CHEMISTRY 112A FALL 2013

FINAL EXAM

Answer key

DECEMBER 18, 2013

NAME- WRITE BIG ______________________________

STUDENT ID: ________________

SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: ______________________

- **You will have 2 hours 50 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

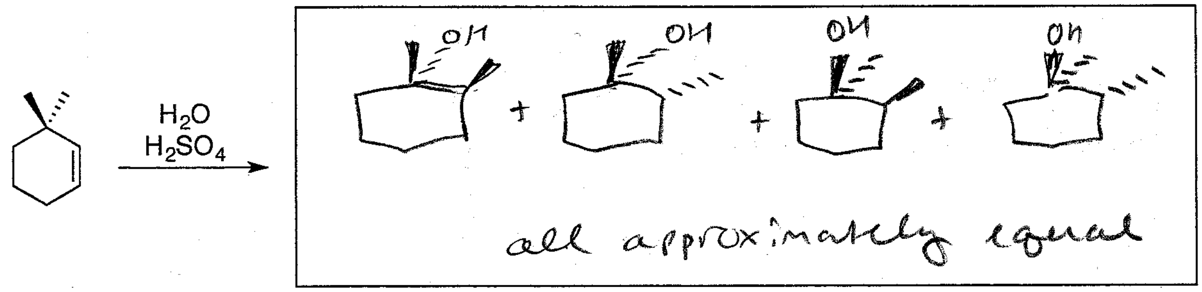
Problem	Points (Maximum)	Points (Obtained)
1	25	
2	25	
3	18	
4	18	
5	28	
6	25	
7	22	
8	18	
9	34	
10	28	
11	15	
12	24	
13	20	
Total	*300*	

1. (25 points) For each reaction:

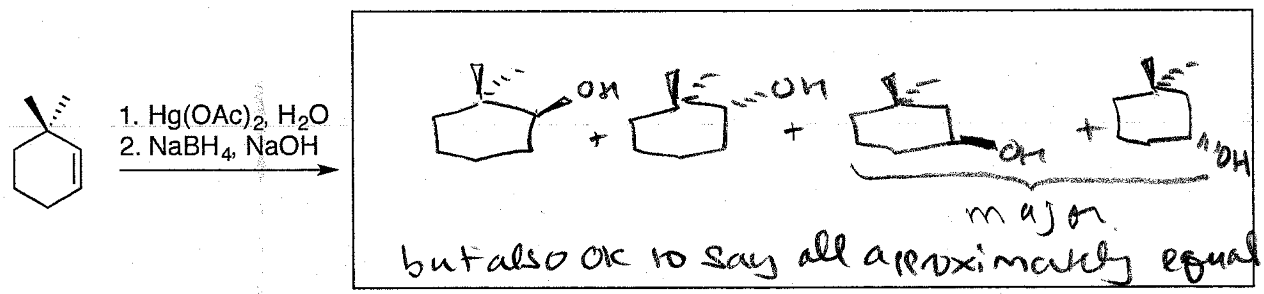
(i) Draw the major and minor organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

(ii) Label each product you draw as major or minor or equal.

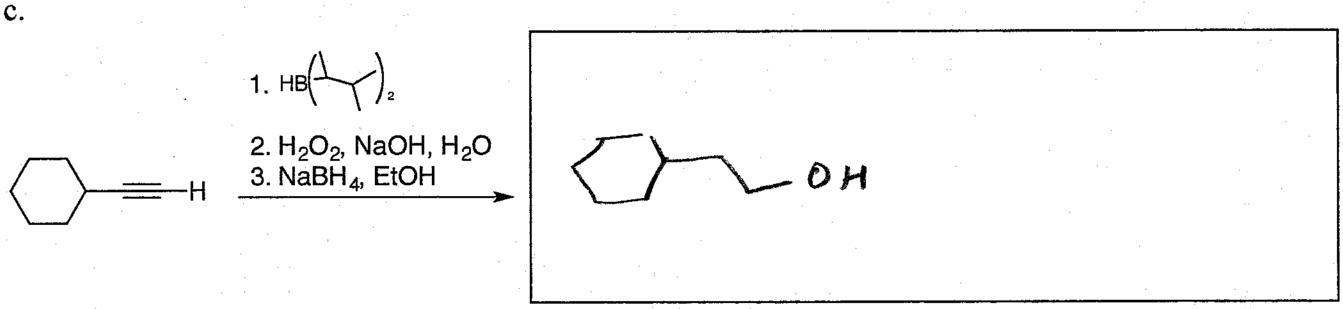
a.



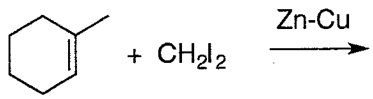
b.

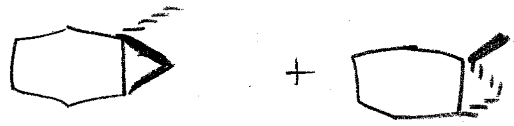


c.



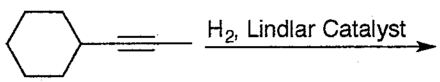
d.





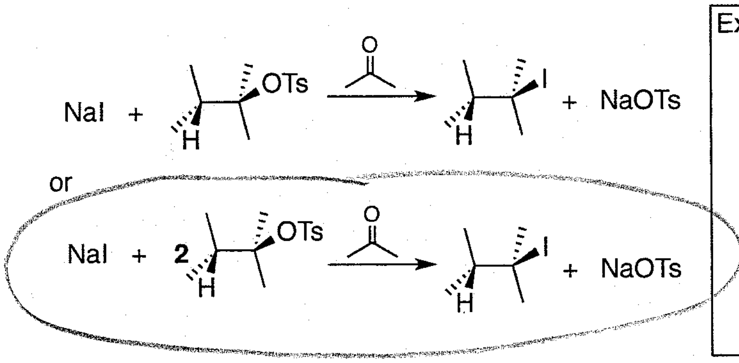
equal

e.



