CHEMISTRY 12A FALL 2018

FINAL EXAM Answers

DECEMBER 12, 2018

NAME- WRITE BIG _____

STUDENT ID: _____

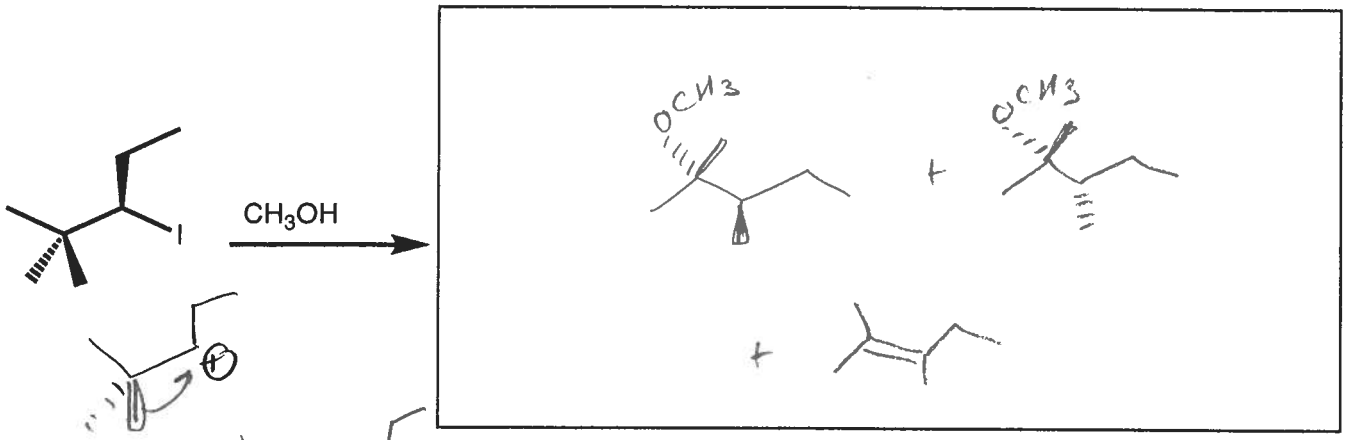
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **You will have 3 hours 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**
- **No stencils**
- **Molecular models may be used**

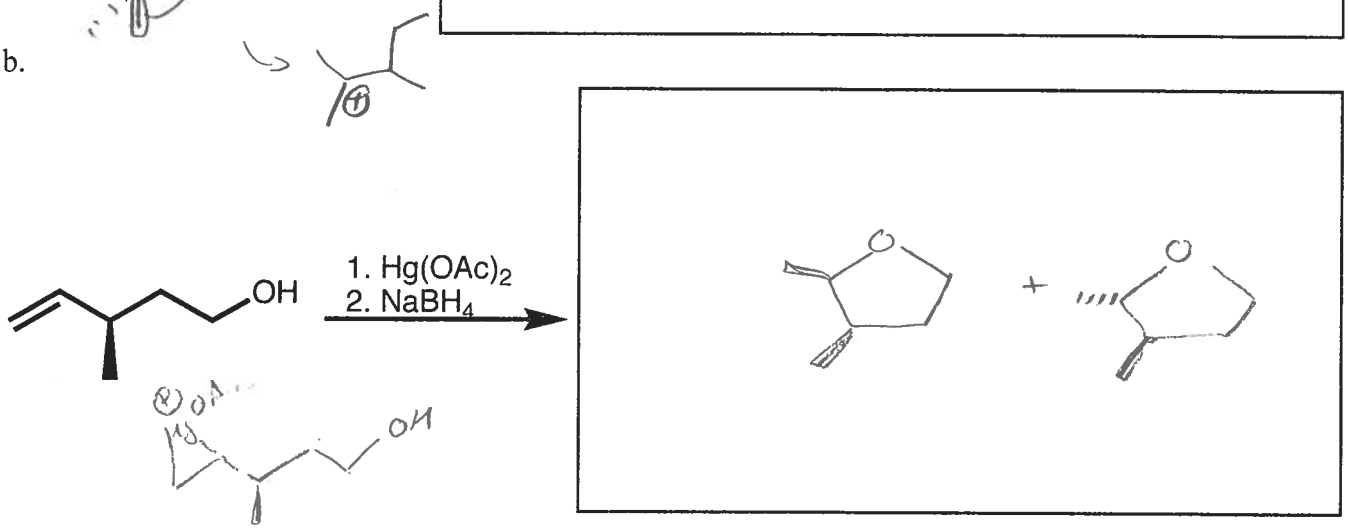
Problem	Points (Maximum)
1	38
2	18
3	18
4	21
5	18
6	24
7	24
8	17
9	15
10	23
11	39
12	23
13	22
Total	*300*

1. (38 points) For each reaction, draw the major organic products, **including all stereoisomers** or fill in the reagent boxes. The reagent boxes may require multiple steps to complete the reaction. Write NR if you think there will be no reaction.

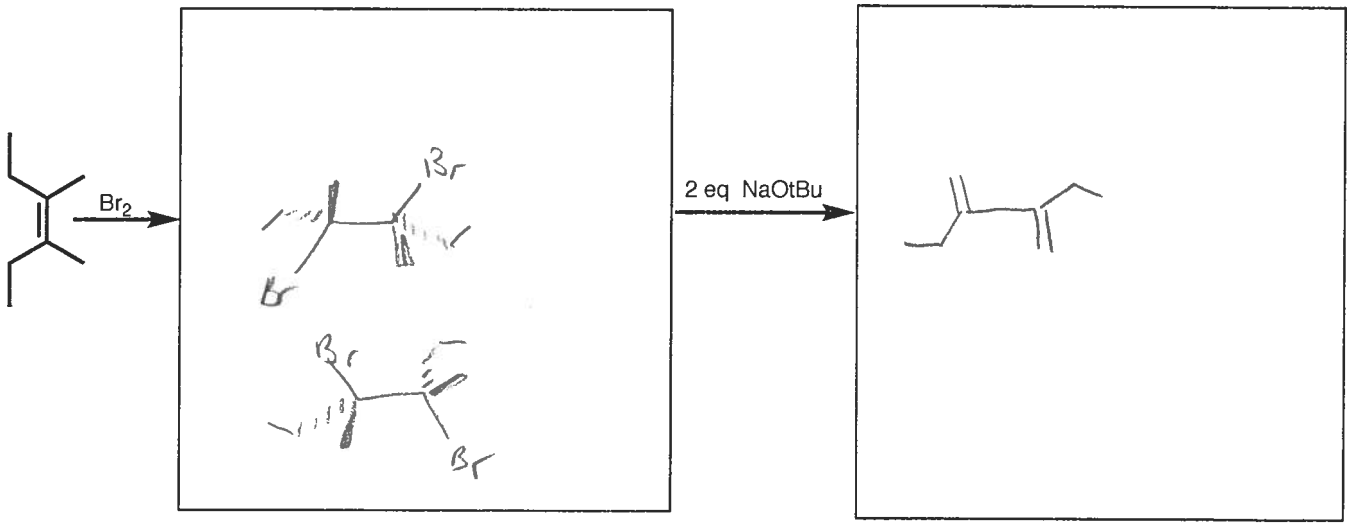
a.



