1. Calculate the degree of unsaturation for each of the following compounds:

C_{60} 61

$C_6H_{11}NO_2$ 2

$C_6H_4OCl_2$ 4

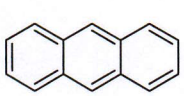
$C_{10}H_8$ 7

$C_9H_{11}N_2O_4Br$ 5

$C_{24}H_{24}N_3OP$ 15

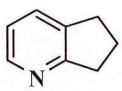
2. How many degrees of unsaturation are present in each compound below?

10

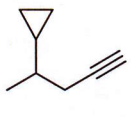


3

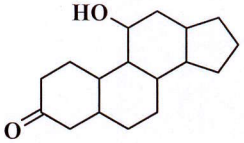
5



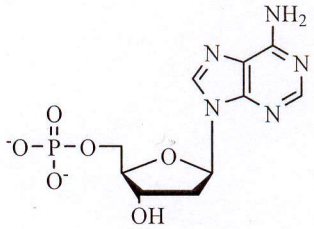
3



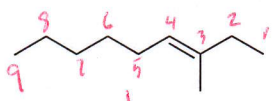
5



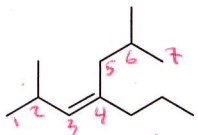
8



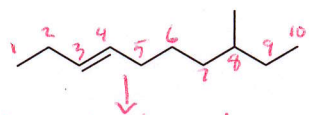
3. Name each of the following compounds according to IUPAC rules.



