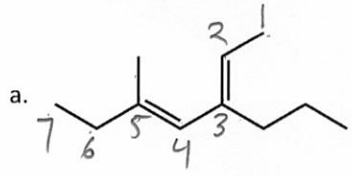
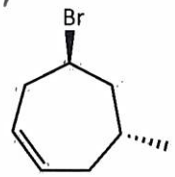
1. Name the following compounds. Don't forget to assign any stereochemistry using the correct notation (where appropriate) (15 points)

a. 

(2E,4E)-
5-methyl-3-propylhepta-2,4-diene

b. 

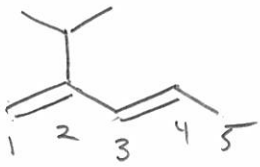
bicyclo[2.2.1]hept-2-ene

c. 

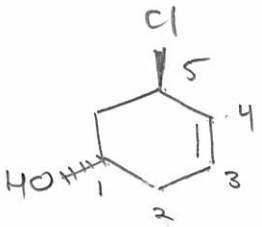
(4S,6R)
4-bromo-6-methylcycloheptene

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

a. (3*E*)-2-isopropylpenta-1,3-diene

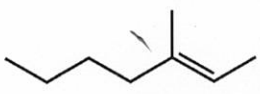


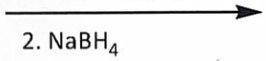
b. (1*S*,5*R*)-5-chlorocyclohex-3-enol

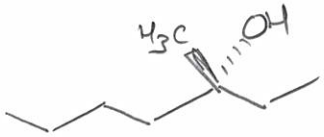


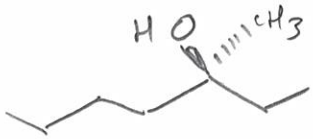
3. Consider the reaction of the alkene shown below. (20 points)

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



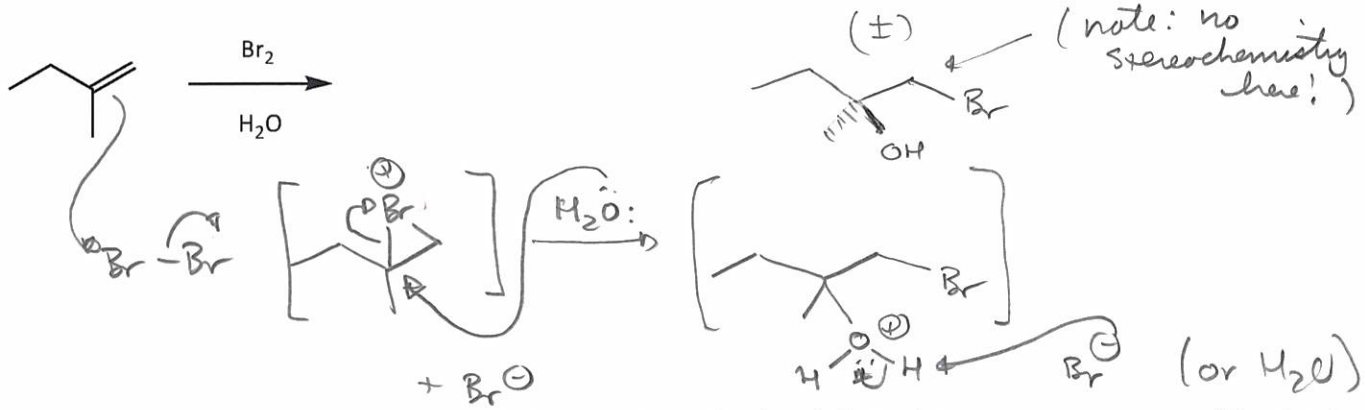




a. 

b. the reaction adds H-OH across the double bond and the more electronegative element ends up on the more substituted carbon, so yes it follows Markovnikov's rule!

