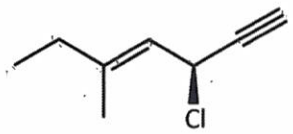
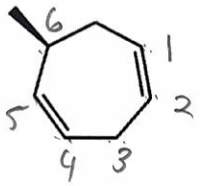
1. Name the following compounds. Don't forget about stereochemistry. (10 points)

a. 

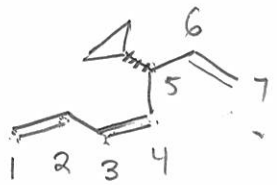

(3S,4E)-
3-chloro-5-methylhept-4-en-1-yne

b. 

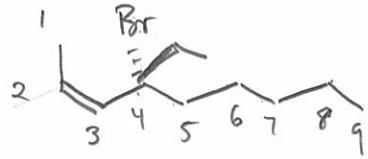

(S)-6-methylcyclohepta-1,4-diene

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

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

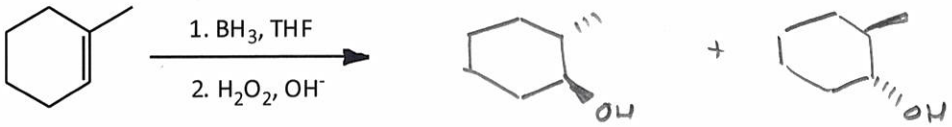



b. (2Z,4*R*)-4-bromo-4-ethylnon-2-ene




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

a. Show *all* of the products formed in this reaction (be clear about the number of stereoisomers produced and the stereochemistry of the product).
b. Indicate whether the addition proceeds with *anti* or *syn* addition.
c. Does the addition follow Markovnikov's rule? Explain.




a.

b. syn-addition

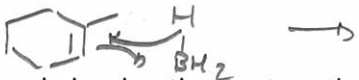
c. anti-markownikov, since the more electronegative element, ends up on least substituted carbon

H—OH

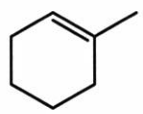
more E.N. element

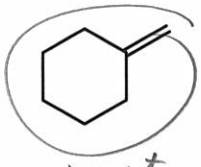
$H-BH_2$

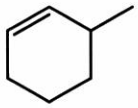
4. Does the first step, the hydroboration step, of the reaction in Question 3 (above) obey Markovnikov's rule? Explain. (5 points)

The first step is addition of $H-BH_2$ across the double bond.  since H is more E.N. than B, this is officially

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

a 

b 

c 

least exothermic

most exothermic

Even though this is di substituted like in b., endo-cyclic is more stable | markovnikov

(didn't cover this, but exocyclic double bonds are more reactive

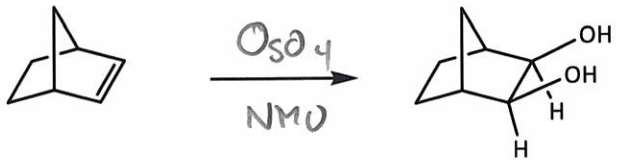
6. Which alkene in the above set (Question 5) would have the largest value for heat (enthalpy) of hydrogenation ($\Delta H_{hydrog.}$)? Explain. (a, b, or c when treated with $H_2$/Pt give the same product) (10 points)

b. also, because it's the most reactive

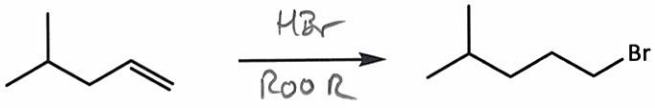
all three would give methylcyclohexane

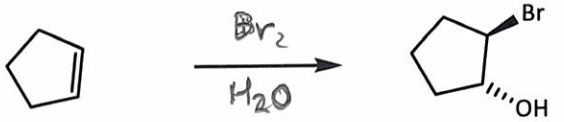
7. Show the product (or products) from the ozonolysis (1. $O_3$, then 2. DMS) of compound b. in Question 5. (5 points)