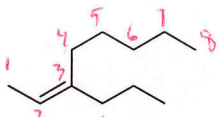
(E)-3-methyl-3-nonene



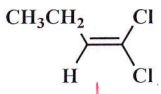
(trans)8-methyl-3-decene



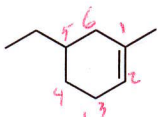
(Z)-3-propyl-2-octene



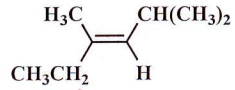
(Z)-2,6-dimethyl-4-propyl-3-heptene



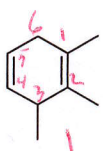
1,1-dichloro-1-butene



5-ethyl-1-methylcyclohexene

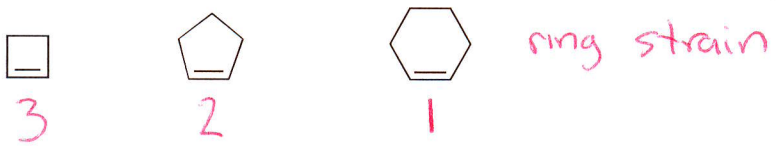


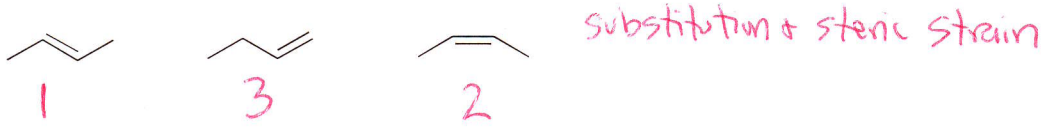
(E)-2,4-dimethyl-3-hexene

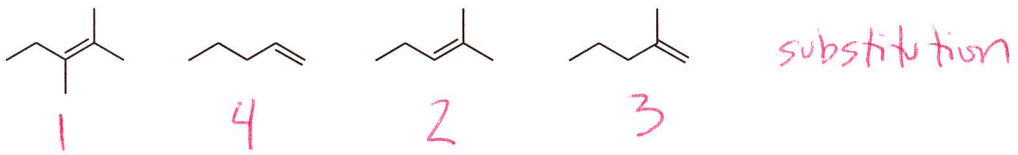


1,2,3-trimethyl-1,4-cyclohexadiene

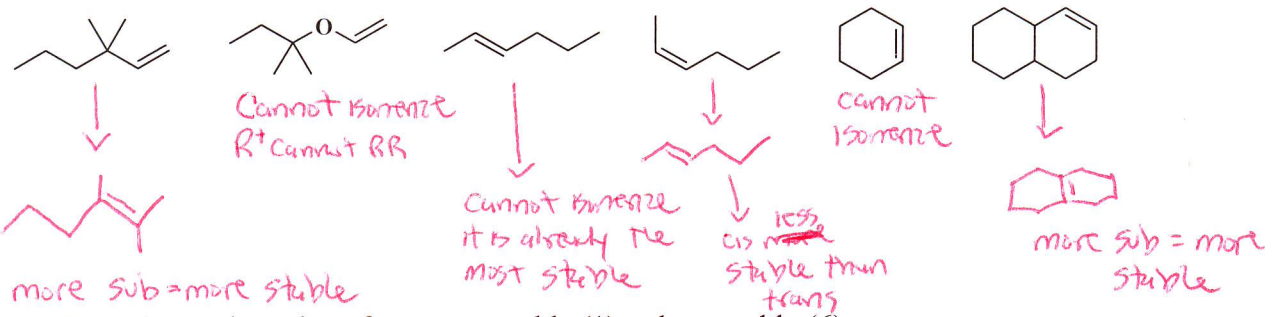
4. For each group of alkenes shown below rank them in increasing order of stability (most stable = 1). For each series, what is the main principle determining this stability?

(a) 

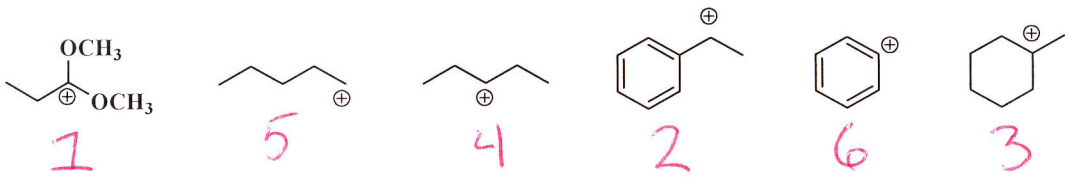
(b) 

(c) 

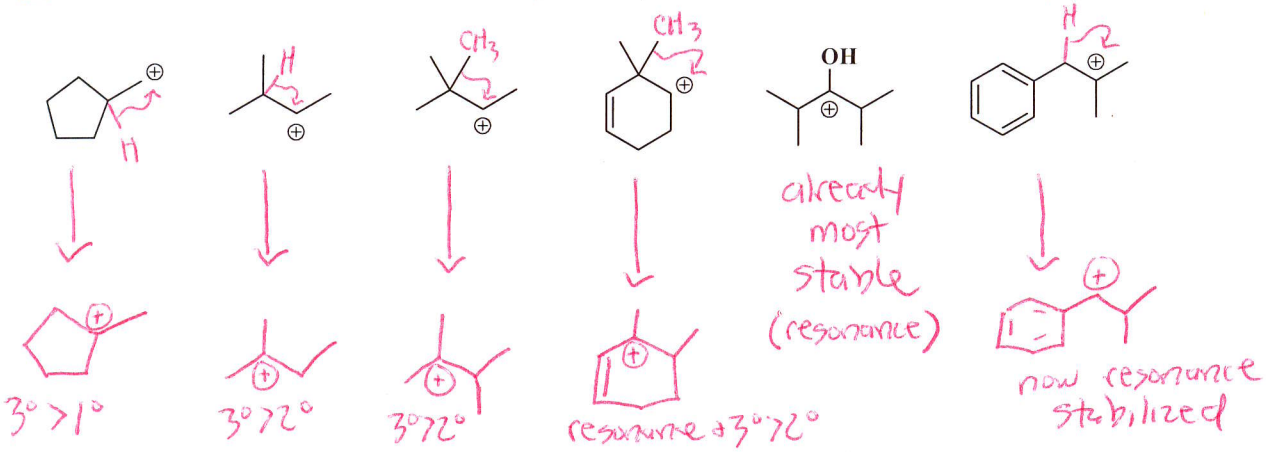
5. If the following alkenes can isomerize to a more stable alkene, draw the strucure of the more stable alkene and state why it is more stable. If it cannot isomerize to a new alkene, state why.