2. (25 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

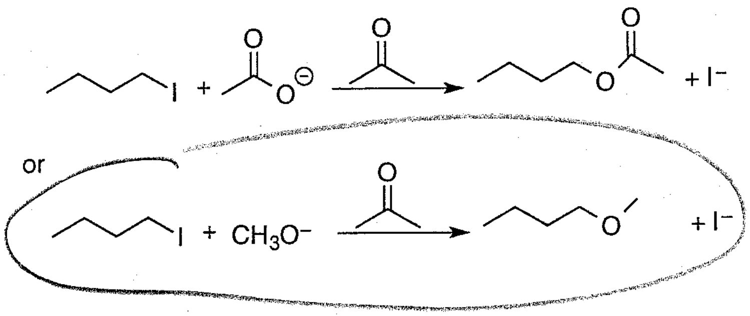
a.



Explanation

SN1 reaction.

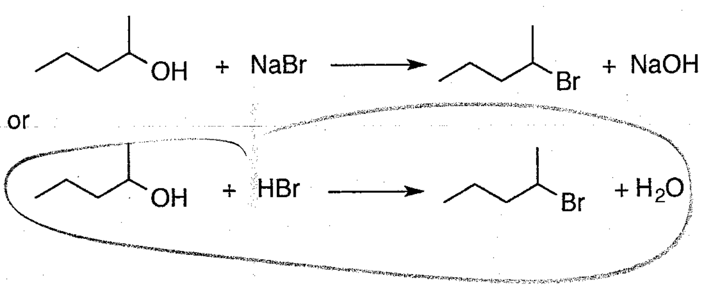
Faster w/ larger concentration of alkyl halide b.



Explanation

SN2.
−OCH3 better nucleophile than $CH_3CO_2^-$ because more basic

c.

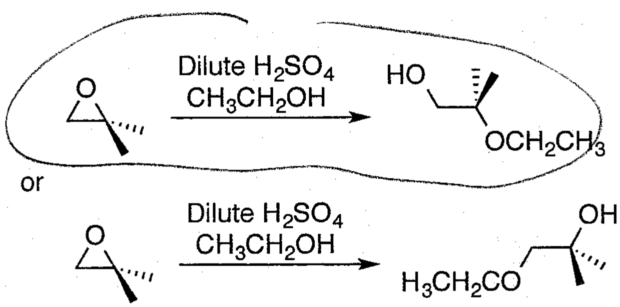


Explanation

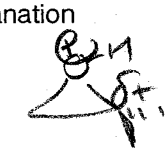
−OH very poor leaving group

H2O good leaving group

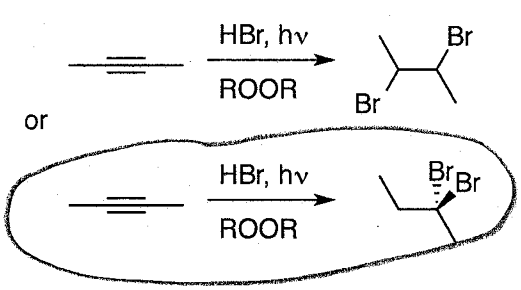
d.

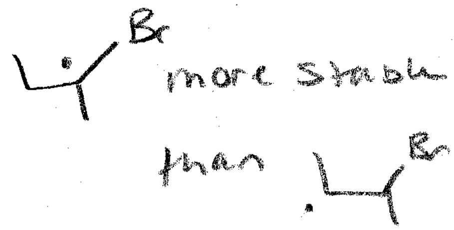


Explanation



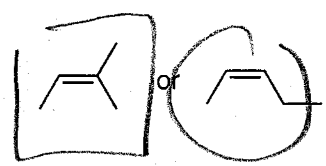
more partial positive charge on more substituted carbon e.





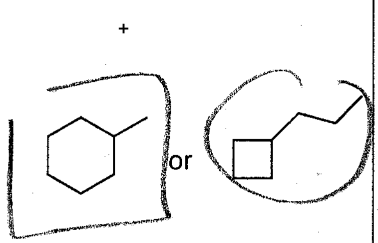
3. (18 points) Put a square around the most stable molecule and circle the molecule that has the more negative heat of combustion. Explain your choices.

a.



Explanation:
more substituted alkene is more stable

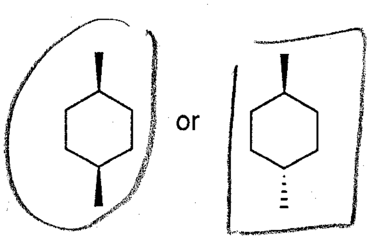
b.



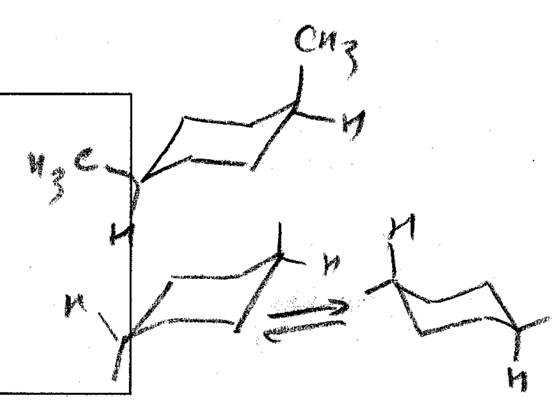
Explanation:
Ring strain makes

less stable

c.

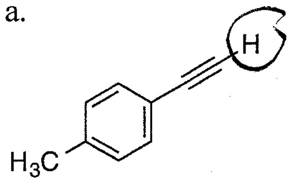


Explanation:
conformation w/ both the groups equatorial is most stable



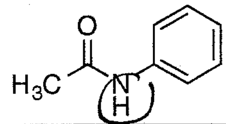
4. (18 points) For the following molecules, circle the most acidic hydrogen. Explain your choice in the box provided.

a.



