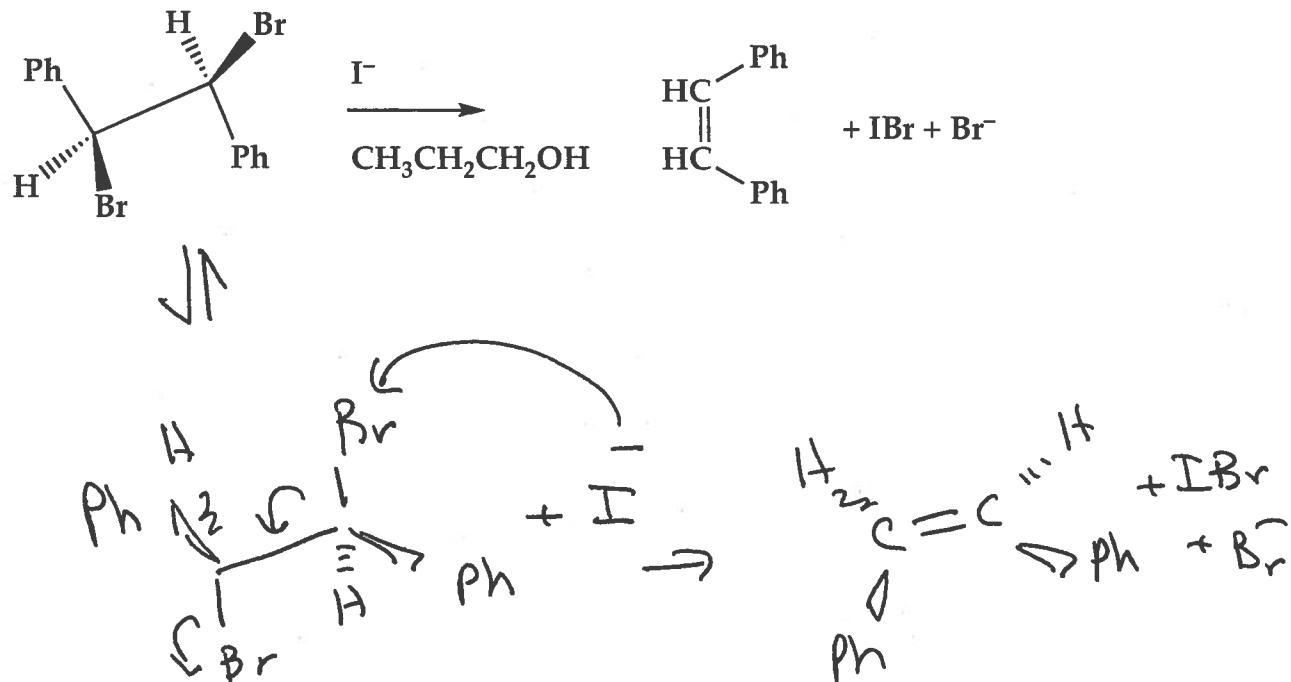


hexethal

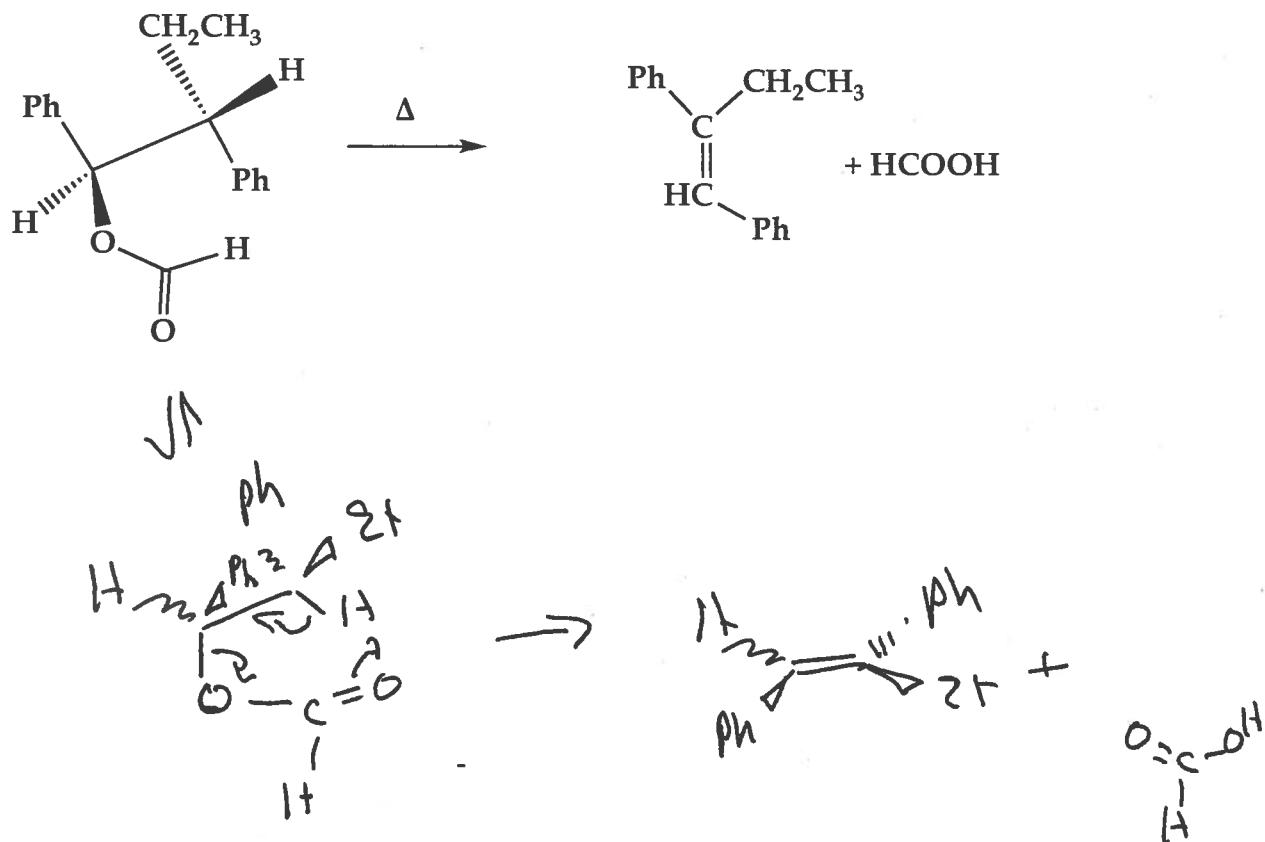
Hexethal is more soluble in lipid bilayers because of the longer alkyl tail.

