CHEMISTRY 112A FALL 2014

FINAL EXAM

DECEMBER 17, 2014

NAME- WRITE BIG _____

STUDENT ID: _____

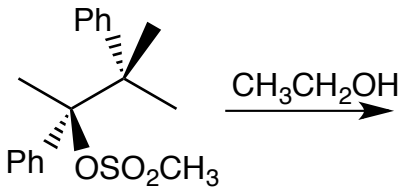
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **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)
1	30
2	21
3	18
4	17
5	18
6	16
7	19
8	26
9	32
10	34
11	25
12	20
13	24
Total	***300***

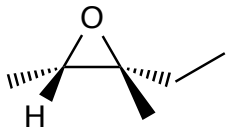
1. (30 points) For each reaction:
(i) Draw the major and minor organic products, **including all stereoisomers**. Write NR if you think there will be no reaction. (ii) Label each product you draw as major or minor or equal.

a.

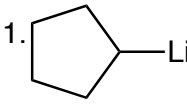


CH_3CH_2OH

b.



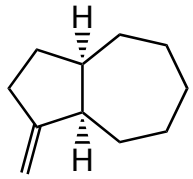
1.



$CH_3CH_2OCH_2CH_3$

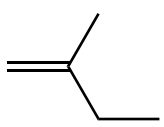
2. H_3O^+, H_2O

c.



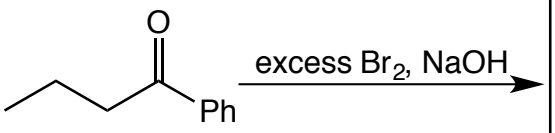
1. BH_3 THF
2. H_2O_2, NaOH, H_2O

d.



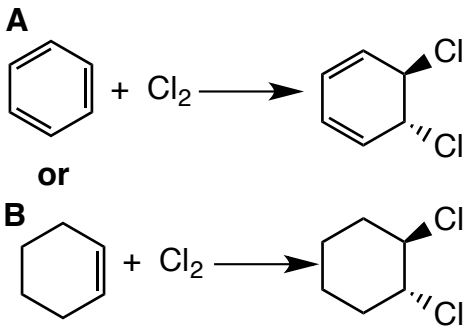
1. CH_3COOOH
2. H_3O^+, H_2O

e.

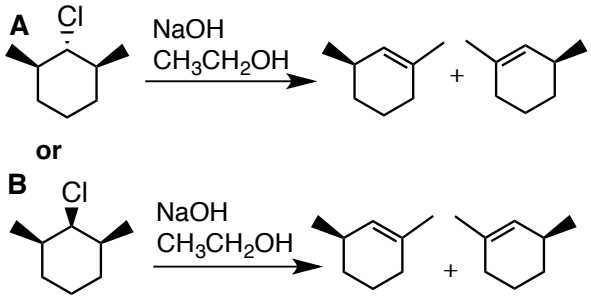


2. (21 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

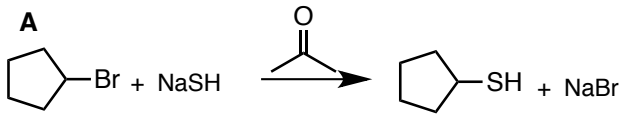
a.



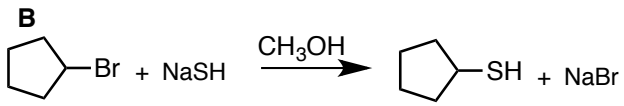
b.



c.

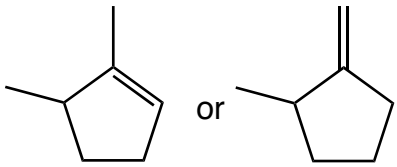


or

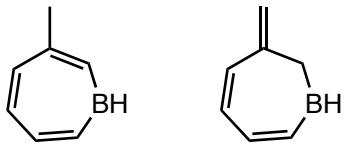


3. (18 points) Circle the most stable (lowest energy) molecule of each pair. Explain your choices.

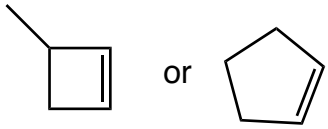
a.



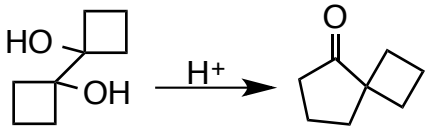
b.