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

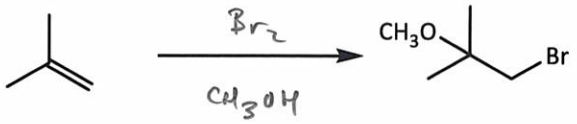
a 


or $\xrightarrow[2.\ NaHSO_3]{1.\ OsO_4}$ or $\xrightarrow[\text{dilute, cold}]{KMnO_4}$ OH

b 


c 

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



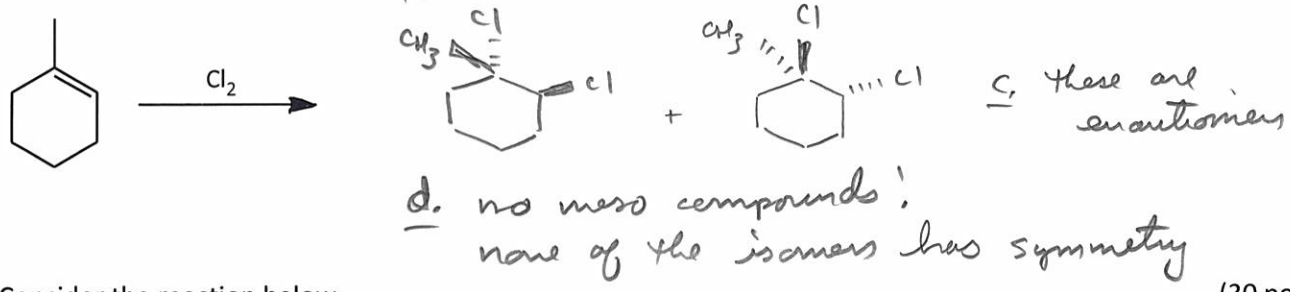

10. Consider the reaction of the alkene below with chlorine ($Cl_2$), which gives a *vicinal* dichloride.

a. Is the addition *syn* or *anti*?

b. Show the resulting stereochemistry of the product(s) using the correct line (——), dash (┈┈┈), and wedge (▬) notation.

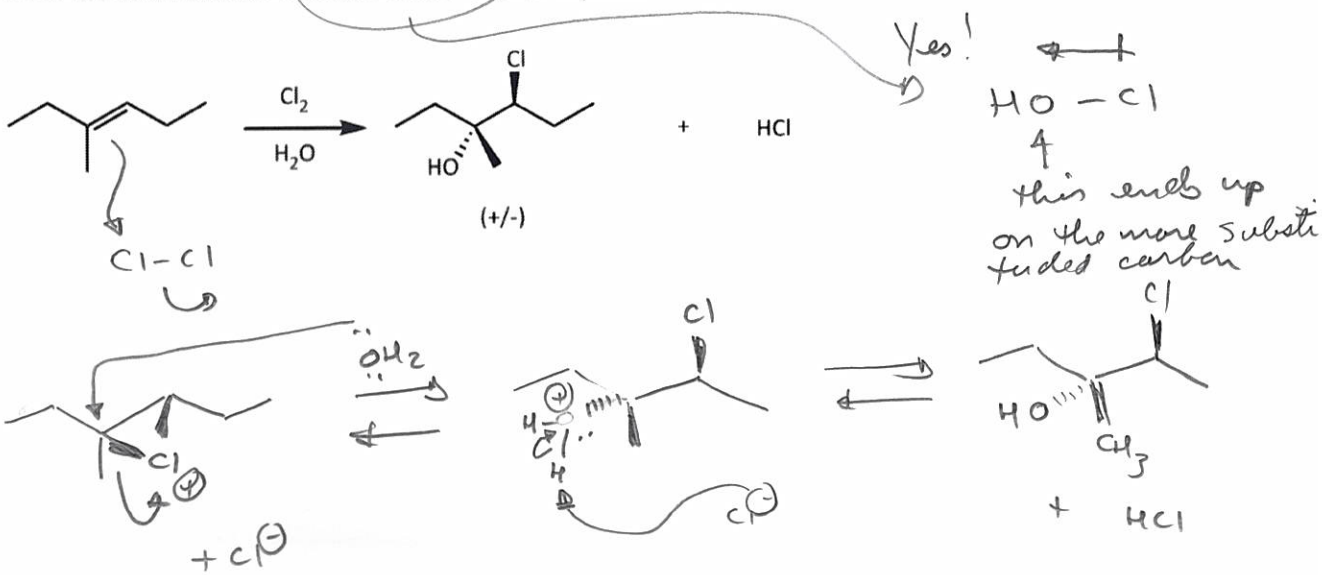
c. If any other stereoisomers are produced, show them and indicate any isomer relationships (diastereomers, enantiomers).