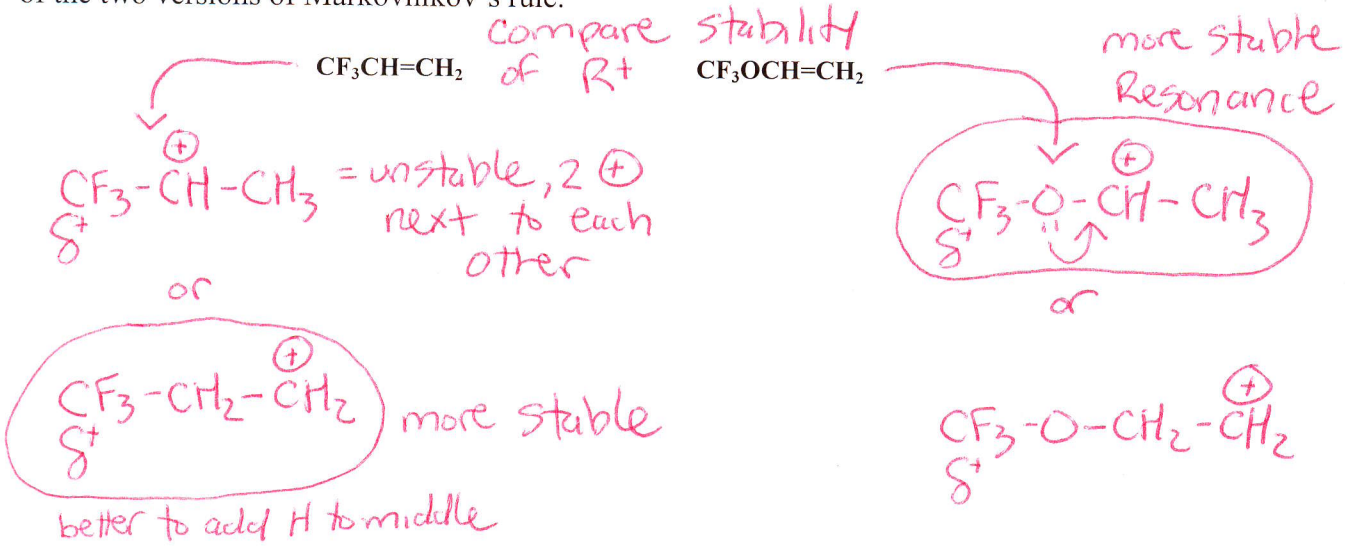
6. Rank following carbocations from most stable (1) to least stable (6).