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)

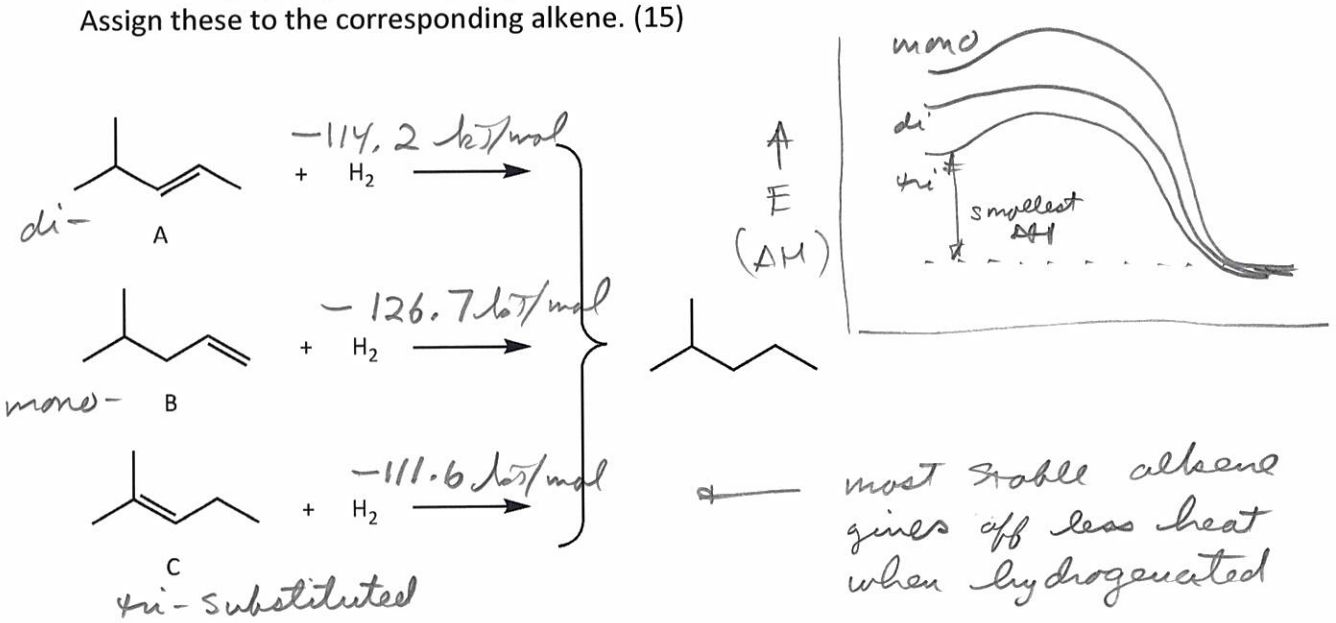
Yes, the more electronegative element of HO–Br adds to the more substituted carbon.

6. Consider the series of isomeric alkenes shown below. (20 points)

a. Arrange the alkenes in order from most stable to least stable (use the letters A, B, and C and the > and < symbols. (5)

C > A > B

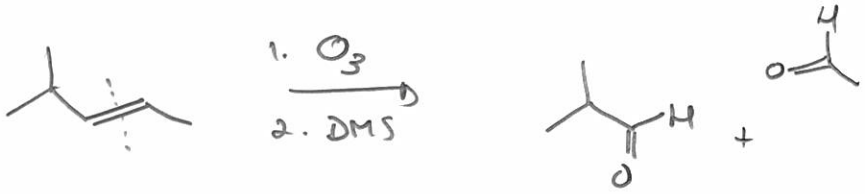
b. The *heats of hydrogenation* ($\Delta H_{hydrog.}$) are -111.6, -114.2, and -126.7 kJ/mol, *irrespectively*. Assign these to the corresponding alkene. (15)



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

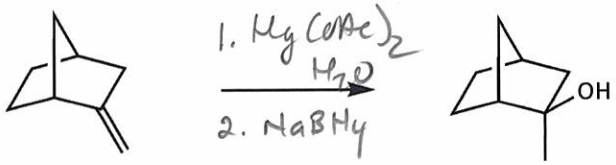
alkene B give off the most heat during combustion because it is the least substituted alkene, which is least stable

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



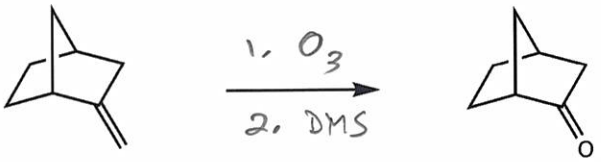
9. Fill in the *reagents* required to accomplish the following reactions. (15 points)

a.

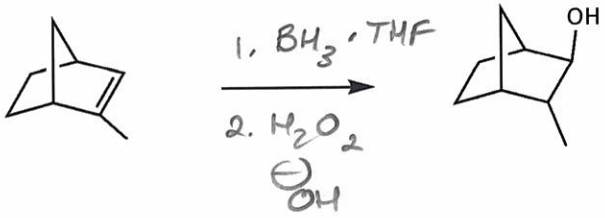


or H_3O^+ (dilute H_2SO_4) though is ones + rearrangements possible

b.



c.



