CHEMISTRY 112A FALL 2016

Answer Key

EXAM 3

NOVEMBER 22, 2016

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**
- **No stencils**
- **Molecular models may be used**

Problem	Points (Maximum)
1	28
2	12
3	24
4	18
5	26
6	12
Total	***120***

1. (28 points) For each reaction draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

a.

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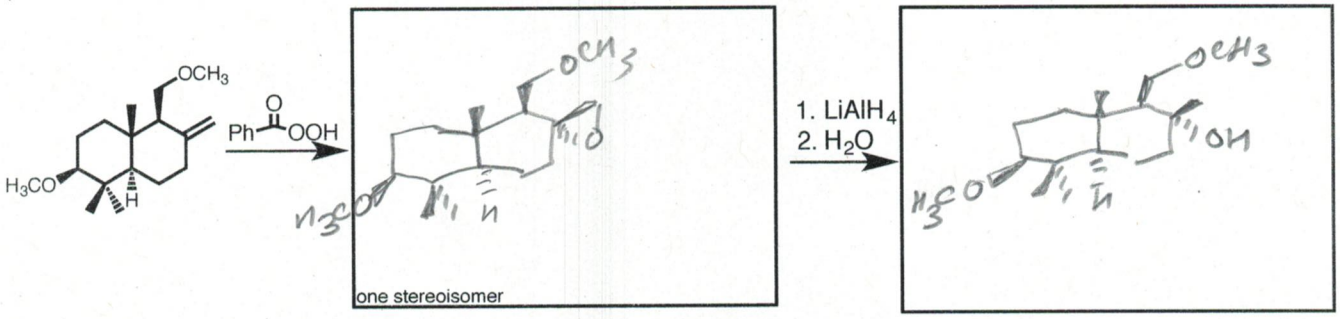
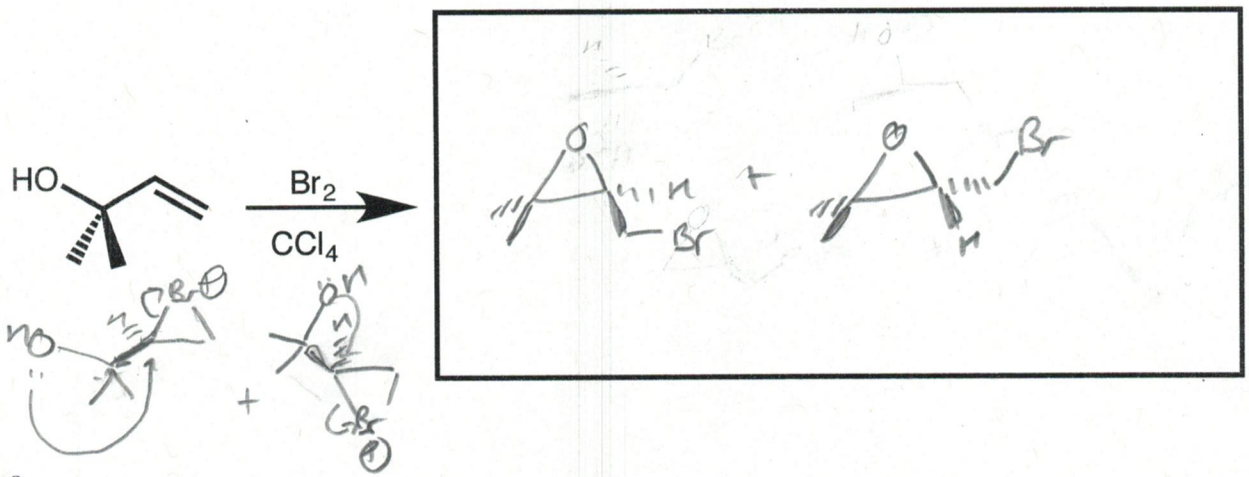
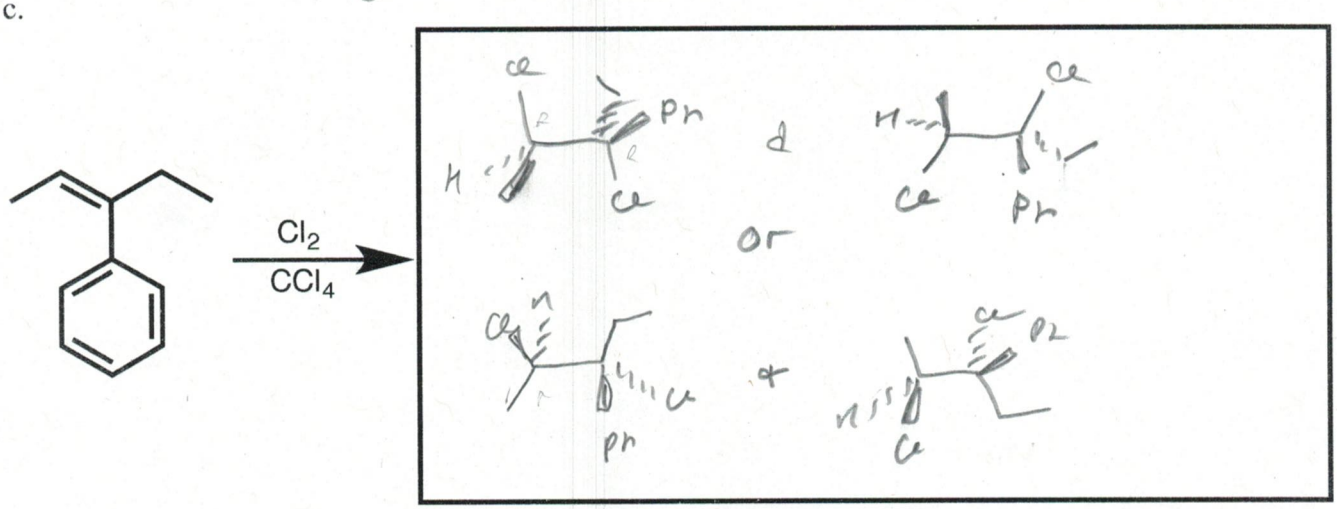


