CHEMISTRY 112A FALL 2015

EXAM 1

SEPTEMBER 29, 2015

NAME- WRITE BIG _____

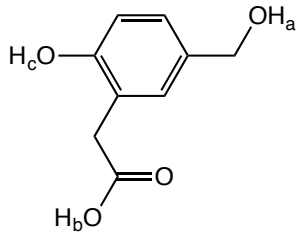
STUDENT ID: _____

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

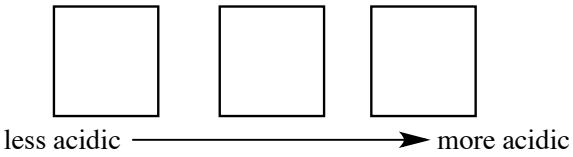
- **You will have 75 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **No stencils**
- **Molecular models may be used**

Problem	Points (Maximum)
1	16
2	16
3	17
4	22
5	24
6	15
7	10
Total	***120***

1. (16 points) Consider the molecule shown below.



a. Place in order of increasing acidity H_a, H_b, and H_c.



b. Explain why the hydrogens follow the order of acidity you listed in part a.

c. The three hydrogens in this molecule have pKa's: of 4.5, 10, and 16. Draw a picture of the major form of this molecule at the following pH's:

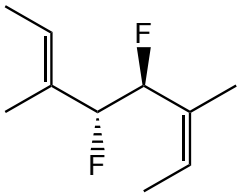
pH = 1

pH = 7

pH = 12

2. (16 points) For each of the following molecules:
i. Circle chiral or achiral
ii. If the molecule is chiral, draw the enantiomer. Write N/A if there is no enantiomer.
iii. Draw <u>one</u> diastereomer of each molecule. Write N/A if there are no diastereomers.

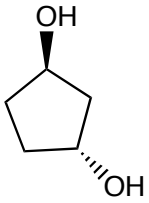
a.



Chiral or Achiral

enantiomer	**diasteriomer**

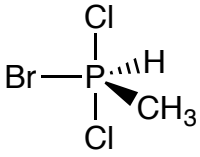
b.



Chiral or Achiral

enantiomer	**diasteriomer**

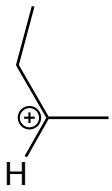
c. Assume that this conformation is stable and does not convert to another conformation.



Chiral or Achiral

enantiomer	**diasteriomer**

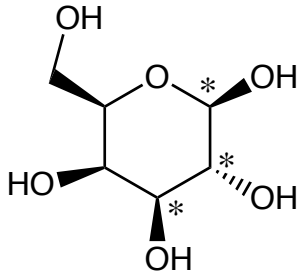
d.



Chiral or Achiral

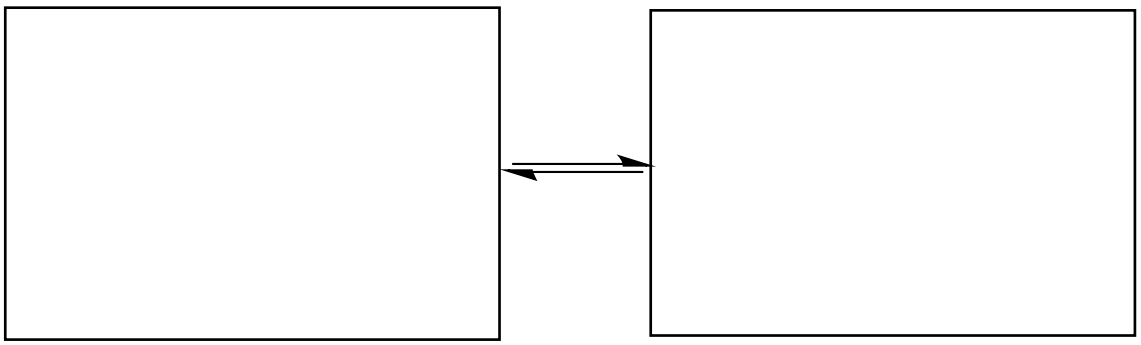
enantiomer	**diasteriomer**

3. (17 points) β-D-galactopyranose is shown below.



a. Assign the <u>three</u> starred tetrahedral stereocenters as *R* or *S* in the above drawing.