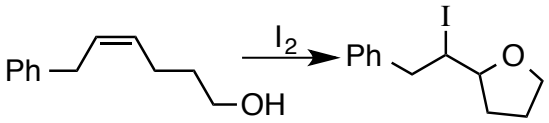
c.



4. (17 points) The following reaction is called a pinacol rearrangement. Draw the mechanism of this reaction using arrows to show the flow of electrons.

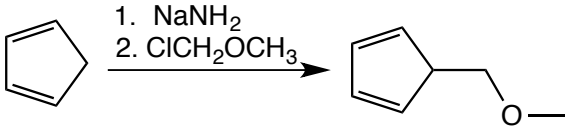


5. (18 points) Draw the mechanism of this reaction using arrows to show the flow of electrons. Indicate the stereochemistry of the products formed.

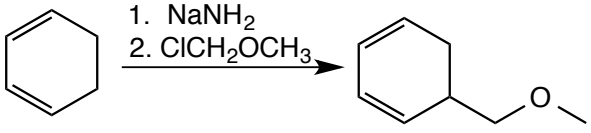


6. (16 points) Place the following reactions in order of reaction rate. Explain your answer.

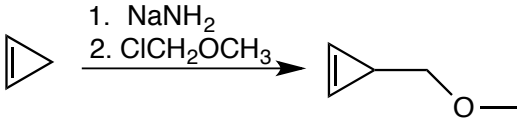
A.



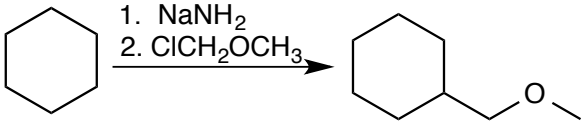
B.



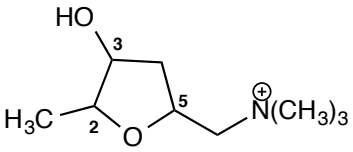
C.



D.



7. (19 points) The natural product muscarine is shown below.

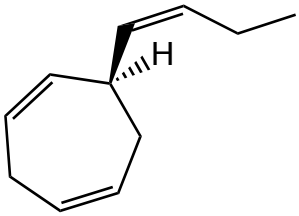


a. Redraw the structure below to be the 2*S*, 3*R*, 5*S* isomer, which is the natural product.

b. Draw the enantiomer of this structure.

c. Draw a diastereomer of this structure.

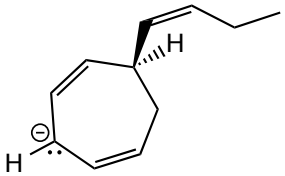
8. (26 points)The molecule shown below is called Ectocarpene and is an algae pheromone



a.Assign stereocenters as *R* or *S*.

b. Ectocarpene is isolated from natural sources. The enantiomer of ectocarpene is also found naturally. The specific rotation of the molecule shown is -117°. If a researcher purifies a sample ectocarpene and measures a specific rotation of -11.7°, what percent of the desired molecule, (-)-ectocarpene, is present in the sample? Show your work.

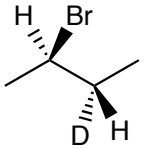
c. The anion of Ectocarpene shown below is relatively stable because of conjugation with the adjacent double bonds.



Draw a molecular orbital diagram of the π molecular orbitals of the conjugated system. You may simplify your drawing by drawing the orbitals in a line, rather than as part of a ring.

i. Draw dashed lines to indicate any nodes.
ii. Label each orbital as bonding, non-bonding, or antibonding.
iii. Fill the orbitals with electrons of the anion.
iv. Label the HOMO and LUMO.

9. (32 points) The molecule shown below undergoes an E2 elimination reaction in NaOEt to form cis-2-butene, trans-2-butene, and 1-butene.