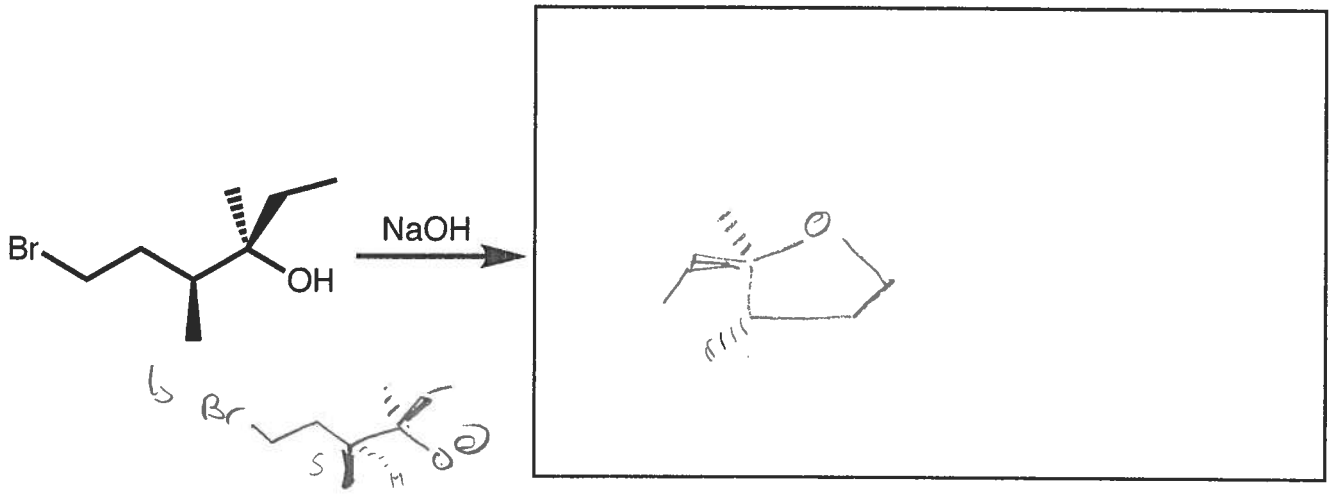
b.



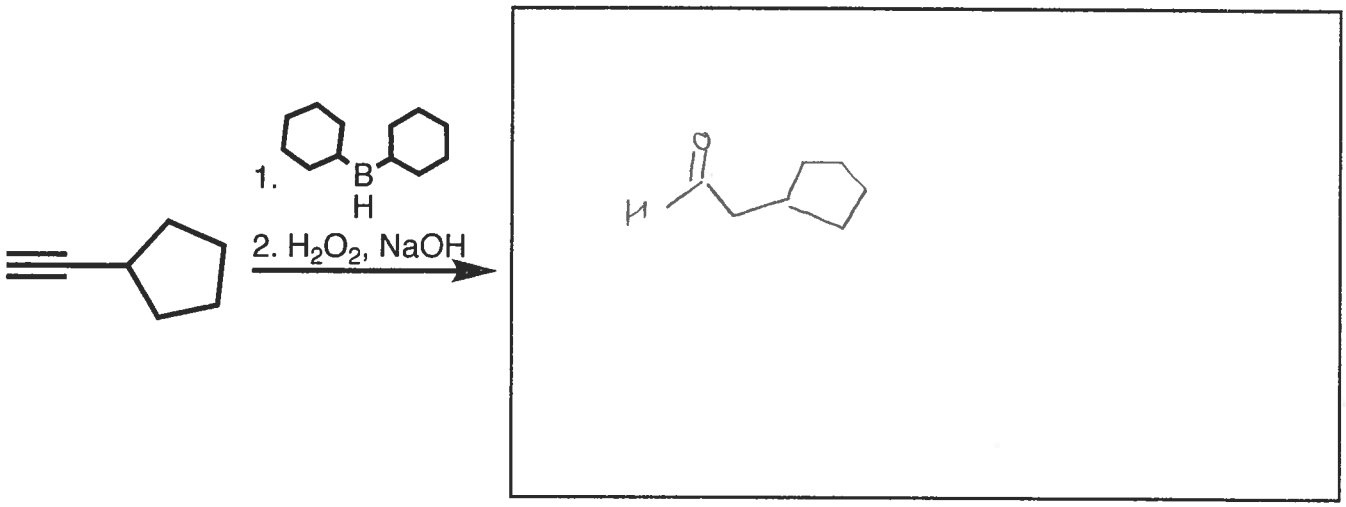
c.



d.

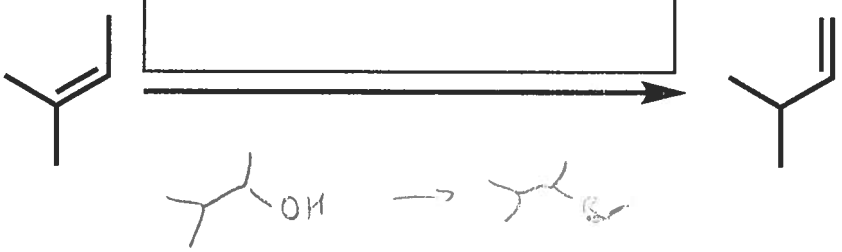


e.

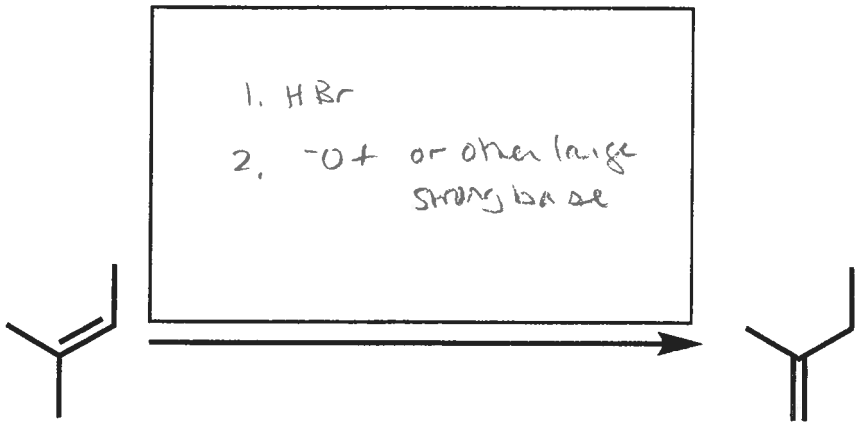


f.

1. BH_3 - THF
2. H_2O_2, NaOH
3. PBr_3 or TsCl/pyridine
4. $+ O^{\ominus}$ or other large base

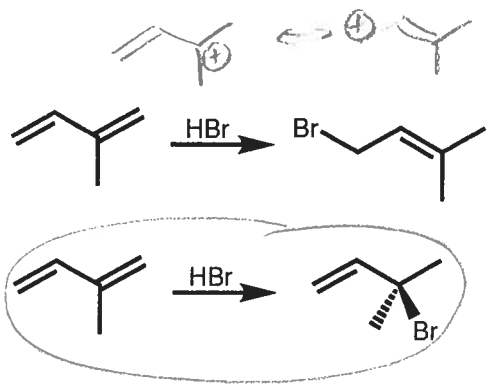


g.



2. (18 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 or that one of the reactions does not occur at a measurable rate. You may disregard any other products besides the ones pictured that may form under the reaction conditions. Give brief explanations in the boxes provided and include relevant structures.

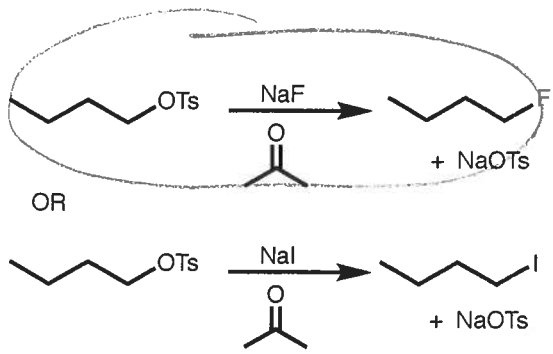
a.