4. (10 pts) Consider the elimination reactions. a) shows 2<sup>nd</sup> kinetics but b) is 1<sup>st</sup> order. Show a mechanism for each.

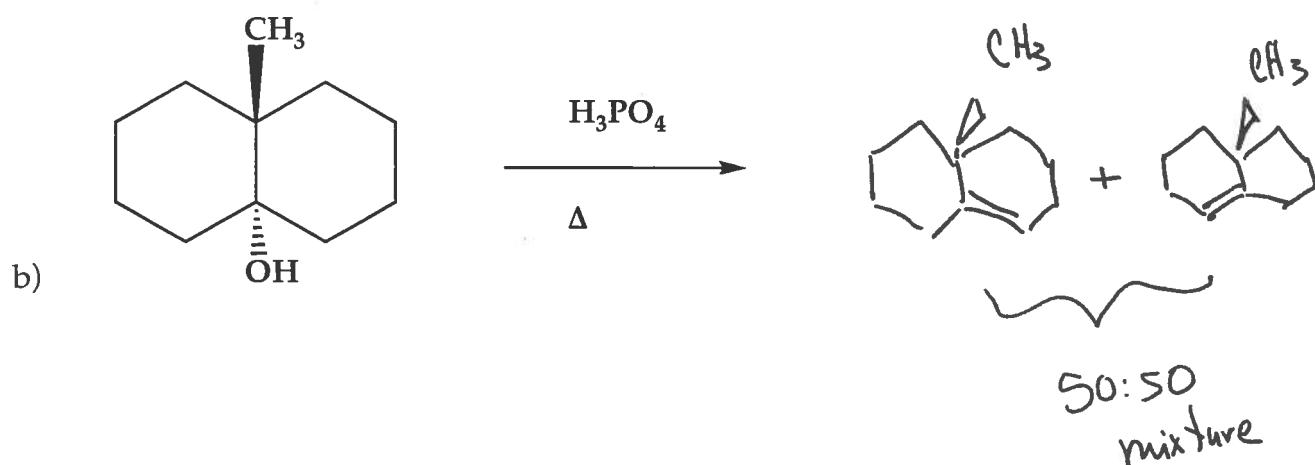
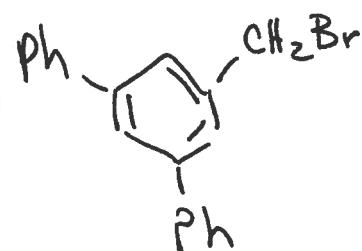
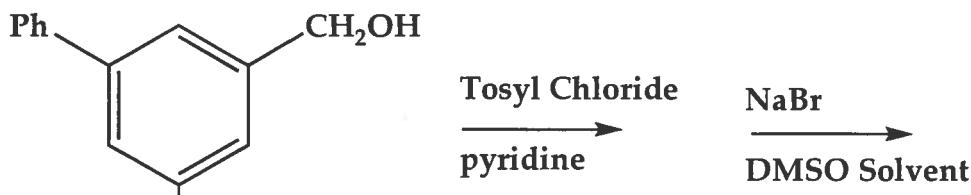
a)



b)



5. (10 pts) Complete the following reactions.



6. (15 pts) Consider the 3 compounds below. Show a mechanism that accounts for the following observations. a) In 80% aqueous ethanol, compound A reacts to form compound B. The *trans* isomer of B is the only stereoisomer formed; none of the *cis* isomer is observed. b) Optically active A gives completely racemic B. c) The reaction of A is  $10^5$  times faster than the analogous reaction of C.

*trans* isomer

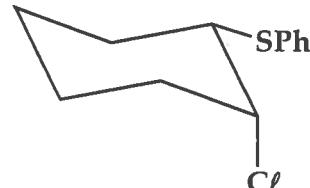


A

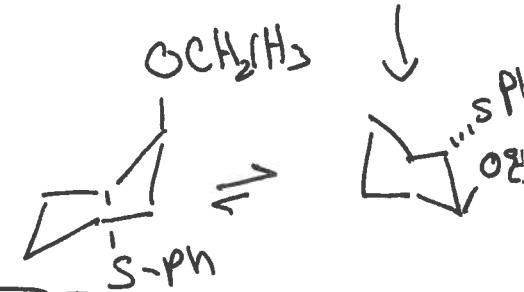
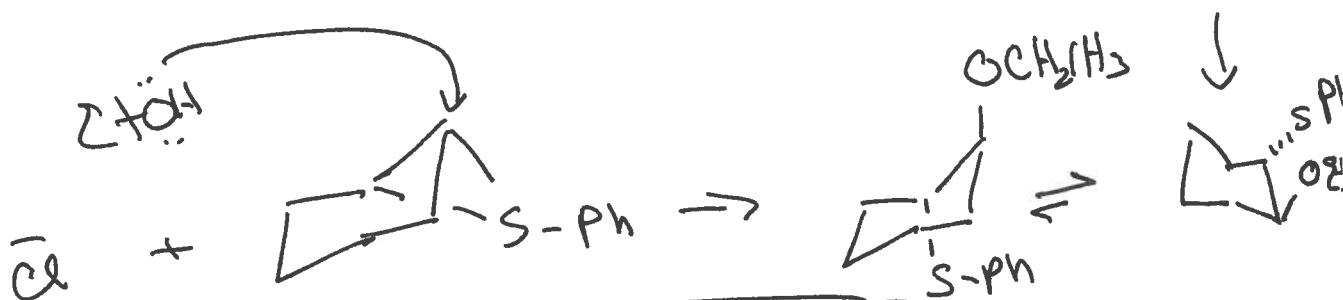
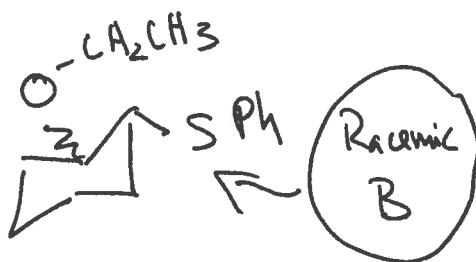
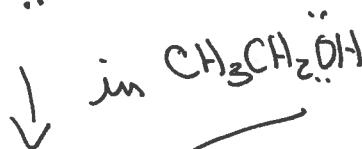
*cis* isomer



