# CHEMISTRY 112A FALL 2015

## FINAL EXAM

DECEMBER 16, 2015

**NAME- WRITE BIG** ________________________________________

**STUDENT ID:** __________________

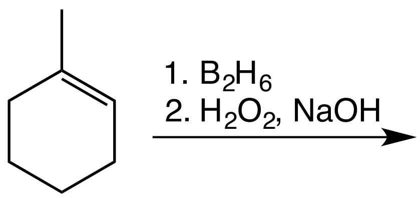
**SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE:** ________________________

- **You will have 2 hours 45 minutes 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**

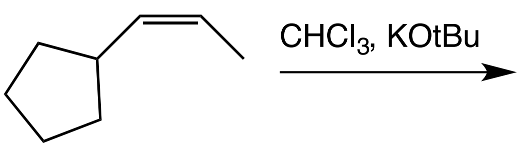
| Problem | Points (Maximum) |
|---|---|
| **1** | 36 |
| **2** | 24 |
| **3** | 18 |
| **4** | 18 |
| **5** | 43 |
| **6** | 39 |
| **7** | 38 |
| **8** | 30 |
| **9** | 14 |
| **10** | 24 |
| **11** | 16 |
| ***Total*** | ***300*** |

1. (36 points) For each reaction, draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

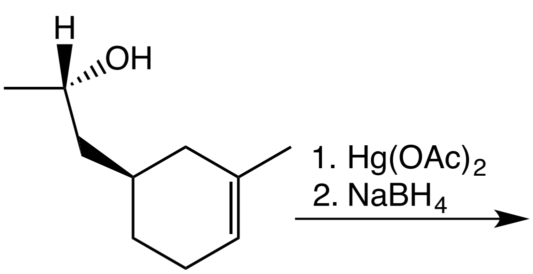
a.



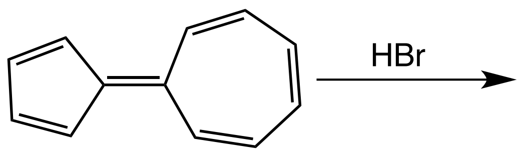

b.




c.

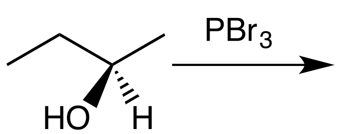


d.

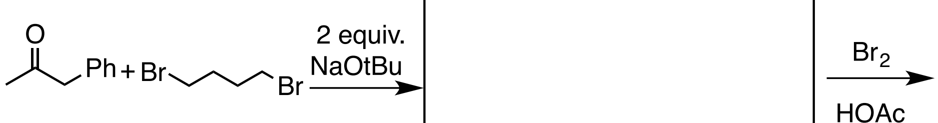



**Draw product of addition of one H-Br**

e.



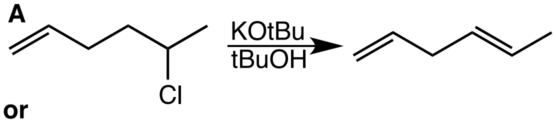

f.



2. (24 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.

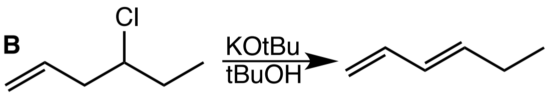
a.

**A**




**or**

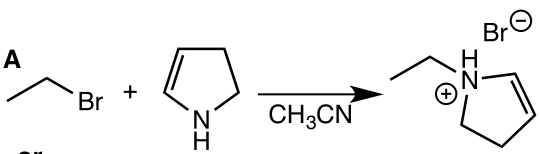
**B**




**Explanation**

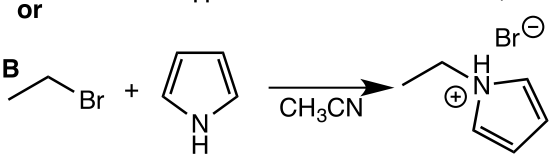
b.

**A**




**or**

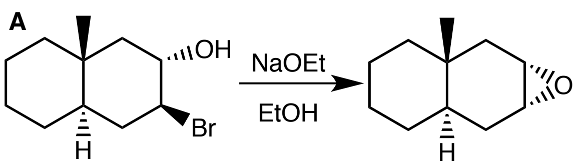
**B**



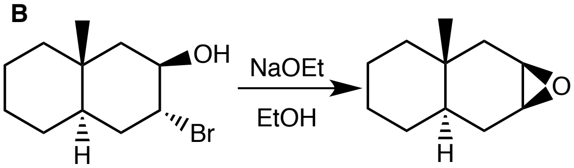

**Explanation**

c. *Hint: think about chair conformation*

**A**

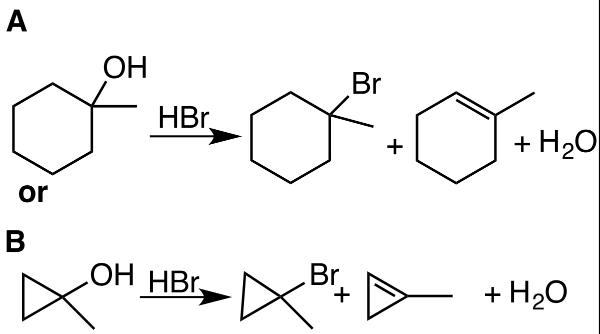



**B**




**Explanation**

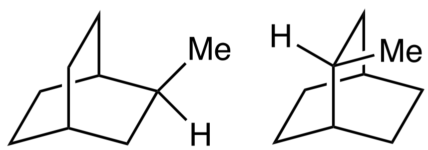
d.



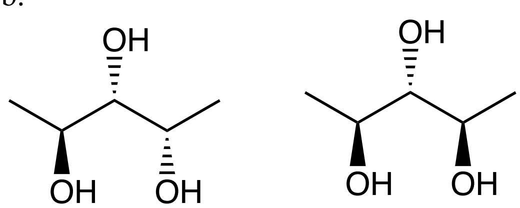

**Explanation**

3. (18 points) Identify the following pairs of molecules as enantiomers, diastereomers, constitutional isomers, or identical.

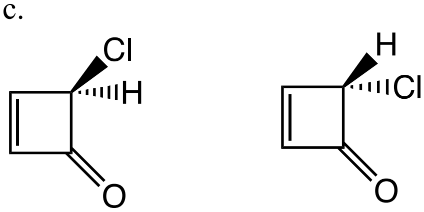
a.




b.

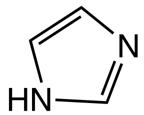



c.

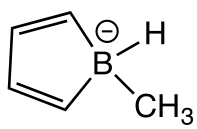


4. (18 points) For each of the following molecules state whether the molecule is aromatic, non-aromatic, or antiaromatic. Explain your answers briefly.

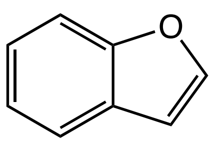
a.



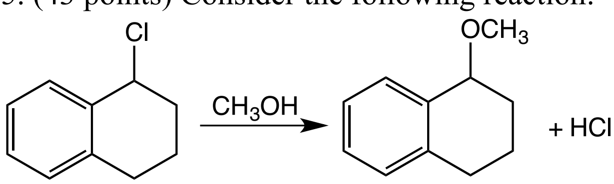

b.




c.



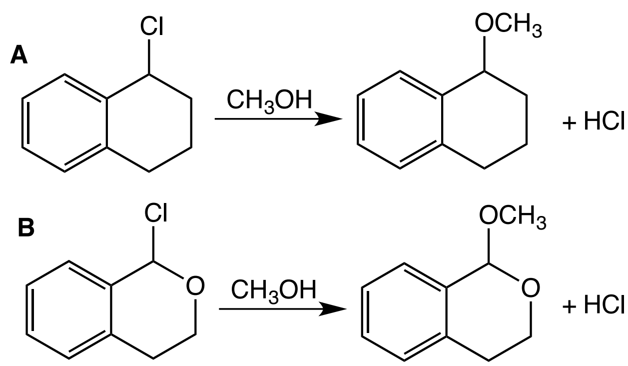

5. (43 points) Consider the following reaction:




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

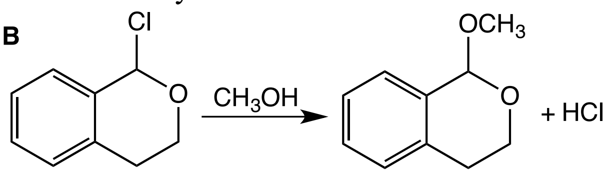
b. What is the rate-limiting step of this substitution reaction?

c. Which of the two reactions shown below is faster? Explain your answer making sure to address why the <u>rate</u> of the reaction is different. Include in your answer sketches of transition states or intermediates that illustrate your explanation.

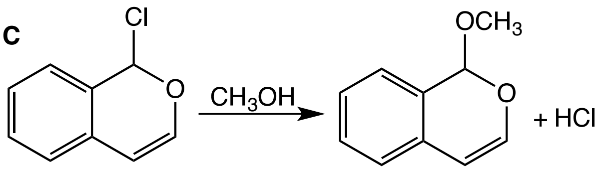


d. Which of the two reactions shown below is faster? Explain your answer making sure to address why the rate of the reaction is different. Include in your answer sketches of transition states or intermediates that illustrate your answer.

**B**

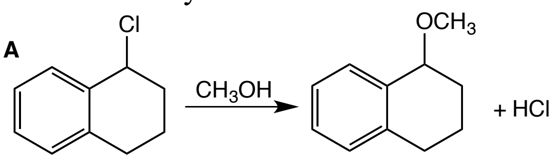



**C**

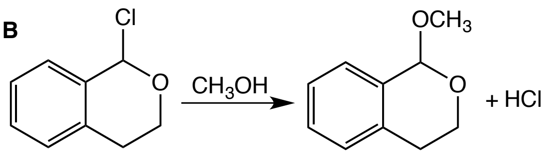


e. Draw a reaction coordinate diagram to illustrate all three reactions, which are redrawn below. You **do not** need to include drawings of starting materials, products, intermediates, or transition states. Clearly label each curve as reaction **A**, **B**, or **C**. You may assume the starting materials and products have similar stability.

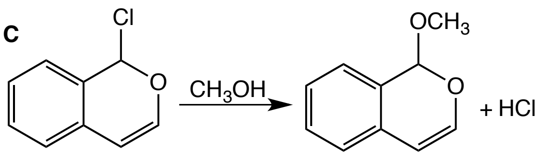
**A**



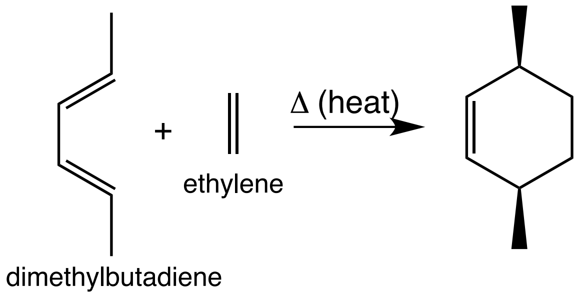

**B**




**C**

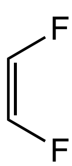


6. (39 points) The Diels-Alder reaction is shown below. This is a reaction that you have not yet learned. In this reaction, a diene reacts with an alkene to form a cyclohexene in one step.




a. Draw a mechanism for this reaction using arrows to show the flow of electrons. All of the bonds are formed or broken in one step.

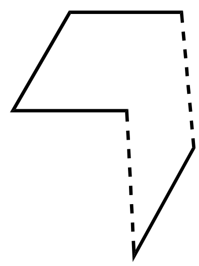
b. In this reaction, ethylene is reacting as the electrophile, while the diene is the nucleophile. Would you expect the molecule below to be a more reactive or less reactive electrophile than ethylene? Explain your answer.



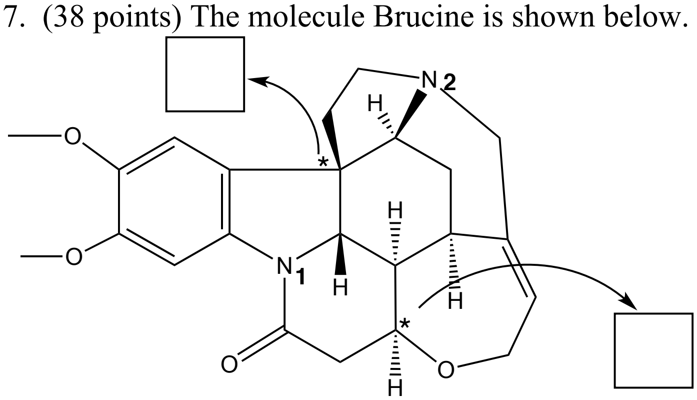
c. Draw the formation of the molecular orbitals to form both bonds of the double bond of ethylene from atomic orbitals. Fill the orbitals with electrons, label and sketch the orbitals, and label the HOMO and LUMO.

d. Draw all of the molecular orbitals of the conjugated pi bonds of the butadiene. Fill the orbitals with electrons, sketch the orbitals, indicate nodes, and label the HOMO and LUMO.

e. In this reaction, the HOMO of the butadiene reacts with the LUMO of ethylene. Sketch the HOMO of butadiene and the LUMO of ethylene on the line drawing below. Note that the dotted lines indicate the formation of the new sigma bonds to form the cyclic product.



7. (38 points) The molecule Brucine is shown below.




a. Assign *R* and *S* to the indicated carbons.
b. Indicate the hybridization for each nitrogen in the molecule. Indicate the type of orbital for each lone pair on nitrogen.

**N$_1$** Type of orbital for lone pair: ___________

Hyrbridization of nitrogen: ___________

**N$_2$** Type of orbital for lone pair: ___________

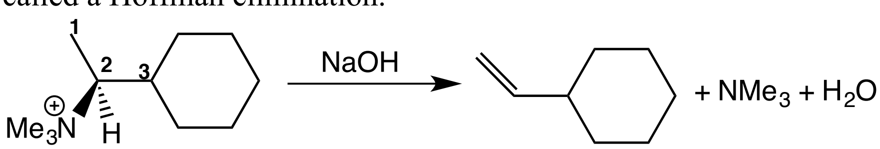
Hyrbridization of nitrogen: ___________

c. Which is the most basic atom in the molecule? Explain your choice.

d. Which is the most acidic proton in the molecule? Explain your choice.

e. Brucine is often used to resolve mixtures of enantiomers of carboxylic acids. You decide to use brucine to purify the *R* enantiomer from racemic 3-hydroxybutyric acid. The pure *R* enantiomer of 3-hydroxybutyric acid has a specific rotation of -20°. If the product you isolate has a specific rotation of -15°, what is percentage of each enantiomer is present in your isolated mixture? Show your work.

8. (30 points) The elimination below yields the less substituted alkene as the major product. This is called a Hoffman elimination.




a. Draw the staggered Newman projections of this molecule looking down the C2-C3 bond.

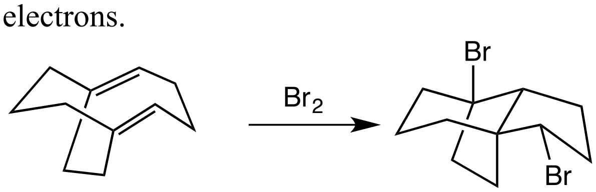
i. Indicate which conformation is **<u>least</u>** stable.

ii. Indicate which conformation is preferred for an elimination reaction to form the more substituted alkene with a double bond between C2 and C3 (the Zaitsev product).

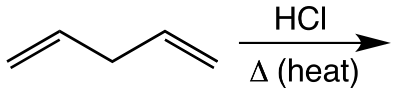
b. Draw the staggered Newman projection(s) of this molecule looking down the C1-C2 bond.

c. Using the Newman projections you drew in part a and b, explain why this reaction produces the less substituted alkene as the major product, while a typical E2 reaction produces the more substituted alkene as the major product.

9. (14 points) Draw the mechanism for the following reaction using arrows to show the flow of electrons.



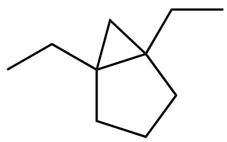
10. (24 points) Consider the reaction below.



a. Draw the mechanism of the reaction to provide the thermodynamic product. Note, that this reaction does not involve an intramolecular cyclization.

b. Explain why this reaction forms the product you drew.

11. (16 points) Synthesize the following molecule from the indicated starting material and any other reagents.



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