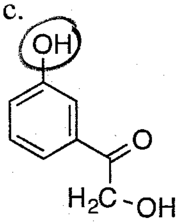
sp hybridization of alkyne C-H stabilizes anion

b.



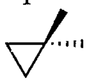
H attached to electronegative atom. Anion stabilized by resonance

c.



Anion stabilized by resonance

5. (28 points) Consider the four isomeric dimethylcyclopropanes below:


A

chiral or achiral
optically active
meso


B

chiral or achiral
optically active
meso


C

chiral or achiral
optically active
meso


D

chiral or achiral
optically active
meso

a. For each compound circle chiral or achiral.

b. Circle 'optically active' for those compounds that are optically active.

c. Circle 'meso' for those compounds that are meso.

d. Would an equal mixture of C and D be optically active?

No

e. Would an equal mixture of B and C be optically active?

Yes

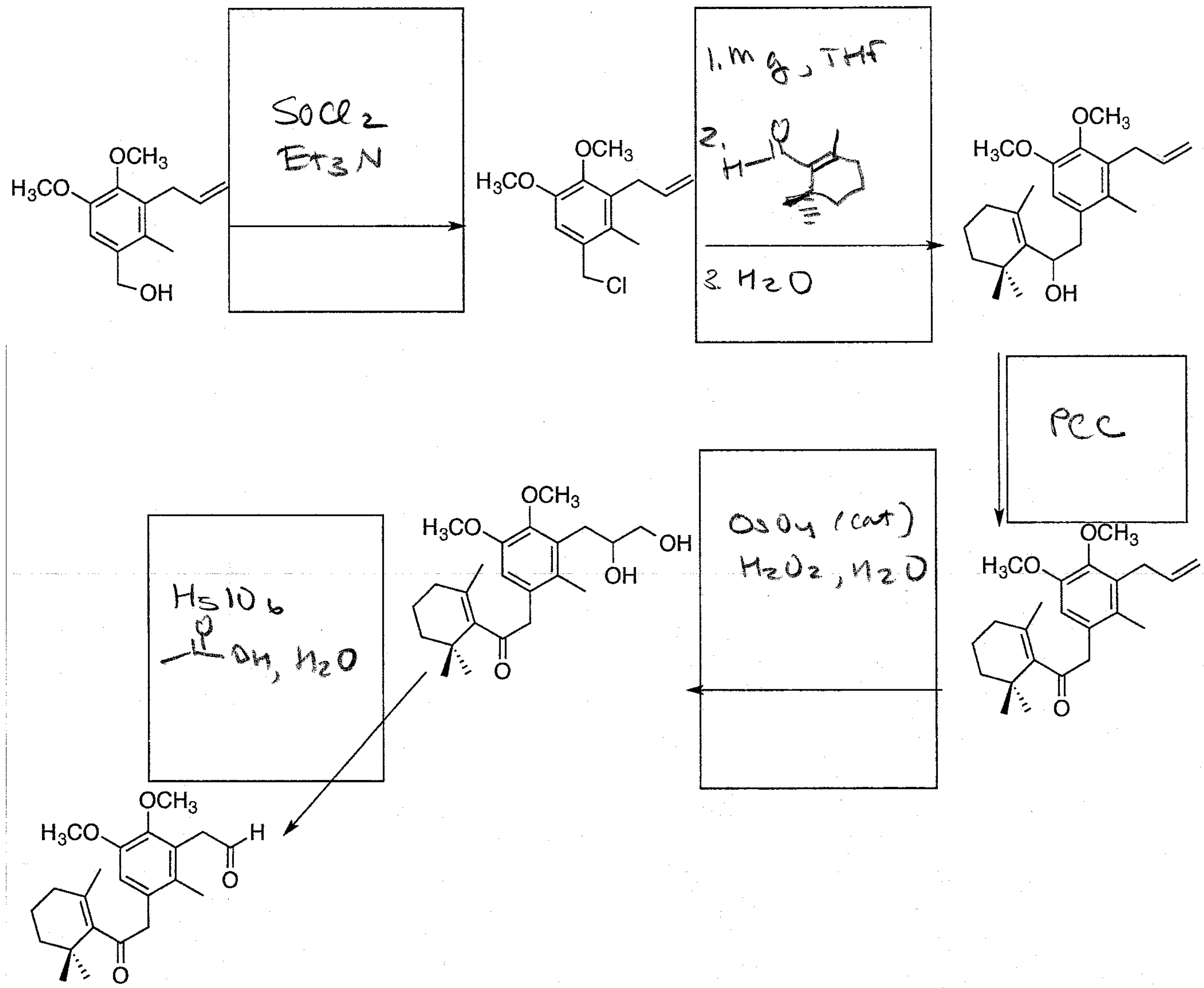
f. Are A and B enantiomers, diastereomers, constitutional isomers, or the same compound?

Costitutional isomers

g. Are B and C enantiomers, diastereomers, constitutional isomers, or the same compound?

