CHEMISTRY 12A FALL 2017

EXAM 1

Answer Key

SEPTEMBER 26, 2017

NAME- WRITE BIG ______________________________

STUDENT ID: ________________

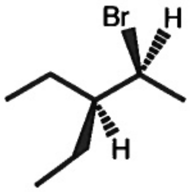
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: ____________________

- **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	8
2	10
3	20
4	11
5	12
6	22
7	11
8	12
9	14
Total	*120*

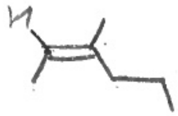
1. (8 points) Fill in either the name or the line drawing of the following molecules:

a.



(S) - 2-bromo-3-ethylpentane

b. (Z)-3-methyl-2-hexene



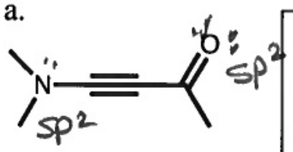
2. (10 points) For each of the following molecules:

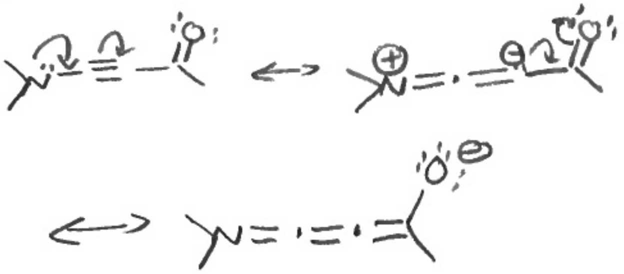
i) Draw in all lone pairs

ii) Identify the hybridization of each oxygen and nitrogen atom.

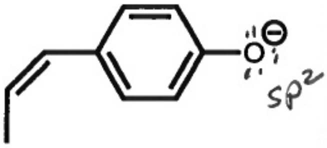
iii) Draw reasonable resonance structures. The atoms in all resonance structures should have full octets.

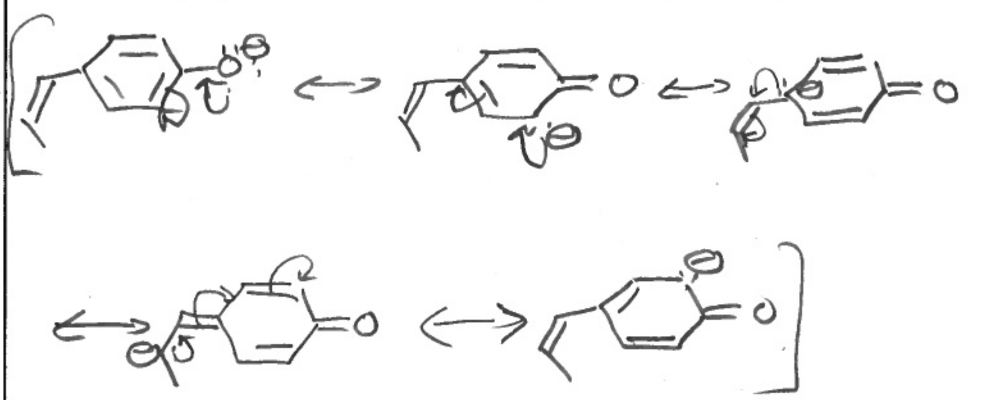
a.





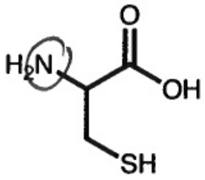
b.





3. (20 points) Circle the indicated atoms in the molecules below. Explain your choice in the box. Include any relevant structures in your explanation.

a. Circle the most **basic** atom.

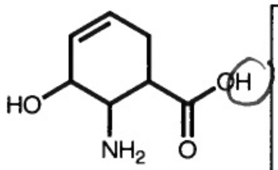


Explanation

Nitrogen is more basic than O because it is to the left in periodic table. Therefore, it is less electronegative & the lone pair is less stable

Sulfur is less basic than O & N because it is farther down a column in periodic table & it is bigger, which stabilizes lone pair.

