CHEMISTRY 112A FALL 2014

Answer Key

EXAM 2

OCTOBER 28, 2014

NAME- WRITE BIG _____

STUDENT ID: _____

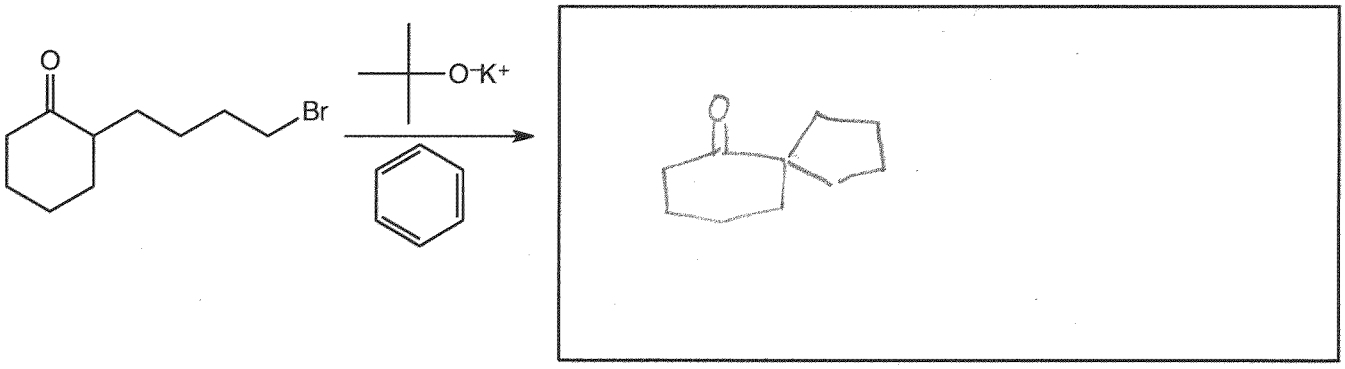
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **You will have 75 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**

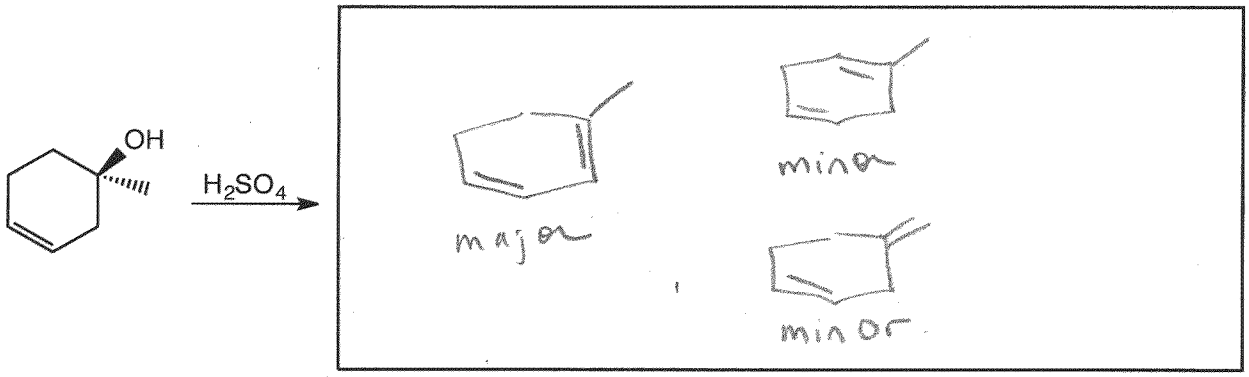
Problem	Points (Maximum)
1	25
2	15
3	11
4	11
5	13
6	25
Total	*100*

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.