Explanation for your choice of faster reaction:

The kinetic product is the 1,2 addition because the $Br^{\ominus}$ adds fastest to the position to which it is closest

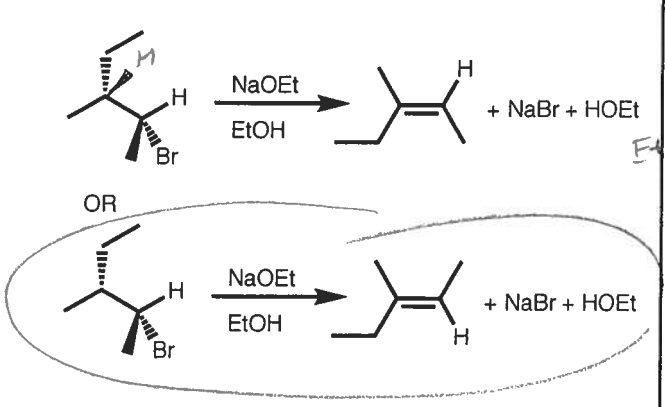
b.



Explanation for your choice of faster reaction:

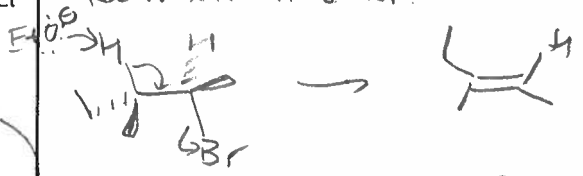
This is an S_N2 rxn. It is a polar aprotic solvent. $F^{\ominus}$ is more basic & more nucleophilic than $I^{\ominus}$ The polar aprotic solvent does not solvate F^- strongly enough to make F^- less reactive than I^-

c.



Explanation for your choice of faster reaction:

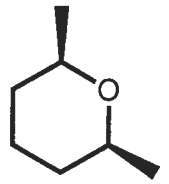
E2 rxn requires anti orientation between H & Br.



Product that forms fastest is the one formed from this orientation of H & Br

3. (18 points) Identify the following molecules as chiral or achiral. If possible draw a diastereomer and enantiomer of each molecule.

a.

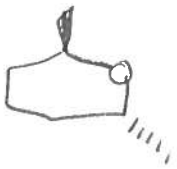


chiral or achiral

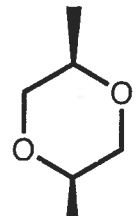
Enantiomer

None

Diastereomer



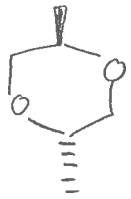
b.



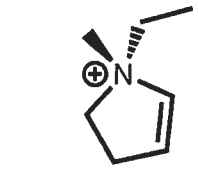
chiral or achiral

Enantiomer

Diastereomer



c.



chiral or achiral

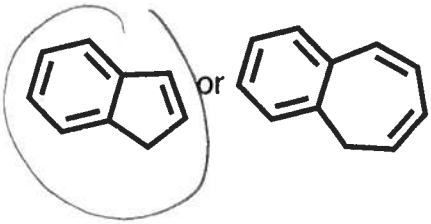
Enantiomer

Diastereomer

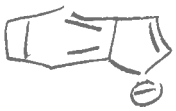
none

4. (21 points) Consider the pairs of molecules below.

a. Circle the more **acidic** molecule. Explain your choice. Draw any relevant structures.



Conjugate base is aromatic & stable

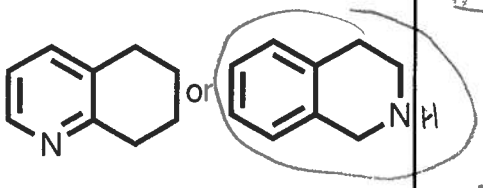


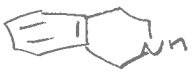
10 π e⁻, cyclic, fully conjugated & planar

In contrast, conjugate base of other molecule

12 π e⁻, cyclic, fully conjugated & if planar → antiaromatic & unstable

b. Circle the more **basic** molecule. Explain your choice. Draw any relevant structures.



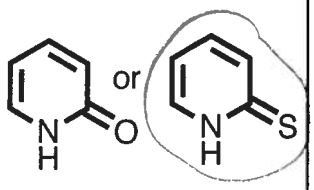


N is sp^3 hybridized

N is sp^2 hybridized

lone pair is more stable & less basic on sp^2 hybridized carbon because orbital has more s character & is closer to the nucleus

c. Circle the more **acidic** molecule. Explain your choice. Draw any relevant structures.

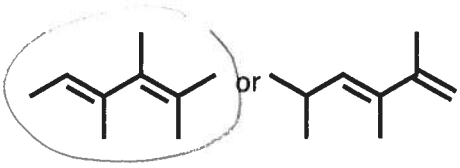


Consider conjugate base of both molecules.

Both are aromatic. In one negative charge is on 'O' & the other on 'S'
Negative charge is more stable on S because it is lower in periodic table & is larger & spreads out charge more. charge is less localized.

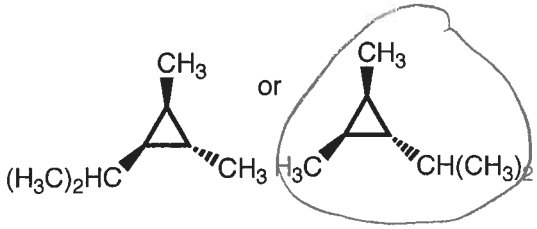
5. (18 points) Circle the molecule that is most stable in the following pairs. Explain your choice.

a.

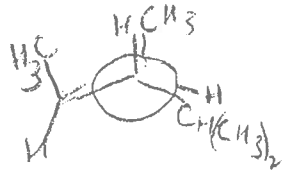


more substituted alkenes are more stable

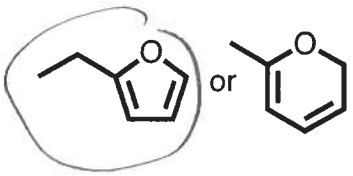
b.



$\sharp CH(CH_3)_2$ is larger than $\sharp CH_3$
Circled molecule has less steric strain because the larger group is directed away from the two methyl groups



c.

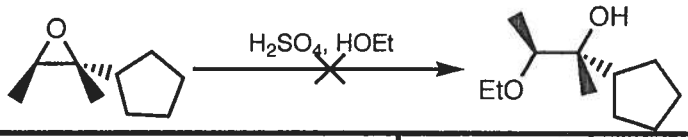


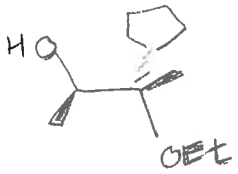
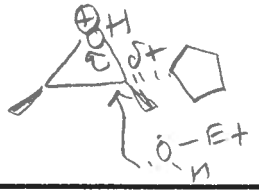
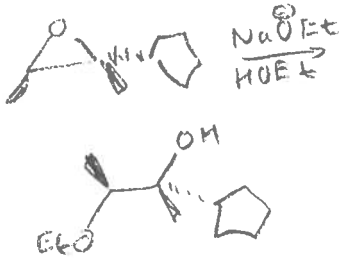
The circled molecule is aromatic 6 πe^-, cyclic, planar, & fully conjugated.

The other molecule is not aromatic because it is not fully conjugated.

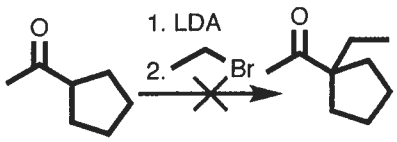
6. (24 points) The following reactions would not occur as written. i. What product would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrates or reaction conditions to give the desired products in as few steps as possible?

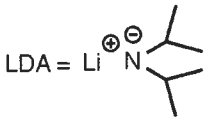
a.