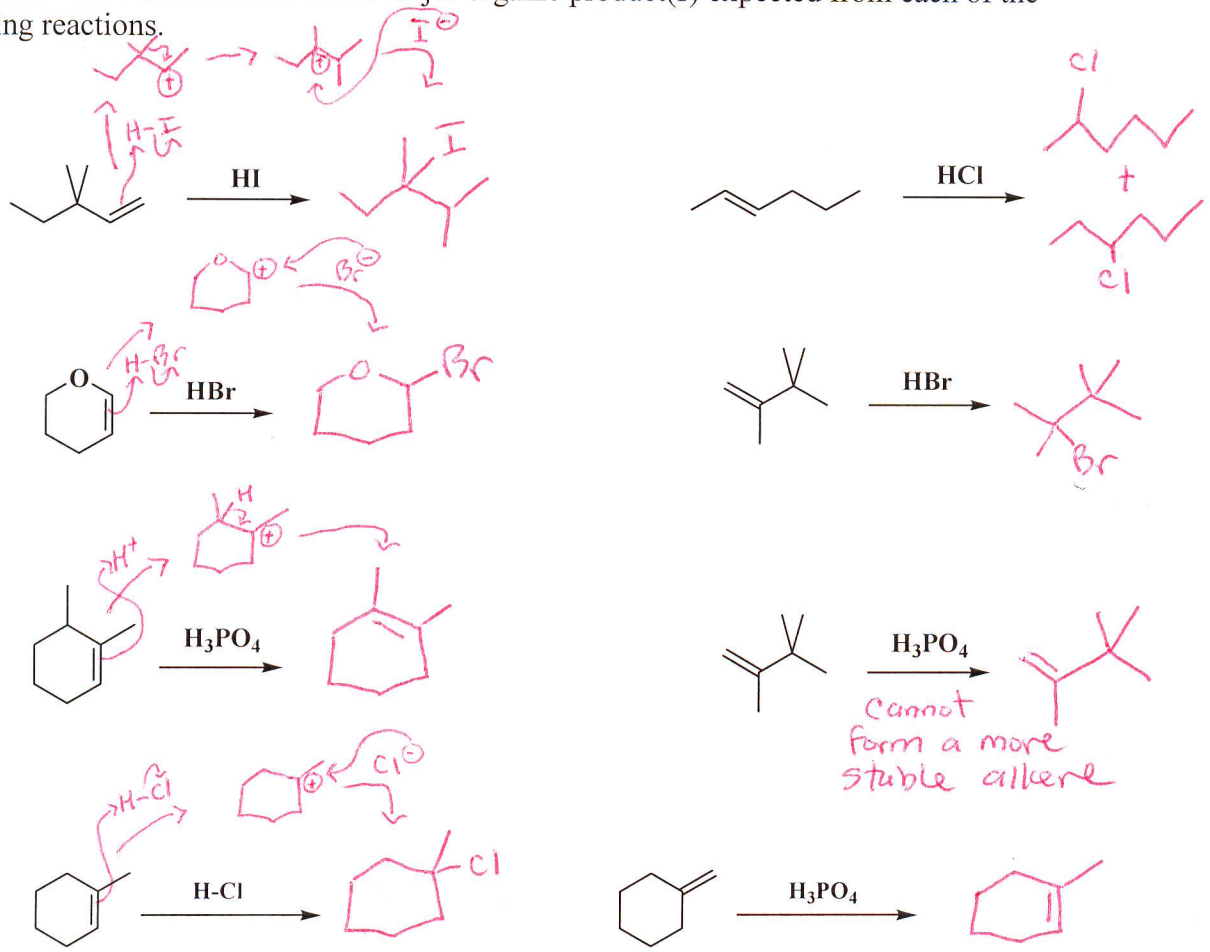
7. If the following carbocations can rearrange to a more stable carbocation, draw the structure of the more stable carbocation and state why it is more stable. If it cannot, state why.



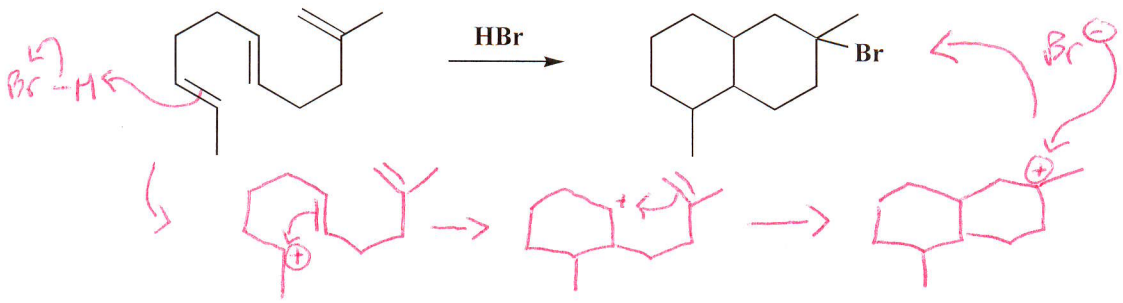
8. In the electrophilic addition of HBr to the following alkenes one is found to add the hydrogen to the end carbon while one adds hydrogen to the middle carbon. Which adds to the middle and which adds to the end? Draw the products of these reactions and explain your product in terms of the two versions of Markovnikov's rule.