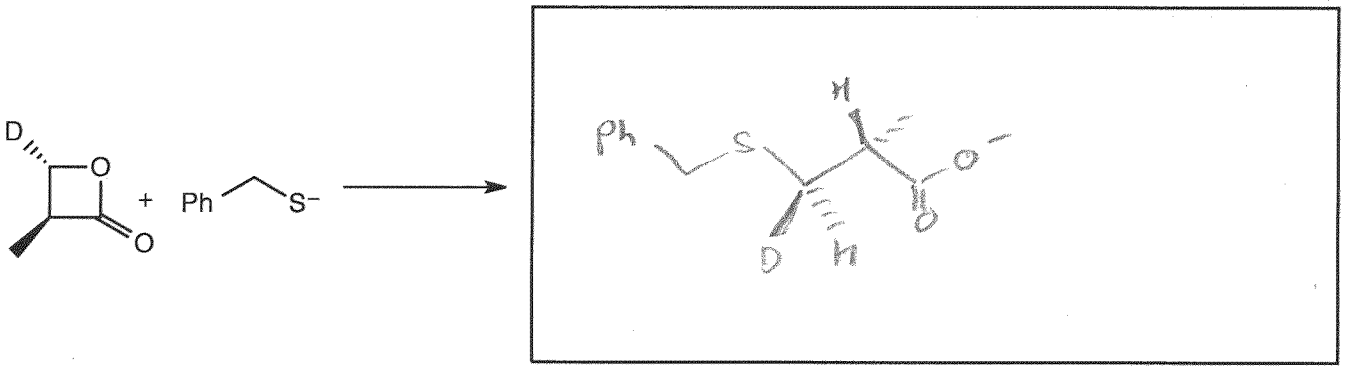
a.



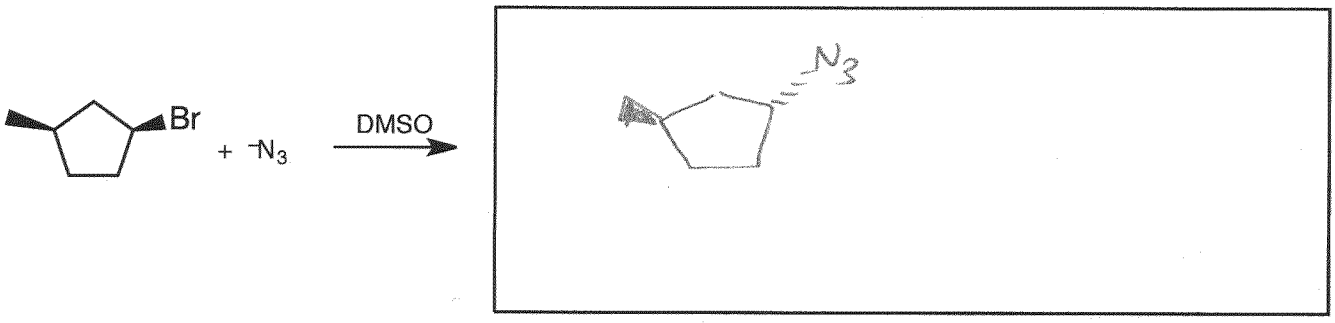
b.



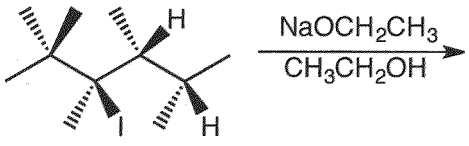
c.

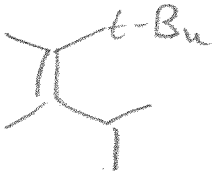


d.



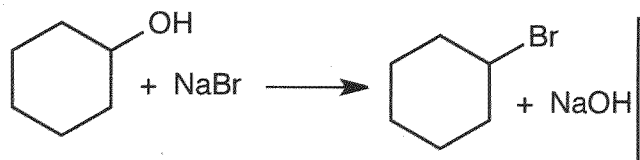
e.



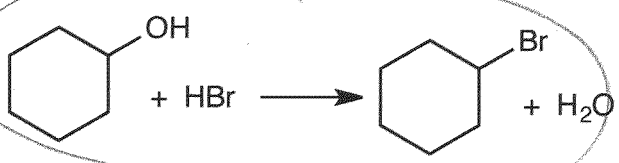


2. (15 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

a.



