Answer key

CHEMISTRY 112A FALL 2015

EXAM 1

SEPTEMBER 29, 2015

NAME- WRITE BIG ______________________________

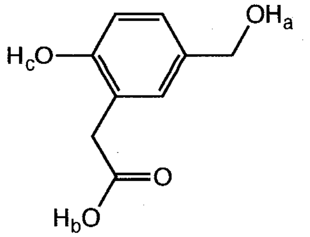
STUDENT ID: ________________

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$_c$.

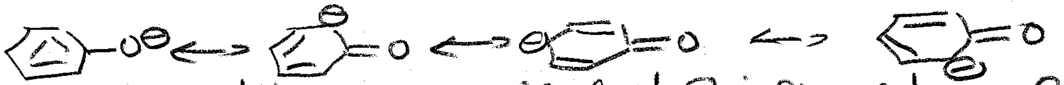
Ha	Hc	Hb

less acidic → more acidic

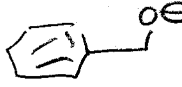
b. Explain why the hydrogens follow the order of acidity you listed in part a.

Justify in terms of stability of conjugate base
more stable conjugate base → less acidic proton

most stable. Stabilized by resonance.
⊖ is shared on another oxygen



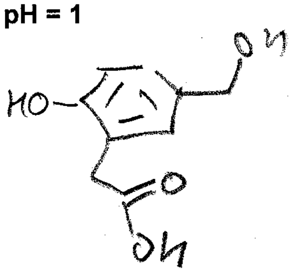
stabilized by resonance, but ⊖ is shared on carbons which is less electroneg than O therefore, less stable conjugate base



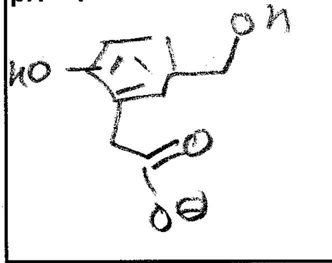
least stable because no resonance stabilization

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:

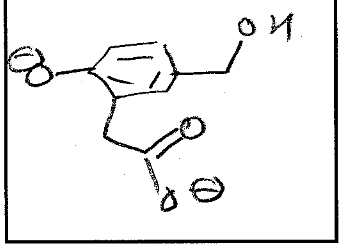
pH = 1



pH = 7

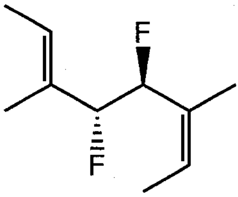


pH = 12



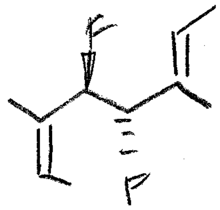
2. (16 points) For each of the following molecules:
i. Circle chiral or achiral
ii. If the molecule is chiral, draw the enantiomer. Write N/A if there is no enantiomer.
iii. Draw one diastereomer of each molecule. Write N/A if there are no diastereomers.

a.

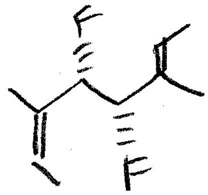


[✓ Chiral] or Achiral

enantiomer

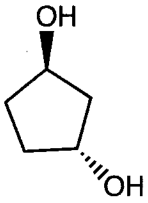


diasteriomer



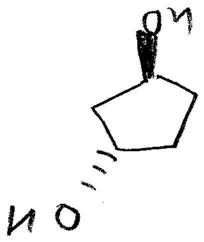
many possibilities

b.

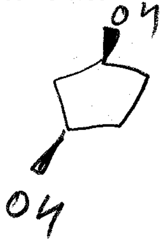


[✓ Chiral] or Achiral

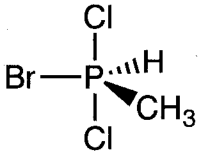
enantiomer



diasteriomer



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

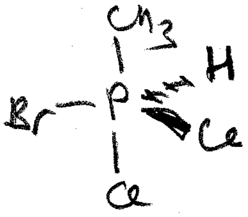


Chiral or [✓ Achiral]

enantiomer

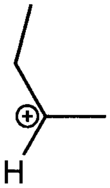
N/A

diasteriomer



many possibilities

d.