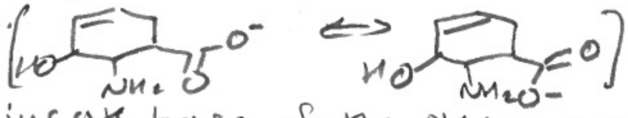
b. Circle most **acidic** H.



Explanation

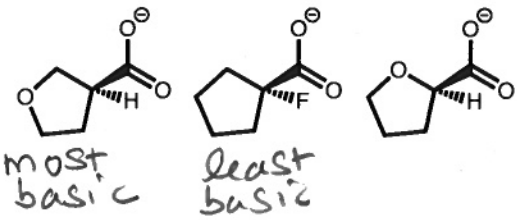
OH more acidic than NH because conjugate base more stable w/ ⊖ because O is more electronegative than N.

The circled O-H is more acidic because conjugate base stabilized by resonance w/ charge spread over two oxygens.



The conjugate base of the other O-H is not stabilized by resonance.

c. What is the order of **basicity** of the following compounds?

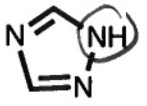


Explanation

Fluorine is more electronegative than oxygen & is therefore more electron withdrawing by induction.
Fluorine stabilizes the base by withdrawing electrons from ⊖ & therefore this molecule is less basic.

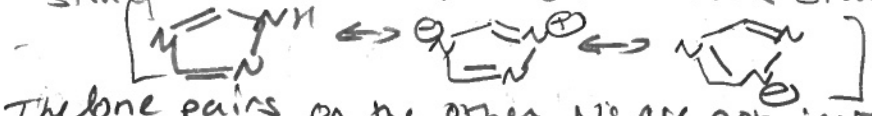
Oxygen is farther away from the base in the most basic molecule. Therefore, it will be less able to withdraw e⁻ density so the base will be less stable & more basic

d. Circle the **LEAST basic** nitrogen

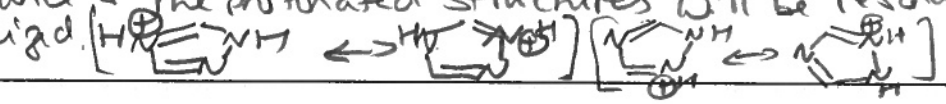


Explanation

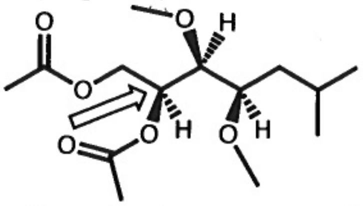
The circled N is least basic because lone pairs are involved in resonance & the protonated structure will have no resonance stabilization.



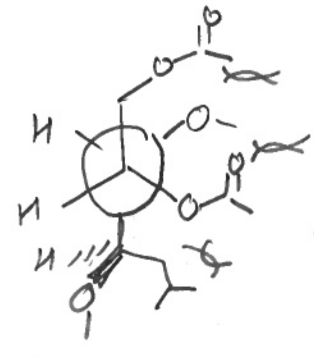
The lone pairs on the other N's are not involved in resonance & the protonated structures will be resonance stabilized.



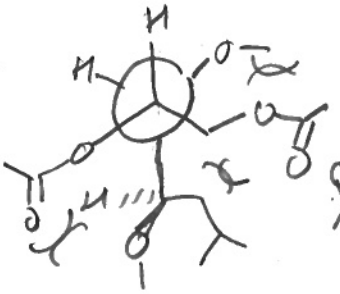
4. (11 points) Consider the molecule shown below:



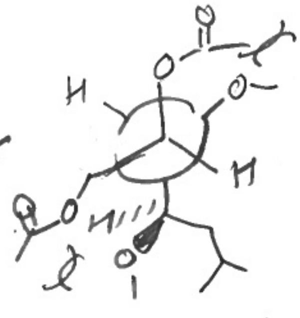
a. Draw the three staggered Newman projections down the bond indicated with the arrow. Identify the most stable conformation and explain your choice.