10. Styrene undergoes addition of I-Cl (iodine monochloride) to give one of the products shown below (but no both). Note that this reaction is similar to the addition of Cl_2. (Hint: electronegativity) (20 points)

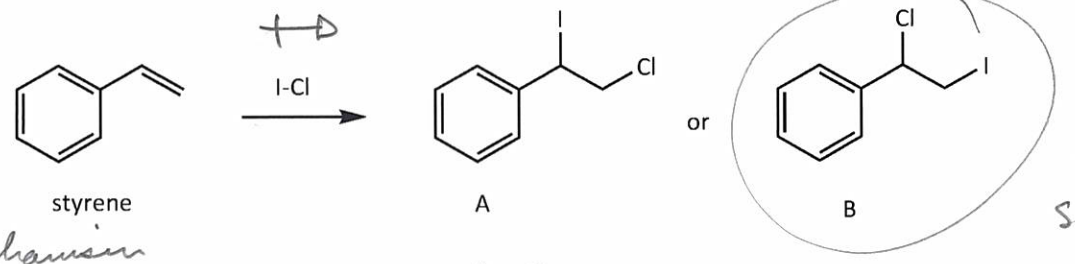
a. Which product is formed, A or B? (5)

B

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

The reaction is similar to addition of Cl_2, which gives a dihalide

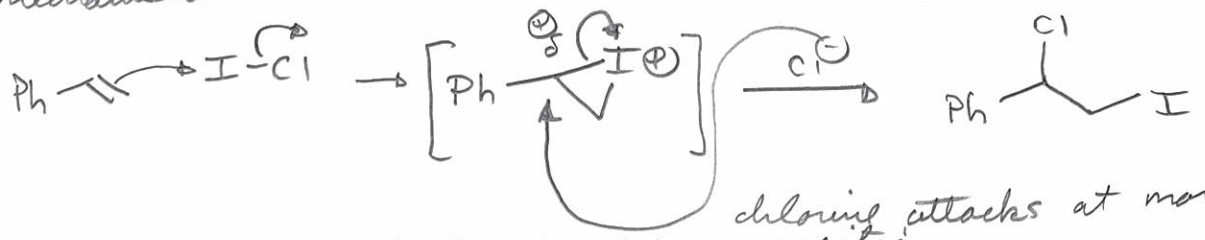
c. Does the formation of this product follow Markovnikov's rule? Explain. (~~10~~ 5)



styrene A B

more E.N. chlorine ends up at more substituted positi

mechanism



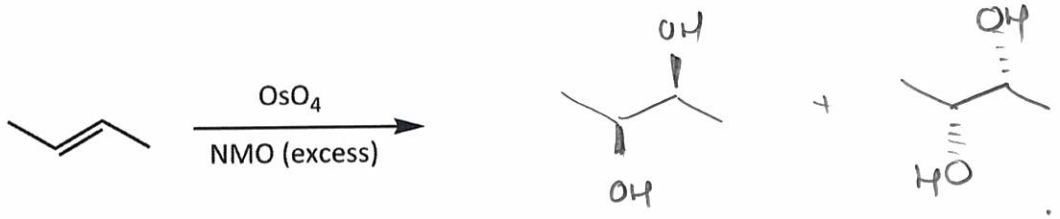
chlorine attacks at more substituted position

11. Consider the reaction of the alkene shown below. (25 points)

a. Is the addition *syn* or *anti*? (5) Syn

b. Show all of the products formed and the resulting stereochemistry of the product(s) using the correct line (——), dash (┅┅), and wedge (▬) notation. (10)

c. Indicate whether *enantiomers* are produced or whether the product is a *meso* compound. Explain your answer. (10)