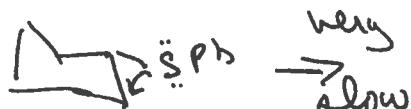
B



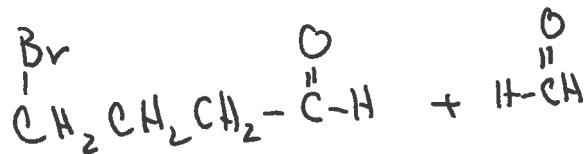
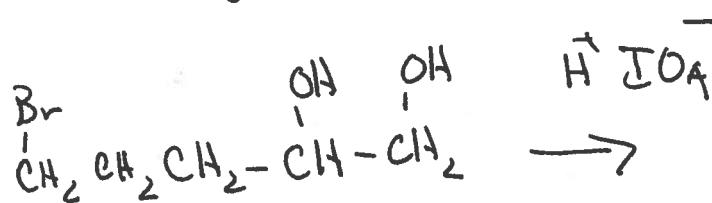
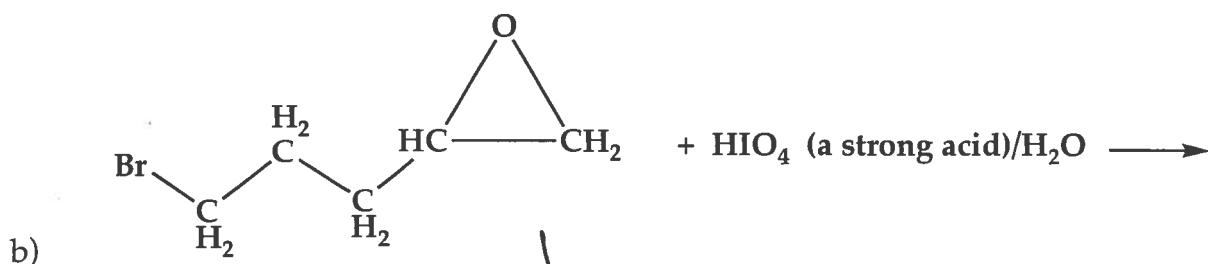
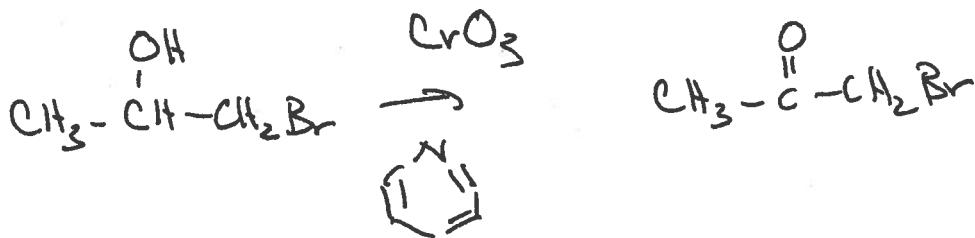
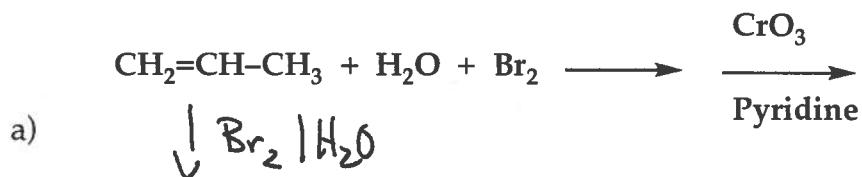
C

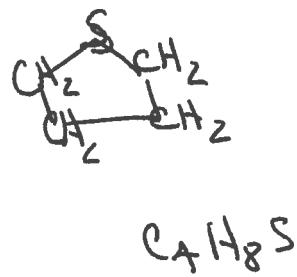
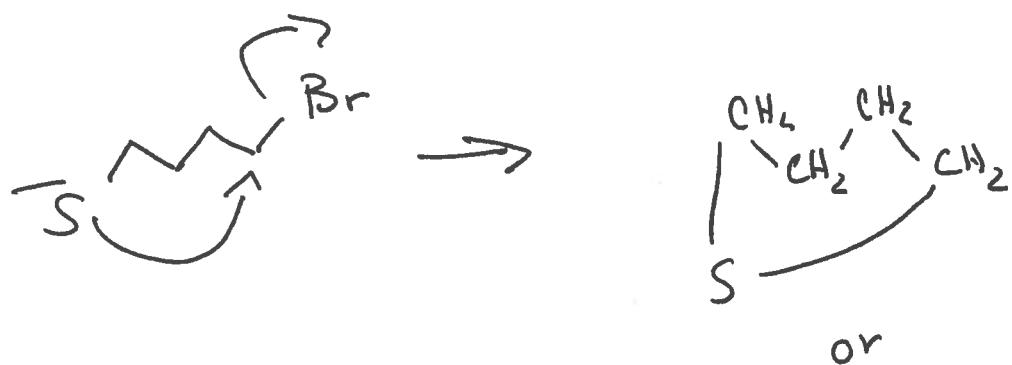
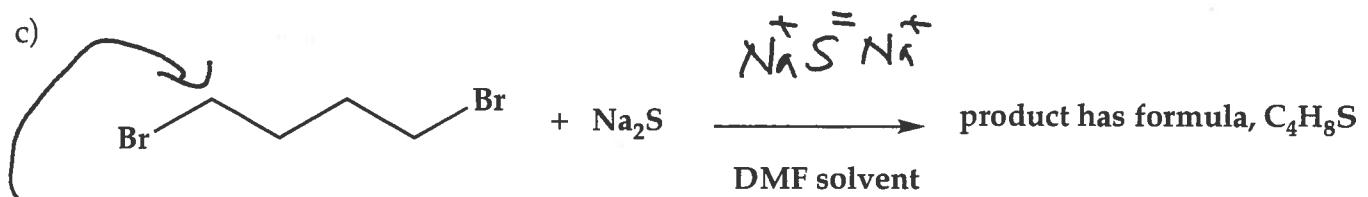


The *cis* isomer cannot form transition state ~~for~~ *trans* & *anti* for internal  $\text{SN}_2$



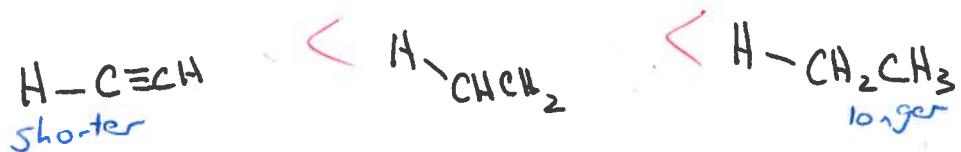
7. (15 pts) Complete the following reactions.