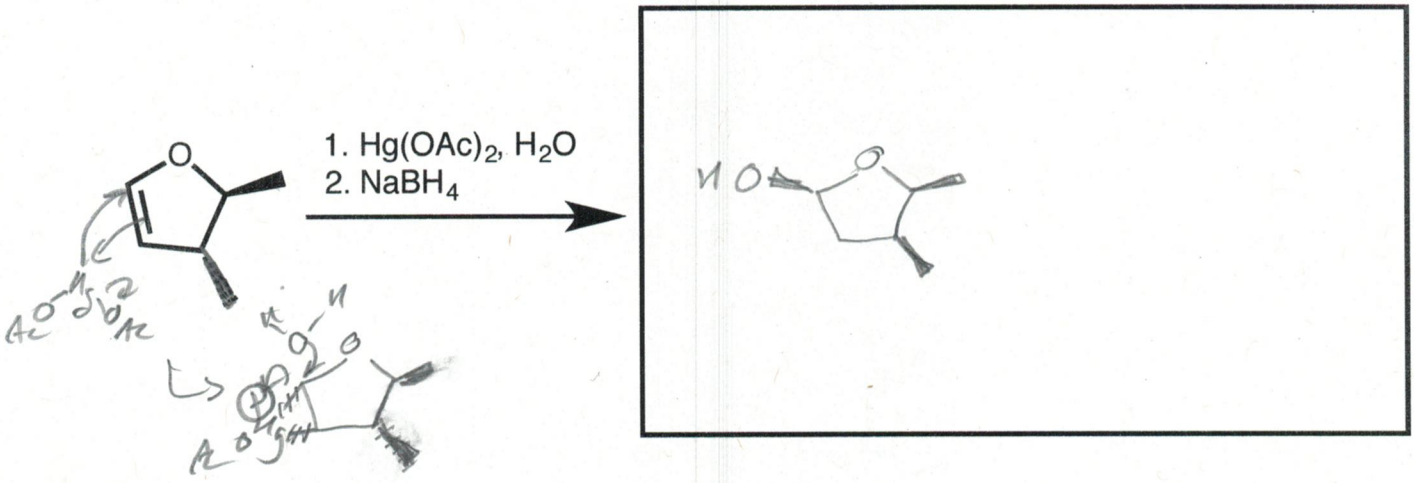
b.



