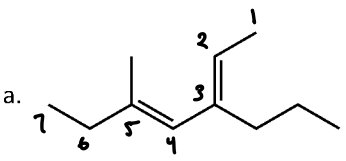
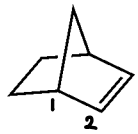
**Name** Key **Date** _____

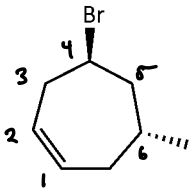
1. Name the following compounds. Don't forget to assign any stereochemistry using the correct notation (where appropriate) (15 points)

a. 


(2E, 4E)-5-methyl-3-propyl-hepta-2,4-diene

b. 

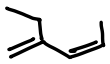

bicyclo[2.2.1]hept-2-ene

c. 

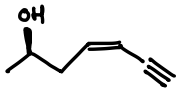

(4S, 6R)-4-bromo-6-methyl-cyclohept-1-ene

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

a. (3*Z*)-2-ethylpenta-1,3-diene

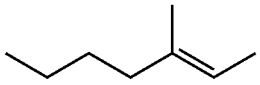


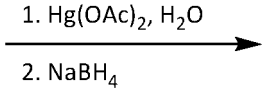
b. (2*R*,4*Z*)-hept-4-en-6-yn-2-ol




3. Consider the reaction of the alkene shown below. (20 points)

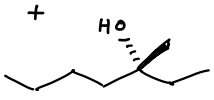
a. Show *all* of the products formed in this reaction. (10)
b. Does the addition follow Markovnikov's rule? Explain (10)





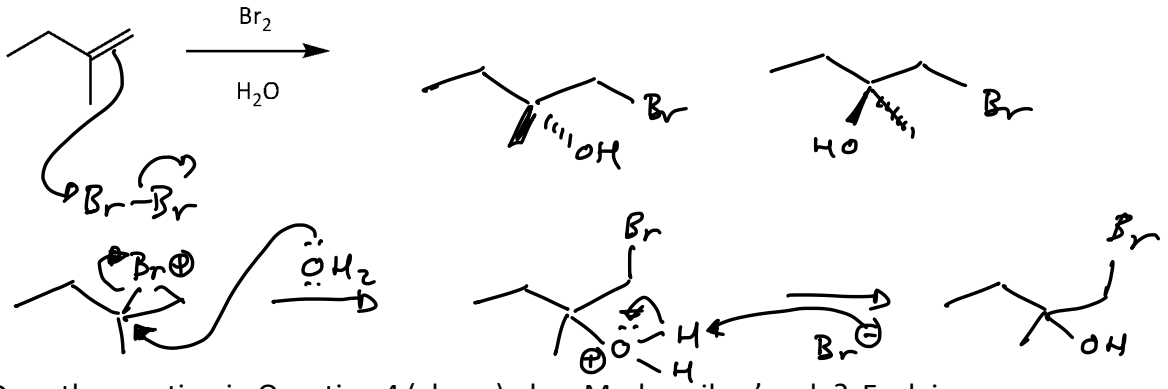

a.


+




b. Yes, because the more electronegative element (of H–OH) adds to the more substituted position of the alkene.

4. Show the product (or products) from the following reaction and show a reasonable and complete *mechanism* for the overall reaction. (Hint: the product is called a *bromohydrin*) (15 points)

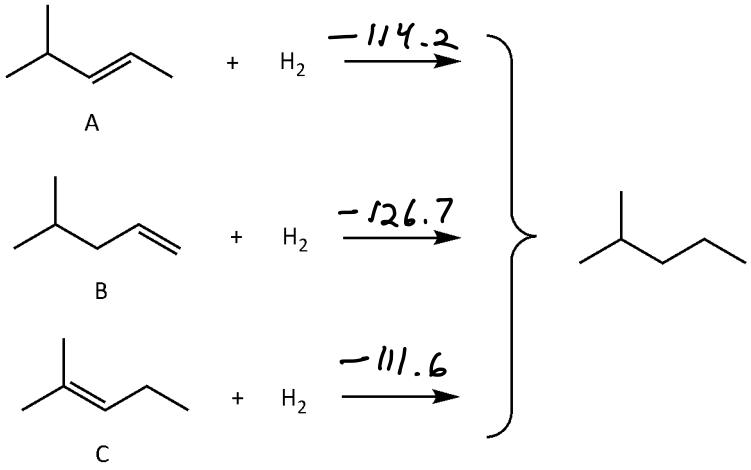



5. Does the reaction in Question 4 (above) obey Markovnikov's rule? Explain. (5 points)

yes, because the more electronegative element ends up on the more substituted carbon