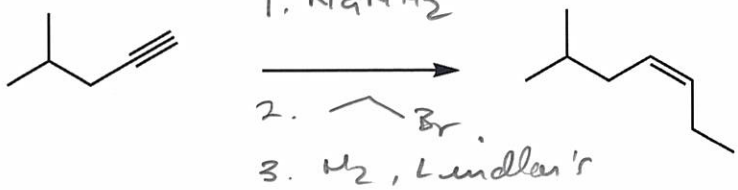


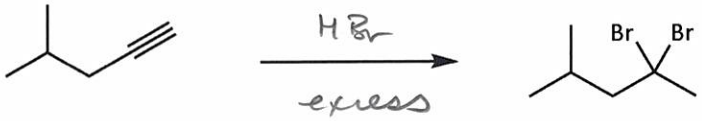
these are enantiomers

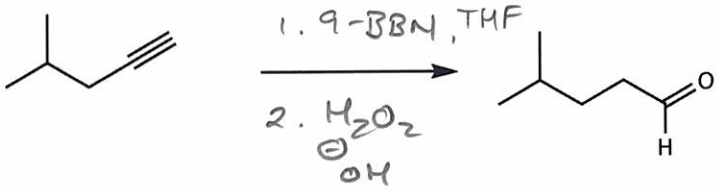
(no meso compounds)

12. 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)

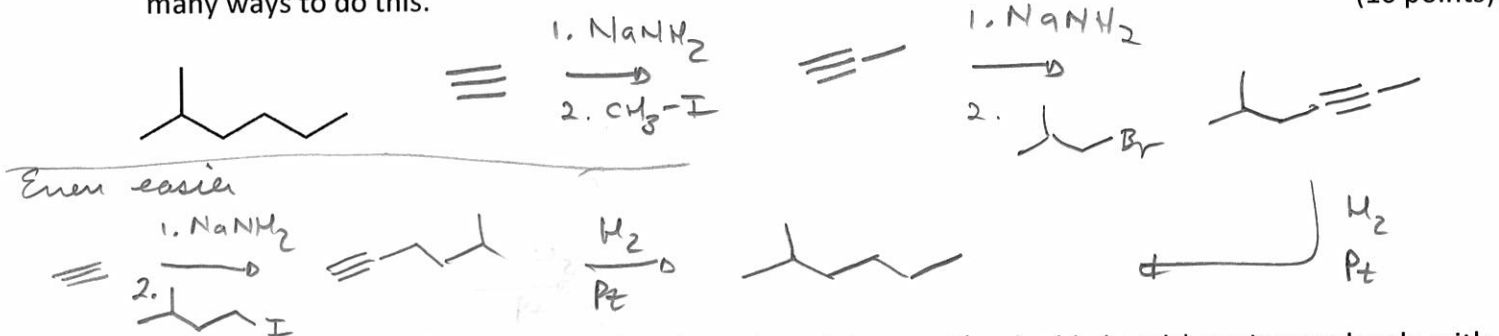
30

a. 

b. 

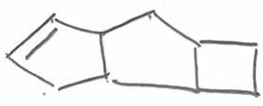
c. 

13. Show how to prepare the following compound start from acetylene and any other reagents. There are many ways to do this. (10 points)

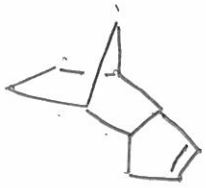


14. How many *degrees of unsaturation* (total number of rings and/or double bonds) are in a molecule with molecular formula $C_{10}H_{14}$? Suggest a *reasonable* structure for a molecule that has only one double bond, but has this formula. (Note that there are *many* possibilities) (10 points)

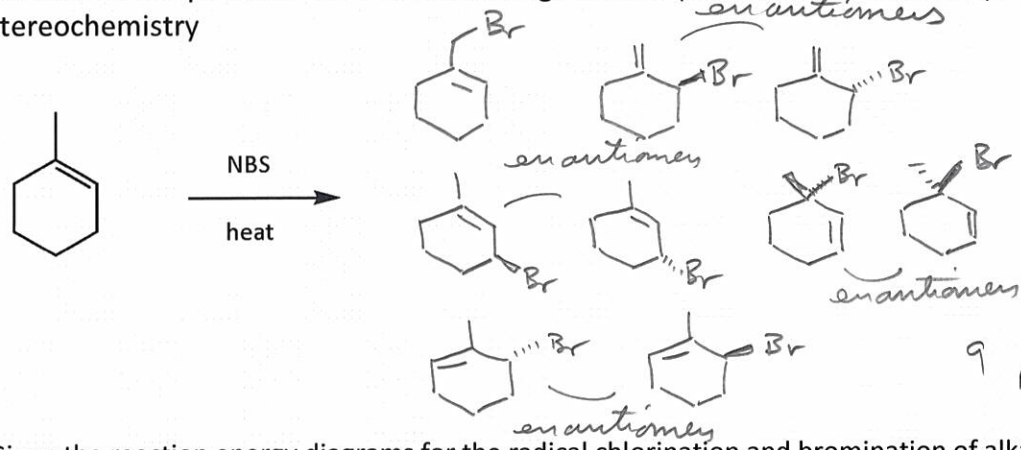
$C_{10}H_{14}$ compared to $C_{10}H_{22}$ (C_nH_{2n+2}) is "missing" 8 hydrogens = 4 H_2 = 4° of unsaturation