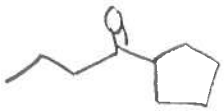
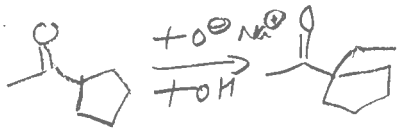


What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	Under acidic conditions, an SN1 type rxn occurs & nucleophile reacts w/ more substituted carbon because it has more $\delta+$ 	Do the reaction under basic conditions 

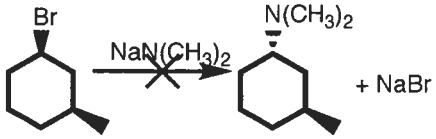
b.

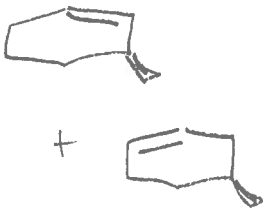
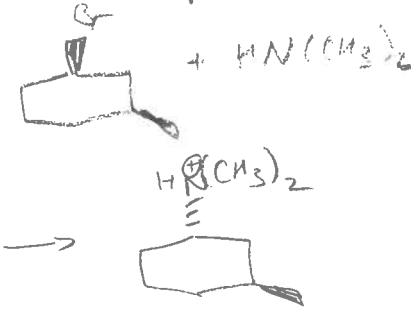




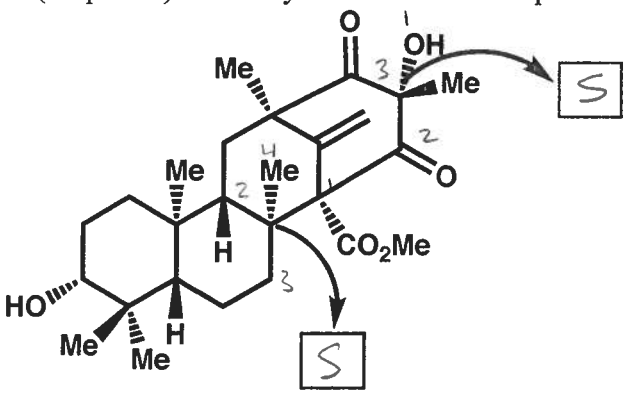
What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	LDA is a large strong base, The formation of the enolate is not reversible. The kinetic enolate is formed by deprotonating most unhindered H This leads to  which reacts w/ 	Use a weaker base so that thermodynamic enolate is formed which is the more substituted enolate 

c.



What product(s) is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	$\ominus N(CH_3)_2$ is a very strong base & will do E2 on 2° alkyl halide	Use less basic N nucleophile. 

7. (24 points) Berkeleyone A is a natural product isolated from the Berkeley pits.



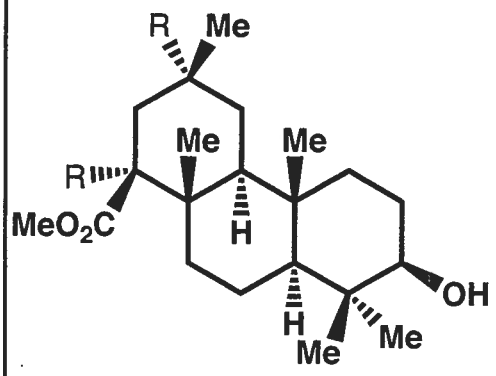
a. Assign the indicated stereocenters as *R* or *S* in the small boxes above.

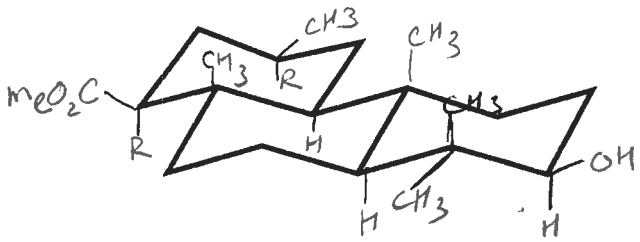
b. The specific rotation of Berkeleyone A is -12°. Your synthesis produces 95% of Berkeleyone A and 5 % of the enantiomer. i. What is the %ee of your product mixture? ii. What is the specific rotation of your product mixture? Calculate numerical values for each. Show your work.

$$\%\,ee = \frac{95-5}{95+5} = 90\%\,ee$$

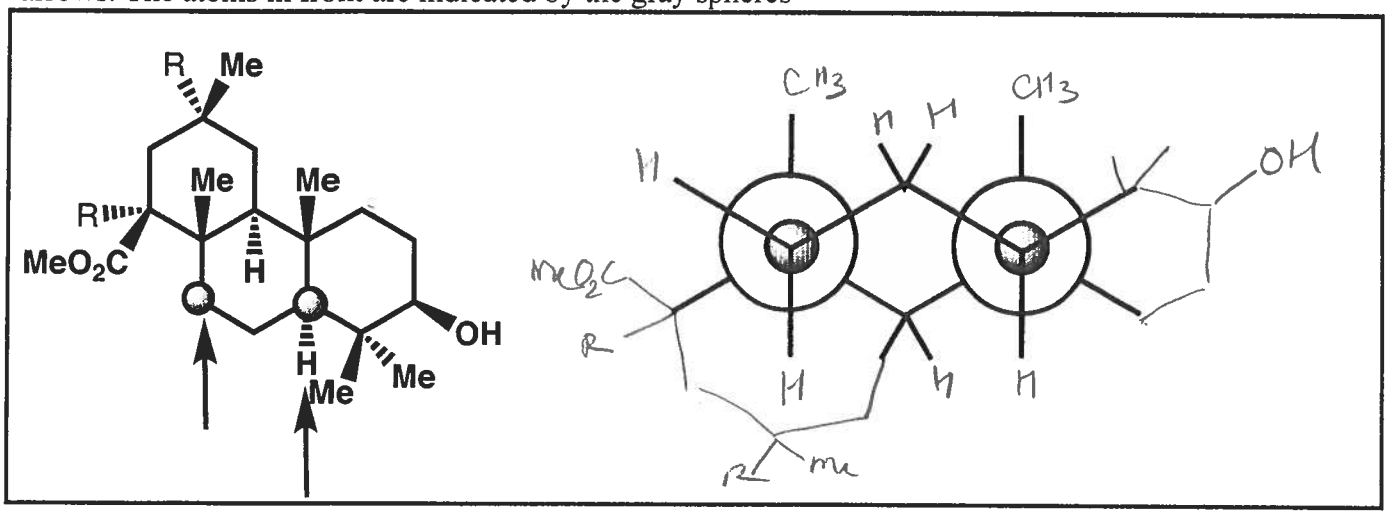
$$-12^\circ \times 0.9 = 10.8^\circ$$

c. Consider the simplified precursor of Berkeleyone A below. Fill in the groups on the three dimensional chair structure. You need only include the H's that are explicitly drawn out on the dash-wedge drawing.