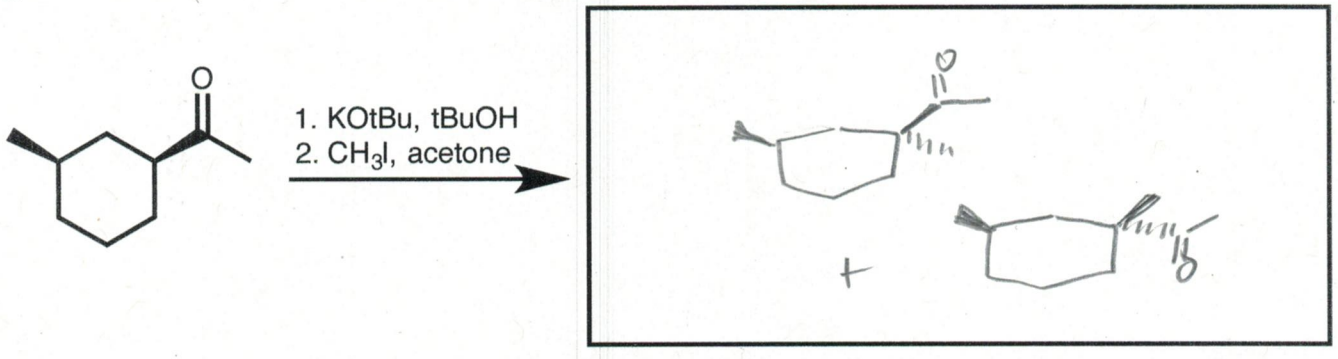
c.



d.

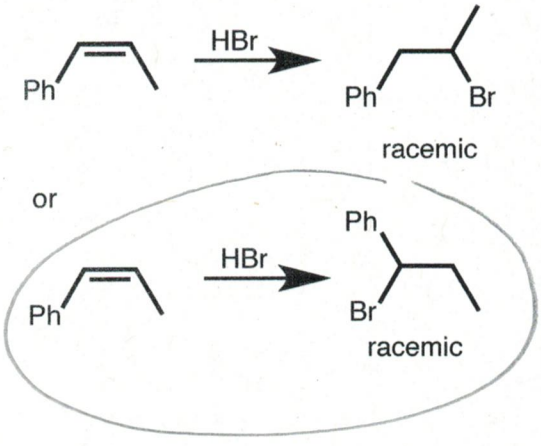


e.



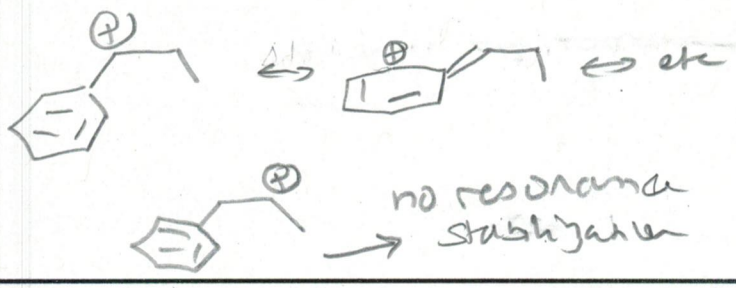
2. (12 points) **Circle** the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. It is possible that one of the reactions shown in each pair does not occur at a measurable rate. You may disregard any other products besides the ones pictured that may form under the reaction conditions. Give explanations in the boxes provided.

a.

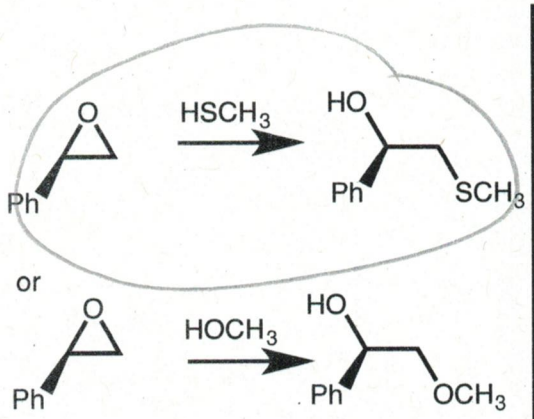


Explanation

more stable carbocation is formed because of resonance w/ Ph ring



b.

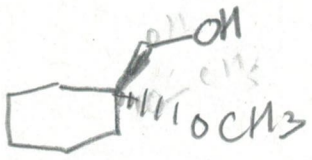


Explanation

this an S_N2 rxn & $HSCH_3$ is a better nucleophile than $HOCH_3$ because S is more polarizable because it is larger because it is one row lower in periodic table than O

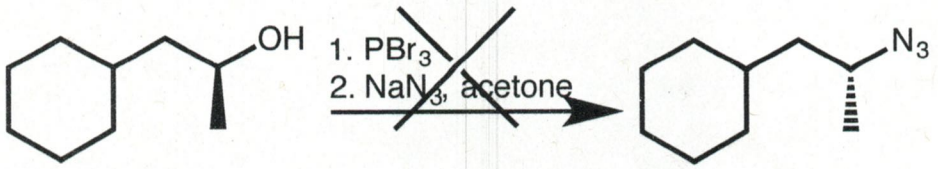
3. (24 points) The following reactions would not occur as written. i. What product would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrate **or** reaction conditions to give the desired product?