d. Is a meso compound produced? Explain your answer. (20 points)



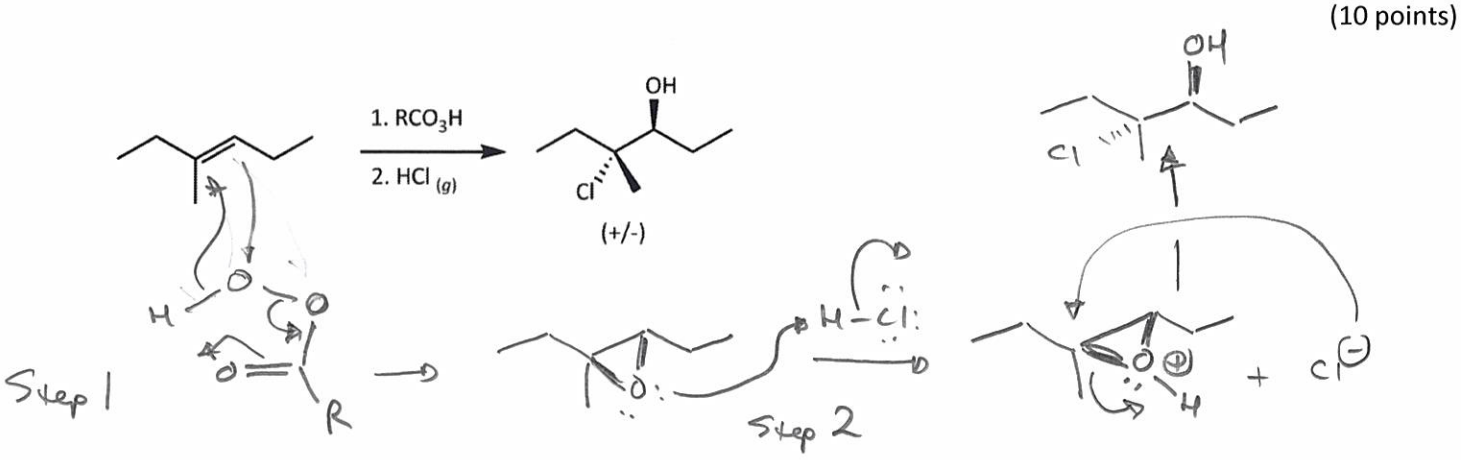

11. Consider the reaction below. (30 points)

a. Show the complete mechanism for the formation of the product, including the HCl.
b. Be sure to account for the formation of the shown stereochemistry of the product (and the (+/-) part).
c. 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 is 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)

(10 points)




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)

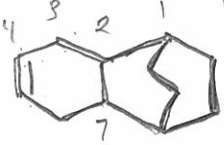
EXTRA CREDIT Name the compound (the more complicated the structure the more EC points you get)

(10 EC points)

$C_{12}H_{18}$ compared to $C_nH_{2n+2}$ or $C_{12}H_{26}$ is missing 8 H's which is 4 $H_2$ molecules = 4° of unsaturation

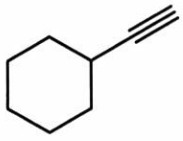
tricyclo[6.2.2.$0^{2,7}$] dodecane

or



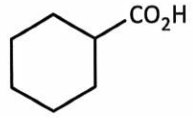

14. Show how to convert the alkyne below to each of the following compounds. List the reagents and conditions below each compound (some of these may require more than one step!). You don't need to show any intermediates (if there are any).

(25 points)

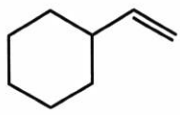


or
$Na, NH_3, ROH$

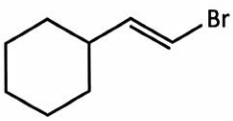
1. $NaNH_2$
2. 
3. $H_2$, Pt

a. 

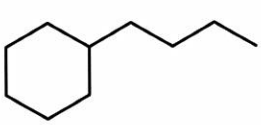

1. $O_3$
2. $H_2O$

b. 

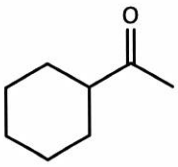
$H_2$
Lindlar's

c. 