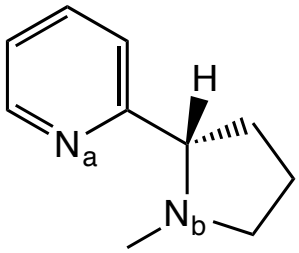
b. Draw both chair conformations of this molecule. *<u>Include all hydrogen atoms</u>*.



c. Circle the most stable chair conformation. Explain why it is most stable.

Explanation

4. (22 points) a. The alkaloid **nicotine** is found in tobacco and is shown below.
i. Label the hybridization of each carbon and nitrogen. Use '3' for sp^3, '2' for sp^2, and '1' for sp.
ii. Indicate the type of orbital of each lone pair on nitrogen.
iii. Circle the most basic atom in nicotine. Explain why the atom you chose is the most basic.

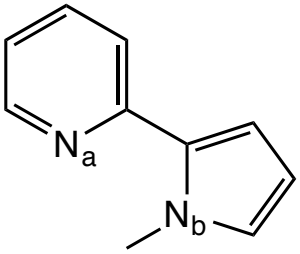


Type of orbital for lone pair on N_a: _____

Type of orbital for lone pair on N_b: _____

Explanation

b. Another alkaloid found in tobacco is **nicotyrine**, which is shown below.
i. Label each carbon and nitrogen with hybridization. Use '3' for sp^3, '2' for sp^2, and '1' for sp.
ii. Indicate the type of orbital of each lone pair on nitrogen.
iii. Circle the most basic atom in nicotyrine. Explain why the atom you chose is the most basic.



Type of orbital for lone pair on N_a: _____

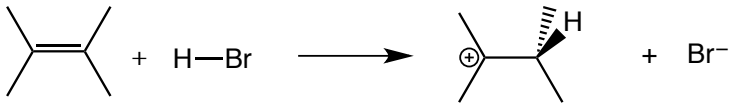
Type of orbital for lone pair on N_b: _____

Explanation

c. The specific rotation of nicotine is -166°. A chemist tries to isolate **nicotine**, but isolates a mixture of enantiomers that has a specific rotation of 16.6°,
i. What is the % ee of the mixture? Show your work.
ii. What is the ratio of nicotine to its enantiomer in the solution? Show your work.

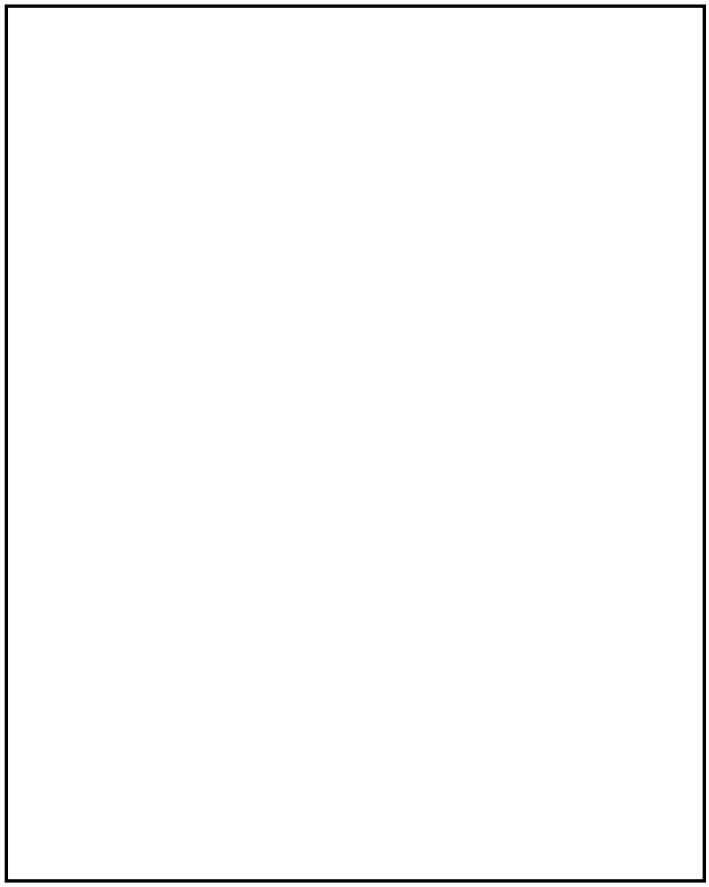
d. If a chemist tries to isolate nicotine, but isolates only **nicotyrine** by accident, what will the specific rotation of the isolate be? Explain your answer.