Chiral or [✓ Achiral]

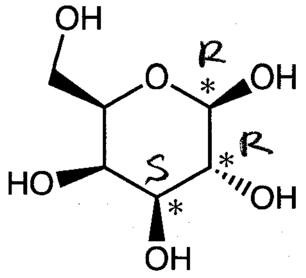
enantiomer

N/A

diasteriomer

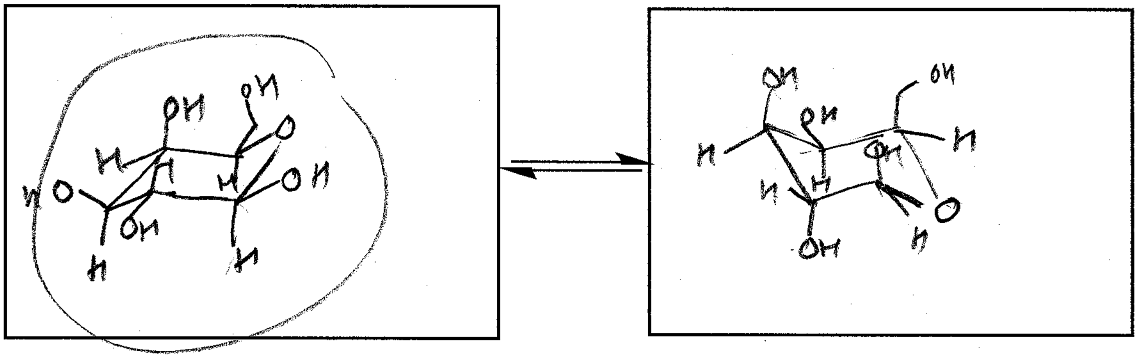
N/A

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. *Include all hydrogen atoms.*

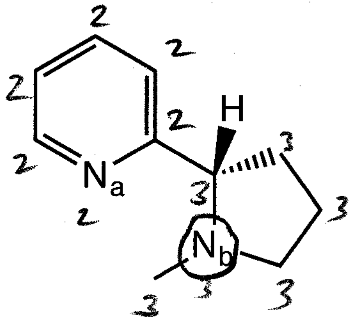


c. Circle the most stable chair conformation. Explain why it is most stable.

Explanation

The circled conformation has four groups equatorial & one axial, while the other conformation has four groups axial & one equatorial. The axial groups are destabilizing due to 1,3-diaxial interactions which are gauche interactions & destabilizing by steric strain

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: sp^2

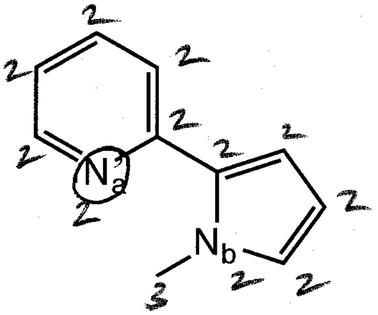
Type of orbital for lone pair on N_b: sp^3

pKa  ~5 pKa $R_3\overset{\oplus}{N}H$ ~ 10
although resonance stabilized ⊕; aromaticity is broken in resonance structures which makes resonance less stabilizing

Explanation

The lone pairs on both nitrogens are not involved in resonance. The main difference between them is their hybridization. Nb is sp^3 hybridized while Na is sp^2 hybridized. The lone pair is more stable in an sp^2 than sp^3 orbital. The higher percentage of s increases the effective electronegativity of N making it a more stable, weaker base.

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: sp^2

Type of orbital for lone pair on N_b: p

Explanation

The basicity of Na is similar in the two molecules. However, Nb is less basic because the lone pair on Nb is involved in resonance. Protonating Nb would disrupt this resonance. Therefore Nb is less basic than Na

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.

i. $\frac{16.6}{166^\circ}$ = 10% ee of enantiomer of nicotine

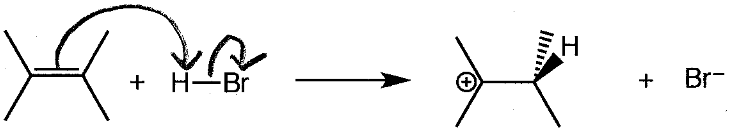
90% racemate → 45% nicotine & 45% enantiomer

Total: 45% nicotine : 55% enantiomer

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.