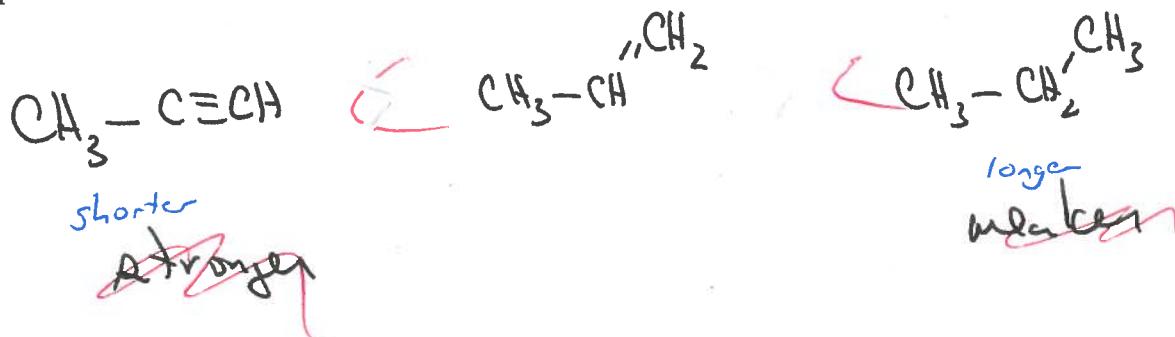
8. (10 pts) On the basis of the hybrid orbitals, arrange the bonds in order of increasing length.

- a) C-H bond of ethylene, C-H bond of ethane, C-H bond of acetylene

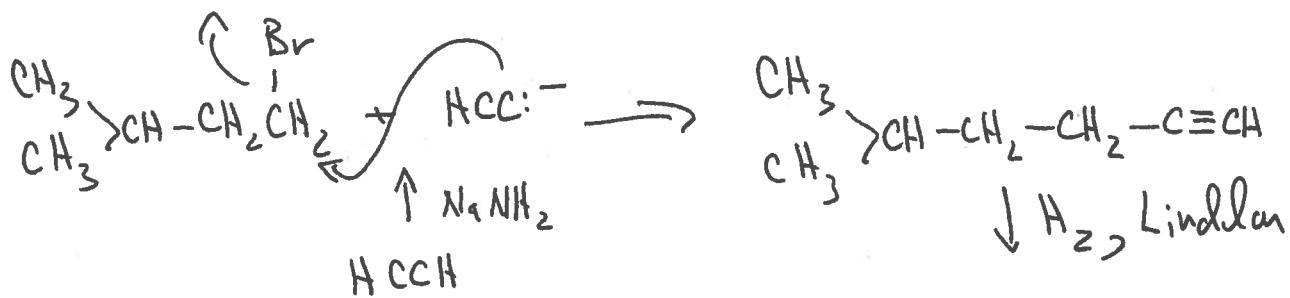
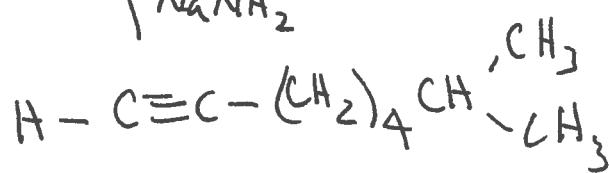
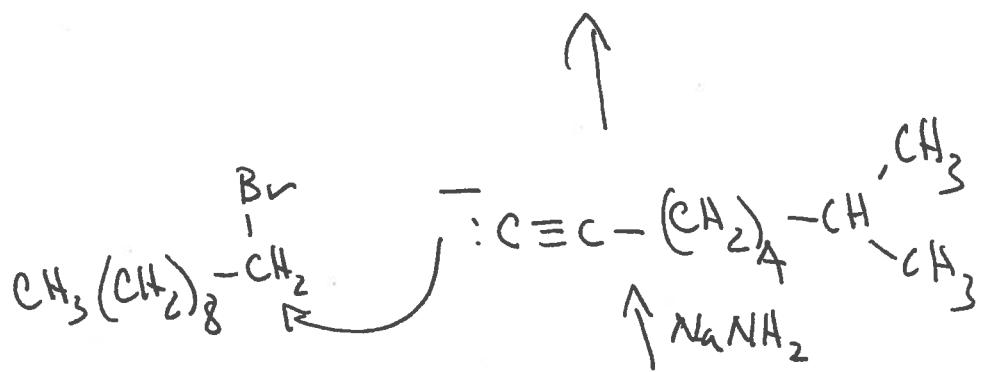
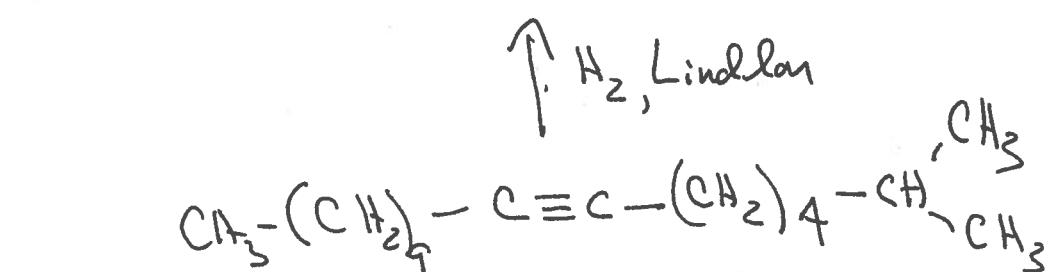
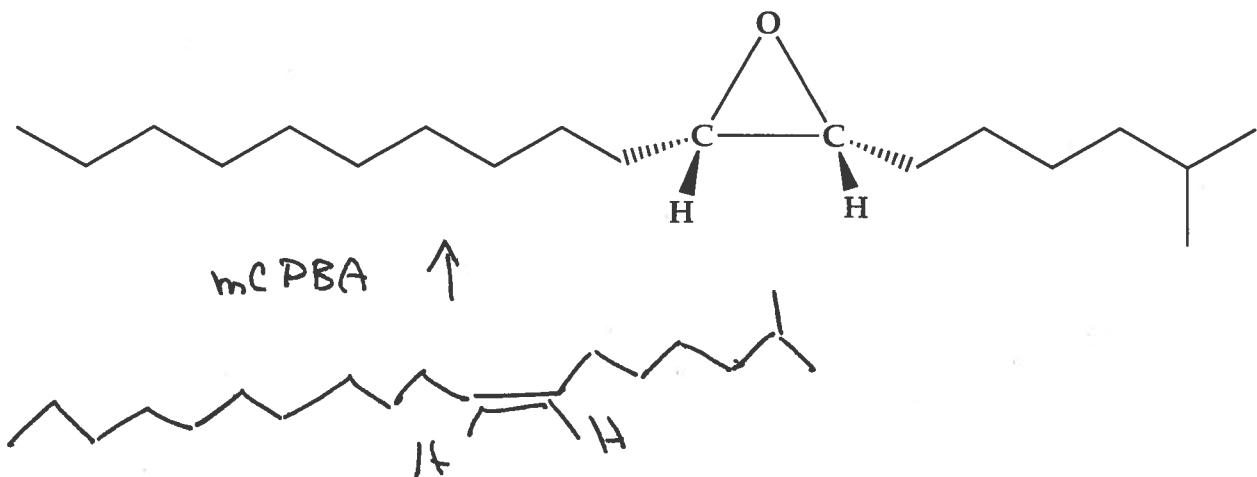