3 gauche interactions



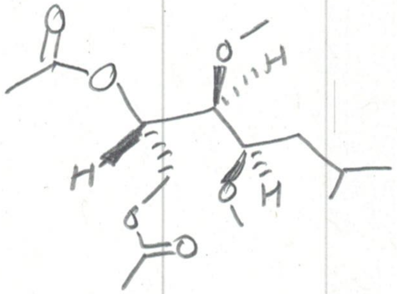
3 gauche interactions



2 gauche interactions

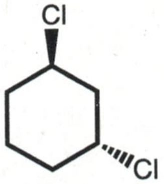
most stable because fewer gauche interactions so less steric destabilization

b. Draw a line drawing of the most stable conformation that you identified in part a of this question.



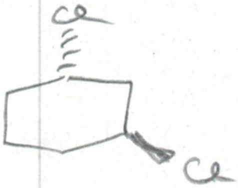
5. (12 points) For each compound, circle whether it is chiral or achiral, and draw the enantiomer and a diastereomer. If no enantiomer or diastereomer exists, then write 'none'.

a.

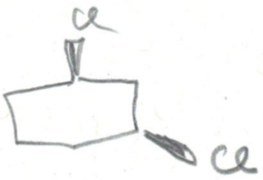


[✓ **Chiral**] or **Achiral**

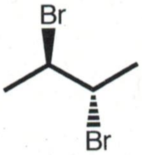
Enantiomer



Diastereomer



b.

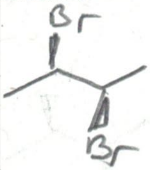


Chiral or [✓ **Achiral**]

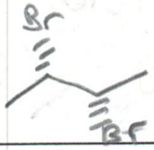
Enantiomer

none

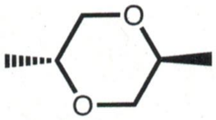
Diastereomer



OR



c.



Chiral or [✓ **Achiral**]

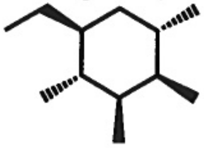
Enantiomer

None

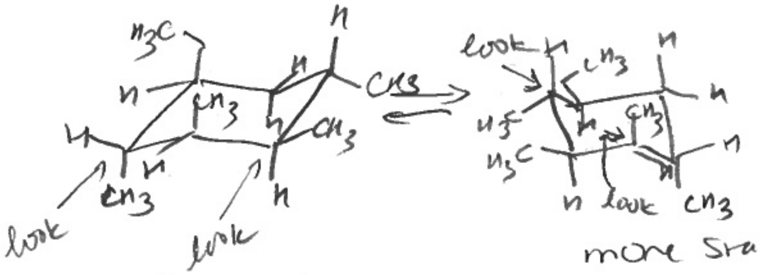
Diastereomer

or

6. (22 points) Consider the molecule shown below.



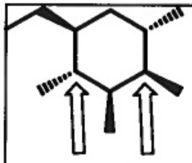
a. Draw both chair conformations, drawing in all of the hydrogens.

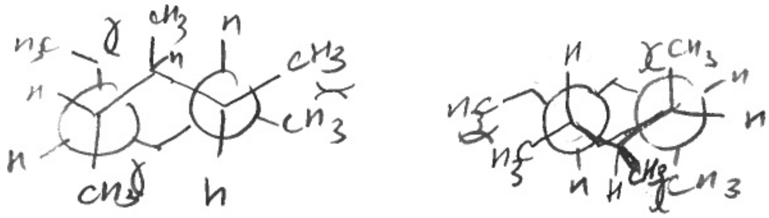


3 axial groups - less stable

more stable two axial groups

b. Draw Newman projections looking down the indicated bonds for both conformations that you drew in part a.



