CHEMISTRY 3A SPRING 2012

EXAM 2

MARCH 21, 2012

Answer Key

NAME _____

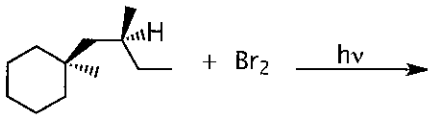
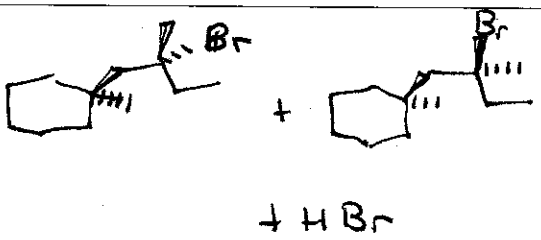
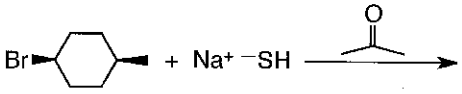
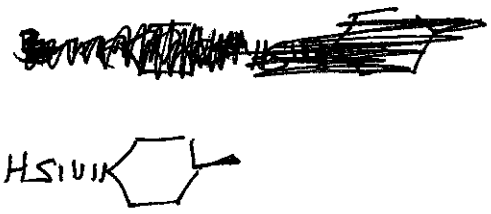
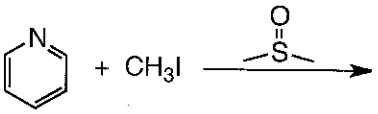
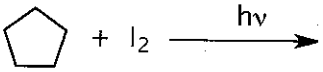
SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: _____

STUDENT ID: _____

- **You will have 2 hours in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

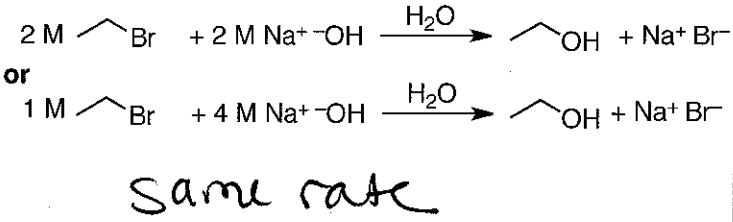
Page	Points (Maximum)	Points (Obtained)
2	30	
3	30	
4	24	
5	22	
6	23	
7	21	
8	29	
9	21	
Total	*200*	

1. (30 points – each part is 6 points) **Predict the major products** formed in the reactions below. For each reaction **identify the type of mechanism**: S_N2, S_N1, E1, E2, radical halogenation, or Brønsted acid/base. Write NR if you think there will be no reaction. Be careful to indicate the stereochemistry of the products.

	Product(s)	**Mechanism Type**
a. 	 + HBr	radical halogenation
b. 		S_N2
c. 		S_N2
d. 	NR	
e. $CH_3O^-Na^+ + HBr \longrightarrow$	$CH_3OH + NaBr$	Acid/ Base

2. (14 points – 7 points each part) Which reaction in the following pairs of reactions would you expect to go faster? It is possible that both reactions have the same rate. Give brief, 2 sentence, explanations for your answers in the box provided.

a.



Same rate

Explanation: SN2 reactions are bimolecular or 2nd order

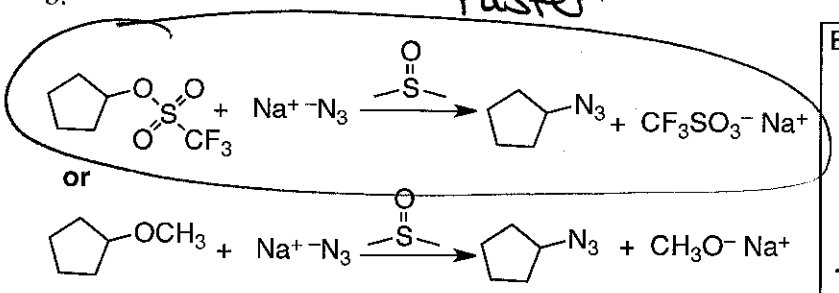
Rate = k_2[Br][OH]