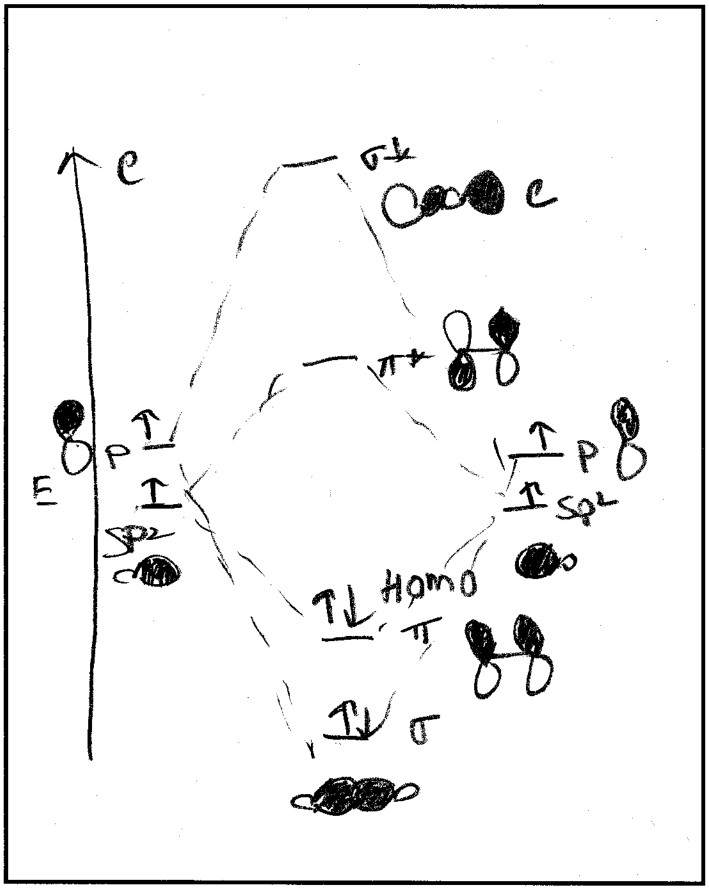
$[\alpha] = 0$ nicotyrine is not chiral & will not rotate light.

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.

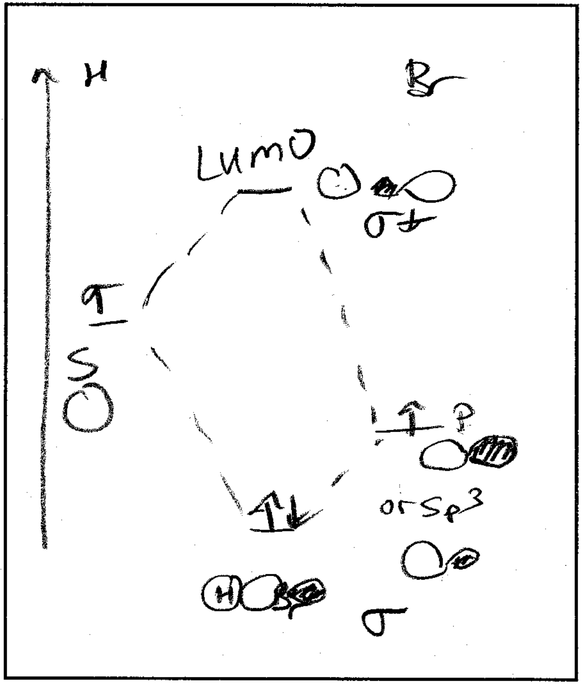


a. Use arrows to represent the flow of electrons in this reaction.