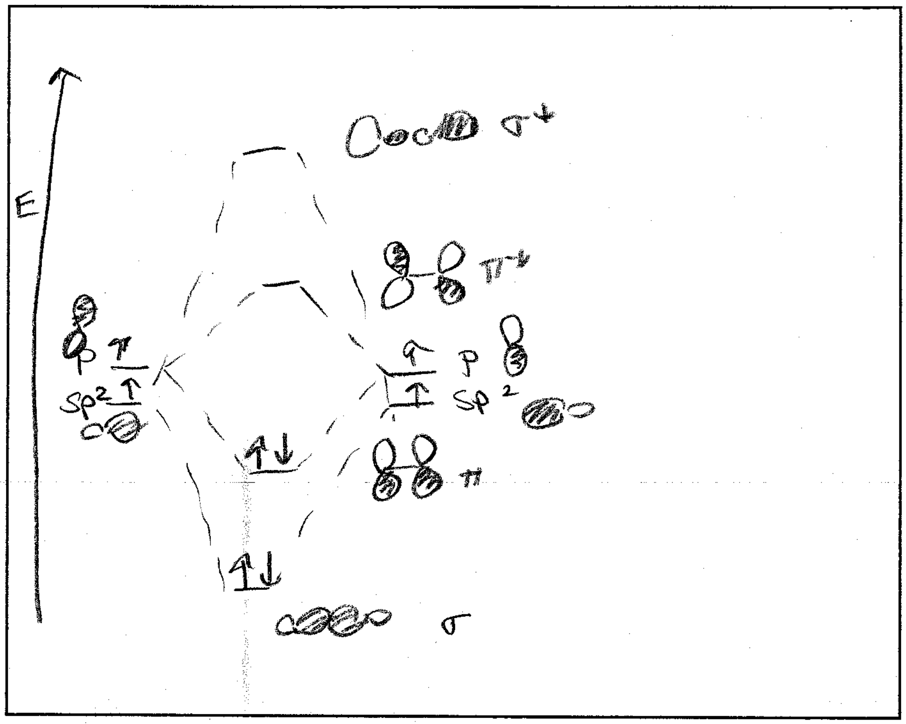
diastreomers

6. (25 points) The total synthesis of an antifungal diterpenoid was reported in the *Journal of Organic Chemistry* this year. A portion of the synthesis is shown below. Fill in the boxes with the reagents most likely used by the authors of this paper. Note that only the organic products have been drawn.



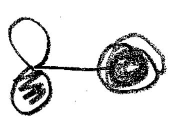
7. (22 points) Consider the alkene *cis*-2-butene:

a. Draw a molecular orbital diagram for the formation of the double bond of *cis*-2-butene. Include pictures and labels of the atomic and molecular orbitals.



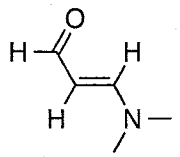
b. The conversion of *cis*-2-butene to *trans*-2-butene requires an activation energy of approximately 66 kcal/mol. Explain why this bond rotation requires so much energy.

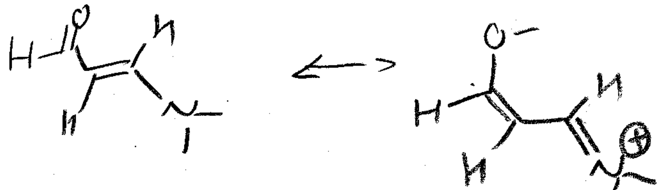
Rotation breaks π bond



No overlap when bond rotated 90°

c. In contrast to the alkenes discussed above, the bond strength of the double bond of the alkene shown below is 14.6 kcal/mol. Explain why this double bond is unusually weak. Use drawings of structures in your explanation.

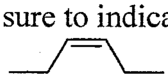


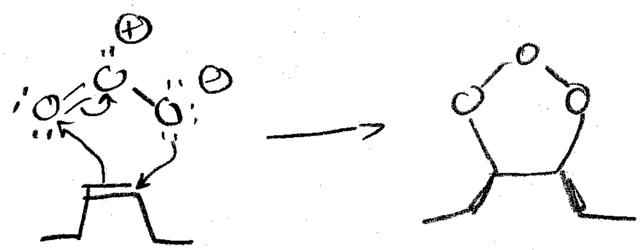


Because of resonance, the bond has single bond character & therefore, rotates relatively easily

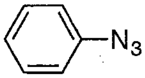
8. (18 points) You learned about 1,3-dipolar additions to alkenes this semester.

a. Draw the mechanism for the 1,3-diploar addition of ozone to *cis*-3-hexene. You only need to draw the first 1,3-dipolar addition to form the initial ozonide. Use arrows to show the flow of electrons. Make sure to indicate the stereochemistry of the product(s).

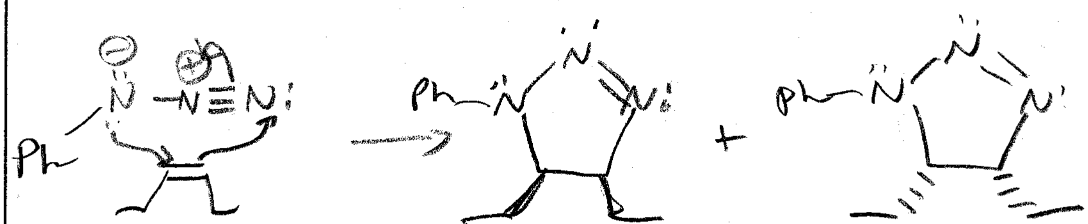




b. Similar 1,3-dipolar additions to alkenes can take place with other reagents, such as azides. Draw the mechanism for the 1,3-dipolar addition of the azide shown below to *cis*-3-hexene. Use arrows to show the flow of electrons. Make sure to indicate the stereochemistry of the product(s).



phenylazide

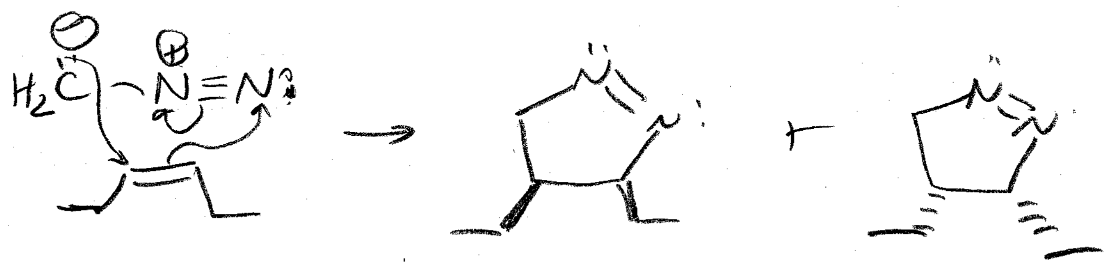


c. In class, we discussed diazomethane as a starting material to form a carbene. However, diazomethane can also react with alkenes by a 1,3-dipolar addition mechanism similar to those you drew in parts a and b.