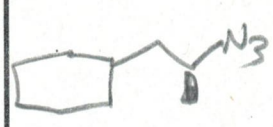
a.

What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence)	How could substrate **or** reaction be changed to give desired product?
	Because protonated epoxide will open at more substituted side because it has more $\delta+$ because carbocation is more stable w/ more alkyl groups	Use CH_3O^- to get an S_N2 rxn at less substituted side.

There are other possible answers

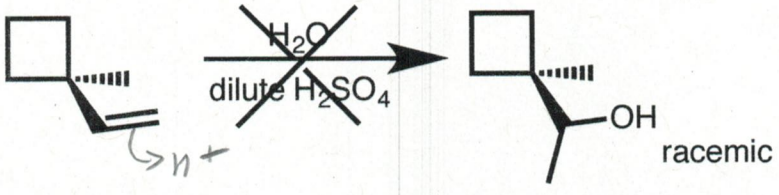
b.

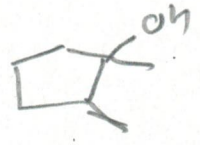


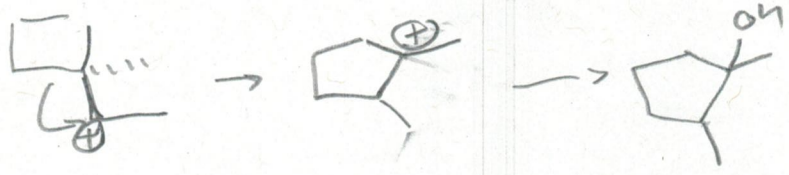
What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence)	How could substrate **or** reaction be changed to give desired product?
	Because PBr_3 does an S_N2 rxn & two successive S_N2 rxns yields retention of configuration	Use TsCl instead of PBr_3 because this does not react w/ inversion of configuration

There are other possible answers

c.

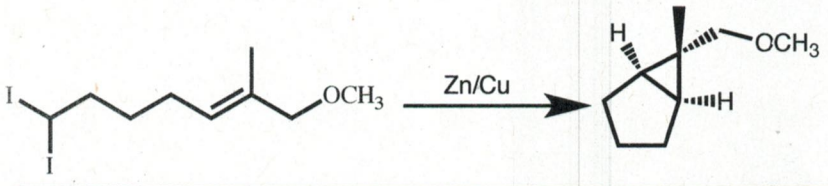


What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence)	How could substrate **or** reaction be changed to give desired product?
 all stereoisomers	Carbocation that is formed will rearrange to form more substituted carbocation & relieve ring strain	Use $Hg(OAc)_2$, H_2O instead.

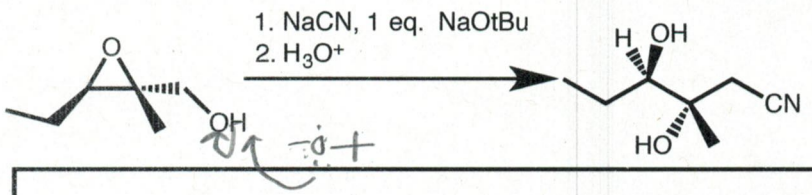


4. (18 points) Draw the mechanism of the following reactions using arrows to indicate the flow of electrons. Make sure to clearly indicate stereochemistry.

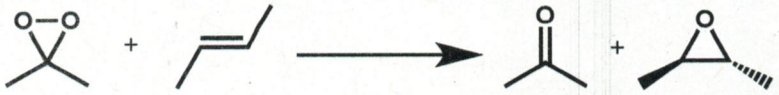
a.