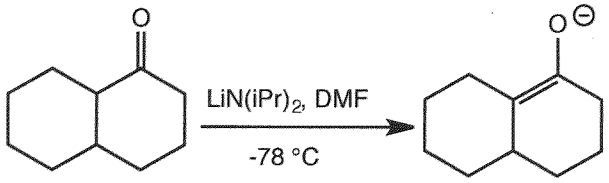
or



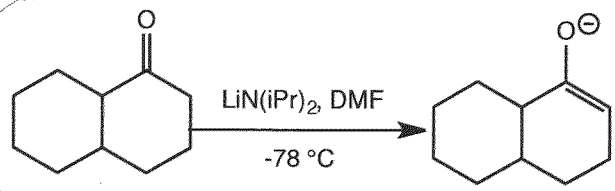
explanation:

Addition of HBr converts poor leaving group -OH to good leaving group H_2O.

b.



or

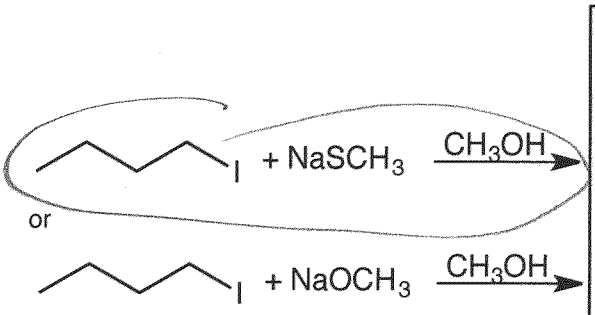


explanation:

less hindered enolate is formed fastest.

(strong base & low temp ensure rxn is not reversible)

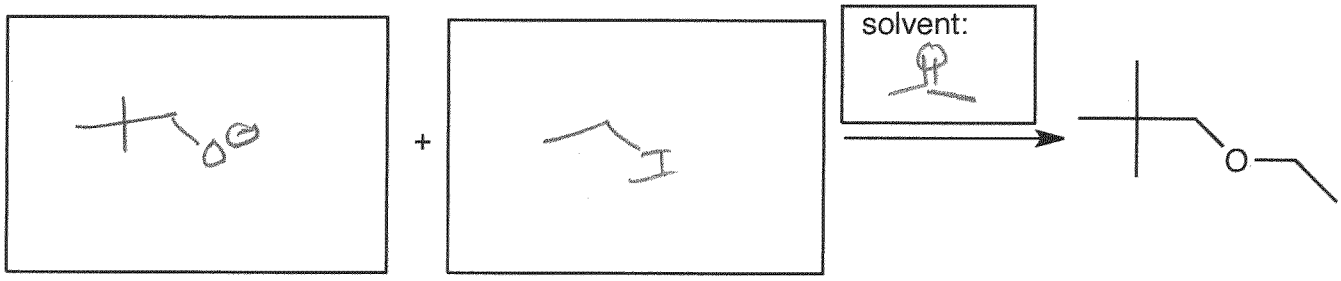
c.



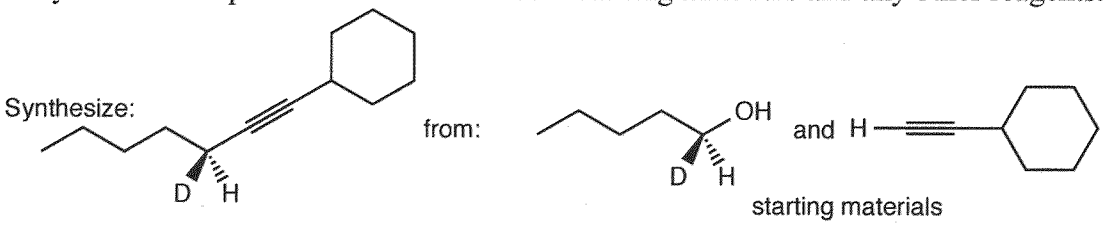
explanation: SN2 – Rate depends on nucleophile
$-SCH_3$ is a better nucleophile in polar protic solvent. The sulfur is down the column of periodic table. Therefore, it is larger and more polarizable & also less solvated than $-OCH_3$