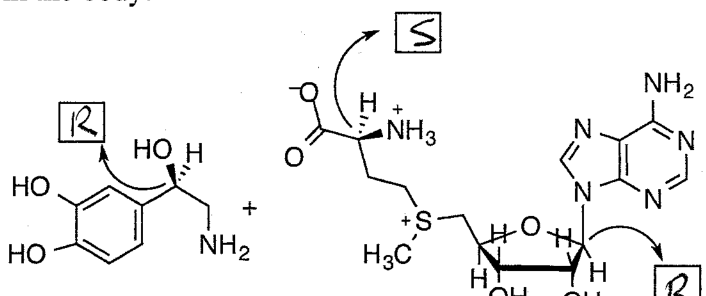
$H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N:$

diazomethane

Draw a mechanism for the 1,3-dipolar addition of diazomethane to *cis*-3-hexene using arrows to show the flow of electrons. Make sure to indicate the stereochemistry of the product(s).



9. (34 point) Epinephrine (adrenaline) is made from norepinephrine and SAM (S-adenosylmethionine) in the body.



Norepinephrine

SAM

a. Assign the indicated asymmetric carbons as R or S in the boxes provided.

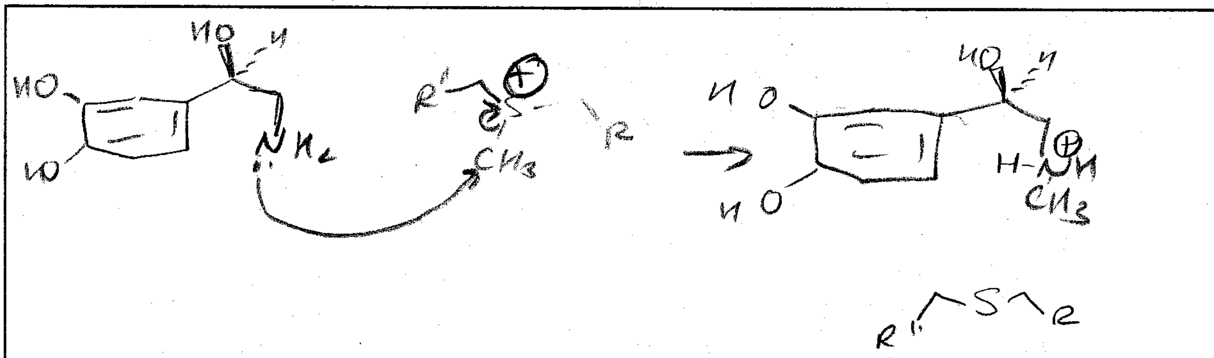
b. What is the most nucleophilic atom in norepinephrine? Explain your choice.

NH_2. most basic & nucleophilic

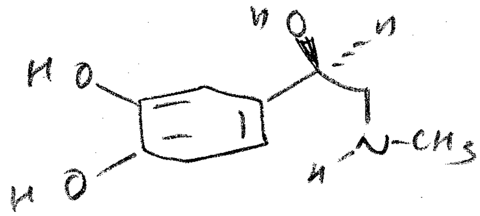
c. What is the most electrophilic and reactive bond in SAM? Explain your choice.

$H_3C-S^{\oplus}$ bond. Good leaving group. least sterically hindered C-S bond

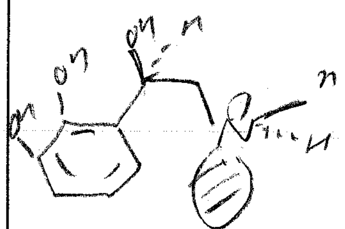
d. Draw a mechanism for the reaction between norepinephrine and SAM, using arrows to indicate the flow of electrons. You may abbreviate sections of the molecules with R or R' in the mechanism.



e. Draw of the full structure of the product (Epinephrine) without abbreviations such as ‘R’.

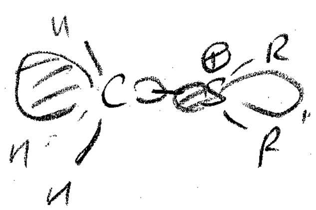


f. Sketch the orbital on norepinephrine that participates in the reaction. Label, identify, and draw a picture of this orbital that shows where the orbital is located in the molecule. You may abbreviate sections of the molecule with R or R’.



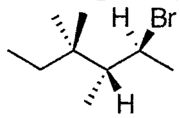
lone pair on N
sp^3 hybridized

g. Sketch the orbital on SAM that participates in the reaction. Label, identify, and draw a picture of this orbital that shows where the orbital is located in the molecule. You may abbreviate sections of the molecule with R or R’.



σ* of C–S bond

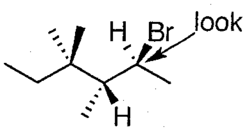
10. (28 points) Consider the molecule below:

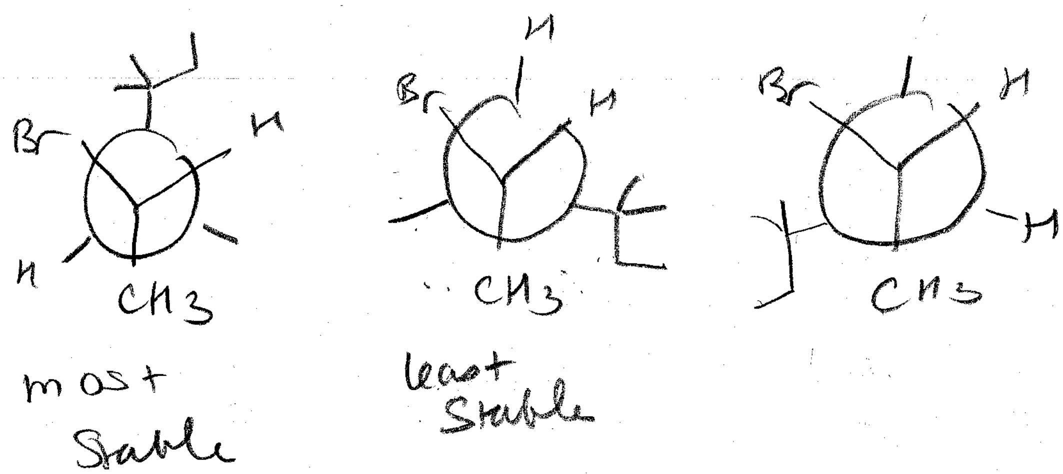


a. What is the name of this molecule?