Rxn 1 = k_2[2M][2M] = 4k_2

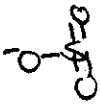
Rxn = k_2[1M][4M] = 4 k_2

Reactions will have the same rate.

b. Faster



Explanation:



is a good leaving group because it is a weak base

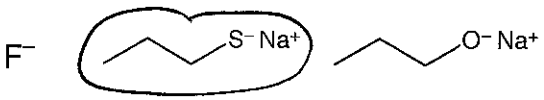
$-OCH_3$ is a strong base & a poor leaving group

3. (16 points – 4 points each part)

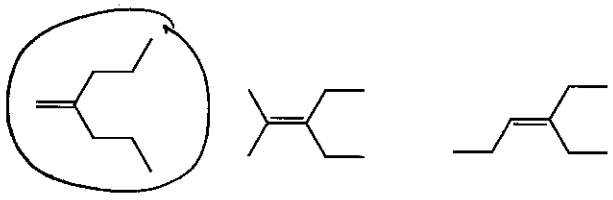
a. Circle the weakest base in the following series.

NH_3 H_2S H_2O

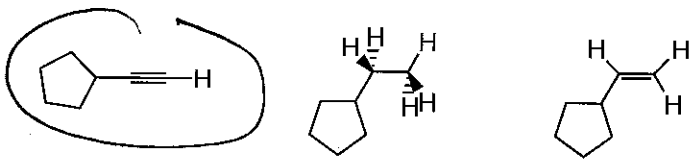
b. Circle the strongest nucleophile in a polar protic solvent:



c. Circle the alkene with the most negative heat of combustion:

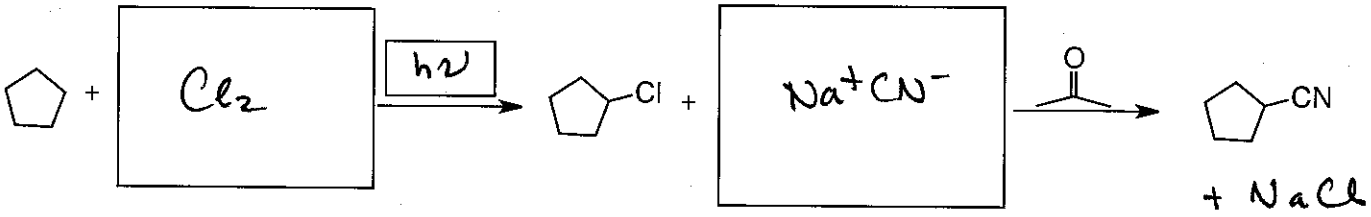


d. Circle the strongest acid of the following molecules:

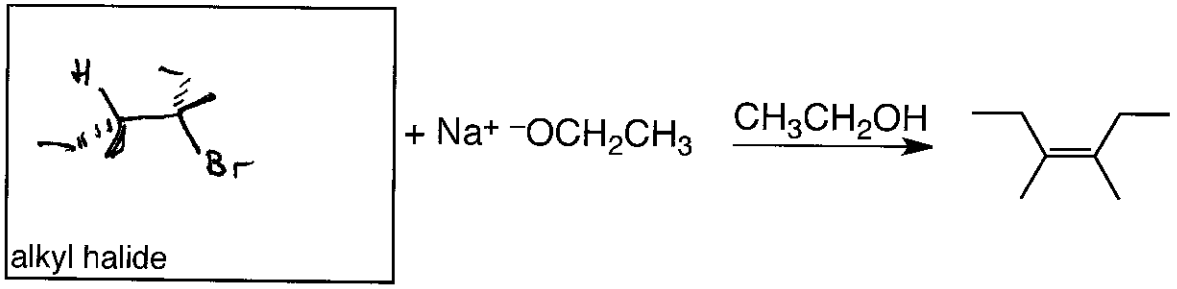


4. (24 points) Fill in the boxes in the following reactions. Note that only the organic products have been drawn.