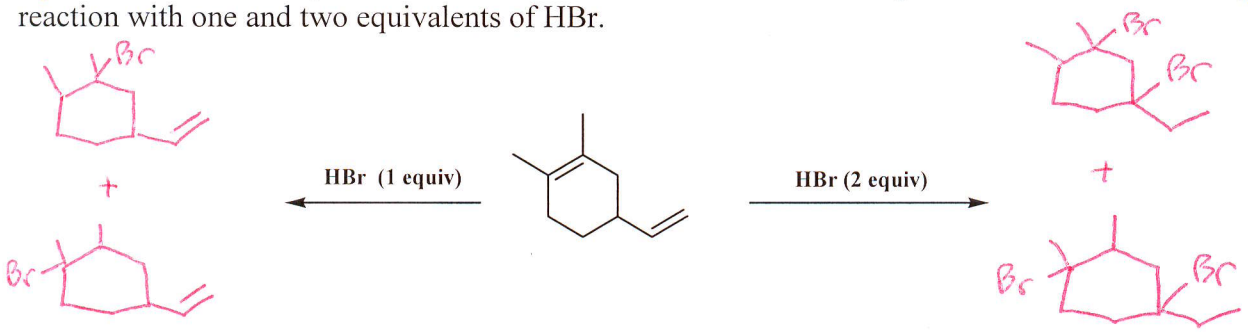
9. **Reactions.** Give the structure of the major organic product(s) expected from each of the following reactions.



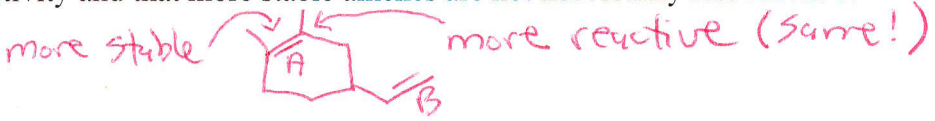
10. **Mechanisms.** Provide a complete stepby-step mechanism for each of the reactions on the left hand column in question 6 and for the reaction below.

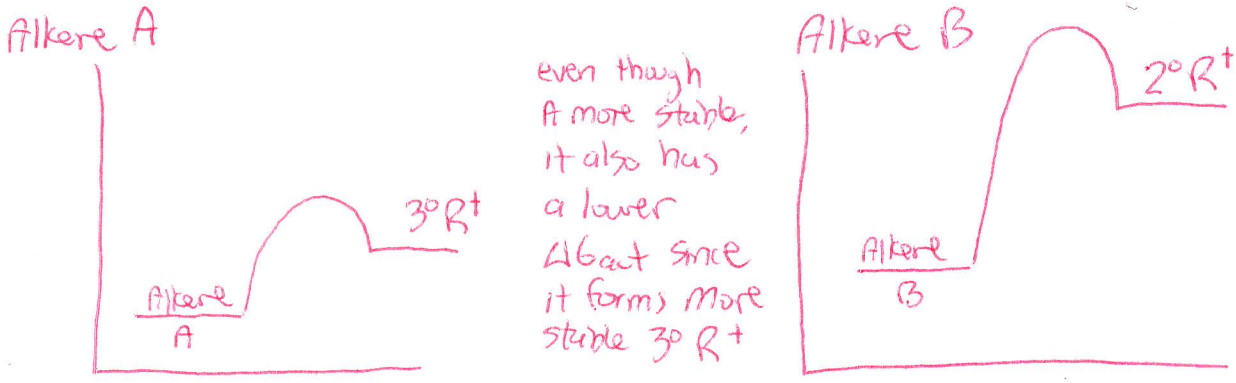


11. When molecules with two alkenes react the product will depend on how many equivalents of HX are added. If two molar equivalents are added, then both alkenes will react. If only one equivalent is added only the more reactive alkene reacts. Predict the products from the following reaction with one and two equivalents of HBr.

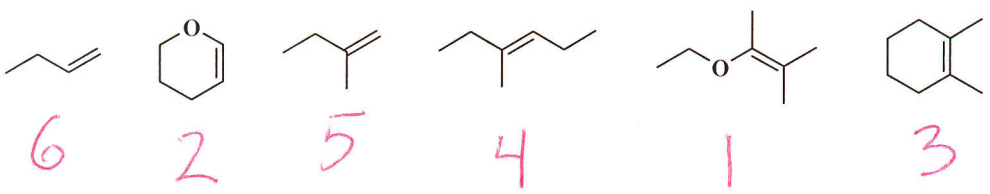


12. For the diene in question 11, which alkene is more stable? Which alkene is more reactive? Draw two reaction energy diagrams (side by side, one for each alkene) illustrating relative energy differences of alkenes, activation energy, transition state energy, and intermediate energy for the addition of HBr. How do these diagrams help explain your answers regarding alkene stability versus reactivity and that more stable alkenes are not necessarily less reactive?