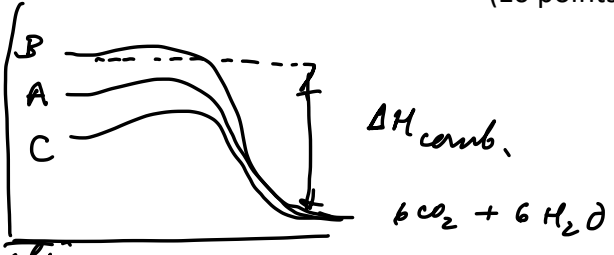
HO–Br

6. Consider the series of isomeric alkenes shown below. The *heats of hydrogenation* ($\Delta H_{hydrog.}$) are -111.6, -114.2, and -126.7 kJ/mol, *irrespectively*. Assign these to the corresponding alkene. (15 points)



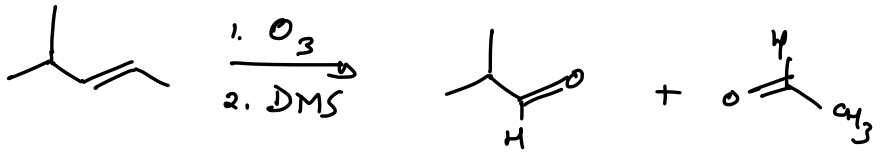

7. Which alkene in the above set (Question 6) has the most *exothermic heat of combustion* ($\Delta H_{comb.}$)? Explain. (10 points)

The alkene shown in B, Since B is the least stable of the alkenes, it gives off the most heat during combustion



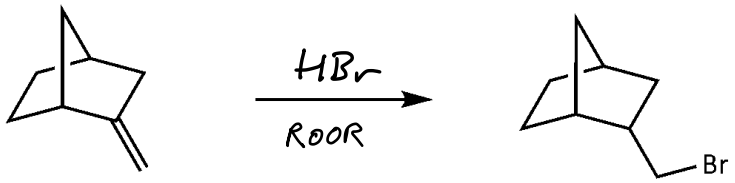

$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$ + heat ($\Delta H_{comb.}$)

8. Show the product (or products) from the ozonolysis (1. $O_3$, 2. DMS) of compound A in Question 6. (5 points)

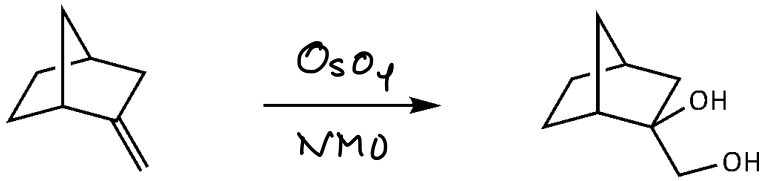



9. Fill in the *reagents* required to accomplish the following reactions. (15 points)

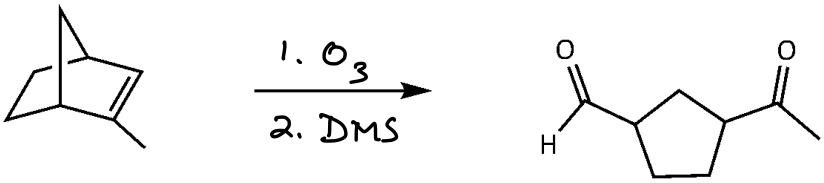
a.




b.




c.



10. Styrene undergoes addition of I-Cl (iodine monochloride) to give one of the products shown below (but not both). Note that this reaction is similar to the addition of $Cl_2$. (Hint: electronegativity) (25 points)

a. Which product is formed, A or B? (5)

B

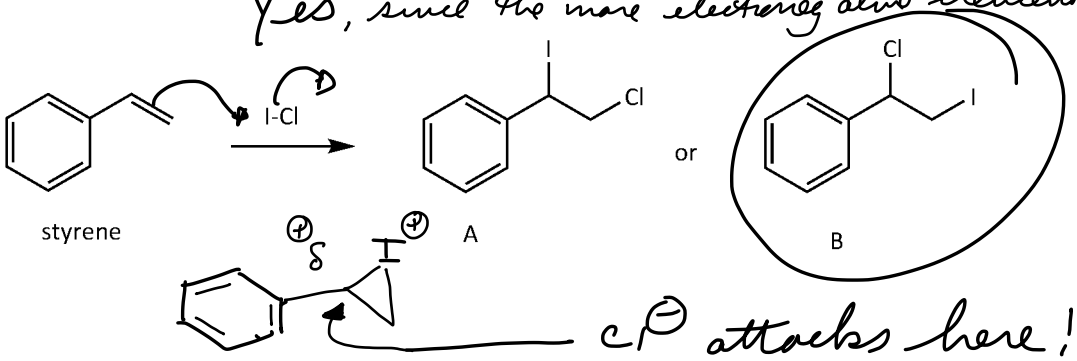
I – Cl

b. Provide a reasonable explanation for your choice in a. (10)