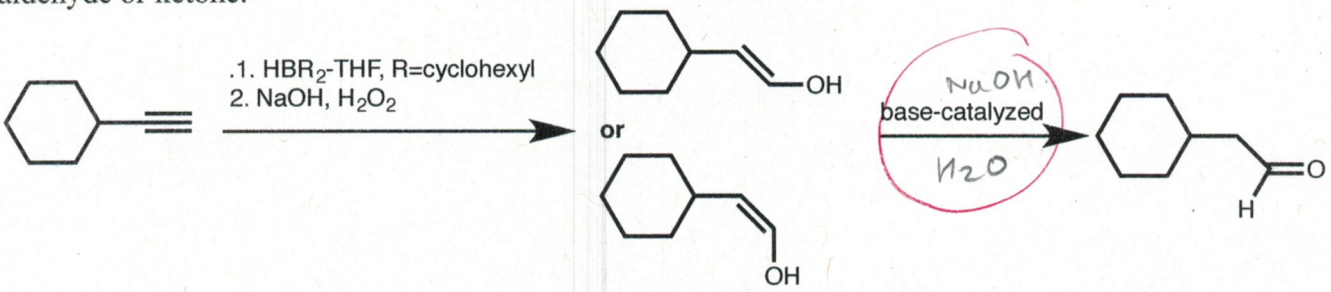
b.



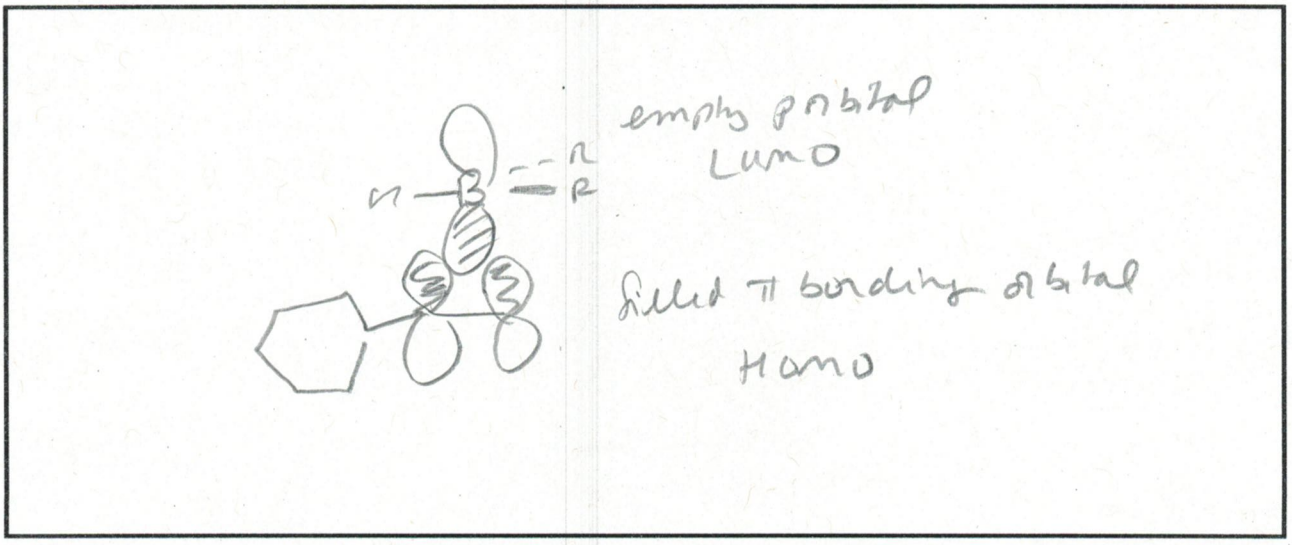
c. 3,3-Dimethyldioxirane is a potent epoxidation reagent. Draw the mechanism for 3,3-dimethyldioxirane epoxidizing the alkene shown below.