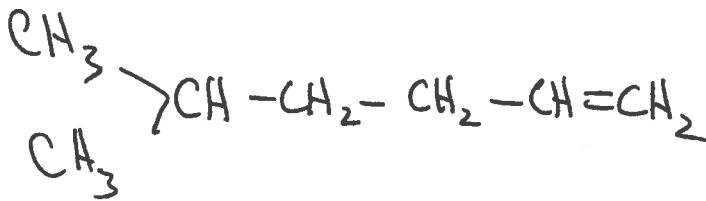
more S character in C-H bond

- b) C-C single bond of propane, C-C single bond of propyne, C-C single bond of propene

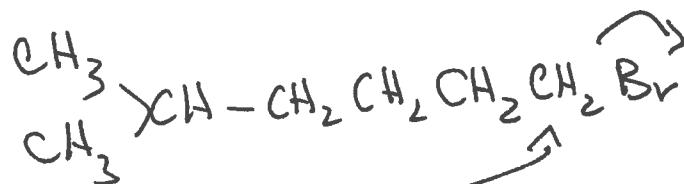


9. (10 pts) Outline a preparation of the racemic epoxide from acetylene and any other compound with 5 carbons or less.

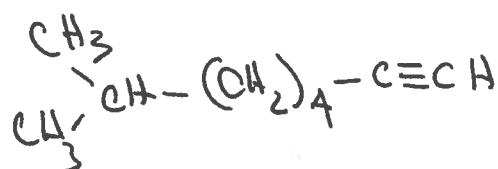




$\downarrow \text{HBr, peroxides}$

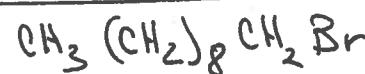


$\leftarrow \text{HCCN}$   
 $\text{NaNH}_2$

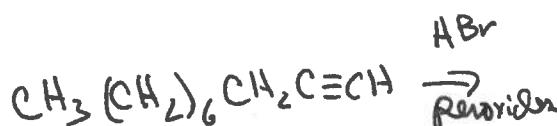
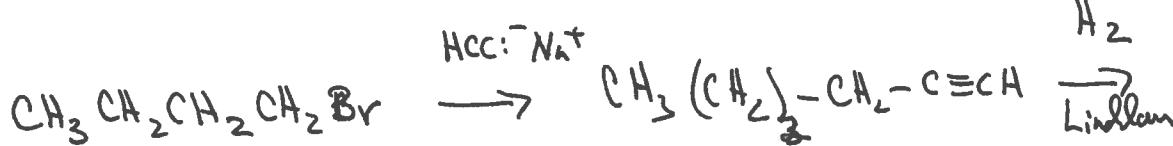


Required alkyne on p. 10

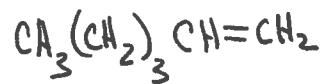
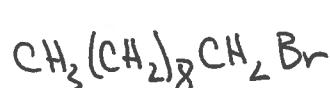
We still need



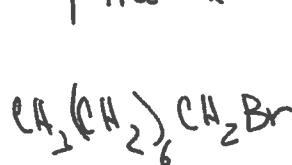
this is ugly!