The more electronegative element of I-Cl, chlorine, ends up on the more substituted carbon

c. Does the formation of this product follow Markovnikov's rule? Explain. (10)

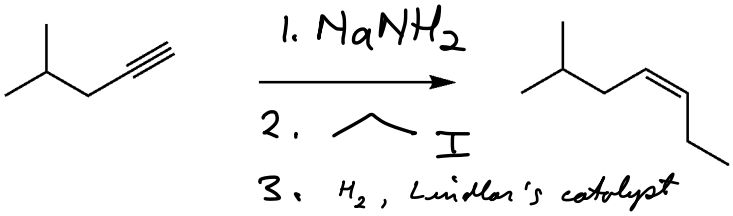
Yes, since the more electronegative element ends up on more substituted carbon



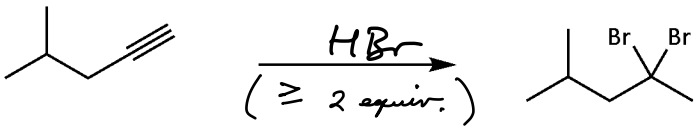

Note the iodonium ion is formed first!

11. 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). (15 points)

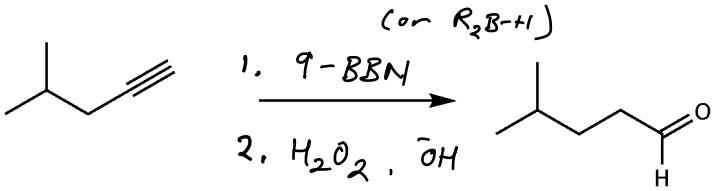
a.




b.

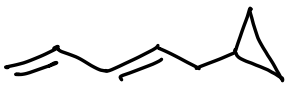



c.



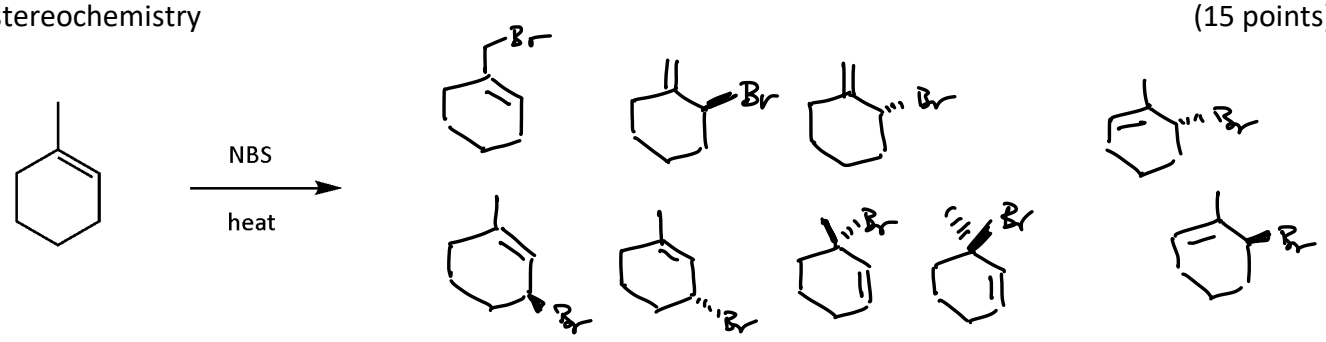
12. How many *degrees of unsaturation* (total number of rings and/or double bonds) are in a molecule with molecular formula $C_8H_{12}$? Suggest a *reasonable* structure for a molecule that has two double bonds *or* one triple bond, but that has this formula. (Note that there are *many* possibilities) (15 points)

$C_8H_{12}$ vs $C_8H_{18}$ (saturated) is missing 3 $H_2$ molecules, so 3 degrees of unsaturation



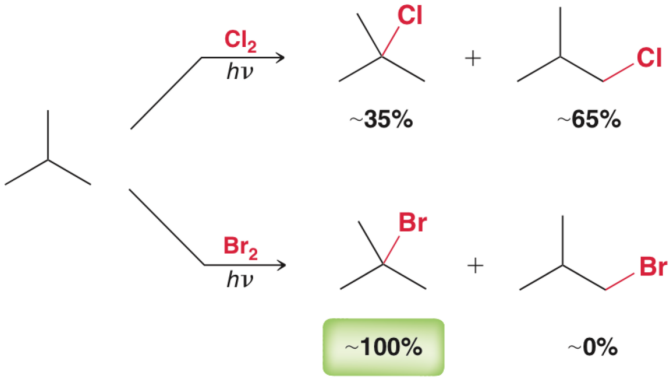
many other possibilities

13. Show all of the products from the following reaction (there is more than one). Clearly show all of the stereochemistry (15 points)