many more

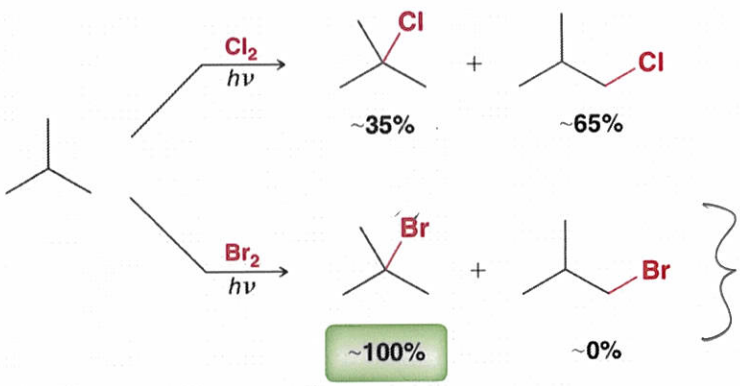


15. Show all of the products from the following reaction (there is more than one). Clearly show all of the stereochemistry (10 points)

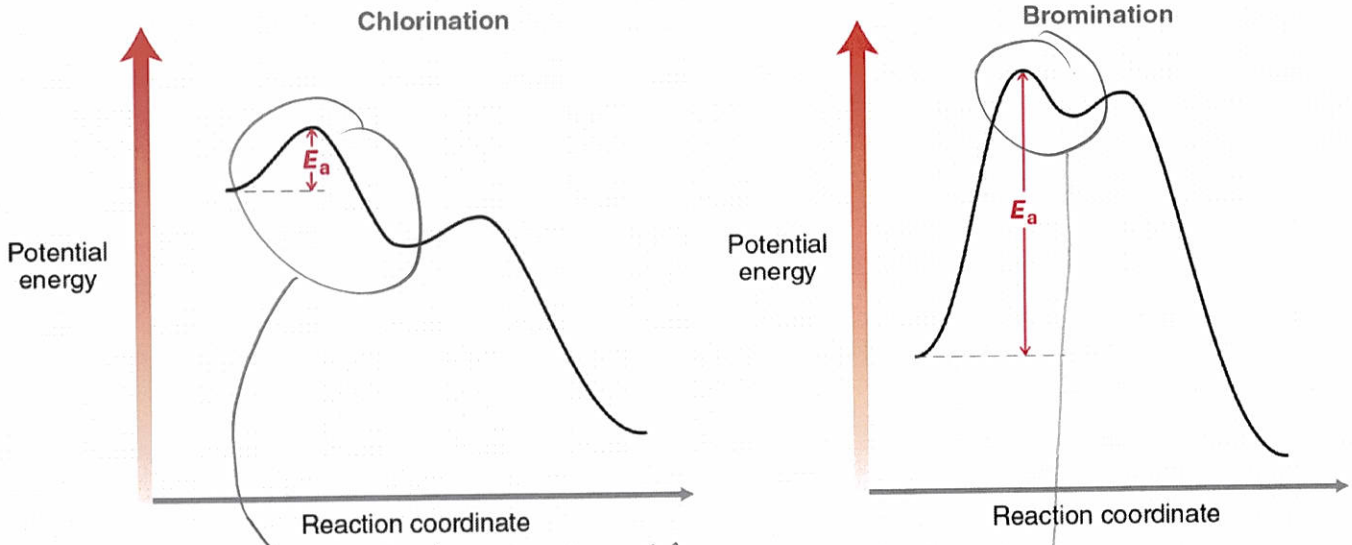


16. Given the reaction energy diagrams for the radical chlorination and bromination of alkanes, provide an explanation for the dramatic difference in the ratio of products produced below. Your answer should mention the Hammond postulate. (10 points)