5. (24 points) Consider the reaction shown below. The carbocation product reacts further, but that reaction isn't shown here. In this reaction, the HOMO of the alkene reacts with the LUMO of the H-Br.

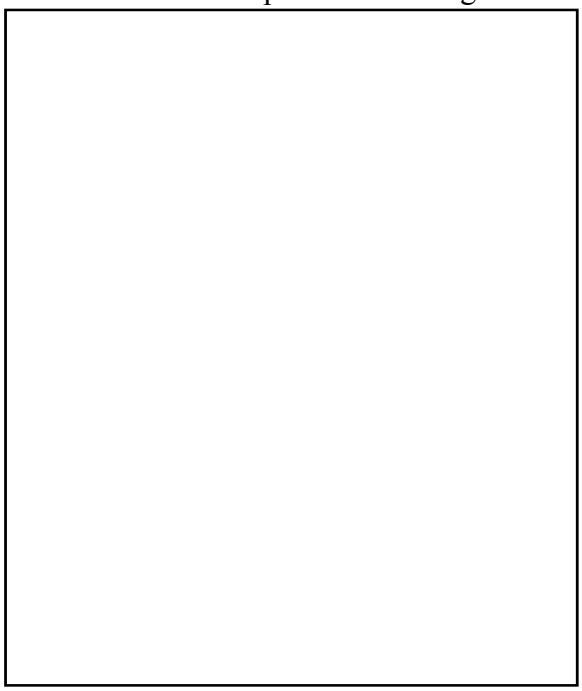


a. Use arrows to represent the flow of electrons in this reaction.

b. Draw an MO diagram of both bonds of the double bond in the alkene. Label and sketch all orbitals. Identify the HOMO of the double bond.

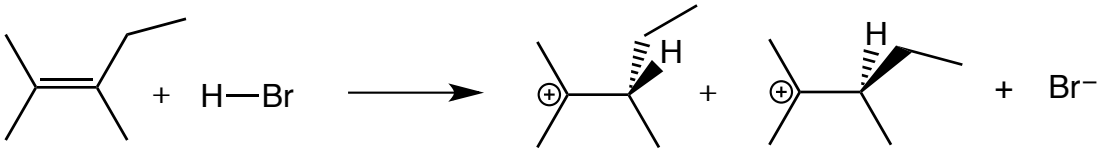


c. Draw an MO diagram of H-Br. Label and sketch all orbitals. Identify the LUMO of H-Br. You do not need to include lone pairs in this diagram. You may assume that bromine is hybridized.

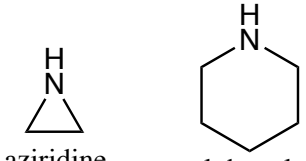


d. The HOMO of the alkene reacts with the LUMO of the H-Br to initiate this reaction. Sketch the interaction of the HOMO of the alkene with the LUMO of the H-Br bond. Overlay the sketch of the orbitals on line drawings of the two molecules.

e. If the alkene shown below is used as a starting material, the two products shown below are formed. What would you expect the ratio of these two products to be? Explain your answer.



6. (15 points) Two cyclic amines are shown below.

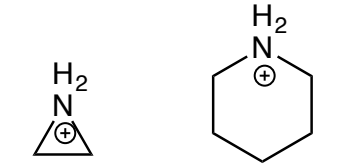


aziridine cyclohexylamine

a. Do you expect aziridine or cyclohexylamine to have more ring strain? Explain your answer. Include in your answer the different kinds of strain that contribute to ring strain in these molecules.

b. How would you set up an experiment to use heat of combustion to compare ring strain in 3-membered and 6-membered cycloamines? You may assume you have access to any organic molecules you need.

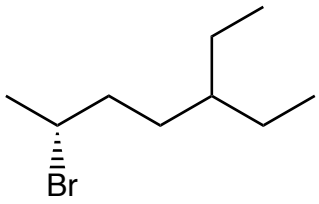
c. The pKa's of the conjugate acids of azridine and cyclohexylamine are given below. Explain why there is a large difference in acidity.



pKa = 7.9 pKa = 10.6

7. (10 points) Name the following molecules. Include *R* and *S* and *E* and *Z* when applicable.

a.



b.