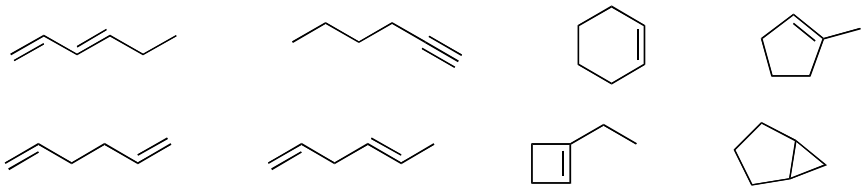


13. Rank the following alkenes from most reactive (1) to least reactive (6) towards electrophiles.



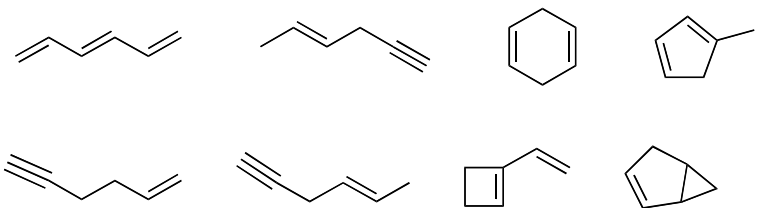
14. Calculate the degree of unsaturation, and draw <u>three</u> constitutional isomers for the molecular formula C_6H_{10}.

2° of unsaturation; possibilities include:



15. Calculate the degree of unsaturation, and draw <u>three</u> constitutional isomers for the molecular formula C_6H_8.

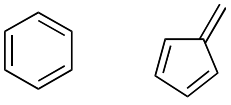
3° of unsaturation; possibilities include:



16. Calculate the degrees of unsaturation and draw two reasonable structures for each of the following molecular formulas.

a. C_6H_6

4° of unsaturation:

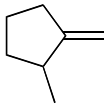


b. C_3H_4

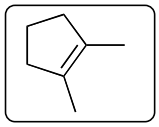
2° of unsaturation

17. For the following pairs, determine which compound is more stable, and briefly explain why.

2 R groups

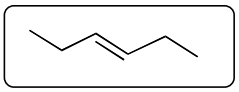


4 R groups

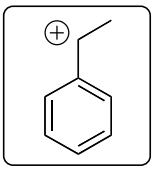


more highly substituted
double bond

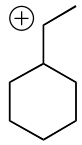
cis



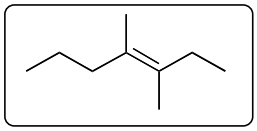
trans-more stable



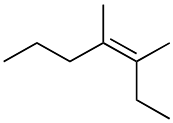
resonance
stabilized

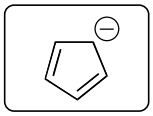


no resonance
stabilization



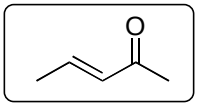
biggest groups trans



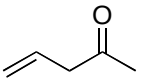


resonance
stabilized

no resonance
stabilization



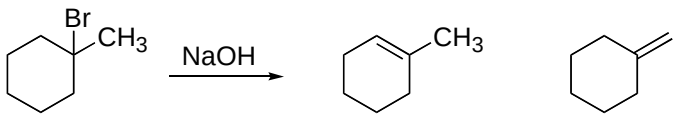
resonance
stabilized



pi bonds are not in resonance
so no resonance stabilization

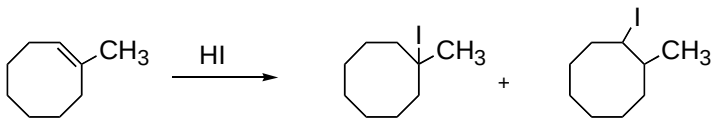
18. Using the stability arguments we have learned, label which product would be major in the following reactions. Briefly explain why.

a.



major
more substituted
double bond

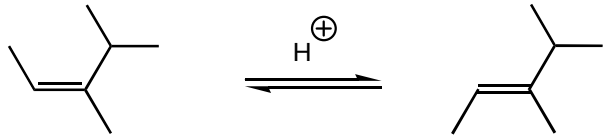
b.



major
more substituted
cation intermediate

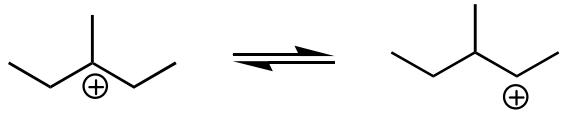
19. Using the stability arguments we have recently learned, indicate whether the product or the reactant would be favored. Briefly explain why.

a.



product: biggest groups are *trans*

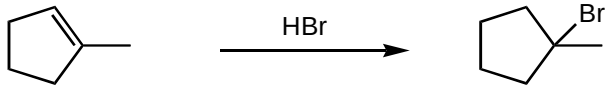
b.