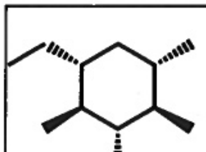


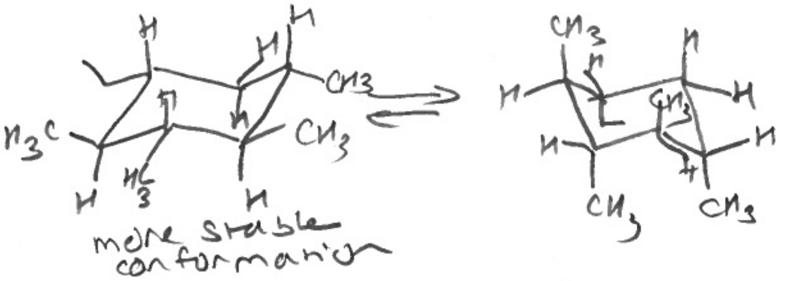
Newman projections needed to be connected.

c. Use both your chair structures and Newman projections to explain which conformation is more stable.

Conformation on the right is more stable because it has fewer axial groups.. These are destabilizing because of the destabilizing gauche interactions they have with the 1,3 CH_2 groups (1,3-diaxial interactions). Some of these gauche interactions are illustrated in the Newman projections. The 1,3 diaxial interaction between the ethyl & methyl group will be particularly destabilizing

d. Will the isomer shown below be more or less stable than the isomer drawn at the beginning of this problem? Explain your answer. In your explanation, draw both chair conformations, decide which is more stable, and compare the most stable conformation to the most stable conformation of the isomer you drew in part a of this question.

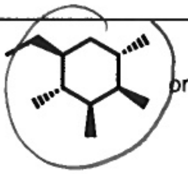




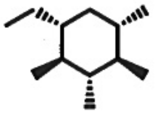
overall, this isomer is more stable because the conformation on the left has all groups equatorial. This conformation will have the fewest destabilizing gauche (steric) interactions

e. Circle the isomer that will have a larger (more negative) heat of combustion?

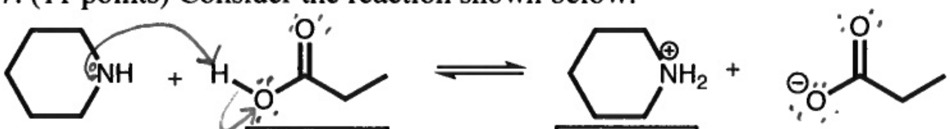
because it is less stable



or



7. (11 points) Consider the reaction shown below:



pKa = 5

pKa = 10

a. Draw in all of the lone pairs in the starting materials and products and the arrows to go from reactants to products in this reaction.

b. Fill in the approximate pK_a's in the boxes below the reaction.

c. Will the equilibrium favor the products or the starting materials of this reaction? By approximately how much will the products or starting materials be favored (ie., K_{eq})? Explain your answer briefly.

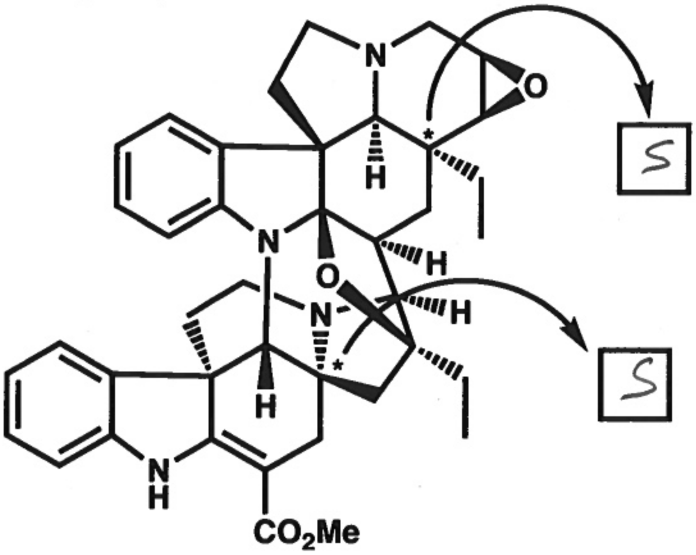
Products will be favored.

