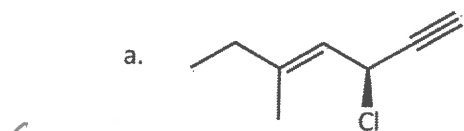
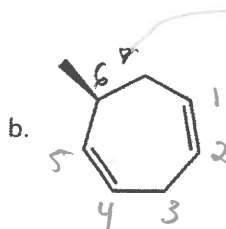


1. Name the following compounds. Don't forget about stereochemistry. (10 points)



(3S,4E)-  
 3-chloro-5-methylhept-4-en-1-yne

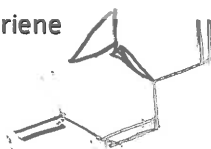


(S)-  
 6-methylcyclohept-1,4-diene

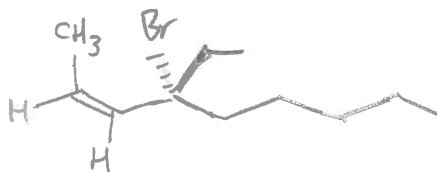
(don't need E/Z for alkenes  
 in ring  $\leq 7$  carbons)

2. Draw the structure of the following compounds. (10 points)

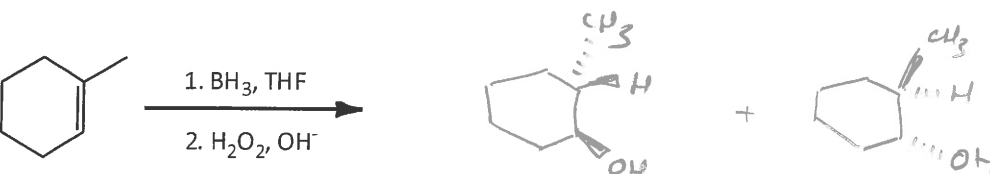
- a. (3Z,5R)-5-cyclopropylhepta-1,3,6-triene



- b. (2Z,4R)-4-bromo-4-ethylnon-2-ene



3. Consider the reaction of the alkene shown below. (15 points)



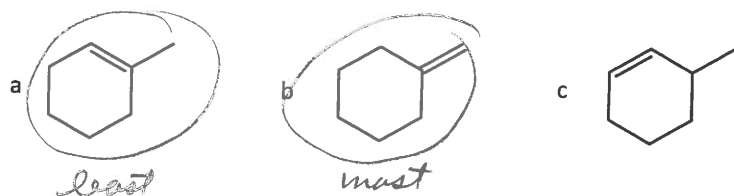
b. syn addition - H & OH add to same side of alkene

c. the addition is anti-Markovnikov. The more electronegative element adds to less substituted carbon, which of opposite to mark. rule.

4. Does the reaction in Question 3 (above) obey Markovnikov's rule? Explain. (5 points)

X

5. Which alkene shown below has the *most exothermic* heat (enthalpy) of combustion ( $\Delta H_{\text{comb}}$ ) and which has the *least exothermic* value? Explain your choice. (Note that the heat of combustion for all three alkenes is negative.) (20 points)



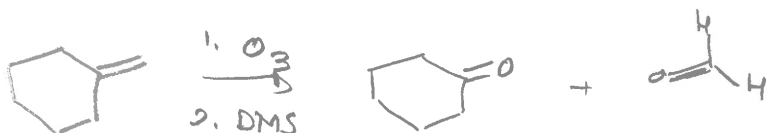
Although b, and c, are both disubstituted, compound c, has more branching which is also found to be more stable