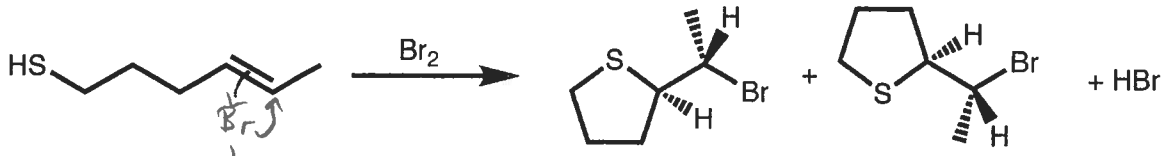


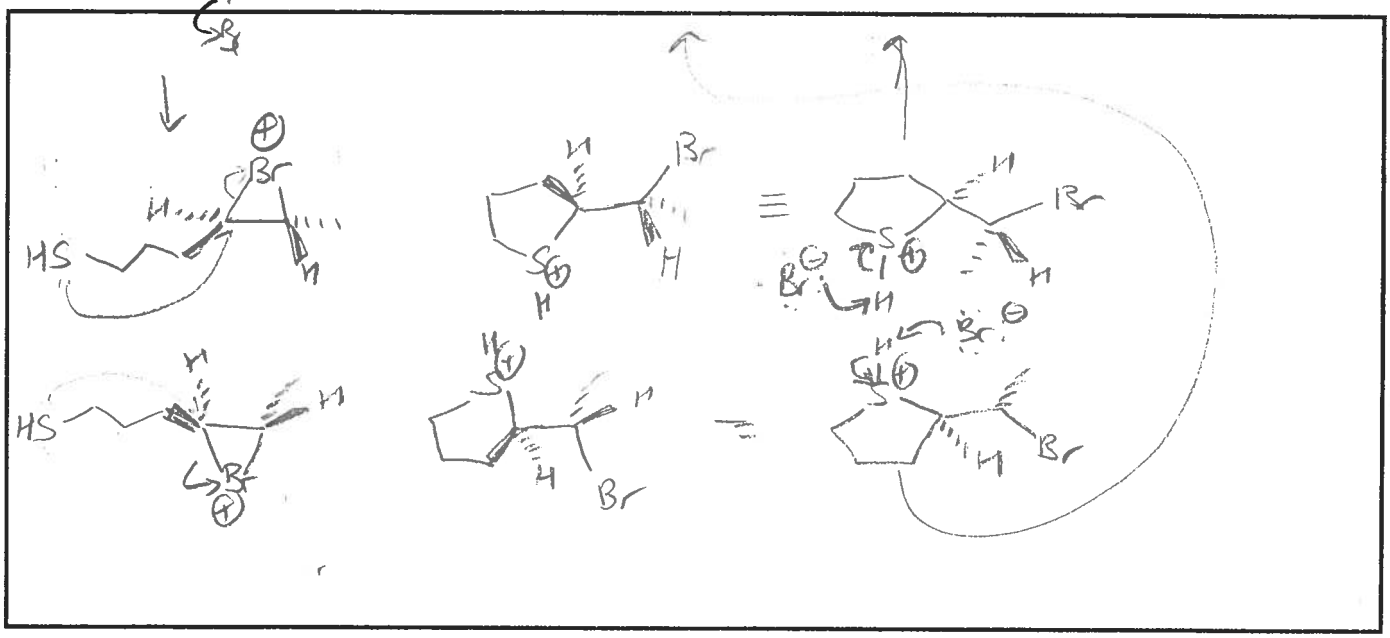
d. Using the 3D structure from part c, fill in the Newman projection looking down the bonds with arrows. The atoms in front are indicated by the gray spheres



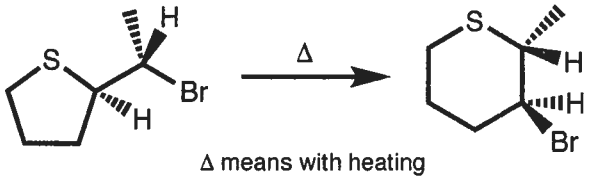
8. (17 points) Draw the mechanism of the following reactions using arrows to indicate the flow of electrons. Make sure to clearly indicate stereochemistry.

a.

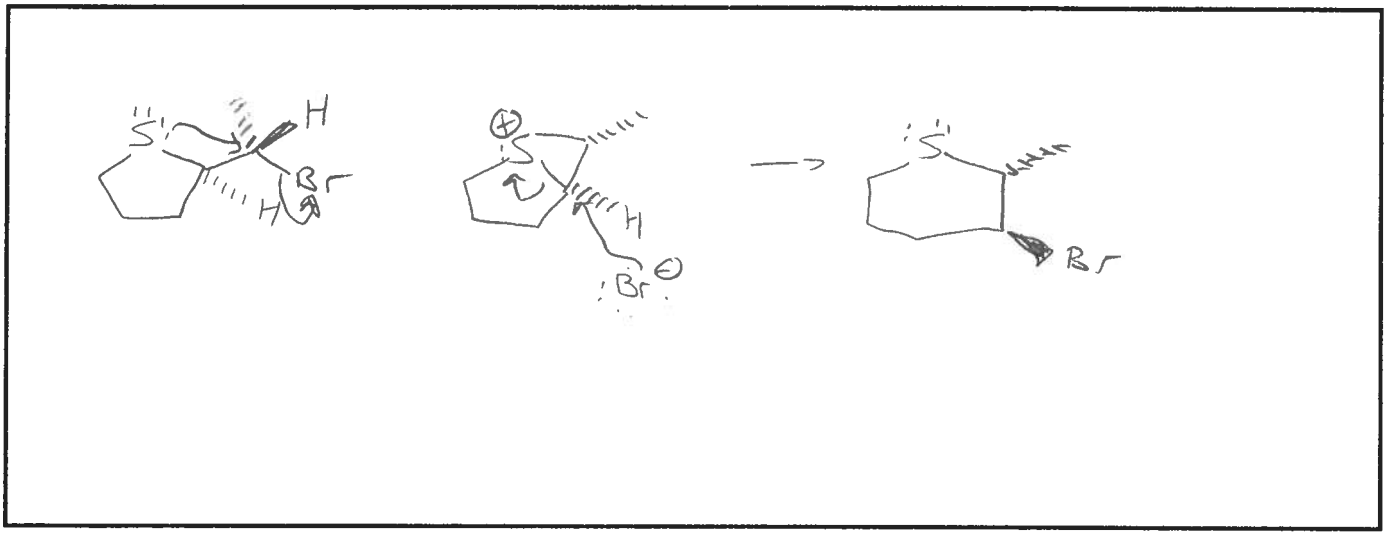




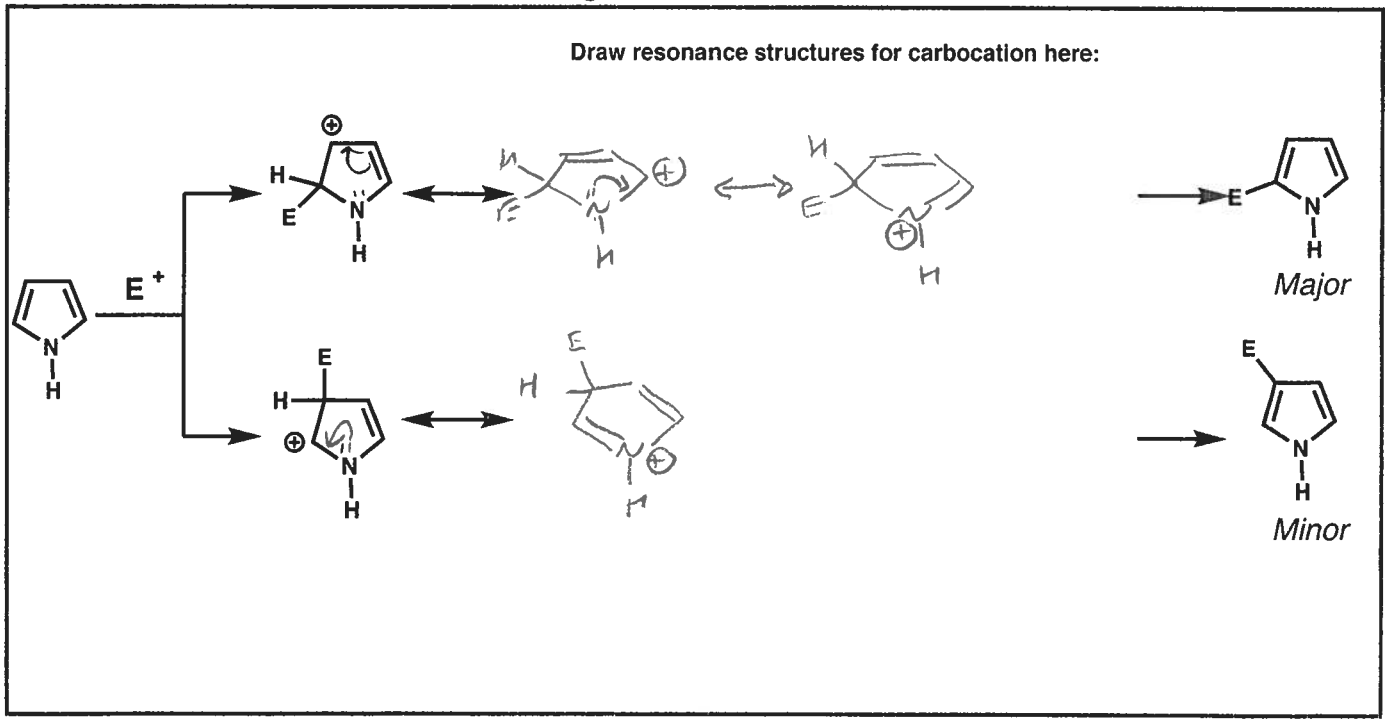
b. The product can react further upon heating. Write the mechanism for the reaction using arrows to show the flow of electrons. Make sure to clearly indicate stereochemistry.