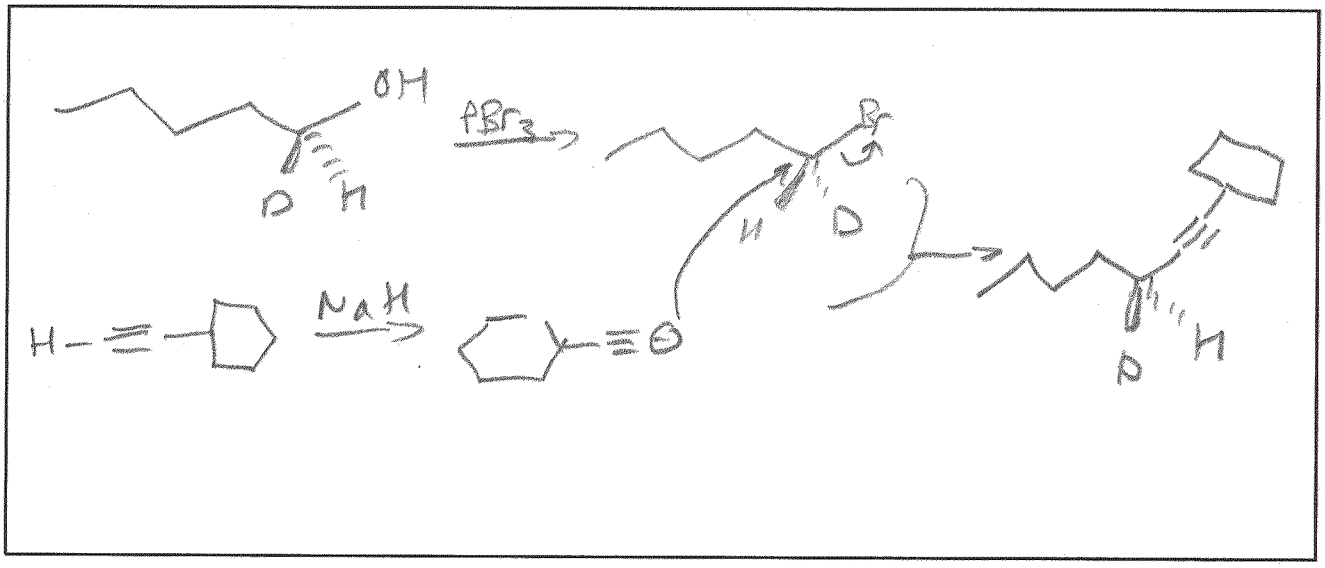
3. (11 points) Predict starting materials and plan synthesis.

a. Fill in the boxes in the following reactions. Note that only the organic products have been drawn.

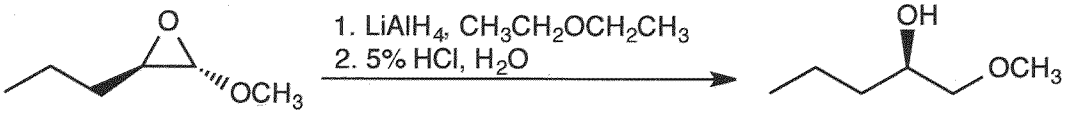


b. Synthesize the product from the indicated starting materials and any other reagents.