HO– is a stronger acid than 

 is a stronger base than -O–

Products favored by 10^5 $10-5=5$ $K_{eq} \approx 10^5$

8. (12 points) The molecule shown below is called Ervafoline.



a. Assign the stereocenters marked with a * as ‘R’ or ‘S’ in the boxes provided.

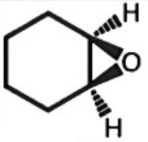
b. If the specific rotation of Ervafoline is -25°, what specific rotation would you measure, if you isolated a mixture of 80% Ervafoline and 20% the enantiomer of Ervafoline? Show your work.

80% - 20% = 60% ee

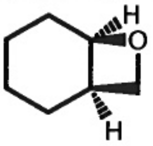
the 20% racemate will not rotate light

$-25 \times 0.6 = -15^\circ$

c. Ervafoline contains a strained 3-membered ring with oxygen, called an epoxide, which will be a site of reactivity in the molecule. Using the two simpler molecules drawn below, how would the ring strain change with a 4-membered ring with oxygen? Compare the sources of strain in each molecule shown below. Which molecule is more strained?



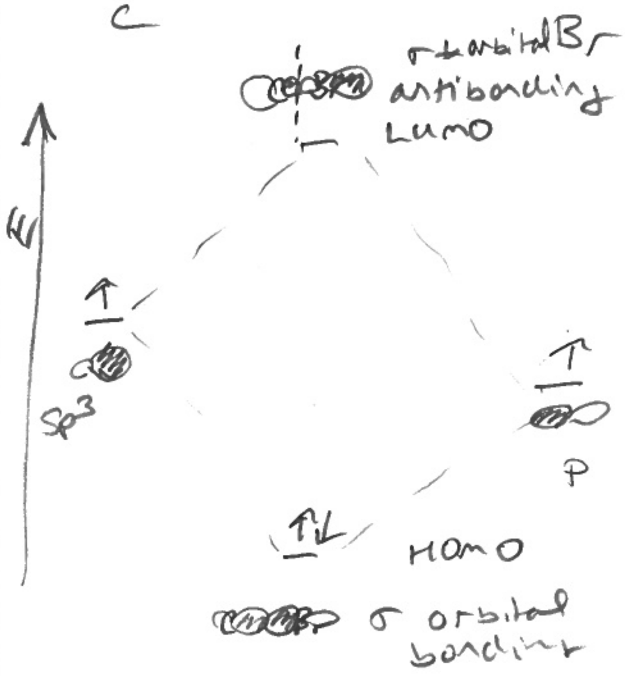
more strained.



The three membered ring has greater bond angle strain per CH_2 or O atom. The angles of a triangle are 60° while a sp^3 C prefers 109.5°. The four membered ring has less bond angle strain per CH_2 or O, but has four instead of 3 atoms in ring - so bond angle strain is similar. The three membered ring also has torsional strain due to eclipsed interactions while the four membered ring puckers to reduce eclipsing. Overall the three membered ring is 1.2 kcal/mole more strained.

9. (14 points) The following reaction shows the formation of 3-membered rings (epoxides) by the reaction of a deprotonated alcohol with a C-Br bond in the same molecule.

a. Draw a molecular orbital diagram for the C-Br bond in the reactant. You do not need to include lone pairs in your diagram. Sketch and label all orbitals. Label the HOMO and LUMO of this bond.



b What is the most reactive pair of electrons on the negatively charged oxygen? Draw a sketch of this orbital.

lone pair on O

c. In this reaction, the most reactive pair of electrons on O reacts with the LUMO of the C-Br bond. Sketch that interaction on the line drawing below