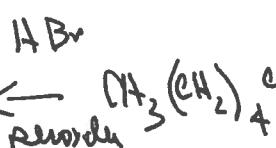
$\uparrow \text{HCCN}^- \text{ Na}^+$



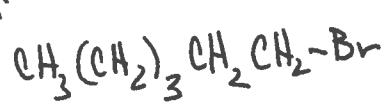
$\downarrow \text{HBr, peroxide}$



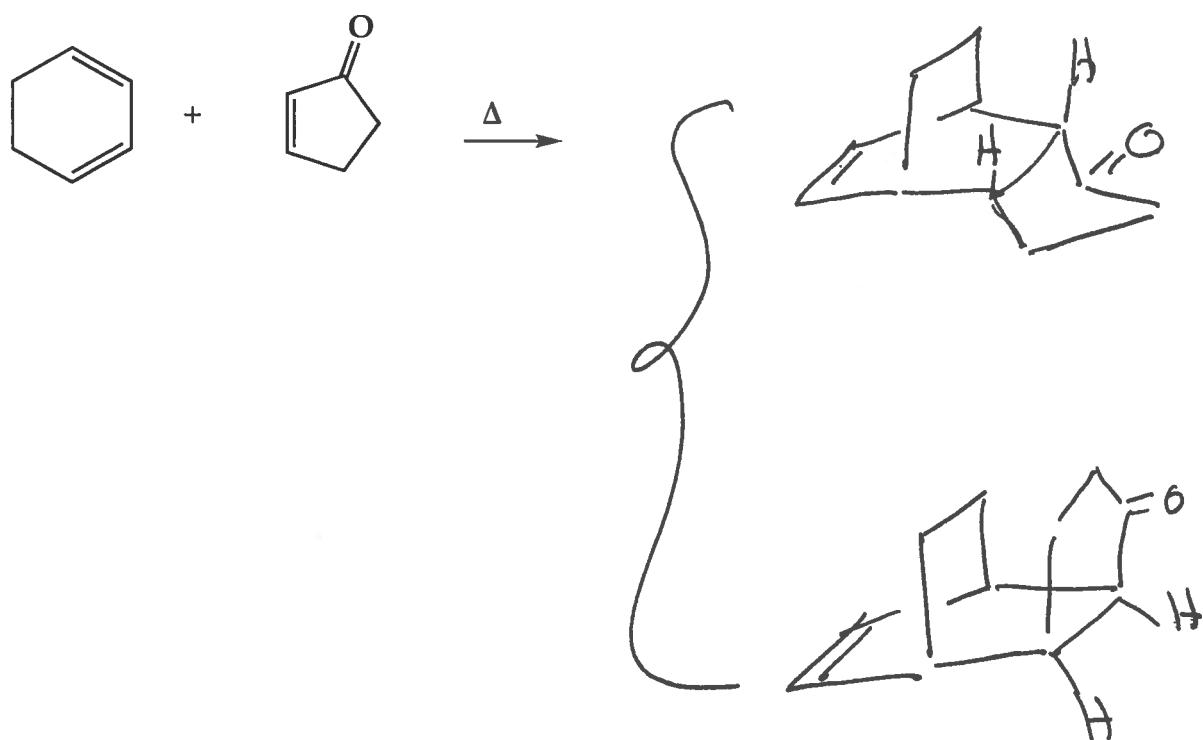
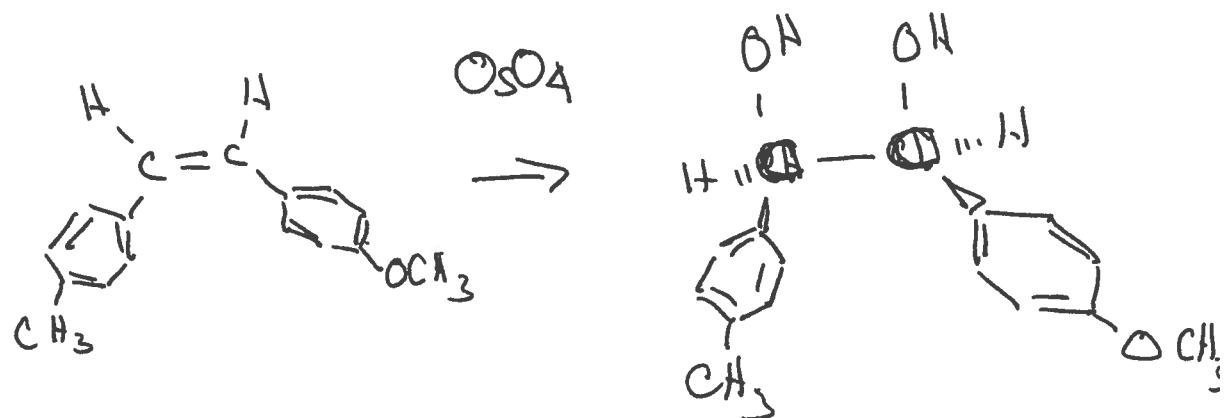
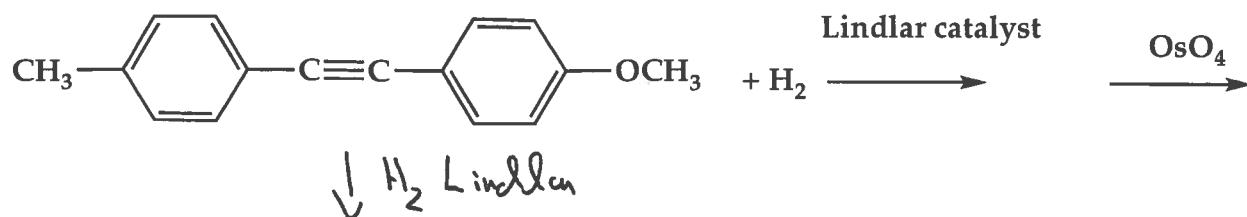
$\xleftarrow[\text{peroxide}]{\text{HBr}}$