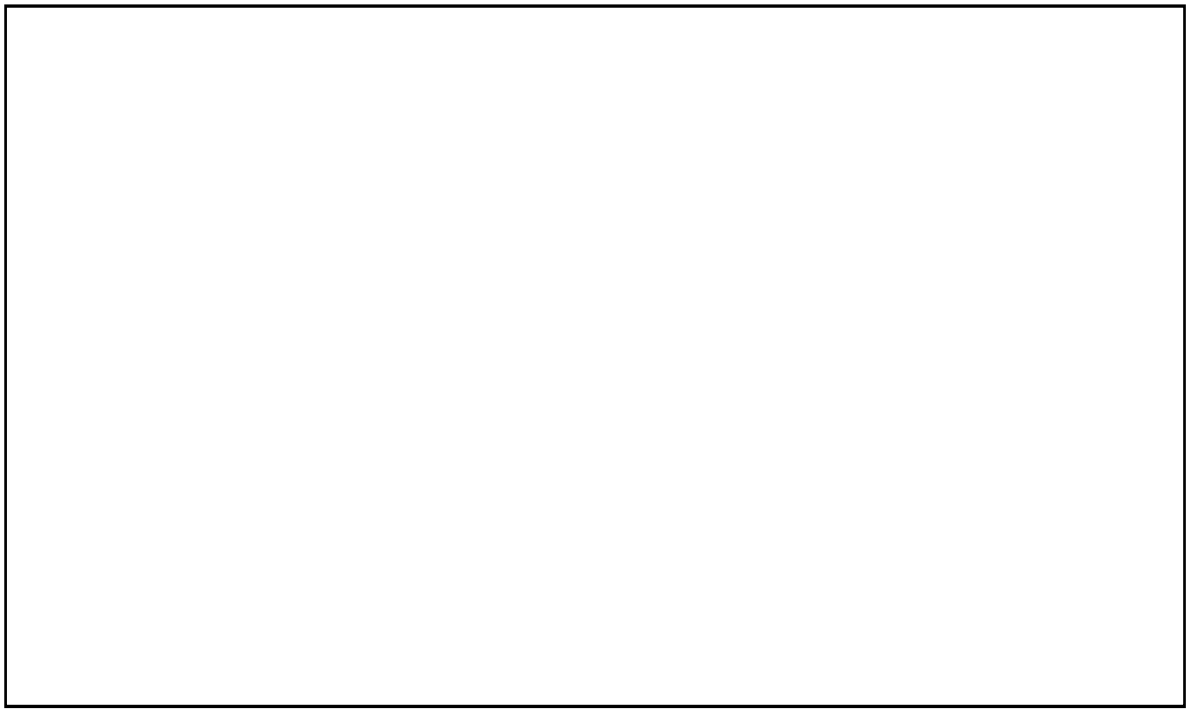


a. Draw mechanisms to form all three of these products, being careful to indicate the presence or absence of deuterium in the products.

b. Which is the major product of this reaction and why?

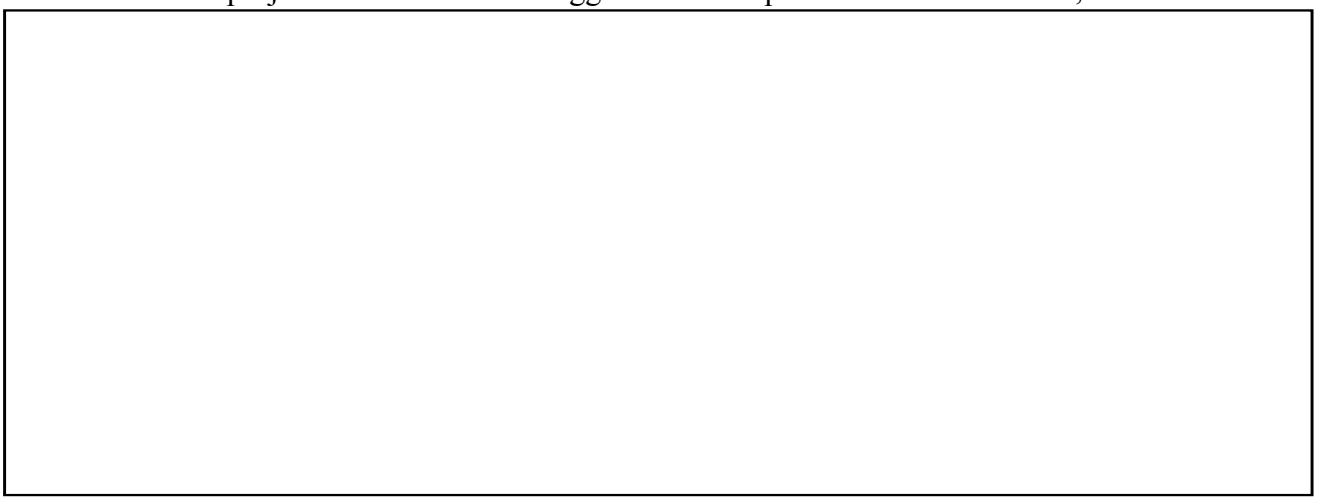
c. Is this reaction thermodynamically controlled or kinetically controlled? Explain.