\* tri-substituted alkene is most stable in the series

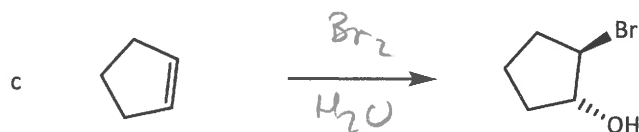
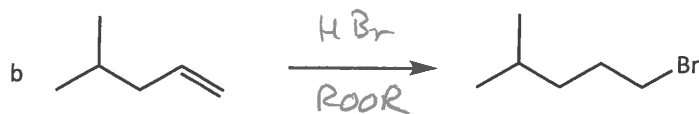
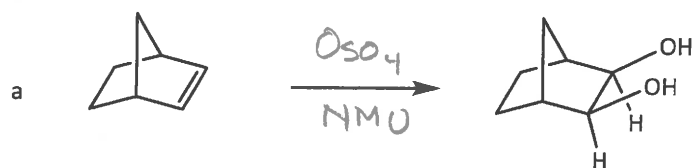
6. Which alkene in the above set (Question 5) would have the largest value for heat (enthalpy) of hydrogenation ( $\Delta H_{\text{hydrog}}$ )? Explain. (a, b, or c when treated with  $\text{H}_2/\text{Pt}$  give the same product) (10 points)

b, show release the most heat since it is the least stable.  
 \* during hydrogenation

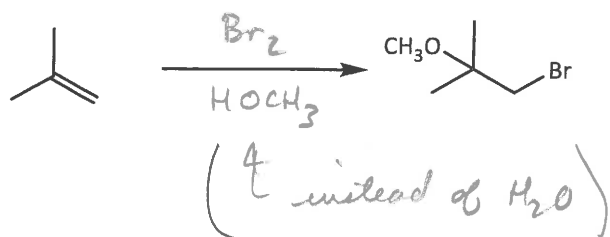
7. Show the product (or products) from the ozonolysis (1.  $\text{O}_3$ , then 2. DMS) of compound b. in Question 5. (5 points)



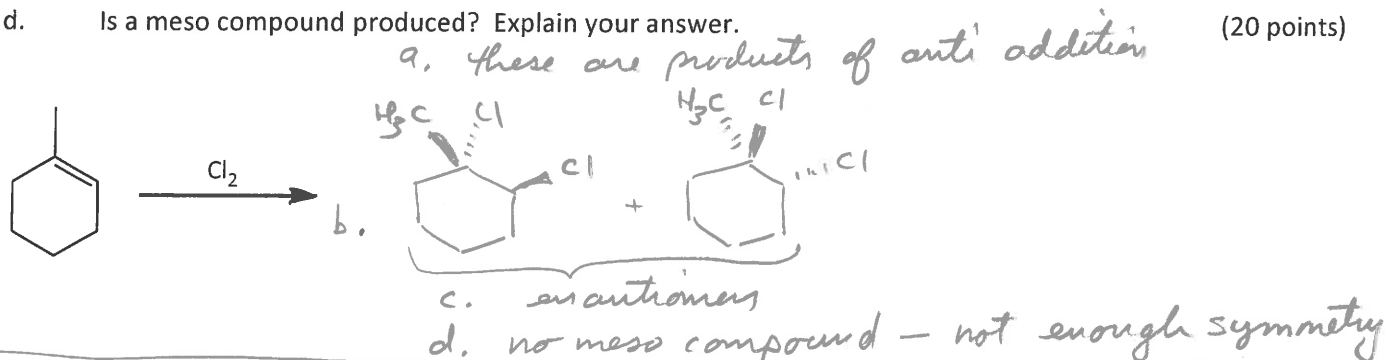
8. Fill in the *reagents* required to accomplish the following reactions. (15 points)