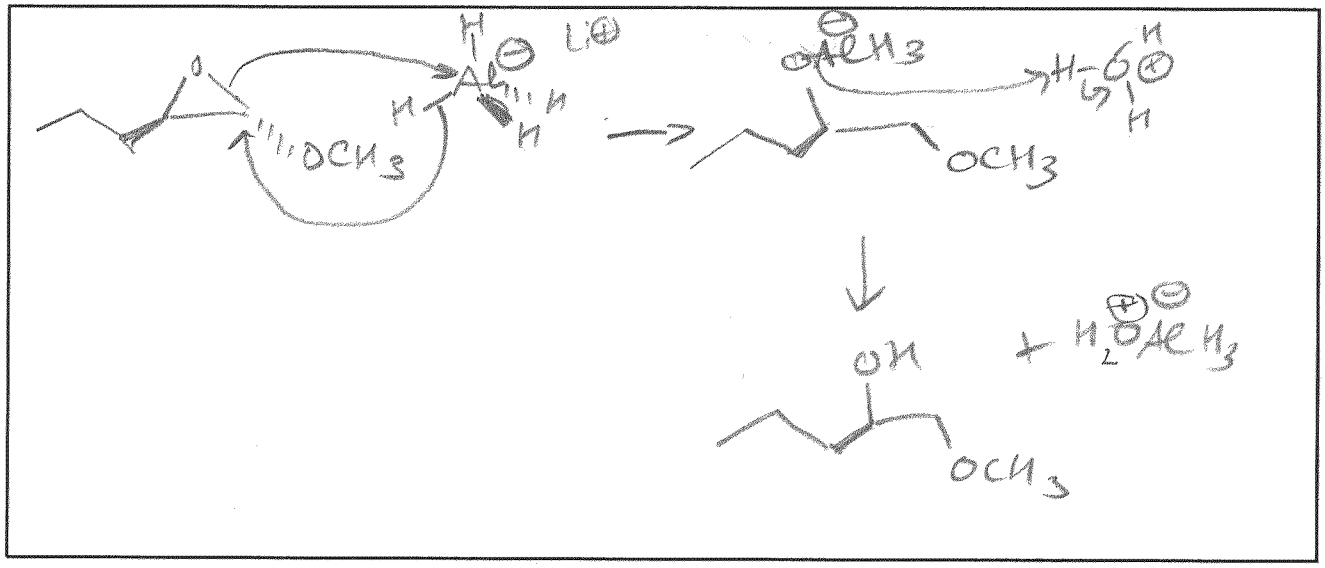




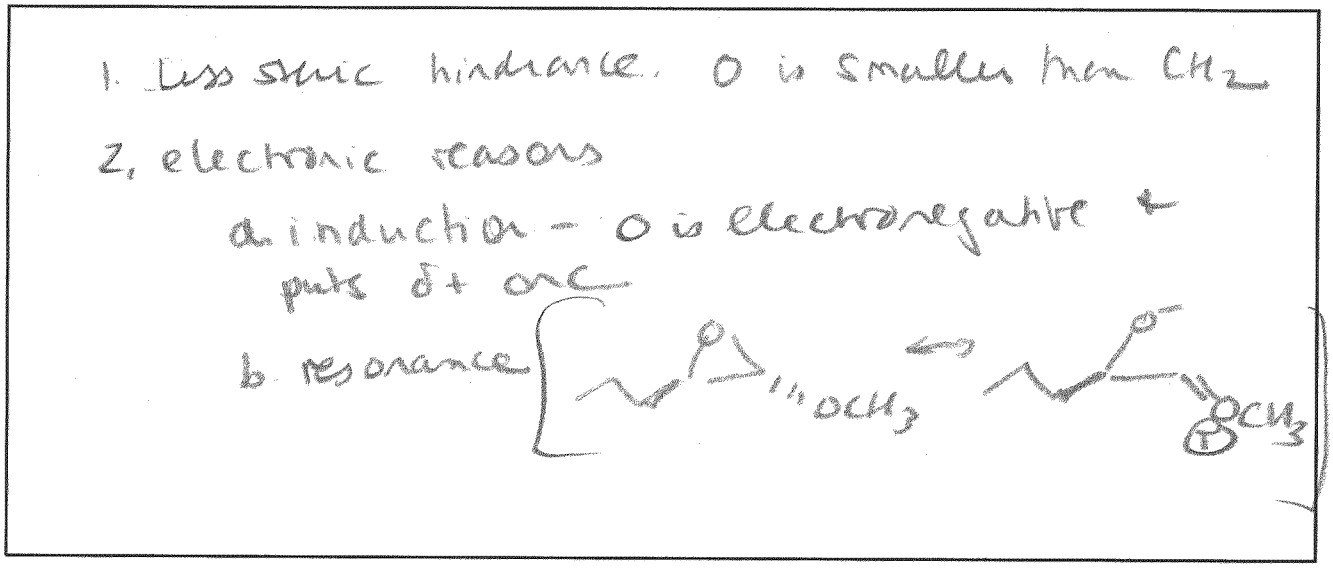
4. (11 points) Consider the following reaction, which produces the major product shown.