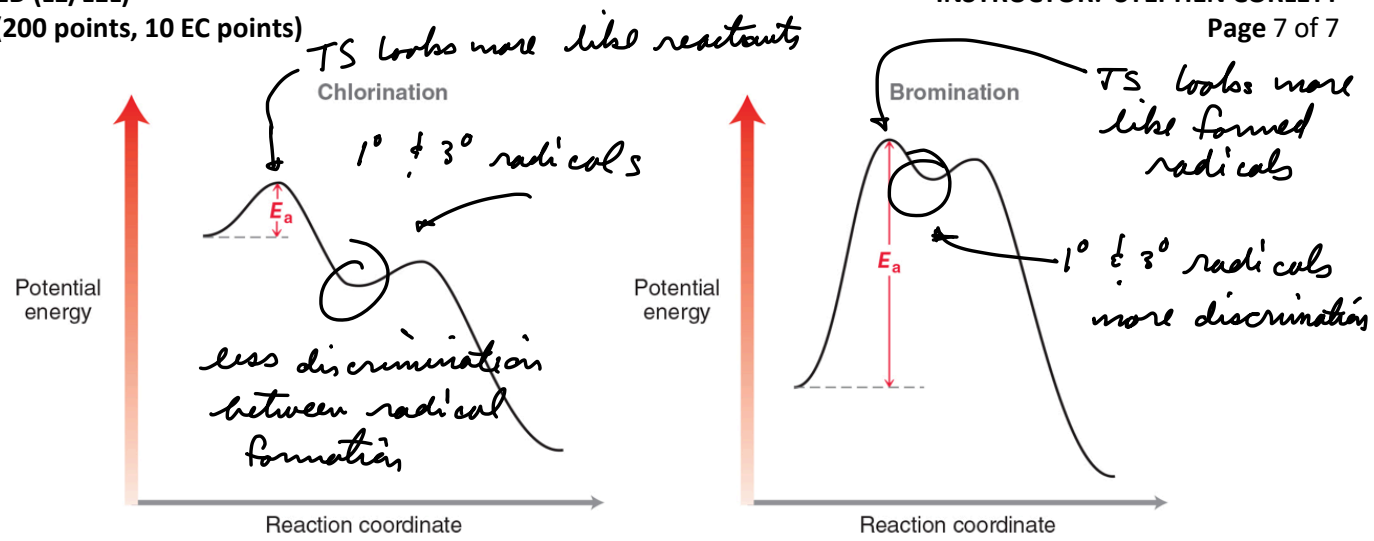



9 products total!

14. Given the reaction energy diagrams for the radical chlorination and bromination of alkanes (next page), provide an explanation for the dramatic difference in the ratio of products produced below. Your answer should mention the Hammond postulate. (10 points)

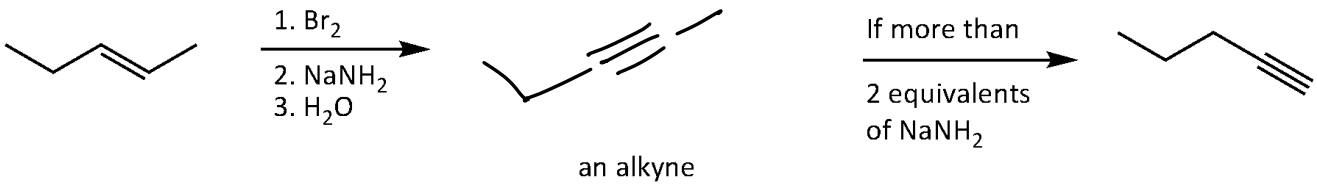



The first step of the chlorination reaction is exothermic, which forms the 1° or 3° radicals that lead to the two products, is less sensitive to stability of the formed radical since the transition state is closer to the reactant energy (the Hammond postulate). In bromination, the first step is highly endothermic, so the transition states leading to the 1° or 3° radical are closer in energy to the formed radicals. This has greater discrimination for the formed radicals, which leads to enhanced (favored) formation of the 3° radical and hence the 3° bromide.




15. Show the product. If excess $NaNH_2$ is used in the reaction (more than 2 equivalents), the product shown on the right is produced. (10 points)

For *Extra Credit,* suggest a mechanism for this *isomerization,* one that includes the role of the $H_2O$. (10 EC points)




This transformation is a series of acid/base reactions