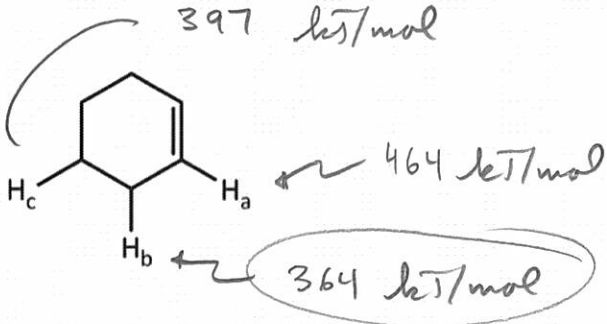

HBr
ROOR

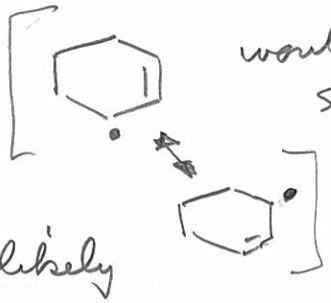
d. 

$H_2SO_4$
$HgSO_4$
$H_2O$

e. 

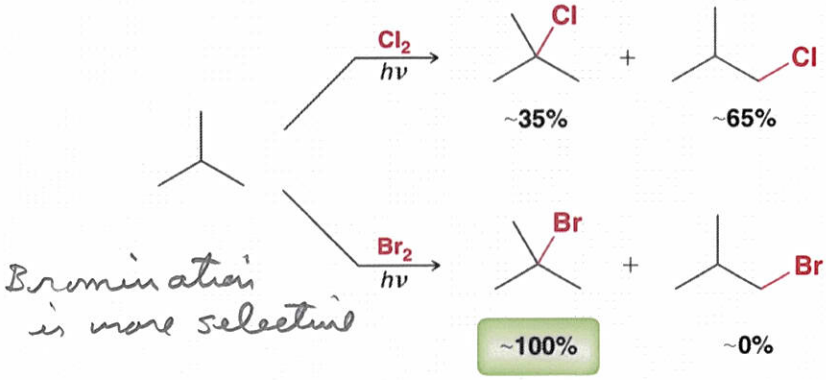
15. For the compound shown below, the carbon-hydrogen bonds to the highlighted hydrogens $H_a$, $H_b$, and $H_c$, have bond dissociation enthalpies (BDEs) of 397, 364, 464 kJ/mol, *irrespectively*. Assign these values to the correct hydrogens and indicate which one is most likely to be abstracted in a *radical* reaction. (20 points)



would give the stable allylic radical

16. Provide an explanation for the dramatic difference in the ratio of products produced below. (10 points)

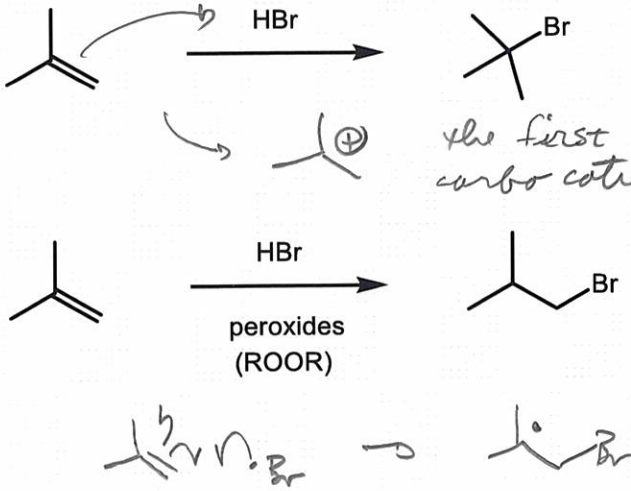



the first step of chlorination is exothermic so formation of 1° vs 3° based on stability of radical is less important

the first step here is endothermic By the Hammond postulate, the intermediate is close in energy to the T.S. and therefore the more stable radical influences the rate more than chlorination

17. In terms of the mechanism of the reaction explain why the addition of peroxides changes the course of the addition reaction shown below. (10 points)

*Extra Credit* Historically, where did the peroxides come from that led to the discovery of the "peroxide effect"? (5 EC points)




impure alkenes typically had peroxide impurities of autoxidation in presence of $O_2$

the first step forms the most stable carbocation

the key step of the mechanism involves addition to give the most substituted radical - this sets where the bromine ends up attached