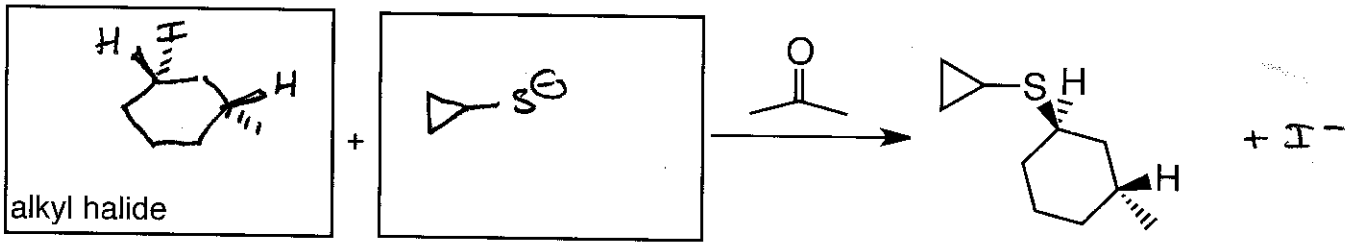
a.



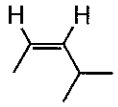
b.



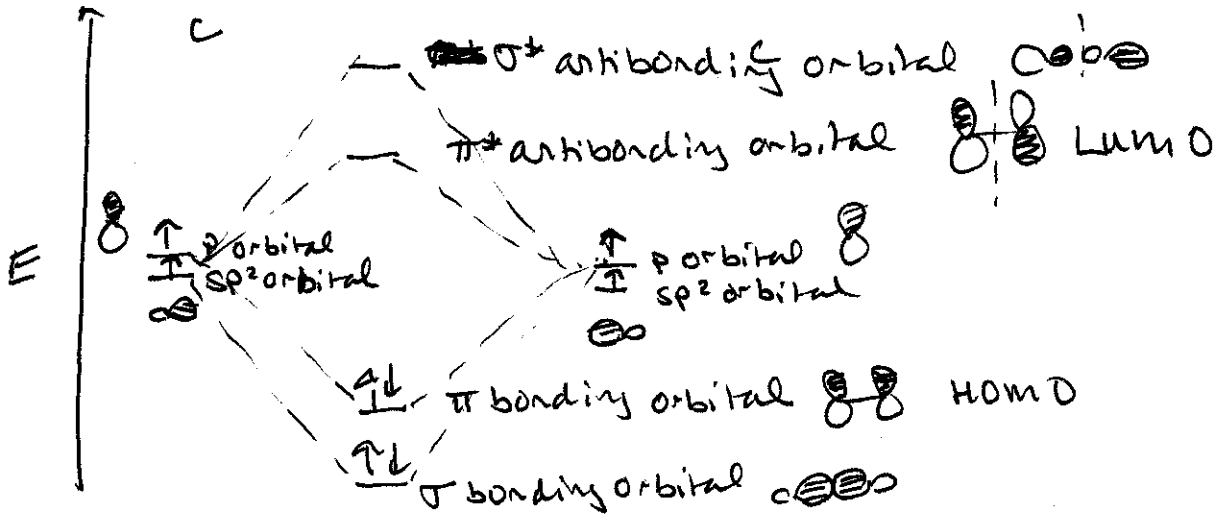
c.



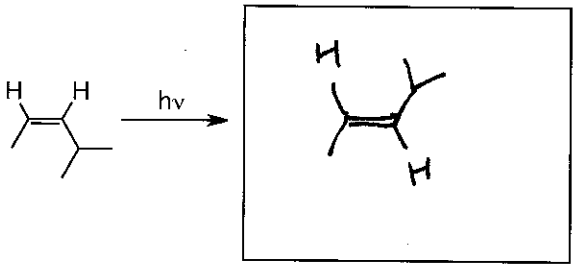
5. (22 points) Consider the alkene below:



a. (15 points) Draw and label a molecular orbital diagram for formation of both the sigma and pi bond of the double bond in the above alkene. Include pictures of the orbitals you use to make the bond and pictures of the molecular orbitals formed. Label the HOMO and LUMO.