d. Draw a reaction coordinate diagram to illustrate formation of the major product. Label your diagram and include drawings of all starting materials, products, intermediates, and transition states.

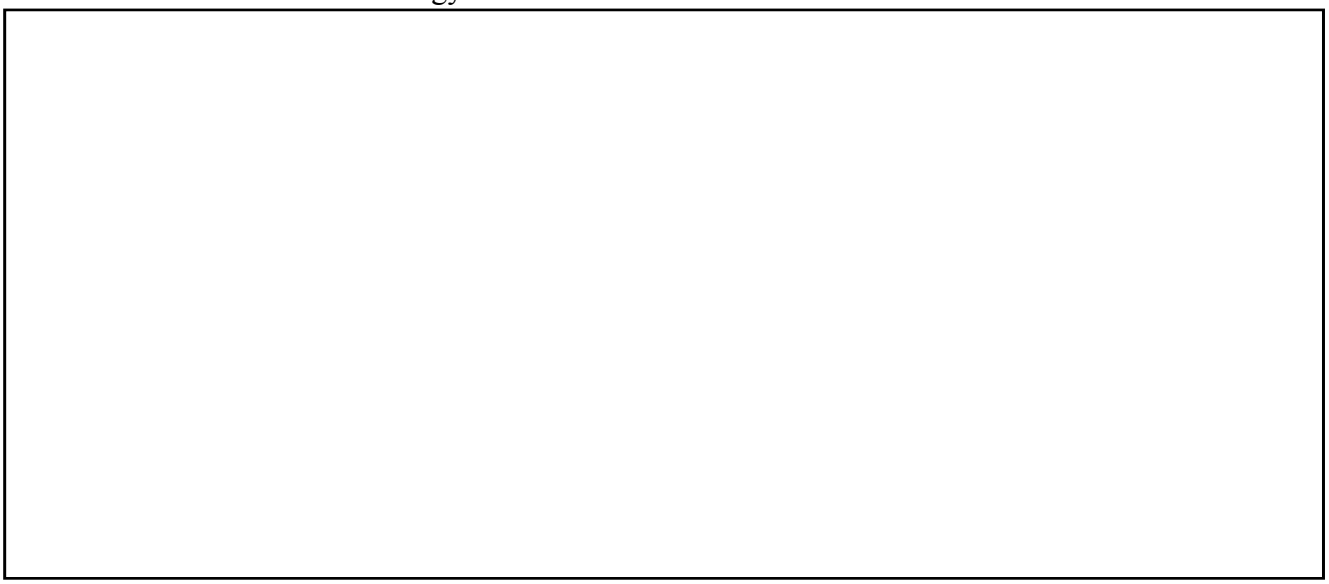


10. (34 points) Interestingly, the gauche conformation of 1,2-difluoroethane is more stable than the anti conformation. This is called the gauche effect.

a. Draw Newman projections of all of the staggered and eclipsed conformations of 1,2-difluoroethane.