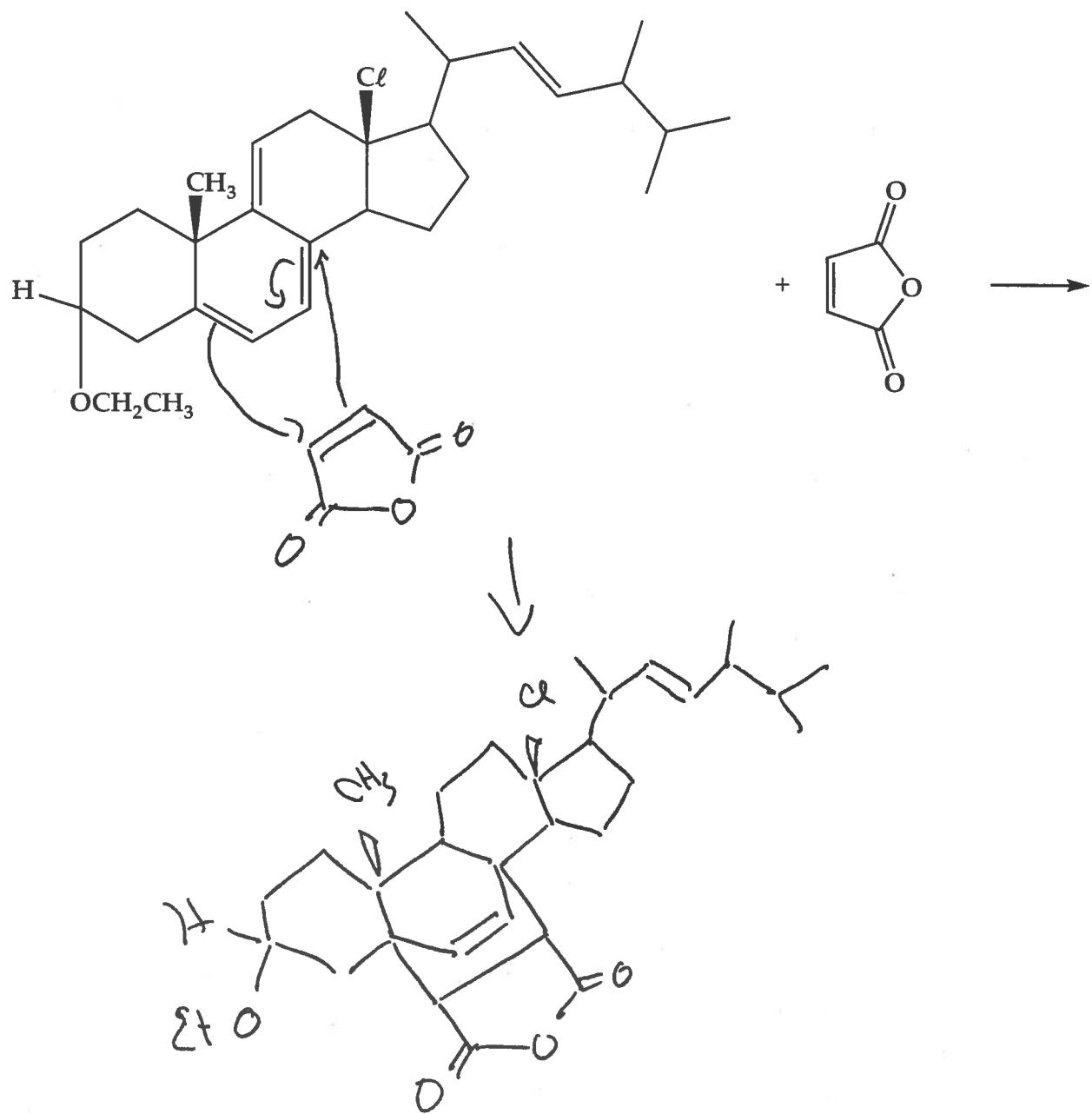


$\xleftarrow{\text{HCCN}^- \text{ Na}^+}$

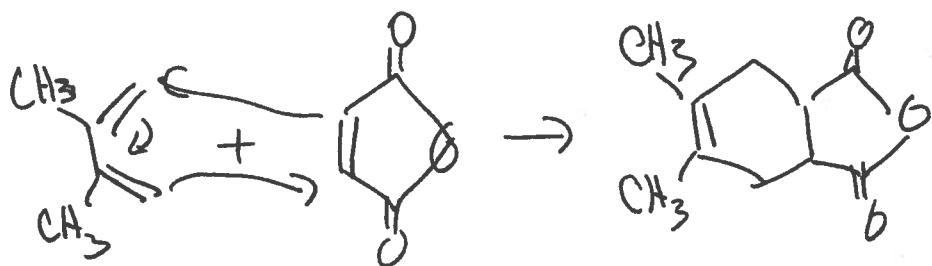
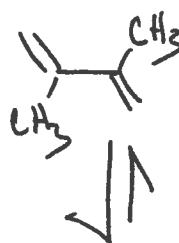
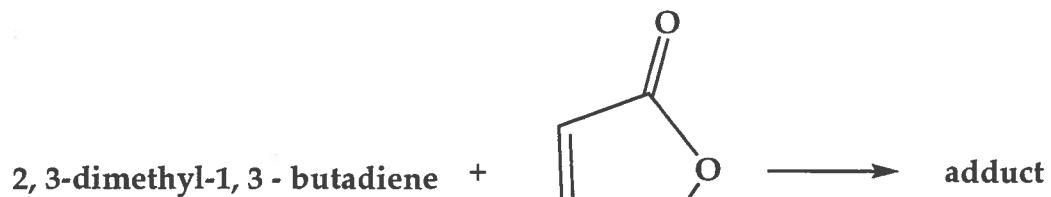


10. (15 pts) Complete the following reactions.

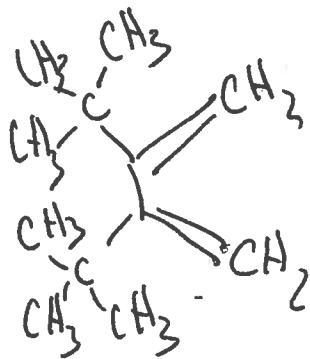
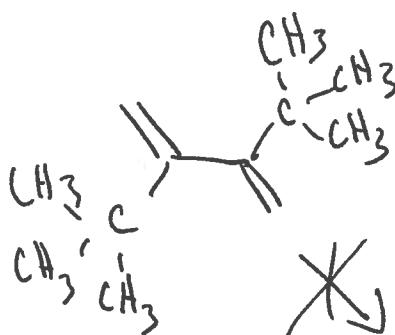
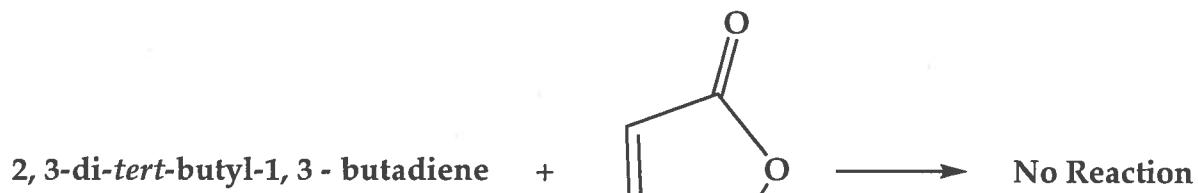




12. (10 pts) What is the product of the reaction?