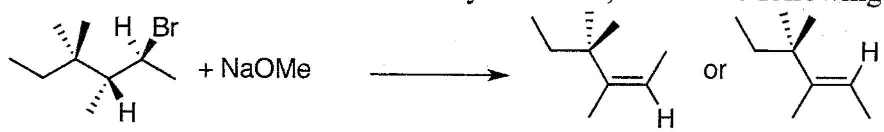
(2S,3R)-2-bromo-3,4,4-trimethylhexane

b. Draw Newman projections of the three staggered structures looking down the bond indicated with the arrow. Label the most and least stable staggered conformation. (*Hint*: Br is smaller than CH_3.)

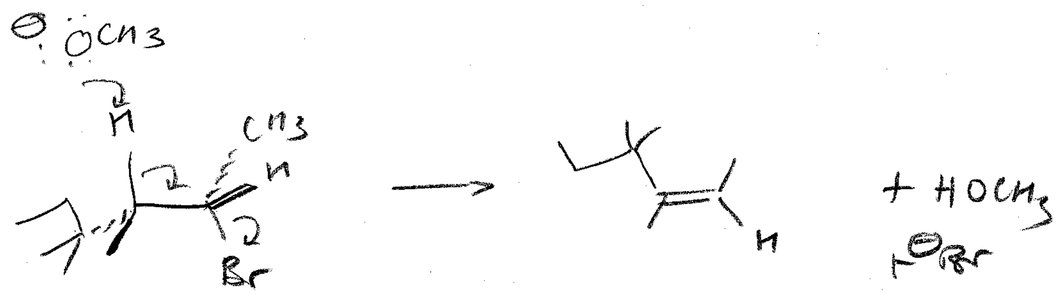




c. When NaOMe is added to this alkyl bromide, one of the following alkenes is formed.

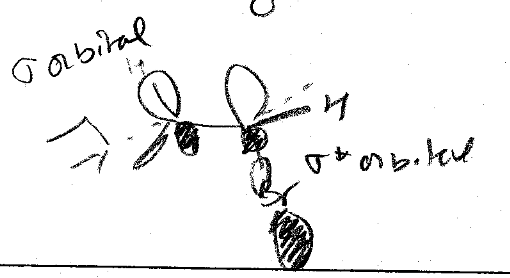


Circle the alkene that forms. Draw the mechanism for the formation of this alkene product using arrows to show the flow of electrons.

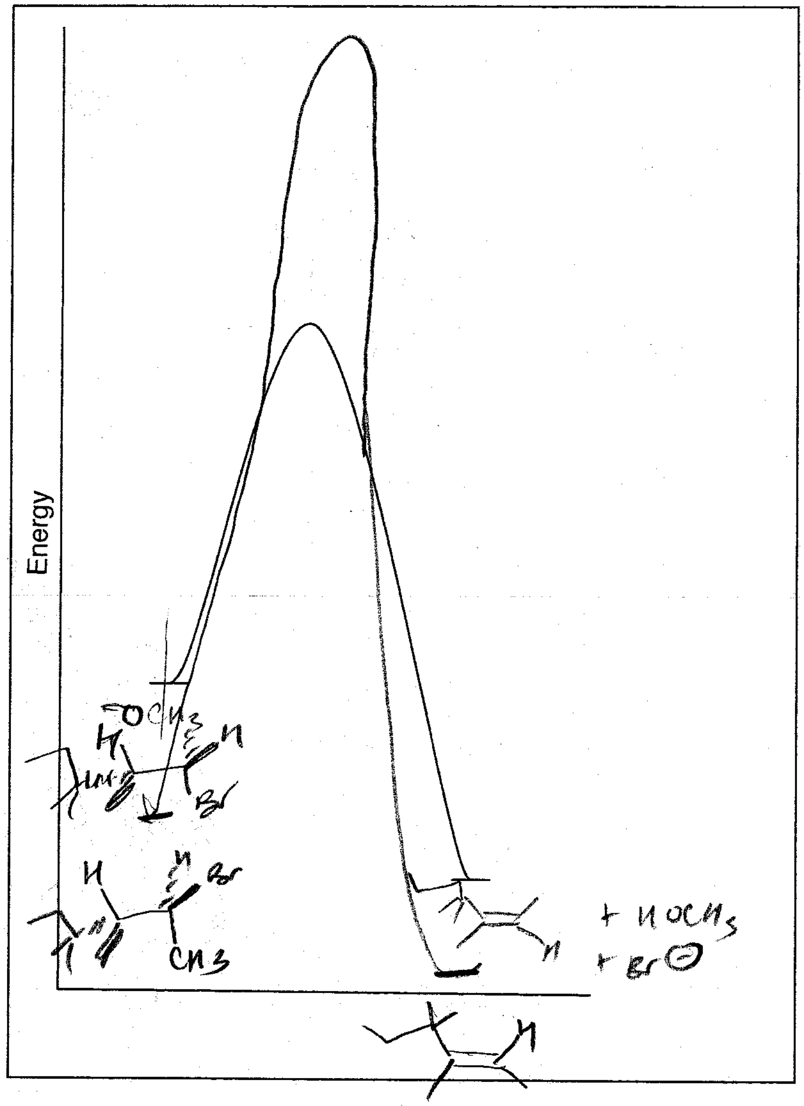


d. Explain why only one of the two alkenes is formed in this reaction.