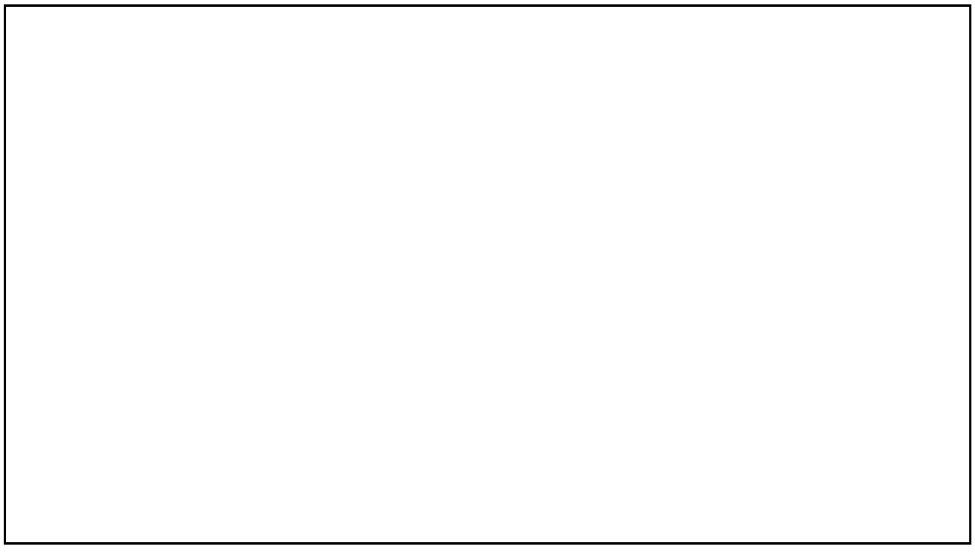


b. Draw an energy vs. dihedral angle plot for 1,2-difluoroethane. You may assume all of the eclipsed conformations have the same energy

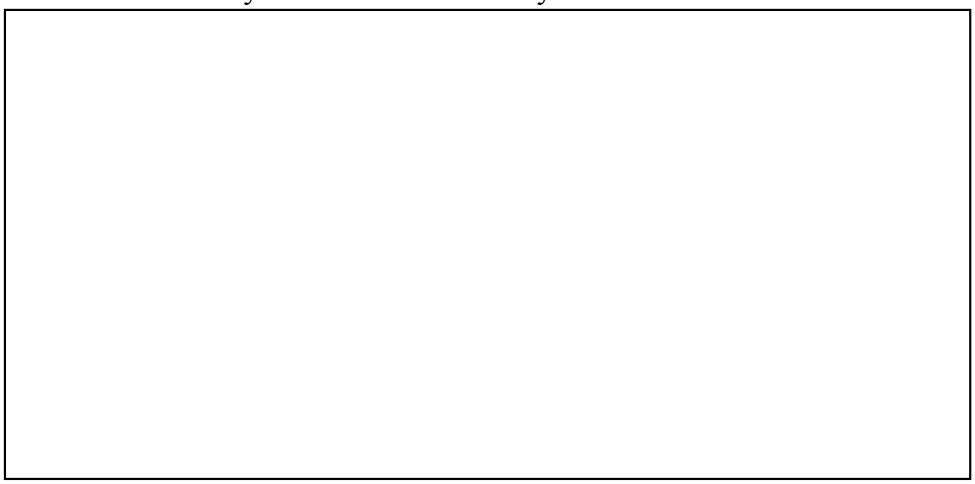


c. It is thought that the main reason for the gauche effect is the interaction between the sigma bonding orbital of one of the C-H bonds and the sigma star antibonding orbital of the anti C-F bond.

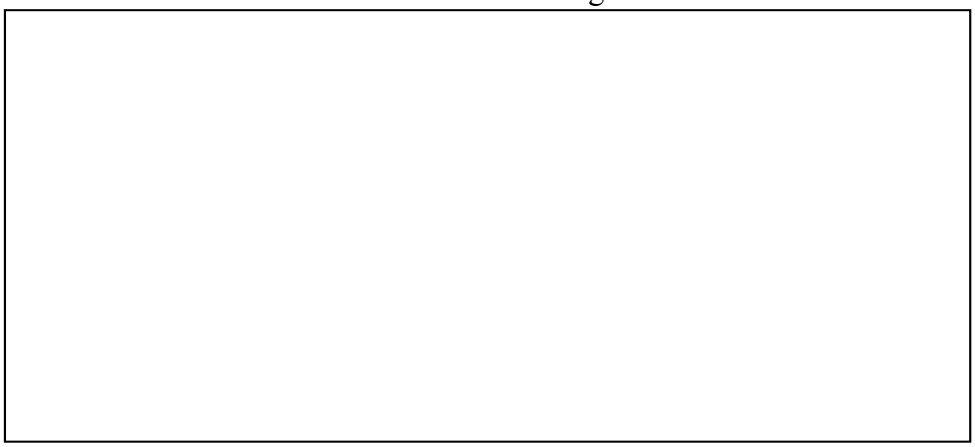
i. Draw the formation of the molecular orbitals of a C-H bond from two atomic orbitals. Label and draw all orbitals.