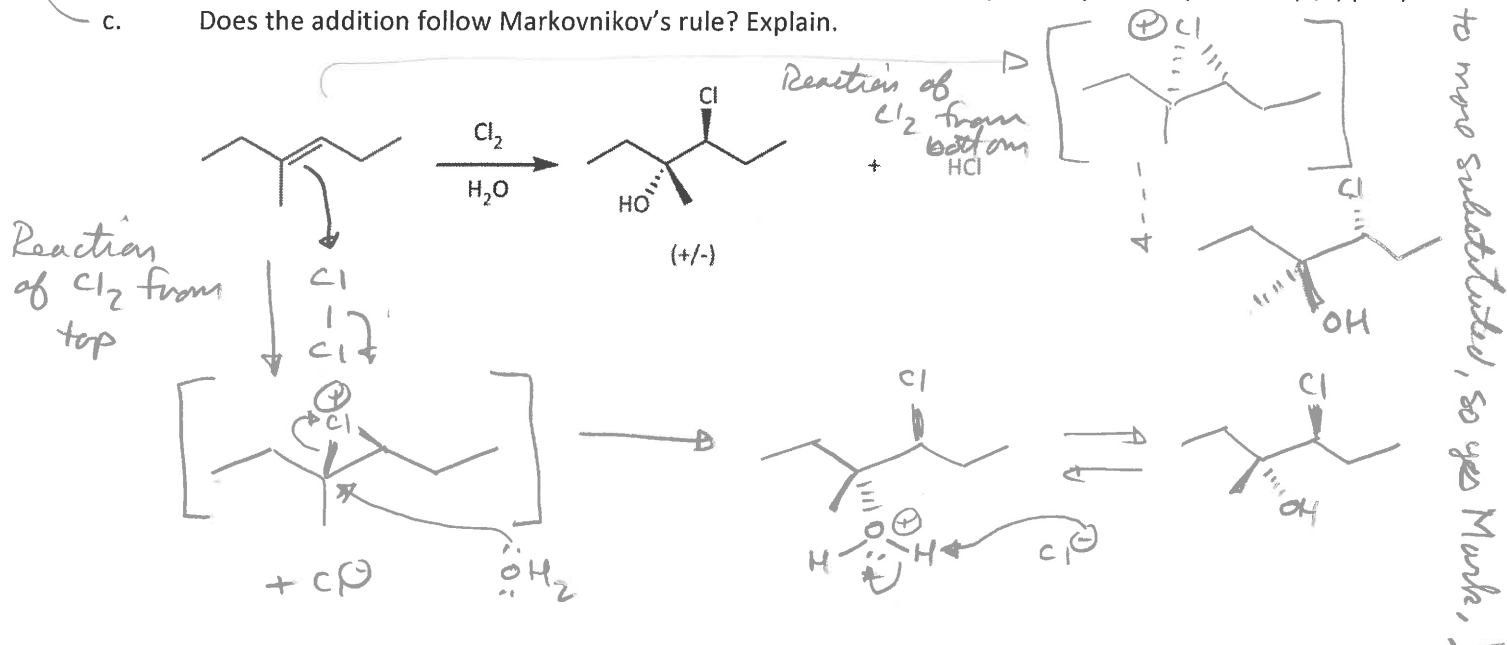
9. Considering your answer from Question 8c, suggest reagents to accomplish the following transformation. (5 points)



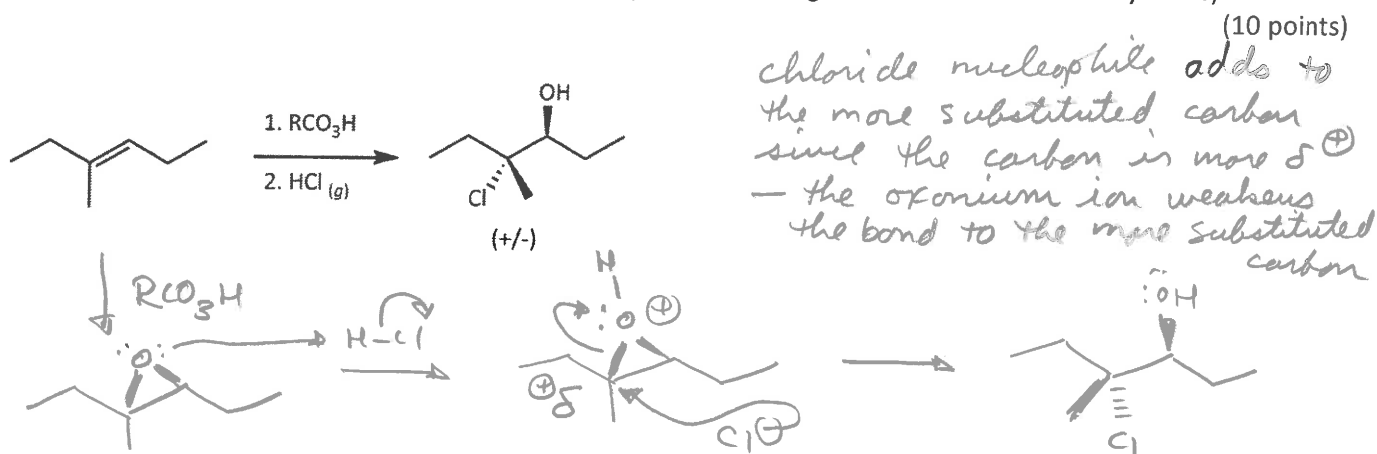
10. Consider the reaction of the alkene below with chlorine (Cl<sub>2</sub>), which gives a vicinal dichloride.
- Is the addition *syn* or *anti*?
  - Show the resulting stereochemistry of the product using the correct line (—), dash (---), and wedge (▲) notation.
  - If any other stereoisomers are produced, show them and indicate any isomer relationships (diastereomers, enantiomers).
  - Is a meso compound produced? Explain your answer. (20 points)