Hammond says: T.S. for bromination resembles the intermediate formed radical



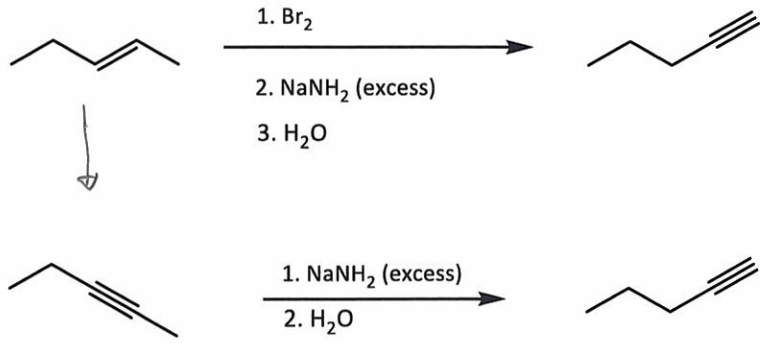
Bromination is more selective for 3° over 1°, than Chlorination



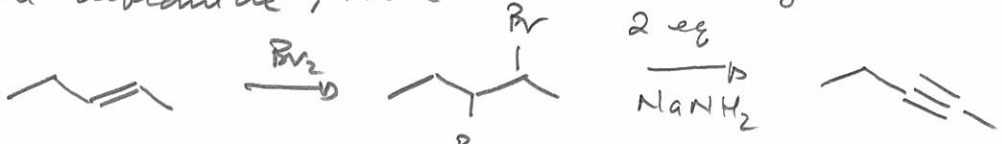
the first propagation step is exothermic, so the TS of reaction depends less on the stability of the intermediate

the TS for bromination is closer in energy to the intermediate radical

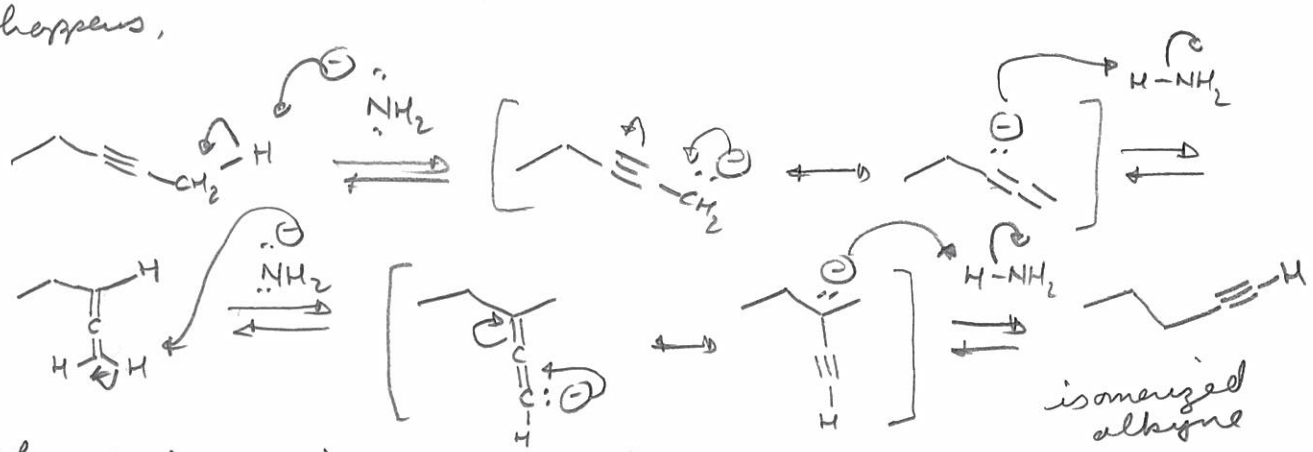
17. *Extra Credit* If excess $NaNH_2$ is used in the above reaction then the *terminal* alkyne is isolated, and H_2O *is* required at the end. The internal alkyne is formed initially, but has been shown to undergo transformation to the terminal alkyne in the presence of excess $NaNH_2$. Suggest a mechanism for this *isomerization,* one that includes the role of the H_2O. (10 EC points)



The question is really about how the internal alkyne undergoes conversion to the terminal alkyne under the reaction conditions. The bromination of the alkene leads the dibromide, then elimination gives the alkyne



If excess base ($NaNH_2$) is present, then the following happens,



The last step is deprotonation of the terminal alkyne,

Under the strongly basic conditions, the terminal alkyne will be deprotonated; the H_2O is added at the end to protonate it!