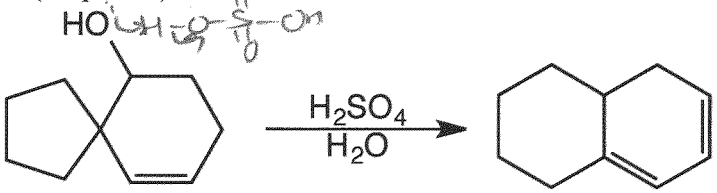
a. Draw a mechanism for the reaction using arrows to show the movement of electrons. You need only show one reaction of $LiAlH_4$ with the epoxide.

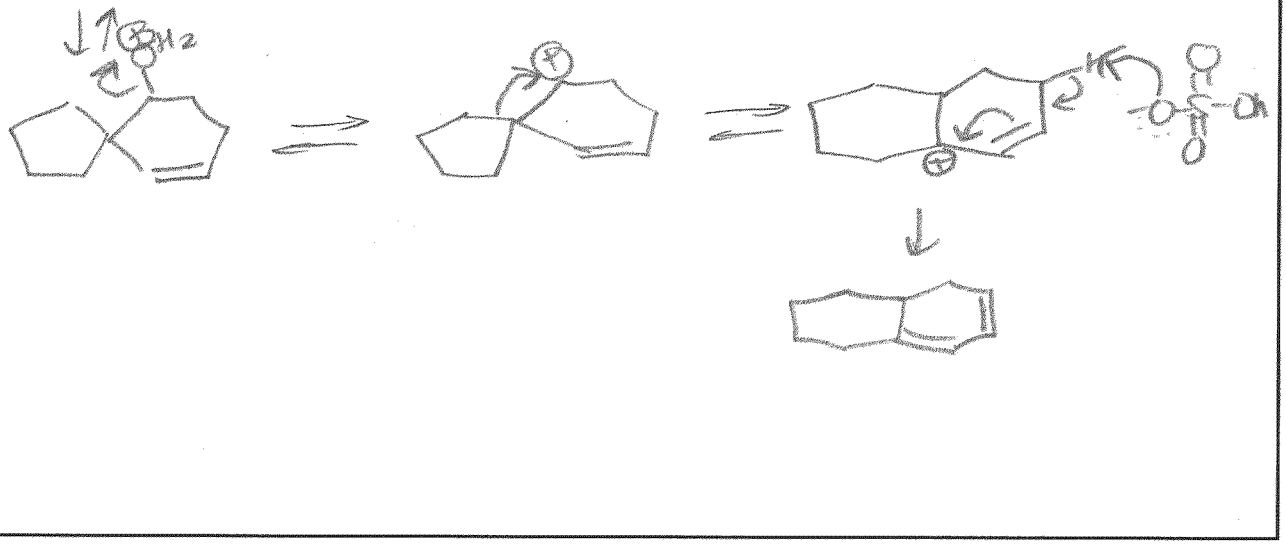


b. Give two reasons for why the epoxide reacts with $LiAlH_4$ at the carbon with the OCH_3 group.