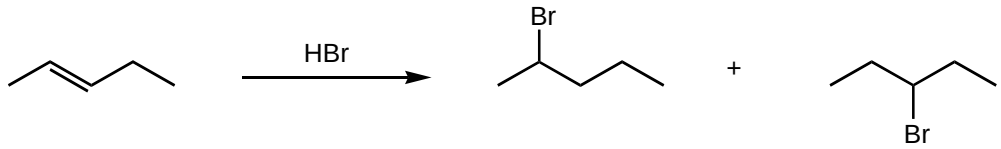
reactant: more substituted carbocation is more stable

20. Predict the major product(s) for the following reactions.

a.

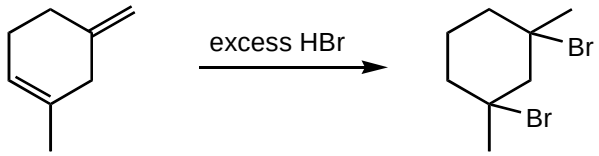


b.



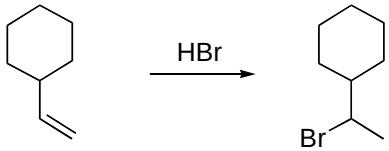
both cation intermediates are 2°, so we get both possible products

c.

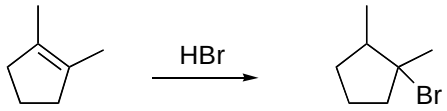


21. Determine the products of the following reactions.

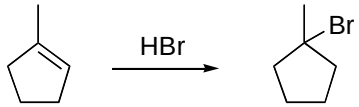
a.



b.

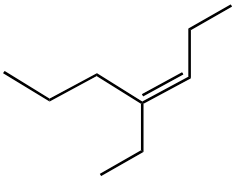


c.



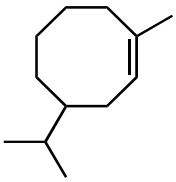
22. Name the following compounds using IUPAC nomenclature. Don't forget to include stereochemical designations where appropriate. (e.g. E, Z, cis, trans)

a.



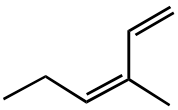
(*Z*)-4-ethyl-3-heptene

b.



(*Z*)-4-isopropyl-1-methyl-1-cyclooctene

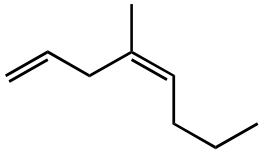
c.