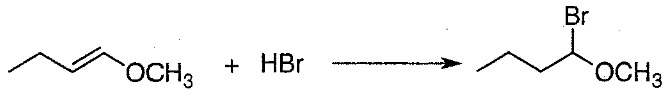
Antiperiplanar geometry is preferred to maximize orbital overlap.



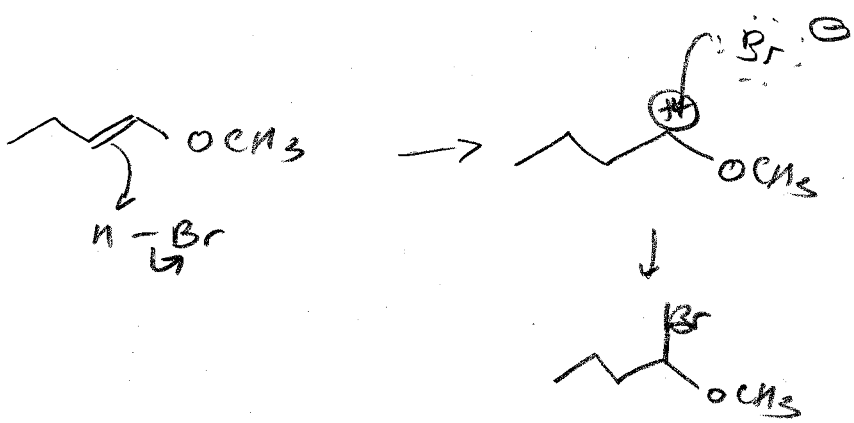
e. A reaction coordinate diagram is shown below.
i. Label the diagram to represent the reaction you drew in part c of this problem.
ii. Add to the diagram a curve that represents the reaction to form the alkene product that is not observed in part c of this problem.



11. (15 points) Consider the following addition of HBr to a methoxy substituted alkene.

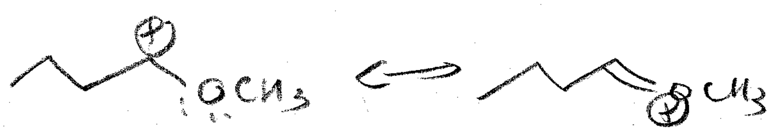


a. Draw the mechanism for this reaction, using arrows to indicate the flow of electrons.

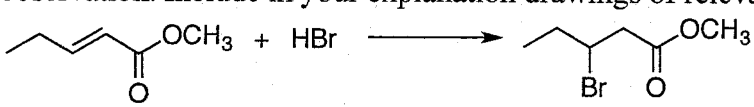


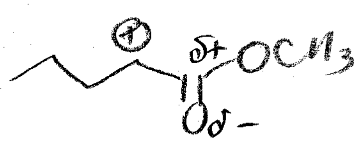
b. Explain why this reaction is regioselective. Include drawings of relevant structures.

Because carbocation is stable:



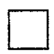
c. The alkene substituted with an ester group gives a different regioselectivity of addition. Explain this observation. Include in your explanation drawings of relevant structures.





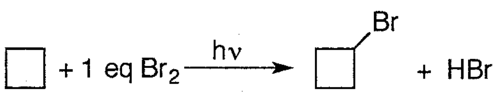
Not stabilized by resonance
Destabilized by inductive effects - ⊕ adjacent to δ+

12. (24 points) Consider cyclobutane and bicyclo[1.1.0]butane shown below:

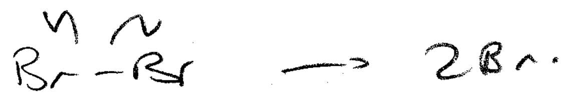

cyclobutane


bicyclo[1.1.0]butane

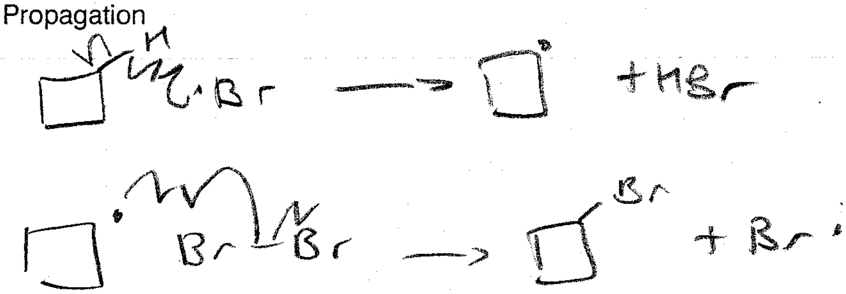
a. Cyclobutane reacts with bromine to give bromocyclobutane. Write the mechanism of this reaction using arrows to show the flow of electrons. Include initiation steps and one termination step.



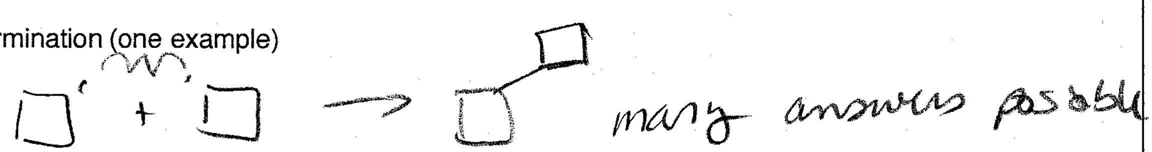
Initiation



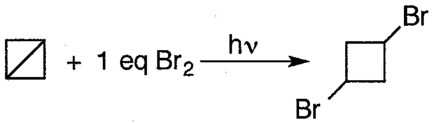
Propagation



Termination (one example)



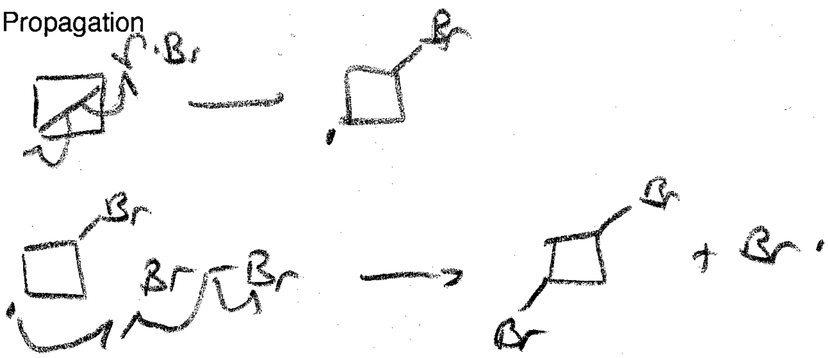
b. Bicyclo[1.1.0]butane reacts with bromine to give 1,3-dibromocyclobutane. Write the mechanism of this reaction using arrows to show the flow of electrons.