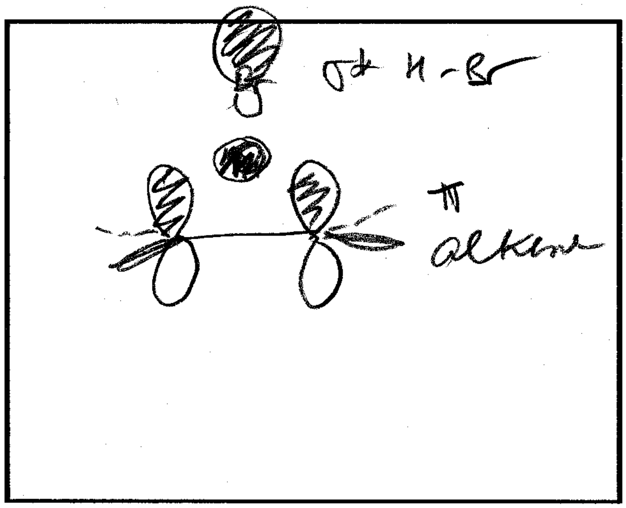
b. Draw an MO diagram of both bonds of the double bond in the alkene. Label and sketch all orbitals. Identify the HOMO of the double bond.



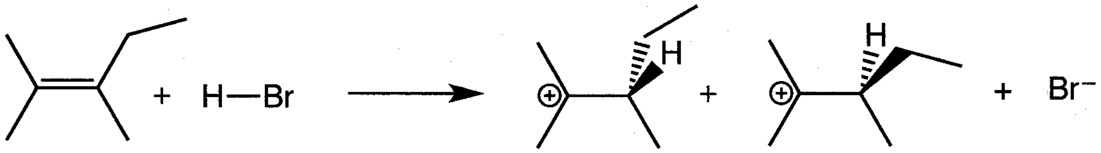
c. Draw an MO diagram of H-Br. Label and sketch all orbitals. Identify the LUMO of H-Br. You do not need to include lone pairs in this diagram. You may assume that bromine is hybridized.



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.



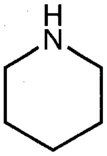
e. If the alkene shown below is used as a starting material, the two products shown below are formed. What would you expect the ratio of these two products to be? Explain your answer.



The ratio will be 1:1. The two products are enantiomers w/ equal stability. The H-Br can react equally well with the two identical faces of the alkene. Reaction with the 'top' produces one of the product enantiomers & reaction with the 'bottom' face of the alkene produces the other enantiomer of product.

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.

Aziridine will have more ring strain. The 3-membered ring will have bond angle strain because sp^3 hybridized atoms are forced to have close to 60° angles due to triangle geometry. Aziridine will also be destabilized by eclipsing interaction & torsional strain. Cyclohexylamine will not have bond angle strain or torsional strain in chair conformation

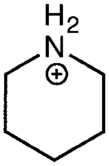
b. How would you set up an experiment to use heat of combustion to compare ring strain in 3-membered and 6-membered cycloamines? You may assume you have access to any organic molecules you need.

It is important to compare isomers. One could compare the heat of combustion of


&


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

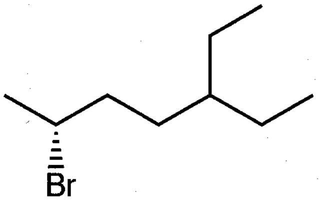

pKa = 7.9


pKa = 10.6

Ring strain means that lone pair of -is in an orbital with more s character. The increased s character will stabilize the lone pair because it will be in a fatter orbital, closer to the nucleus. Therefore  is less basic than .

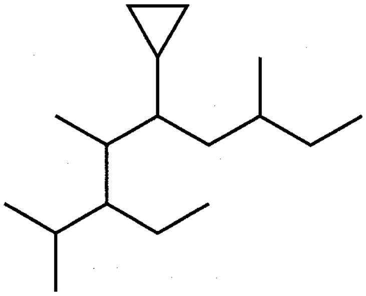
7. (10 points) Name the following molecules. Include *R* and *S* and *E* and *Z* when applicable.

a.



(R)-2-bromo-5-ethylheptane

b.



5-cyclopropyl-3-ethyl-2,4,7-trimethylnonane