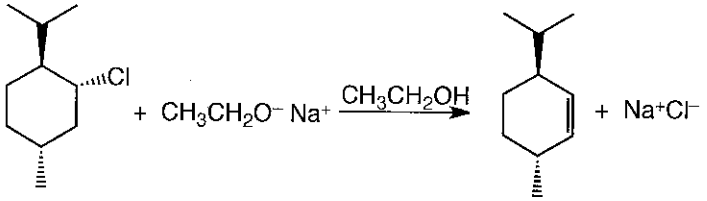


b. (7 points) When one shines the correct wavelength of light on a solution of this alkene, an isomerization reaction occurs. Draw the product of this reaction in the box below. Explain briefly (2 sentences) why this product is more stable than the starting alkene? (An isomerization reaction is one in which an isomer of the starting material is formed).

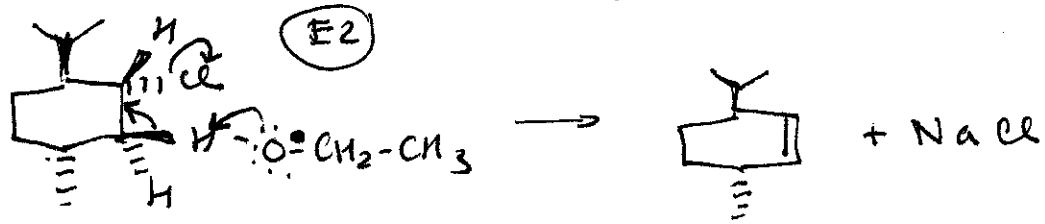


trans is more stable than cis-substituted alkene because the cis-substituted alkene is destabilized by steric interactions between the Me & iPr groups

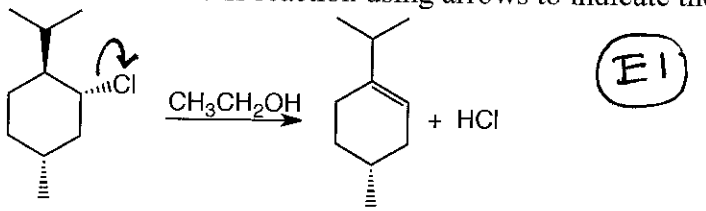
6. (23 points) The following alkyl chloride gives one major alkene product when allowed to react with sodium ethoxide

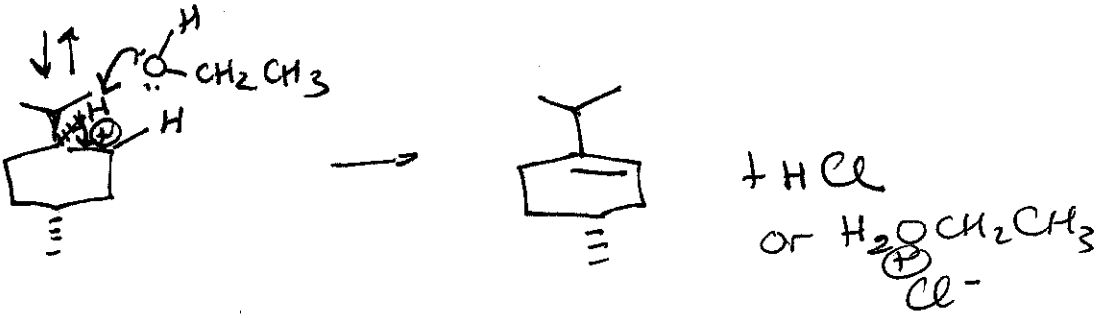


a. (8 points) Draw a mechanism for this reaction using arrows to indicate the flow of electrons.



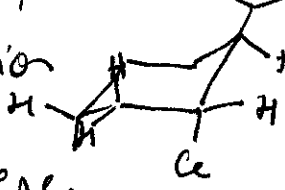
b. (8 points) The reaction gives a different major alkene product when heated in ethanol alone. Draw the mechanism for this reaction using arrows to indicate the flow of electrons.



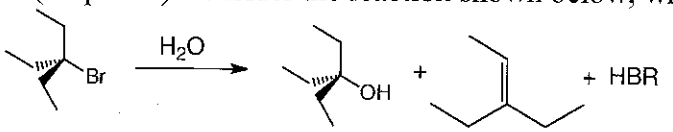


c. (7 points) Explain why each reaction gives a different major alkene product. Draw chair cyclohexane structures as part of your explanation.