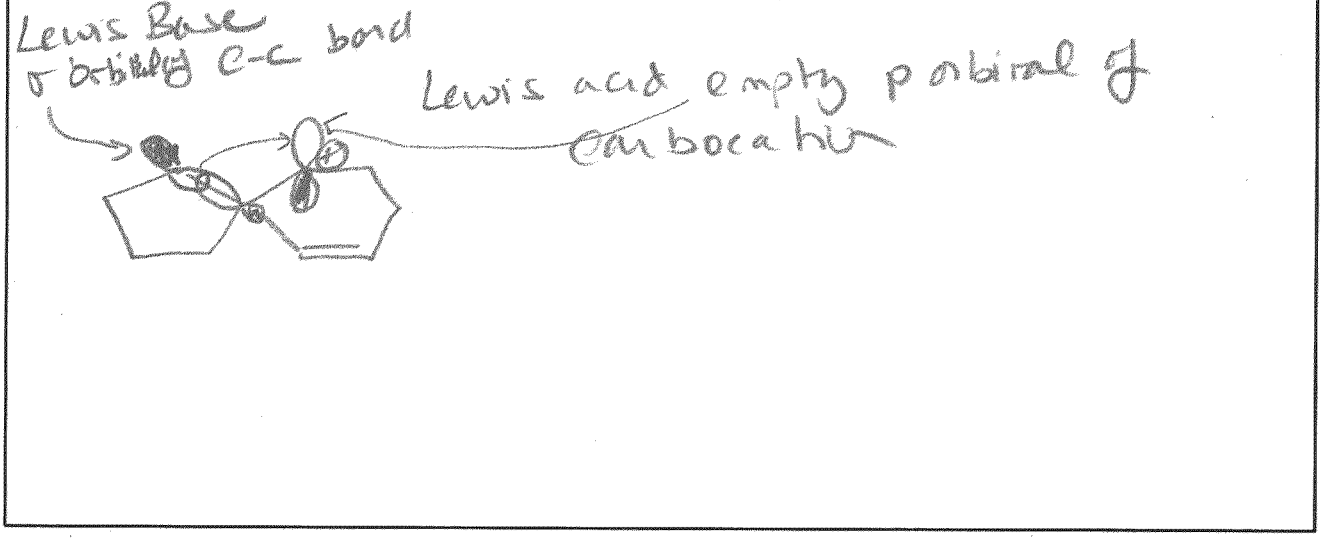


5. (13 points) a. Draw a mechanism for the reaction using arrows to show the movement of electrons.