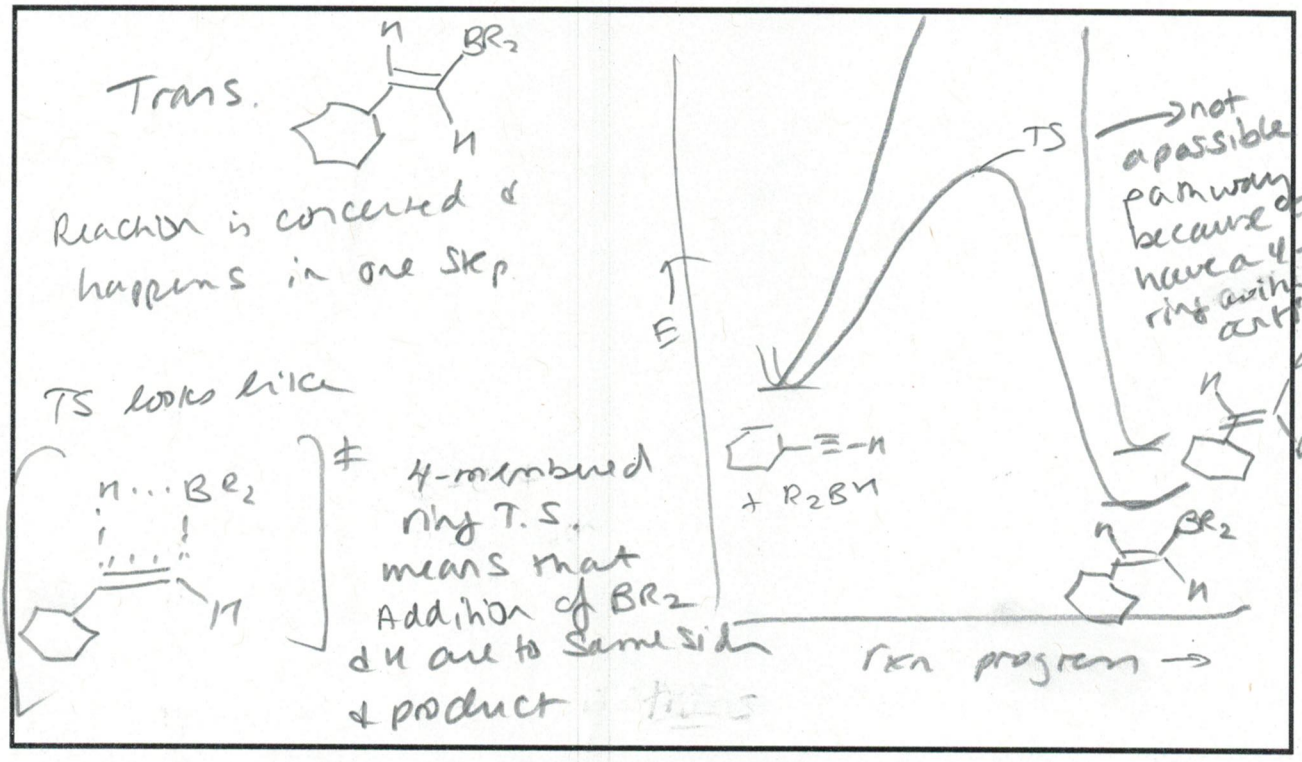
5. (26 points) Alkynes undergo hydroboration to initially form an enolate, which then tautomerizes to an aldehyde or ketone.



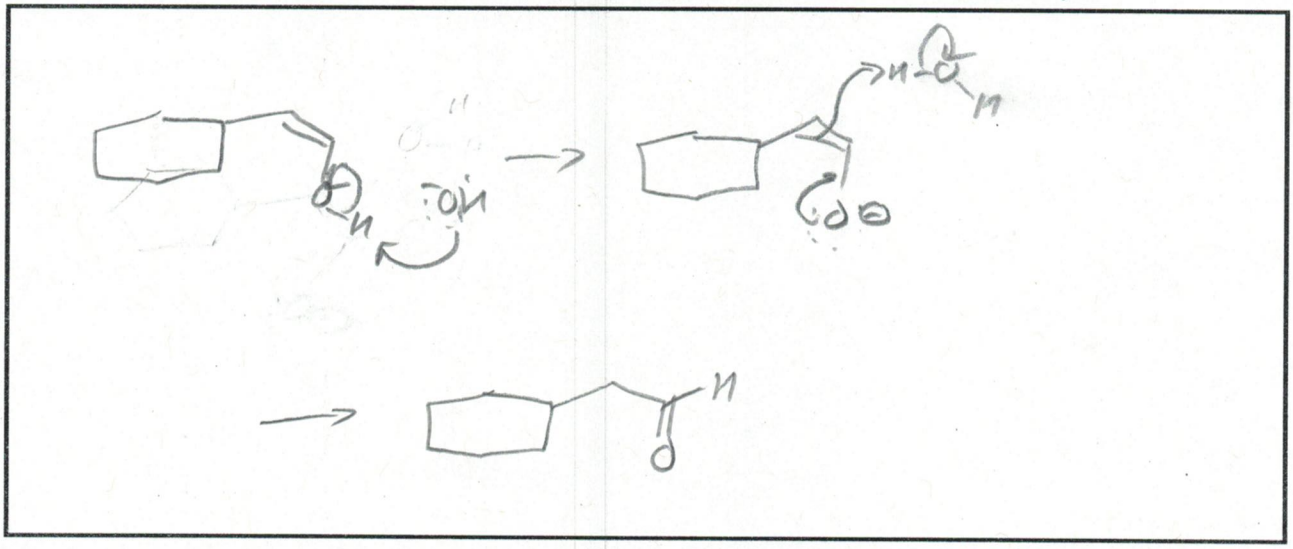
a. Sketch the orbitals that initially interact when HBR_2 reacts with the alkyne. Label each orbital and label it as a LUMO or HOMO.