The E1 reaction yields the most stable alkene, which is the more substituted alkene

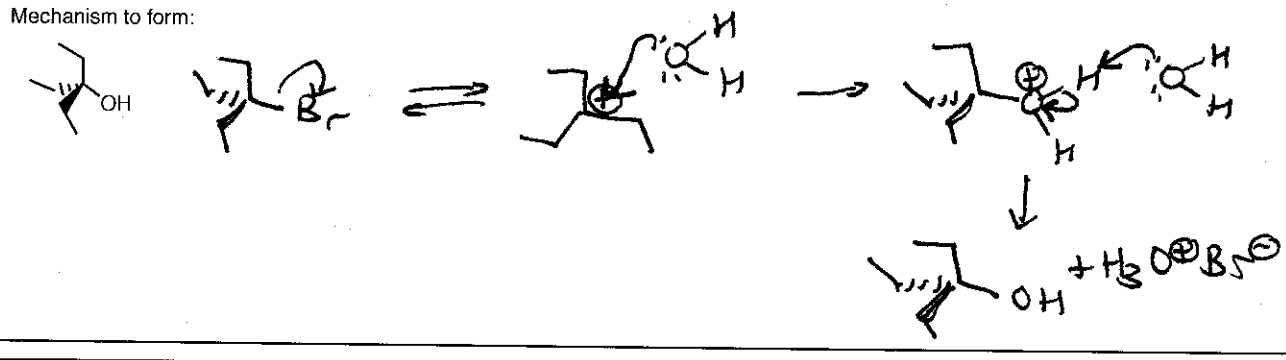
The E2 reaction is fastest when H^+ & Leaving Group are antiperiplanar. Antiperiplanar is only possible with this chair conformation  and thus the major product is the less substituted alkene.

7. (50 points) Consider the reaction shown below, which yields two products.

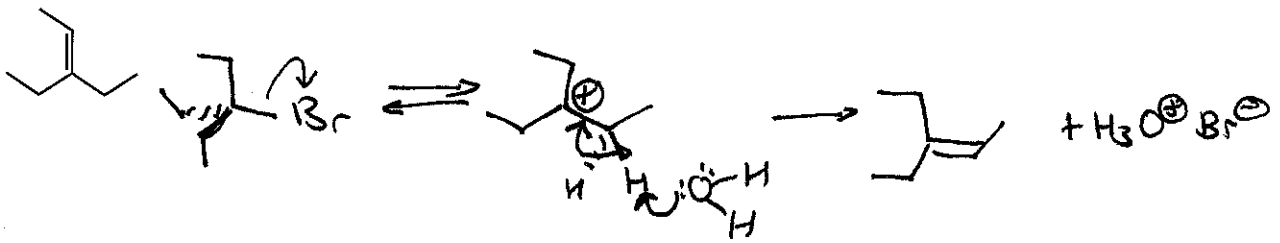


a. (13 points) Draw mechanisms for each reaction using arrows to indicate the flow of electrons.

Mechanism to form:

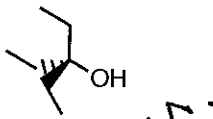


Mechanism to form:



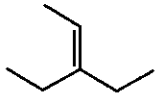
b. (8 points) Write a rate expression that describes the rate of formation of each product. Label each reaction bimolecular or unimolecular.