Δ means with heating



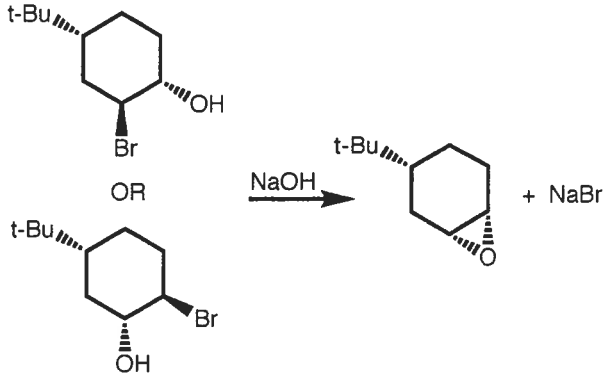
9. (15 points) Pyrrole containing compounds react with electrophiles at the C2 over the C3 position. The reaction below shows a generic electrophile (E^+) reacting with a pyrrole to form a major product with the electrophile attached to C2. Resonance can be used to rationalize this phenomenon.
a. Fill in the resonance structures below using arrows to show the flow of electrons.



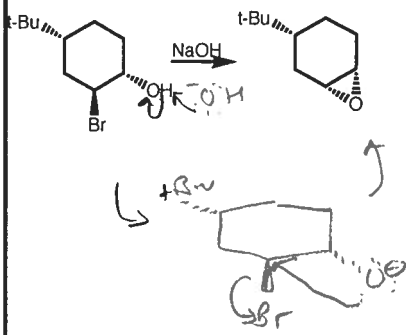
b. Using the resonance structures you drew in part a of this question, explain why the major product has the electrophile substituted at the C2 position.

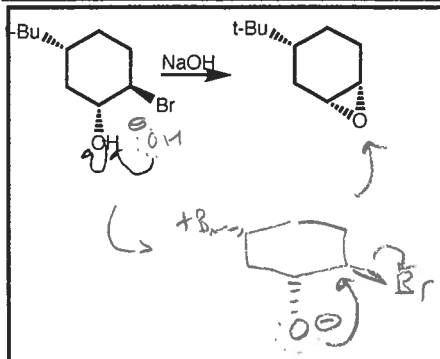
The carbocation intermediate for C2 substitution has one more resonance structure so the charge is spread over more atoms

10. (23 points) You wish to make the epoxide shown below and are trying to decide which of two starting materials to use. You need to decide which reaction will be faster.

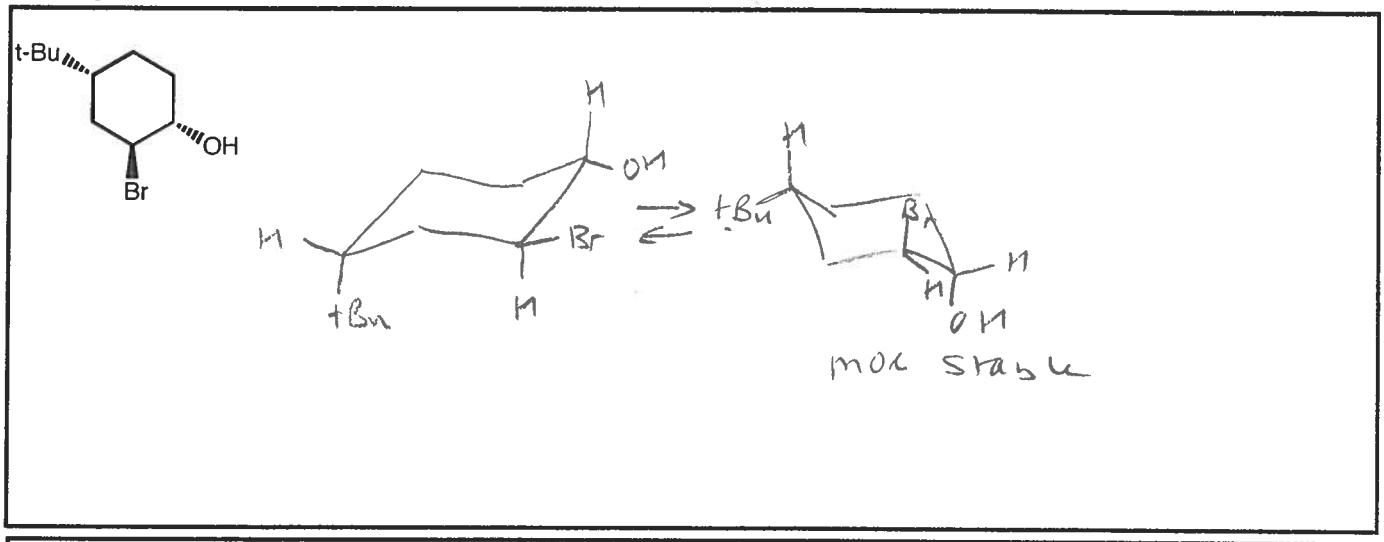


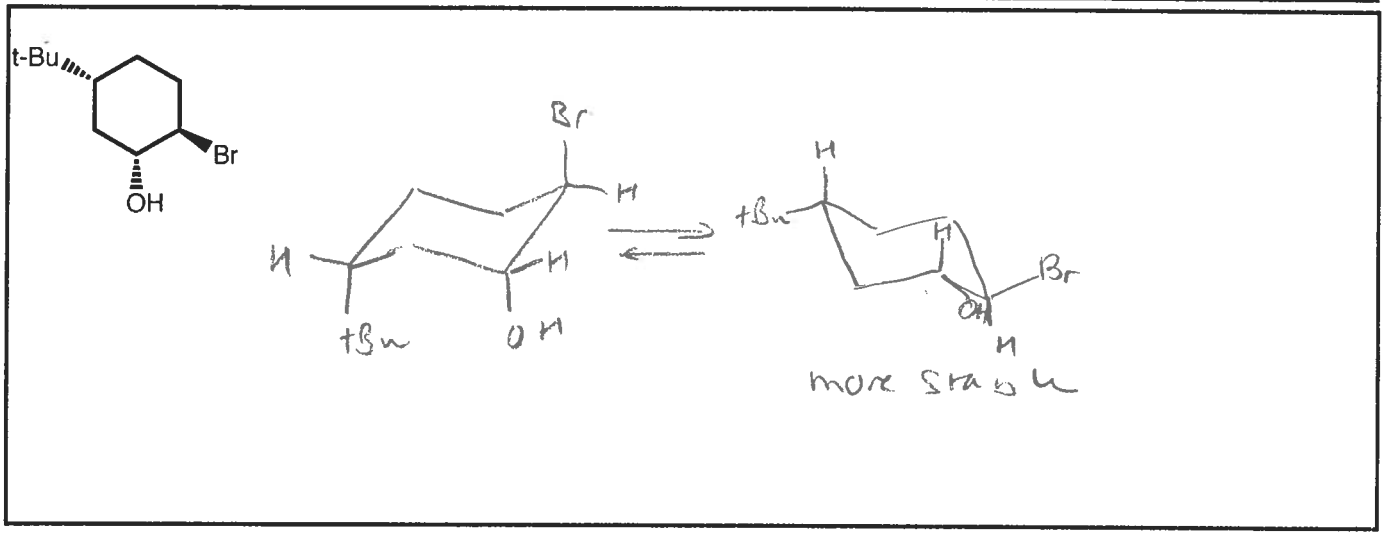
a. Draw the mechanism of the formation of epoxide product from both starting materials below.





b. Draw both chair conformations of both starting materials in the indicated boxes below. For each starting material, indicate which conformation is more stable.