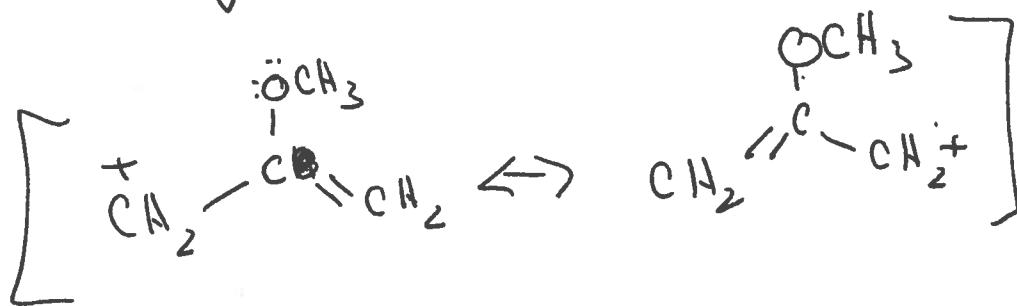
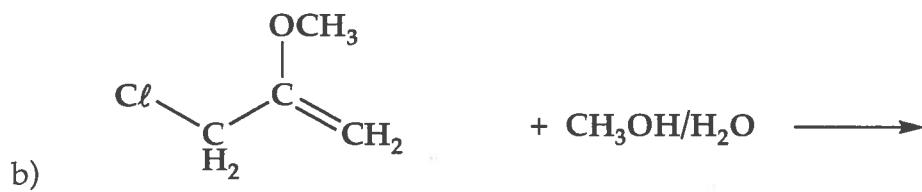
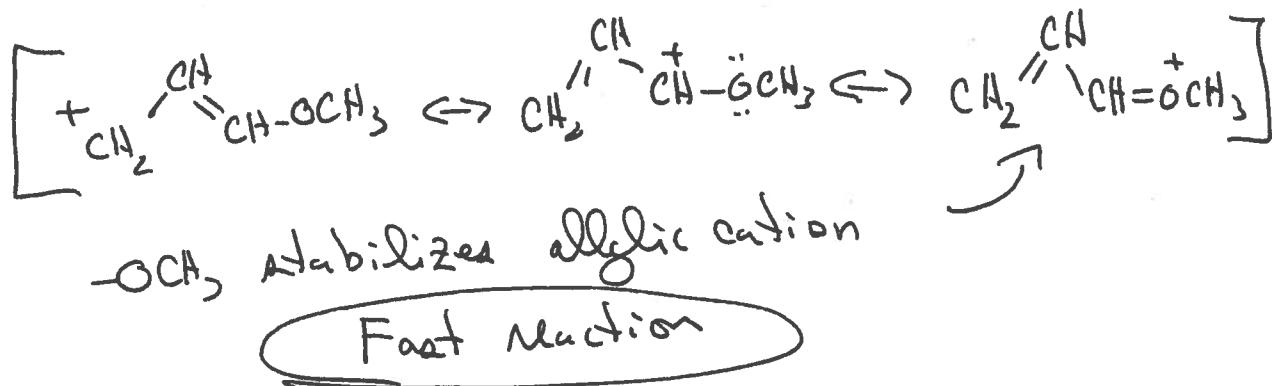
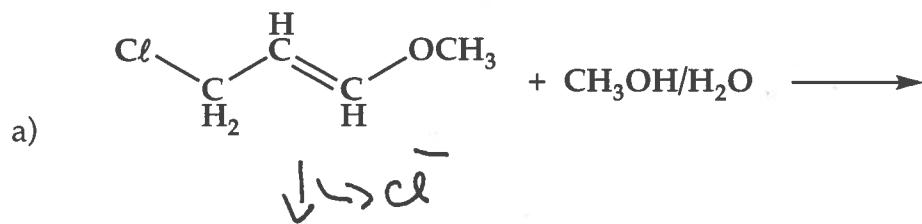
Why does this reaction fail?



no Diels  
alder

can't for cis  
diene

12. (10 pts) Which of the two alkyl halides would react most rapidly in a solvolysis reaction by the S<sub>N</sub>1 mechanism? Why?



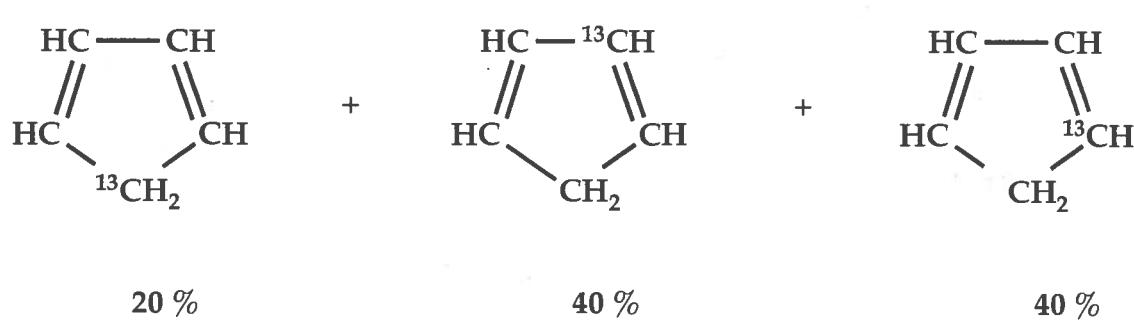
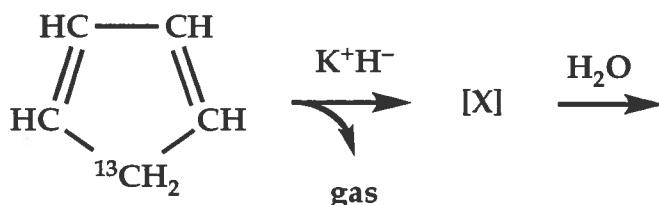
$-\text{OCH}_3$  cannot donate electrons to allylic cation. Inductive effect will destabilize a small amount.

Slow

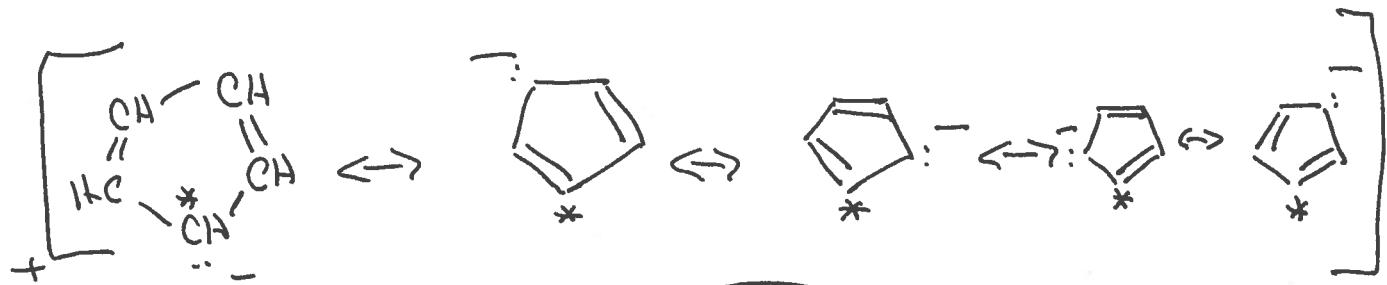
13. (15 pts) When 1,3-cyclopentadiene containing a  $^{13}\text{C}$  label only at C-5 is treated with potassium hydride,  $\text{K}^+\text{H}^-$ , a species X is formed and a gas is evolved. When the reaction is quenched with  $\text{H}_2\text{O}$ , a mixture of  $^{13}\text{C}$ -labeled 1,3 cyclopentadienes is formed.

a) Identify X and the evolved gas

b) Explain the origin and percentages of the three labeled cyclopentadienes



$\text{H}^-$



$\text{A}_2$  gas

$X$  is resonance hybrid of 5 structures

$\text{H}_2\text{O}$   
all sites protonate equally