11. Consider the reaction below. (30 points)
- Show the complete mechanism for the formation of the product, including the HCl.
  - Be sure to account for the formation of the shown stereochemistry of the product (and the (+/-) part).
  - Does the addition follow Markovnikov's rule? Explain.



12. Consider the reaction shown below and note how it gives the opposite result as the reaction in Question 11. Show a reasonable and complete mechanism for the formation of the product of this reaction. (Note that this reaction is a two-step reaction. Also, note that in step 2, the HCl is gaseous and therefore anhydrous)



13. Calculate the degrees of unsaturation for the molecular formula  $C_{12}H_{18}$  and suggest a reasonable structure for a molecule that has only one double bond, but has this formula. (Note that there are many possibilities)

(10 points)

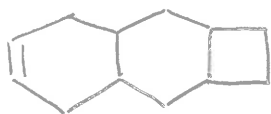
EXTRA CREDIT Name the compound (the more complicated the structure the more EC points you get)

(10 EC points)



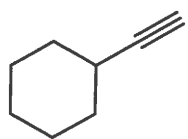
$8H = 4H_2 = 4^\circ$  of unsaturation

difficult



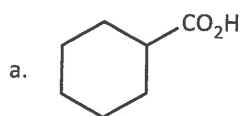
14. Show how to convert the alkyne below to each of the following compounds. List the reagents and conditions below each compound (some of these may require more than one step!). You don't need to show any intermediates (if there are any).

(25 points)

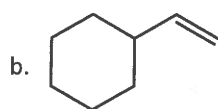


1.  $NaNH_2$   
 2.  $CH_3CH_2Br$   
 3.  $H_2, Pd/C$

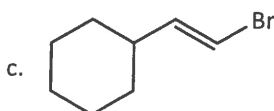
$H_2SO_4$   
 $HgSO_4$   
 $H_2O$



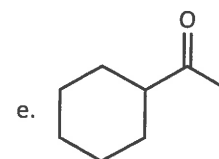
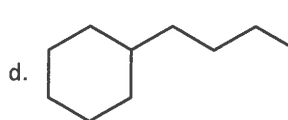
1.  $O_3$   
 2.  $H_2O$