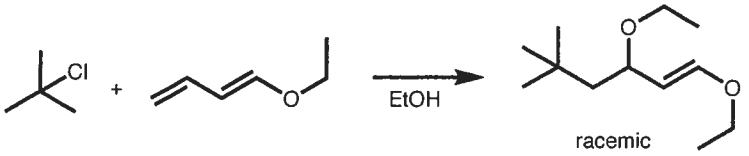




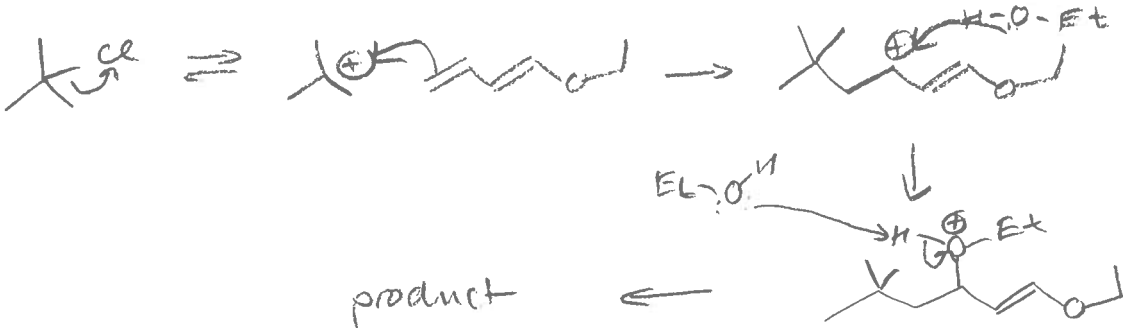
c. Based on the mechanism and chair structures you have drawn, which starting material will you use. Explain your choice.

more stable conformation has OH & Br anti to each other which facilitates a reaction of the alkoxide from the back of the C-Br bond.

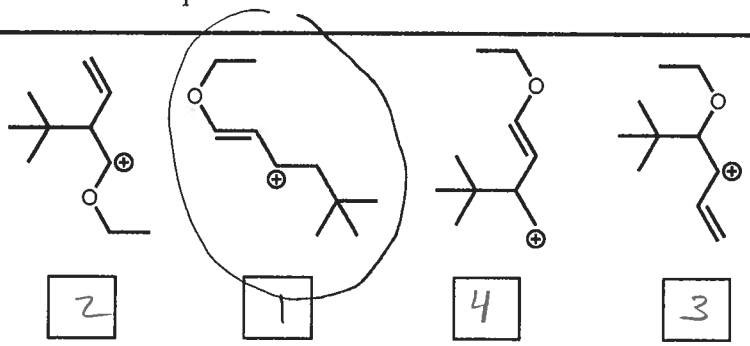
11. (39 points) Consider the reaction shown below.



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



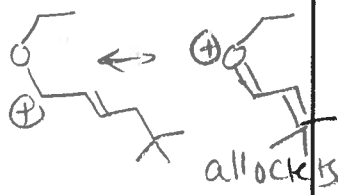
b. In an important step of the mechanism, the diene reacts with a carbocation. Four different possible intermediates that could be formed in this step are shown below. Rank these carbocations in order of increasing stability (1 = most stable, 4 = least stable). Explain your ranking. Circle the carbocation intermediate that forms the observed product.



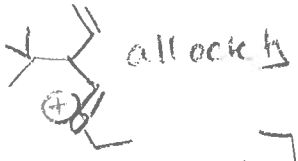
Ranking 2 | 1 | 4 | 3

Give your reasons for each ranking below:

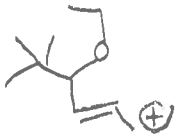
1 Two resonance structures, one of which has all octets



2 One resonance structure w/ all octets

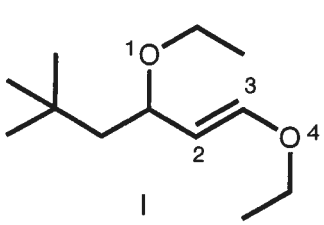


3 One resonance structure, but none w/ all octets

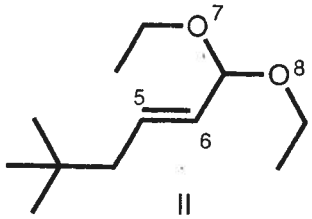


4 Primary carbocation & not resonance stabilized

c. In addition to the product shown at the beginning of this problem (product I below), the product shown below on the right (product II) could also be formed from the same carbocation intermediate. For each of the two products below identify the hybridization of each atom indicated with a number in the structure.



I



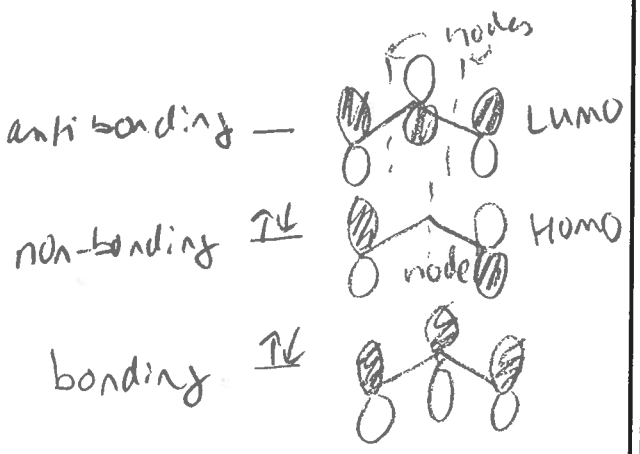
II

Fill in hybridization of numbered ~~carbons~~ atoms in the spaces below:

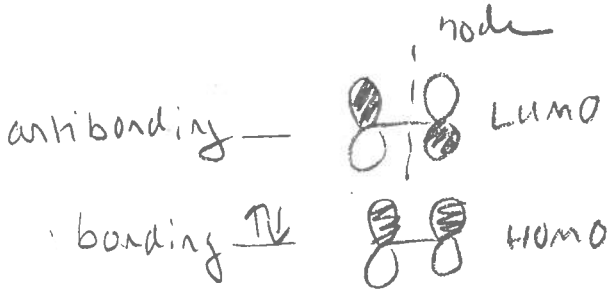
1	sp^3	**5**	sp^2
2	sp^2	**6**	sp^2
3	sp^2	**7**	sp^3
4	sp^2	**8**	sp^3

d. For both molecules I and II, draw the molecular orbitals of all p orbitals that are conjugated in a pi system. Label i. the HOMO and LUMO, ii. All nodes, iii. Bonding, antibonding, and non bonding orbitals, and iv. Fill ~~all~~ the orbitals with electrons.

Orbitals for Molecule I



Orbitals for Molecule II

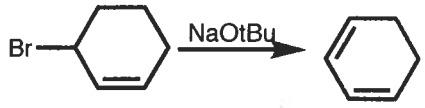


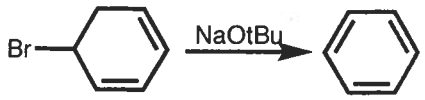
e. Is Molecule I the thermodynamic product? Explain your answer briefly.