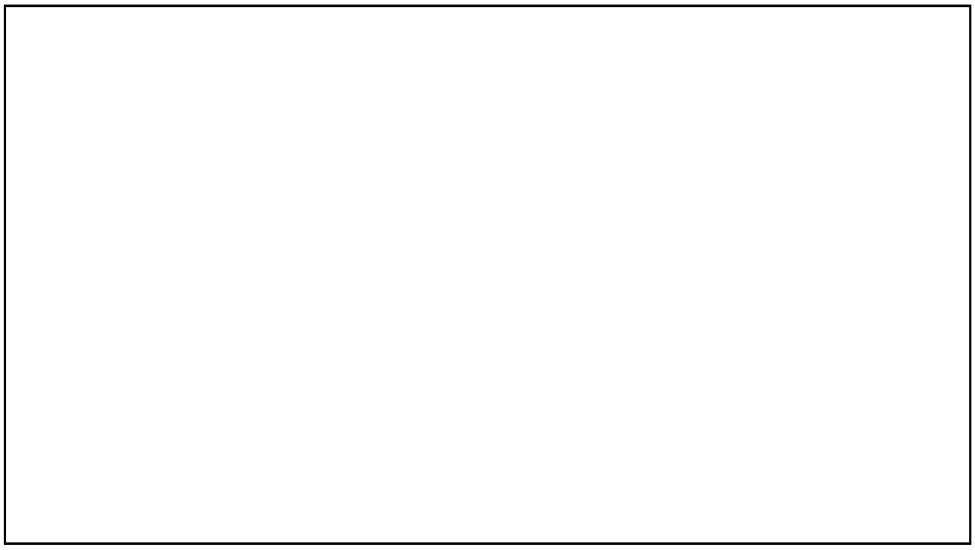
ii. Draw the formation of the molecular orbitals of a C-F bond from two atomic orbitals. Label and draw all orbitals.You may assume the F is not hybridized.



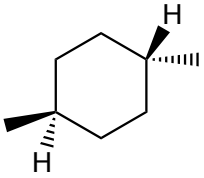
iii. Draw the interaction of the sigma bonding orbital of the C-H bond with the sigma star orbital of the C-F bond. Sketch the orbitals on a line drawing of the molecule.



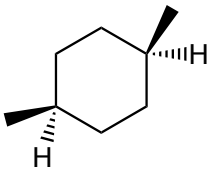
d. Explain why the sigma bonding orbital of the C-H bond interacts with the sigma star orbital of the C-F bond, rather than the sigma bonding orbital of the C-F bond interacting with the sigma star orbital of the C-H bond.



11. (25 points) Consider the two molecules shown below:



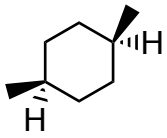
and

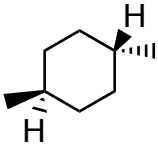


a. Are these molecules diastereomers, enantiomers, constitutional isomers, or the same molecule?

b. Are these molecules chiral?

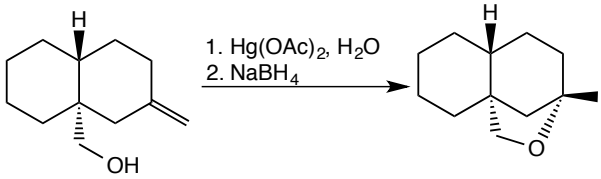
c. Draw both chair conformations of both molecules. Circle the more stable conformation or indicate that they are of equal stability.





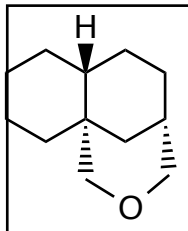
d. Which molecule is more stable? Explain your answer.

12. (20 points) Consider the following reaction:



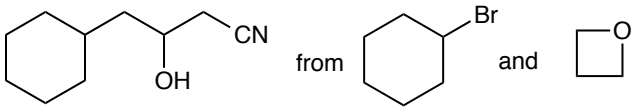
a. Draw the mechanism of the first step of this reaction using arrows to show the flow of electrons. You do not need to show the mechanism for the reaction with $NaBH_4$.

b. Why is the product shown below not formed?



13. (24 points) Synthesize the molecules from the indicated starting materials and any other reagents.

a.



b.