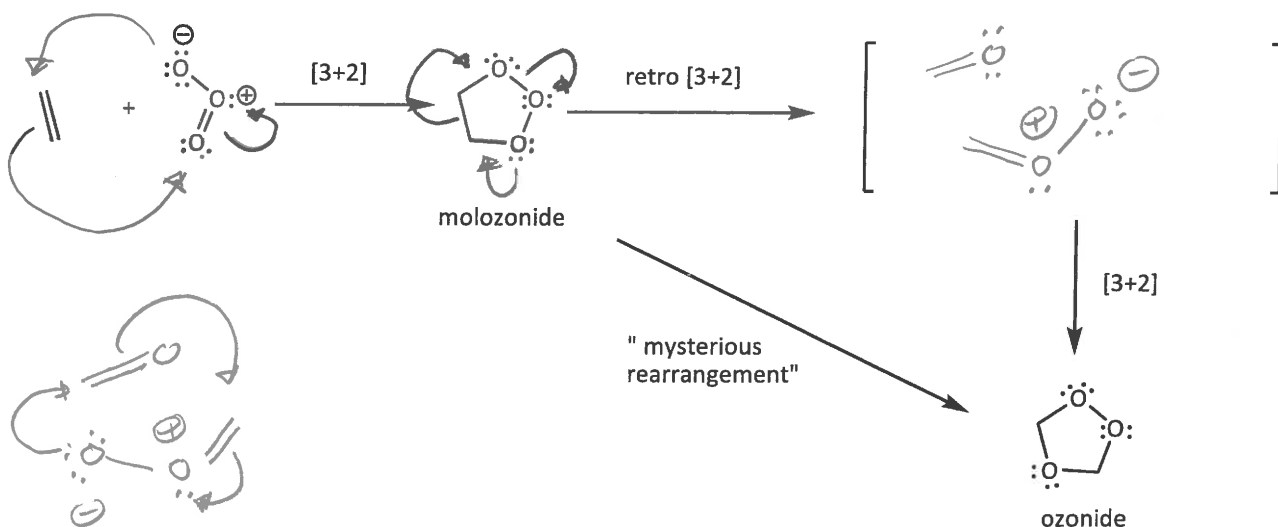
$H_2$   
 Lindlar's



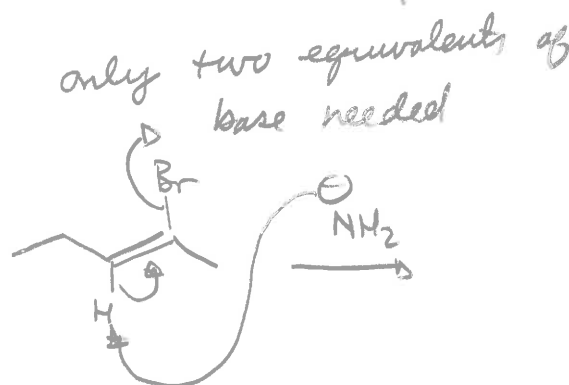
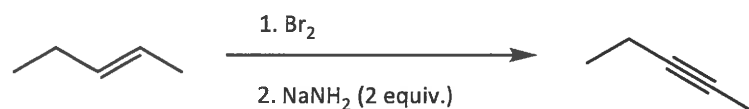
$H-Br$   
 $ROOR$



15. *Challenge Problem.* The first intermediate formed in the ozonolysis of ethylene is called a *molozonide*, which is exceedingly unstable and undergoes a "mysterious rearrangement" to give the intermediate called an *ozonide*. The first step of this reaction is officially called a [3+2] cycloaddition. The mysterious rearrangement step actually involves two steps: a retro (backwards) [3+2] cycloaddition followed by another [3+2] cycloaddition.
- Show the mechanism of the formation of the *molozonide* by using *electron-pushing*.
  - Suggest structures for the two (2) intermediates formed by the "retro" process
  - Show (with *electron-pushing*) how they can recombine to give the *ozonide*. (15 points)



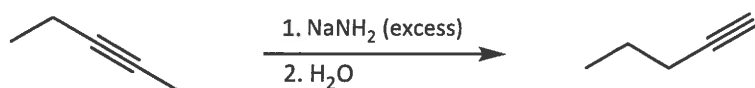
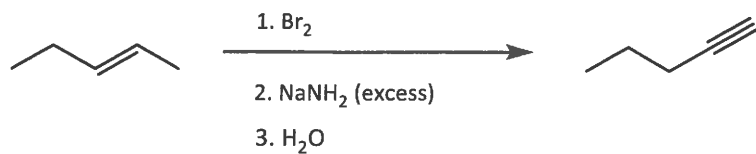
16. The two steps below are a standard method to synthesize an alkyne starting from an alkene. To prepare an internal alkyne, only two equivalents of base are needed and  $\text{H}_2\text{O}$  is not required at the end. In terms of the mechanism, show how this works. (10 points)



only two equivalents of base needed

the internal alkyne doesn't have an acidic hydrogen so not deprotonated w/  $\text{NaNH}_2$

15. *Extra Credit* If excess  $\text{NaNH}_2$  is used in the above reaction then the *terminal* alkyne is isolated, and  $\text{H}_2\text{O}$  is required at the end. The internal alkyne is formed initially, but has been shown to undergo transformation to the terminal alkyne in the presence of excess  $\text{NaNH}_2$ . Suggest a mechanism for this *isomerization*, one that includes the role of the  $\text{H}_2\text{O}$ . (10 EC points)



*this mechanism was shown in class*

*also, see the answer to problem 10.72 in Klein*

*and 10.8*