Yes it is the thermodynamic product because it forms the more conjugated and therefore more stable product

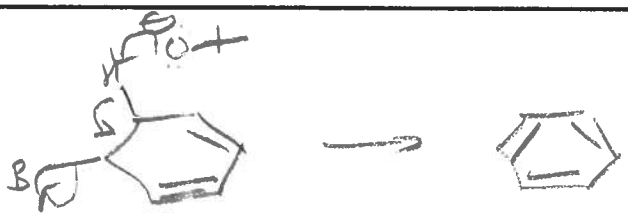
Note: making a kinetic argument does not answer the question.

12. (23 points) Consider the reactions shown below.

i. 

ii. 

a. Draw the mechanism of the second reaction (reaction ii). Use arrows to show the flow of electrons.

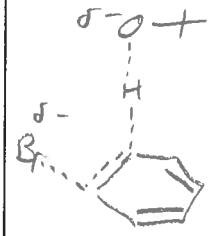


b. Which reaction do you predict to be faster and why? Include a sketch of the transition state for the faster reaction in your answer.

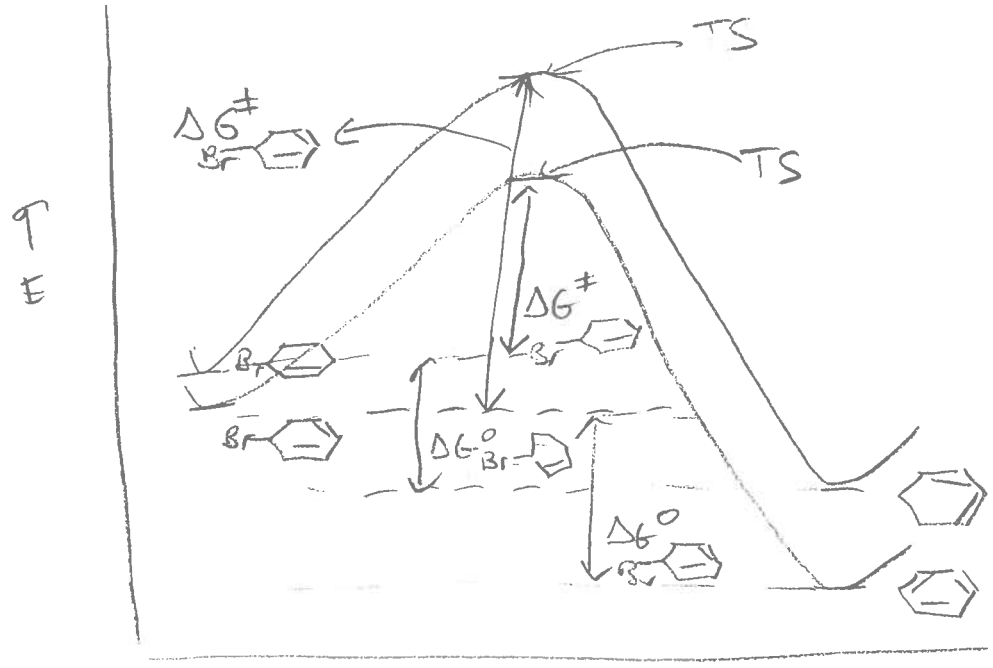
ii will be faster because product is aromatic. T.S. has some aromatic character because of partial bonds forming & therefore, T.S. is more stable & rxn is faster.

The starting material for ii is also more stable than the starting material for i but this difference in energy is smaller than the difference in energy of T.S

Sketch of TS structure

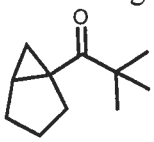


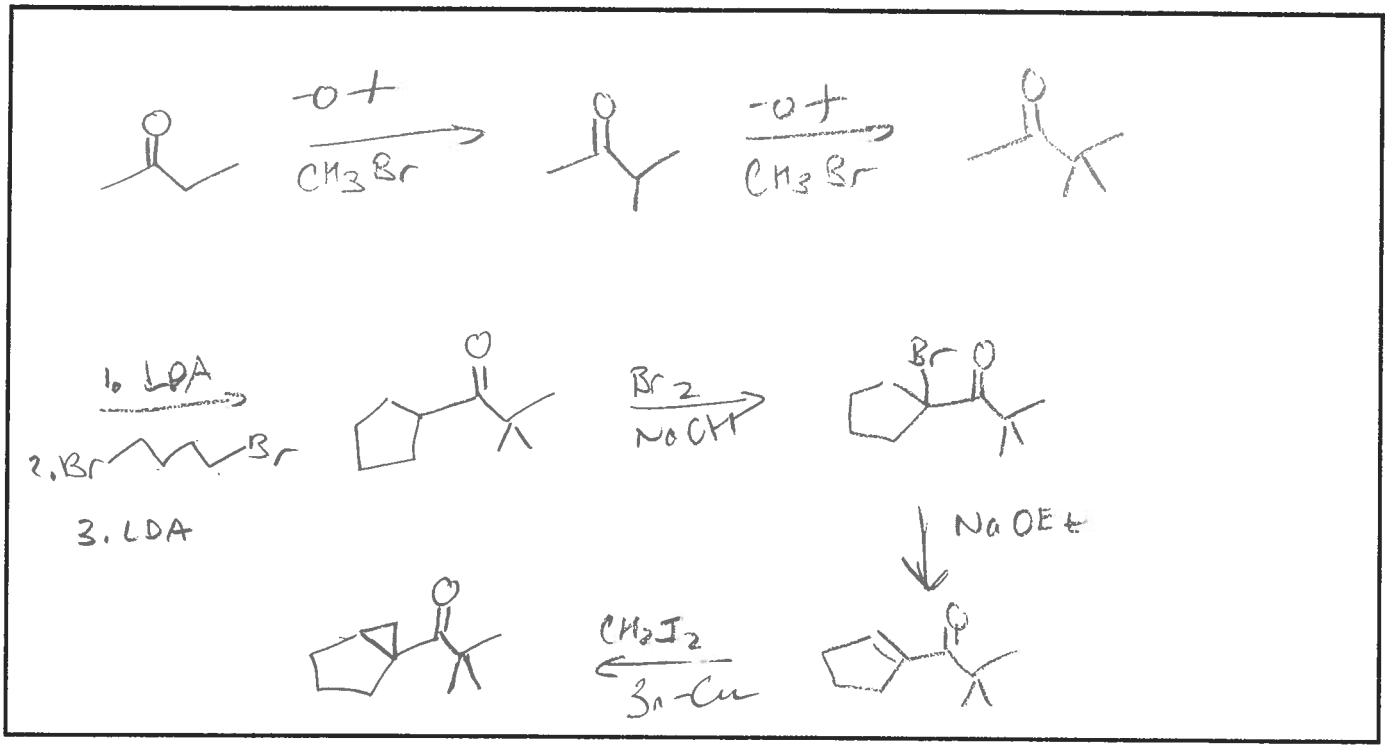
c. Draw a reaction coordinate energy diagram to illustrate your prediction in part b. On your diagram, draw structures of the starting materials and products and label the $\Delta G^{\ddagger}$, and $\Delta G°$, and the transition state for the formation of each product.



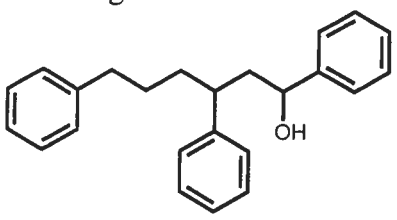
13. (22 points) Synthesize the following molecules,

a. Use reagents containing **4 or fewer** carbon atoms and any other reagents





b. Use the indicated starting material as the only source of carbon in the product. You can use any other reagents.



All stereoisomers

from