Rate expression to form: Unimolecular



$\text{Rate} = \frac{d[\text{OH}]}{dt} = k[\text{Br}]$

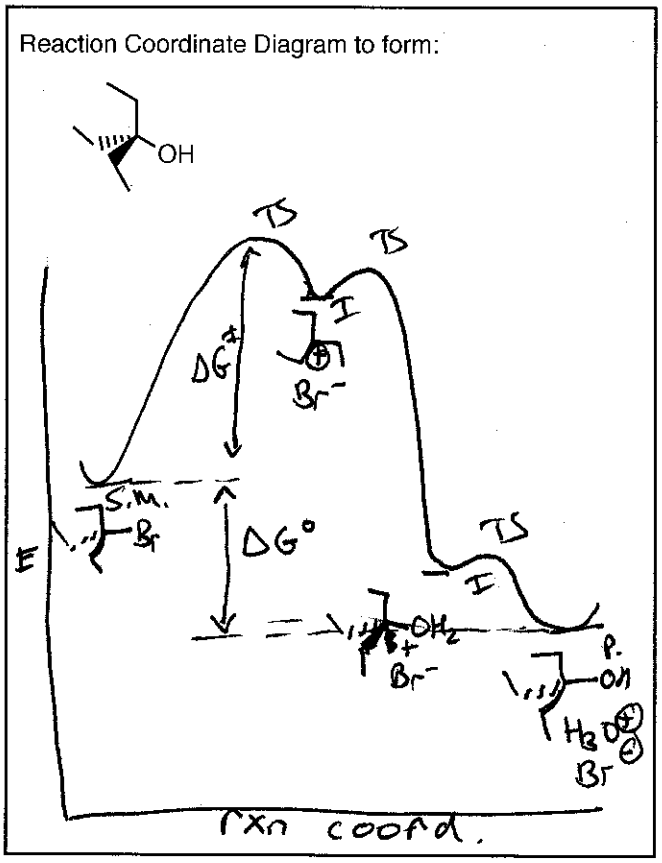
Rate expression to form: Unimolecular



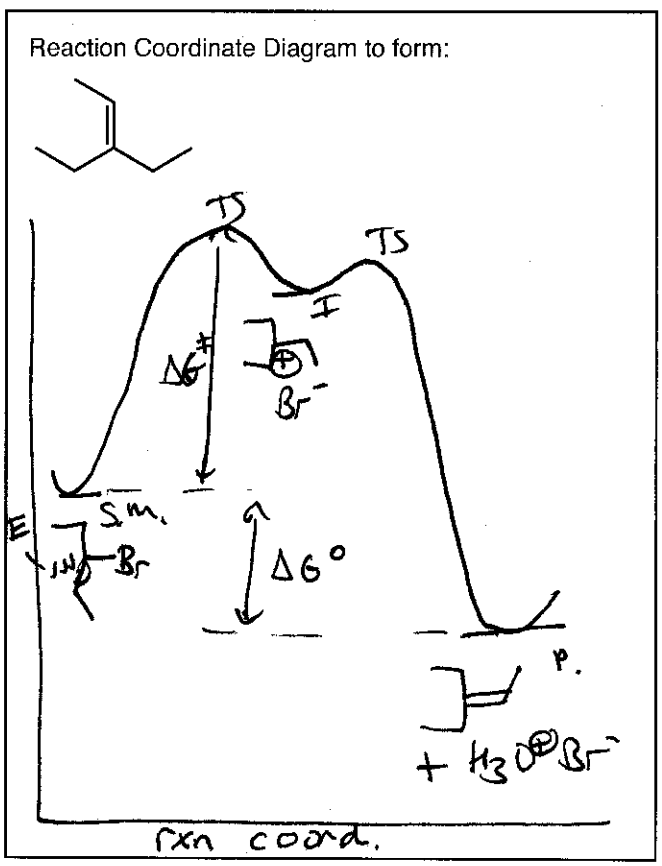
$\text{Rate} = \frac{d[\text{product}]}{dt} = k[\text{Br}]$

c. (16 points) Draw a reaction coordinate diagram for each reaction. Label the axes, starting materials, products, $\Delta G°$, $\Delta G^{\ddagger}$, intermediates, and transition states. Do not draw the structure of the transition state.