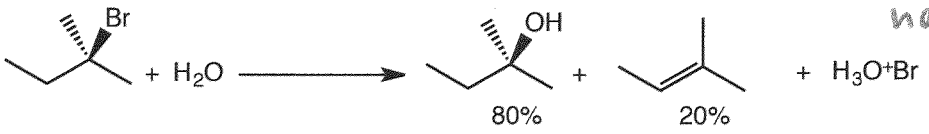




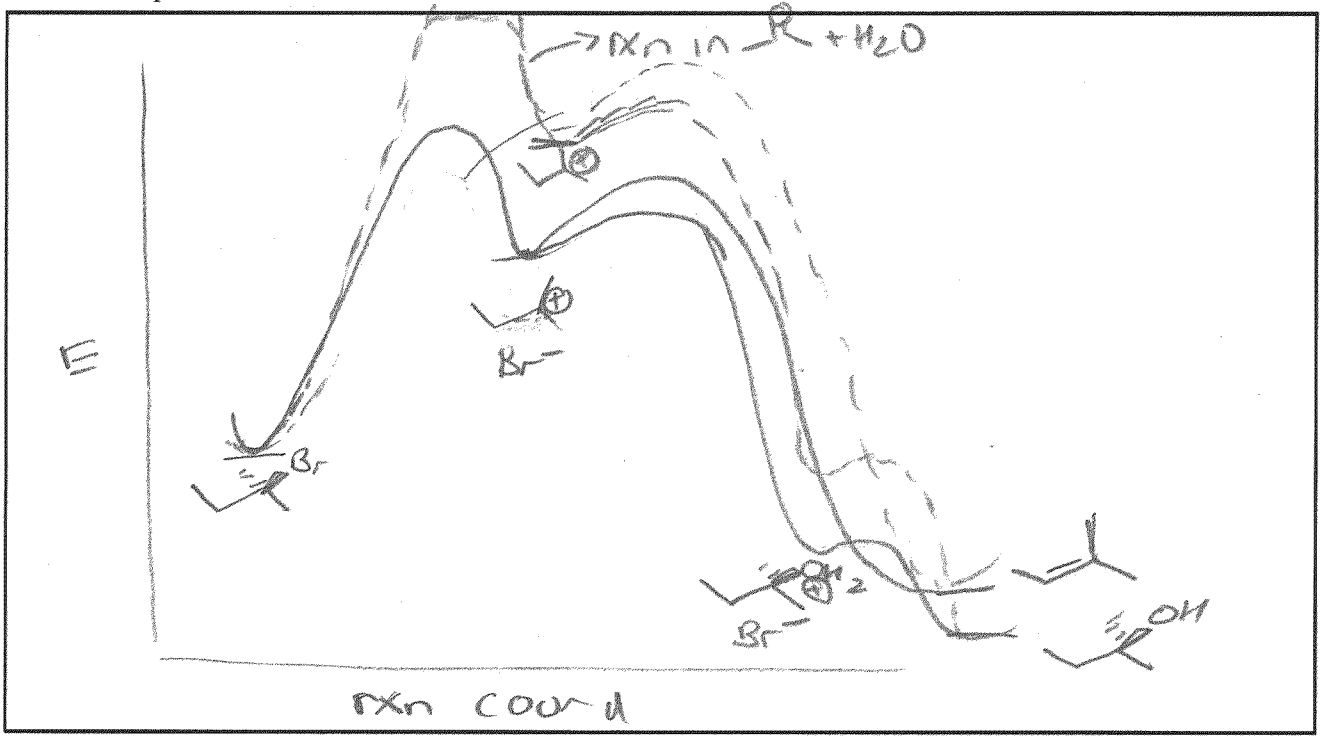
b. Sketch and label the orbitals that are involved in the alkyl shift step of this reaction. Sketch the orbitals on a line drawing representation of this step of the reaction. Identify which orbital is acting as a Lewis acid and which is acting as a Lewis base.



6. (25 points) The ratio of elimination to substitution products for the hydrolysis of 2-bromo-2-methylbutane is shown below. For this question, assume this rxn is under kinetic control & is not reversible



a. Draw a reaction energy diagram below for this reaction showing formation of both substitution and elimination products. Draw all intermediates.



b. Suppose that 90% acetone/10% water is used instead of water.

i. Would you expect the reaction to proceed at a faster or slower rate than is observed in water?

ii. Modify the reaction energy diagram you drew in part A to illustrate your answer. dotted line

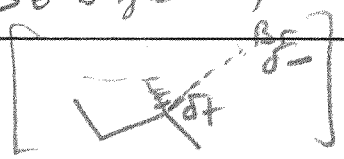
iii. Include in your explanation a sketch of the transition state of the rate determining step.

Slower in 90% R 10% H_2O.

The starting materials are not charged & therefore, stability not affected by solvation.

The 1st step to form carbocation is rate determining.

The carbocation & halide are less stable in less solvating solvent. T.S. for this step resembles carbocation because endothermic & Hammond postulate. Therefore, TS is less stable in less solvating solvent, $\Delta G^\ddagger$ is greater, & rxn is slower



c. If 2-iodo-2-methylbutane is used instead of the 2-bromo-2-methylbutane under the same conditions, will the reaction go faster or slower? Explain your answer.

Faster. RDS is leaving group leaving. I^- is a better leaving group than Br^- because I^- is a weaker base because it is down column in periodic table.

d. Would you expect the same or different product ratios for the hydration of the 2-iodo-2-methylbutane as is observed for the 2-bromo-2-methylbutane? Assume both reactions are under kinetic control and are not reversible. Explain your answer.

Same product ratios. The intermediate carbocation is the same for both reactions; Therefore, the product determining step is the same for both reactions,

(If leaving group does not fully leave, then ratios can be different)