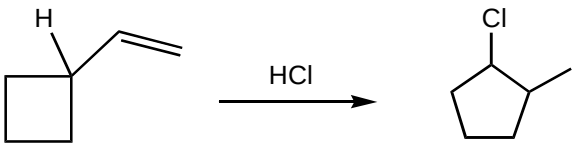
(*Z*)-3-methyl-1,3-hexadiene

23. Draw the skeletal structures corresponding to the following names. Make sure to clearly indicate stereochemistry.

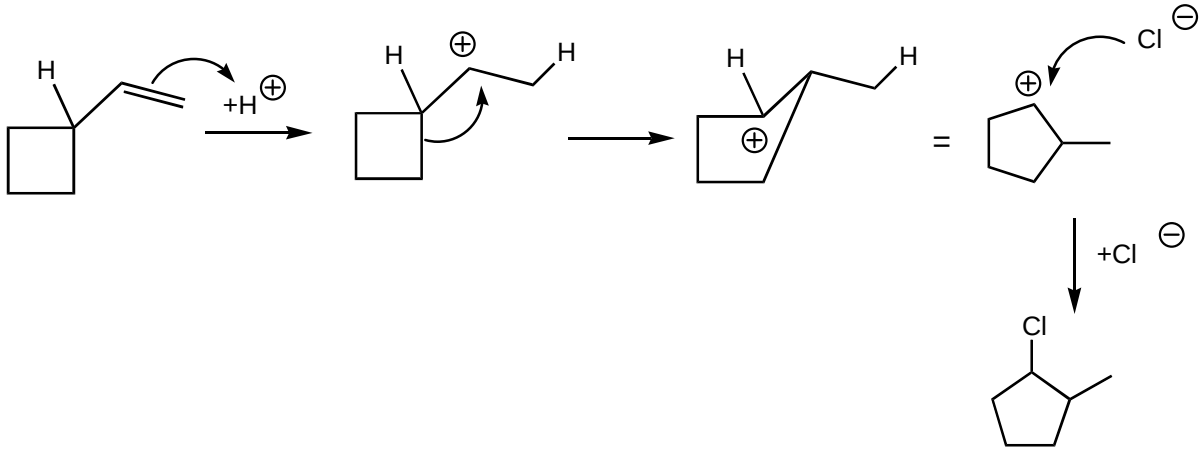
a. (*Z*)-4-methyl-1,4-octadiene



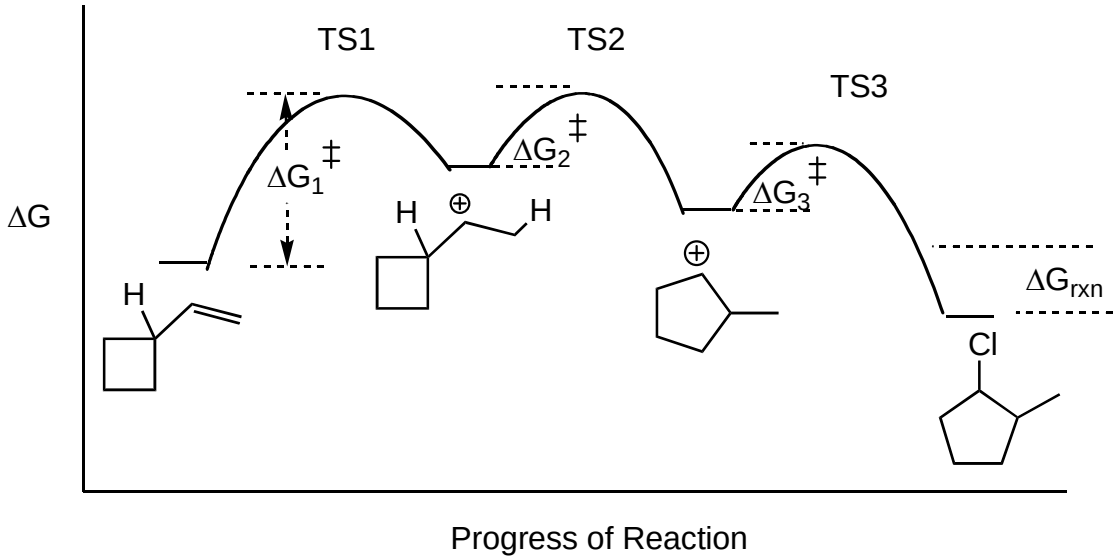
24. Consider the following reaction.



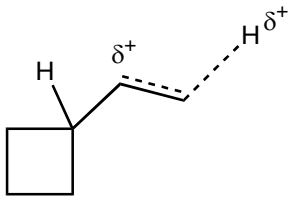
a. Draw a reasonable mechanism that accounts for the observed product. Show all steps and intermediates.



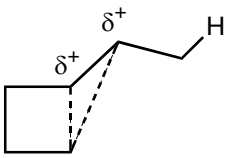
b. Draw a reaction coordinate diagram for the reaction. Label the transition state(s), intermediate(s), the energy of activation(s), and the energy of reaction.



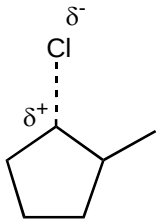
c. Draw the structure(s) of the transition state(s) using the standard conventions.



transition state #1



transition state #2



transition state #3