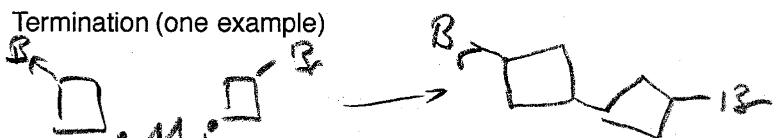
Initiation

$Br-Br \longrightarrow 2\ Br\cdot$

Propagation



Termination (one example)



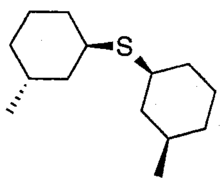
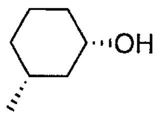
many possible answer

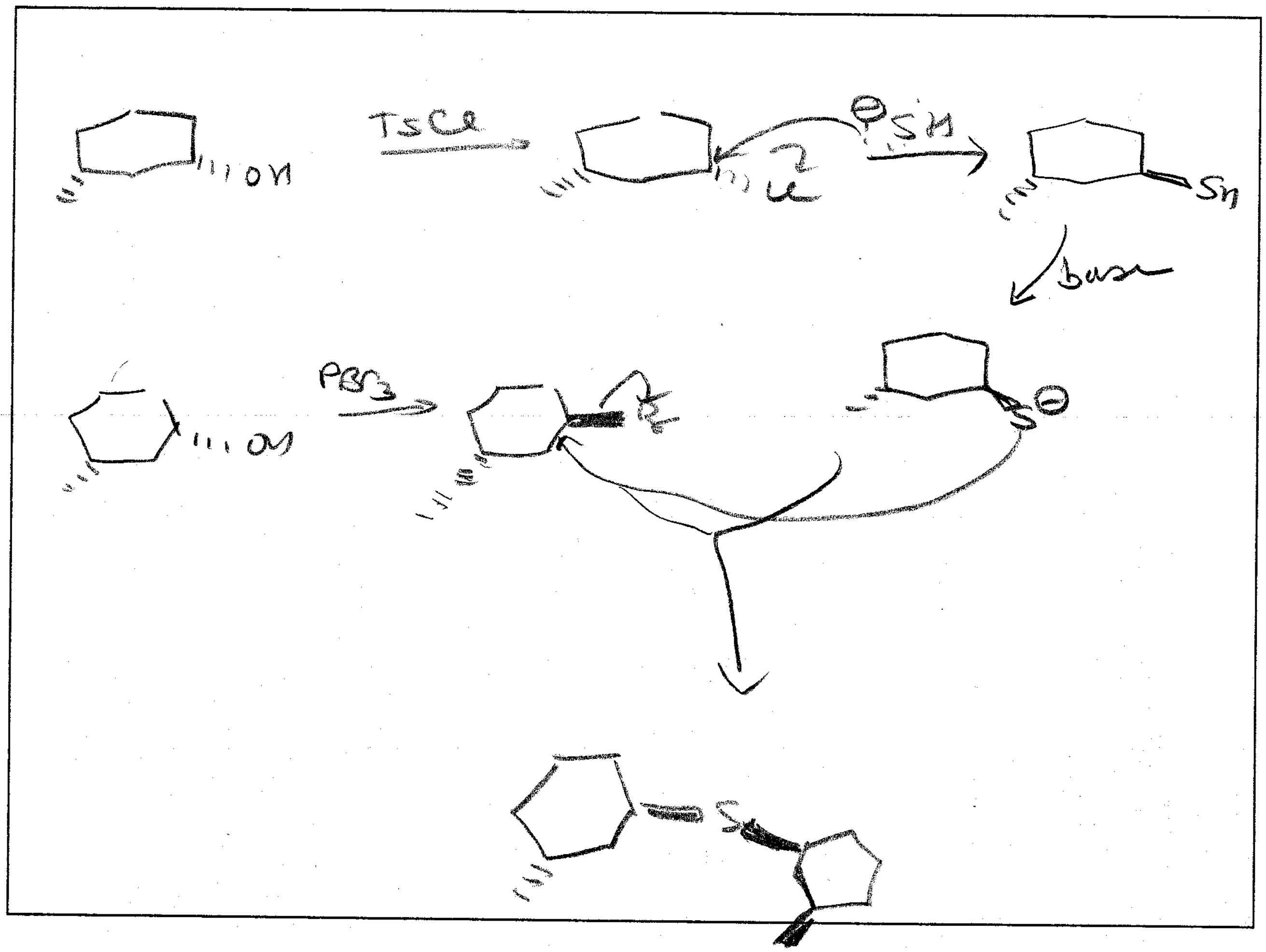
c. Explain why addition of 1 equivalent of bromine to cyclobutane produces a monobrominated product and HBr, while addition of 1 equivalent of bromine to bicyclo[1.1.0]butane produces a dibrominated product and no HBr.

C–C bond in  weak because of ring strain

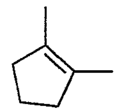
13. (20 points) Synthesize the molecules from the indicated starting materials.

a. Every carbon in the product must come from the indicated methylcyclohexanol.

Make:  from 



b. For the following problem, one of the carbons in the product comes from an added reagent.

Make:  from: