## Chemistry 112A FALL 2016

Final Exam

December 14, 2016

## Name- WRITE BIG

Student ID: $\qquad$
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: $\qquad$

- 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 <br> (Maximum) |
| :---: | :---: |
| $\mathbf{1}$ | 25 |
| $\mathbf{2}$ | 18 |
| $\mathbf{3}$ | 16 |
| $\mathbf{4}$ | 18 |
| $\mathbf{5}$ | 20 |
| $\mathbf{6}$ | 26 |
| $\mathbf{7}$ | 24 |
| $\mathbf{8}$ | 16 |
| $\mathbf{9}$ | 18 |
| $\mathbf{1 0}$ | 26 |
| $\mathbf{1 1}$ | 22 |
| $\mathbf{1 2}$ | 30 |
| $\mathbf{1 3}$ | 21 |
| $\mathbf{1 4}$ | 20 |
| $\boldsymbol{T o t a l}$ | $\mathbf{3 0 0}$ |
| $\mathbf{~}$ |  |

1. (25 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.

e.

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. 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 brief explanations in the boxes provided.
a.

b.

c.

3. (16 points) Identify the following pairs of molecules as enantiomers, diastereomers, constitutional isomers, identical, or different molecules.
a.

b.

c.

d.



4. (18 points) For each of the following molecules state whether the molecule is aromatic, non-aromatic, or antiaromatic. Explain your answers briefly and indicate which lone pairs are part of any aromaticity you identify.
a.



c.

5. (20 points) Consider the molecule drawn below:
a. Circle the two most basic atoms.

b. Explain your choice.
c. Determine the hybridization of the atom and the orbital of the lone pair for each of the numbered nitrogens below.


| Nitrogen | Hybridization of $\mathbf{N}$ | Orbital of lone pair |
| :---: | :---: | :---: |
| 1 |  |  |
| 2 |  |  |
| 3 |  |  |
| 4 |  |  |

6. (26 points) Consider the two molecules below:

A

B

The site of protonation of molecule $A$ is nitrogen, while the site of protonation of molecule $B$ is oxygen. a. Draw the protonated form of each molecule.

| Molecule A | $\left.\begin{array}{\|l\|}\hline \text { Molecule B } \\ \\ \\ \\ \\ \\ \hline\end{array}\right]$ |
| :--- | :--- |

b. Explain way these two similar molecules are protonated on different atoms.
c. Draw resonance structures of the anion shown below. Which resonance structure is the most important contributor? Explain your answer.
d. The reaction shown below forms three products. The first product is given to you. Fill in the other two products.


Two additional products:
7. (24 points) Circle the molecule that is most stable in the following pairs. Explain your choice in the box.
a.


b.




d.



8. (16 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 products in as few steps as possible?
a.




What product is actually made? (Draw structure or NR for no reaction)

Why was desired product not formed? How could substrate or reaction be (Explain in 1 sentence)
changed to give desired product in as few steps as possible?
b.


9. (18 points) Consider the following reaction:

a. Draw the mechanism of the reaction to form product $\mathbf{1}$ using arrows to show the flow of electrons. Illustrate the stereoselectivity of the reaction by drawing the formation of one of the two enantiomers of the product. You do not need to show the mechanism for the formation of both enantiomers.
b. Draw the mechanism of the reaction to form product 2 using arrows to show the flow of electrons. Illustrate the stereoselectivity of the reaction by drawing the formation of one of the two enantiomers of the product. You do not need to show the mechanism for the formation of both enantiomers.

10. (26 points) Consider the reaction below:

a. Fill in R or S in the boxes.
b. Draw the two chair conformations of the cyclohexane ring. Identify which is more stable and explain your choice. Include all hydrogens on the rings in your answer.
c. Draw the mechanism for this reaction, using arrows to illustrate the flow of electrons.
$\square$
d. Based on your answer to part b and c, draw the major product of the reaction. Explain your answer.
11. (22 points) Consider the reaction shown below in which an aziridine (3-membered ring with nitrogen) reacts with an allylic Grignard reagent:

a. Draw a mechanism with arrows for this reaction.
b. Assume the Grignard reagent is ionic and the allyl anion reacts with the aziridine. Draw the molecular orbitals of the allyl anion at the correct relative energy levels. Label i. the HOMO and LUMO, ii. all nodes, iii. bonding, antibonding, and non bonding orbitals, and iv. fill the orbitals with electrons.
$\qquad$
c. Sketch the orbitals that initially interact when the allyl anion reacts with the aziridine. Clearly show the interaction between the orbitals in your drawing. Label each orbital and identify it as a LUMO or HOMO.
12. (30 points) Consider the two reactions shown below.

A


B

a. Write the mechanism for Reaction A, using arrows to show the flow of electrons. Show formation of both products.
b. Which reaction to you expect to be faster, Reaction A or Reaction B? Explain your answer.
$\square$
c. Do you expect the ratio of alcohol to alkene product to be the same for both reactions? Explain your answer.
$\square$
d. Draw a reaction energy diagram that illustrates your answers to parts a-c. Include both reactions on your diagram. Draw structures of starting materials, intermediates, and all products in your diagram.
13. (21 points) Consider the reaction shown below.


mixture of stereoisomers
a. Draw a mechanism for the reaction using arrows to show the flow of electrons. You do not need to indicate stereochemistry. A mixture of stereoisomers is formed.
b. What other products would you expect? Can you predict which would be the major product? Explain your answer.
$\square$
14. (20 points) Synthesize the following molecules from the indicated starting material and any other reagents.
a.

b. All of the carbons in your product should come from the indicated starting material.

$\square$