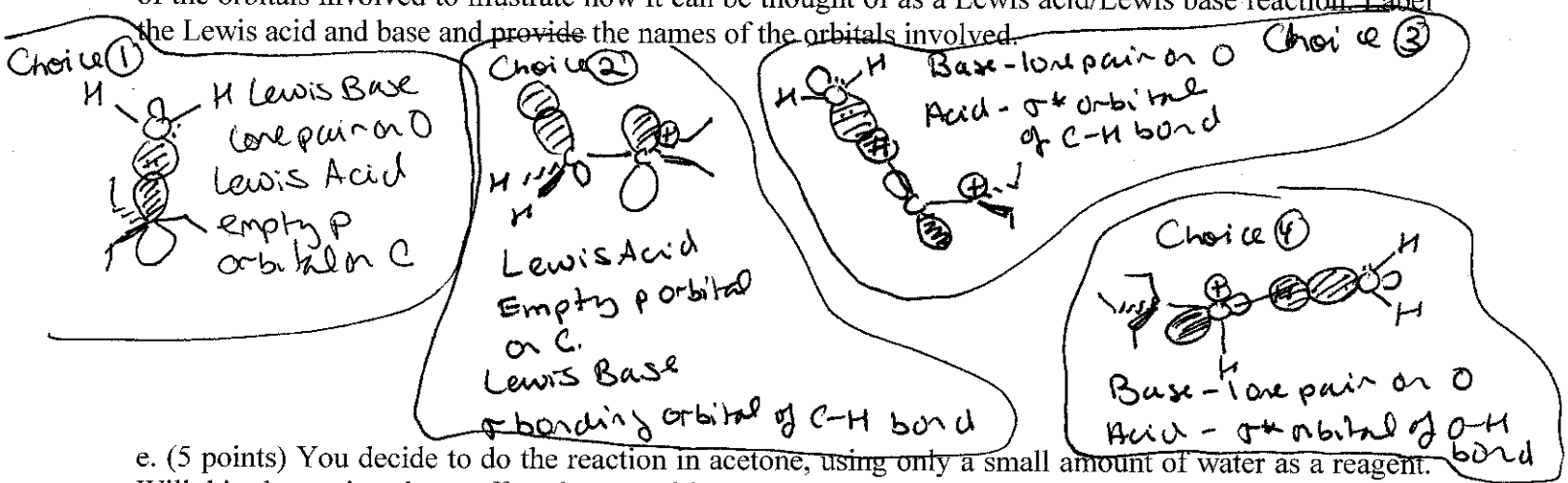
Reaction Coordinate Diagram to form:



Reaction Coordinate Diagram to form:



d. (8 points) Each reaction is a multistep reaction. Choose one step of either reaction and use drawings of the orbitals involved to illustrate how it can be thought of as a Lewis acid/Lewis base reaction. Label the Lewis acid and base and ~~provide~~ the names of the orbitals involved.

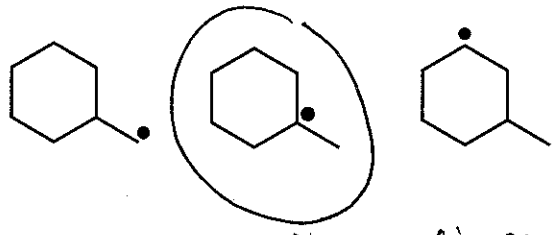


e. (5 points) You decide to do the reaction in acetone, using only a small amount of water as a reagent. Will this change in solvent affect the rate of formation of products? Explain your answer.

Yes- the rate of formation of products will be much slower. The carbocation intermediate & Br^- are stabilized by solvation in protic solvent. The transition state resembles the intermediate and is similarly stabilized by solvation in the polar protic solvent. Therefore the reaction is faster in the polar protic solvent.

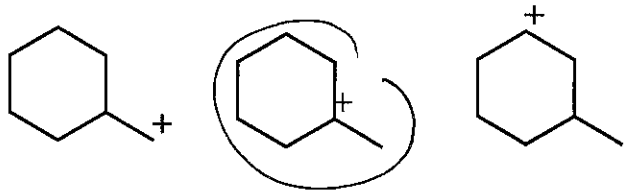
8. (21 points; 7 points each part)

a. Circle the alkyl radical below that is the most stable. Briefly explain your answer.



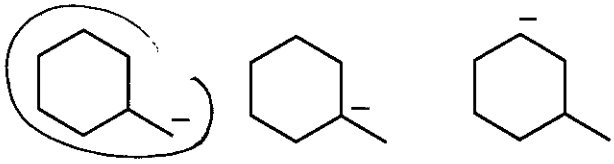
Hyperconjugation with adjacent C-H & C-C bond
There are a greater number of C-H & C-C bonds to participate in hyperconjugation for the 3° radical compared to secondary or 1° radical.

b. Circle the carbocation that is the most stable. Briefly explain your answer.



Answer is the same as for radicals above

c. Circle the carbanion, shown below, that is the most stable. Briefly explain your answer.



Hyperconjugation does not stabilize carbanions
Both bonding & antibonding orbitals have 2e⁻ so there is no net stabilization and the electrons in the alkyl groups destabilize the carbanion