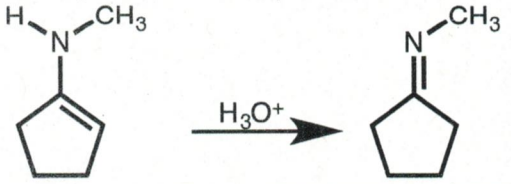
b. Would you expect the initially formed boron addition product to be cis or trans? Explain your choice. Include a reaction energy diagram and a sketch of the transition state of the rate-determining step in your explanation.

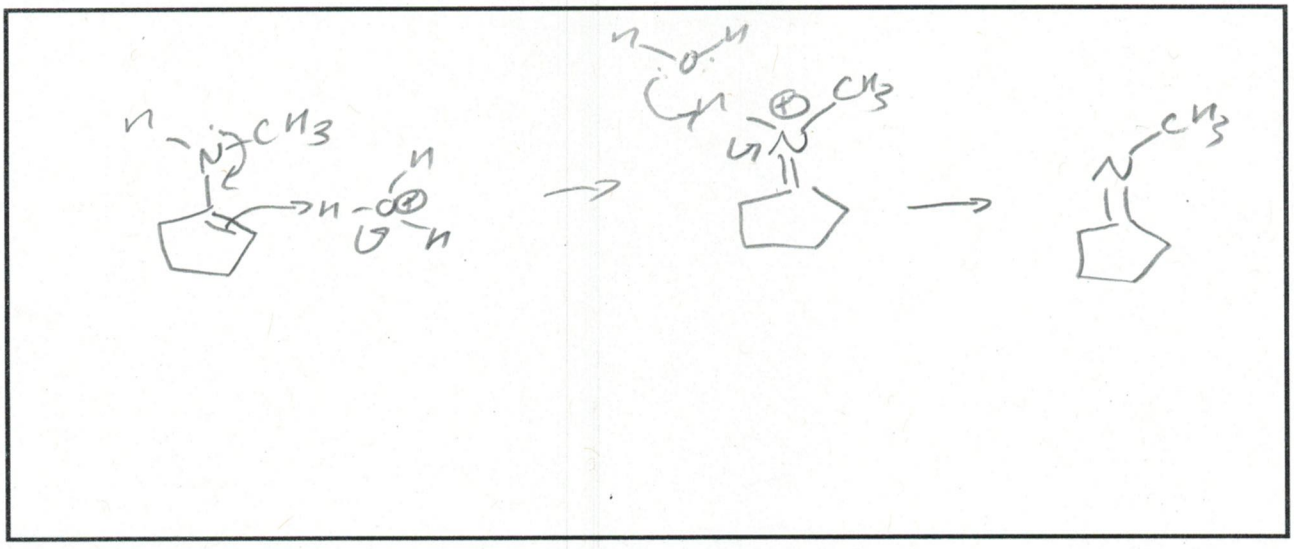


c. Draw a mechanism for the base catalyzed tautomerization of the enol to the aldehyde.

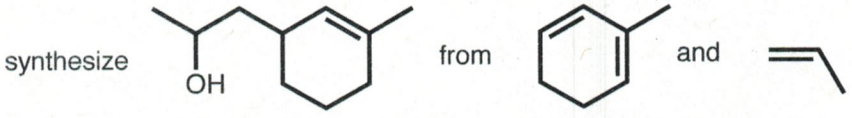


d. Enamines are similar to enols with nitrogen replacing oxygen. The enamine shown below will undergo an acid-catalyzed tautomerization to the imine. Draw the mechanism of this reaction.





6. (12 points) Synthesize the indicated product from the indicated starting materials and any other reagents. In your synthesis, show each product formed by each set of reagents.



all stereoisomers