CHEMISTRY 112A FALL 2015

EXAM 1

SEPTEMBER 27, 2016

NAME- WRITE BIG ____

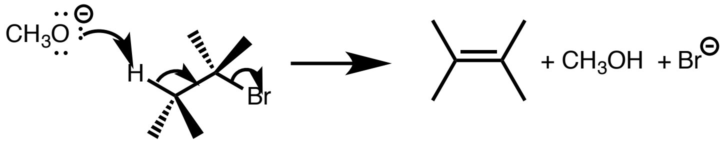
STUDENT ID: __________________

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	12
2	24
3	15
4	20
5	16
6	8
7	15
8	10
Total	***120***

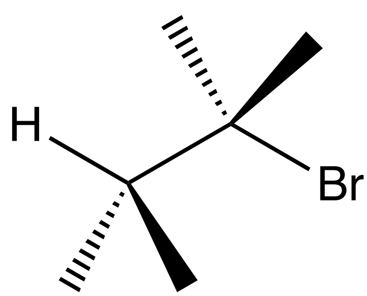
1. (12 points) Alkyl halides undergo E2 elimination reactions as shown below. The proton is removed, the double bond formed, and the halide leaves all in one step as shown with the arrows. The hydrogen and the bromide need to be anti to each other for this reaction to be fast.



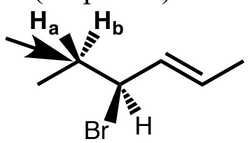
a. In this reaction, the HOMO of the C-H bond interacts with the LUMO of the C-Br bond. Below, draw a molecular orbital diagram for the formation of C-H and C-Br bonds. You do not need to include lone pairs in your diagrams. Sketch and label all orbitals. Label the HOMO of the C-H bond and the LUMO of the C-Br bond.

C-H Bond	C-Br Bond

b. Sketch the HOMO of the C-H bond and the LUMO of the C-Br bond on the line drawing below. Indicate the interaction between the two in this reaction.



2. (24 points) Consider the molecule shown below:

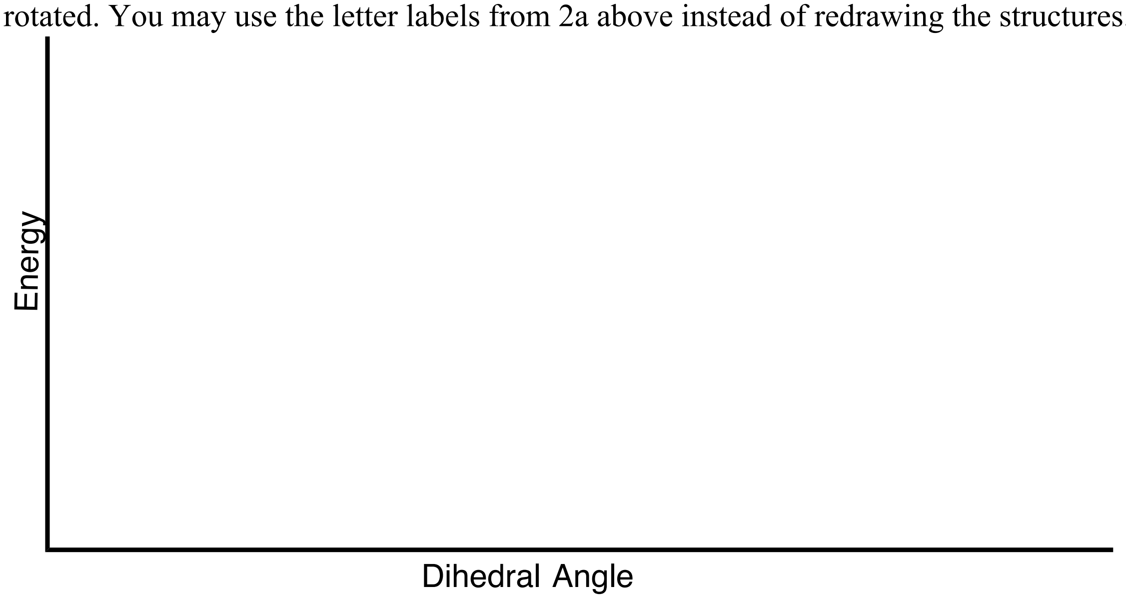


a. Draw Newman projections looking down the indicated arrow. Rotate around the bond to draw all the staggered and eclipsed conformations for a total of 6 conformations. Draw each structure above one of the letter labels A-F.

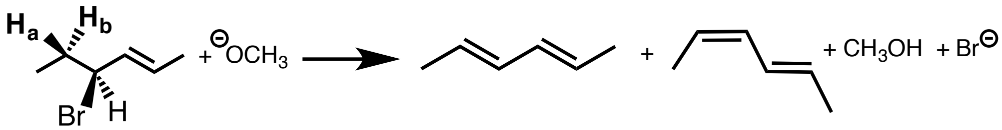
A	B	C
D	E	F

b. In your answer to 2a above, label the **most and least stable staggered** conformation **and** the **most and least stable eclipsed** conformation **Hint**: The group with the double bond is bigger than Br, but smaller than methyl.

c. Draw an energy vs. dihedral angle plot illustrating the change in stability as the indicated bond is rotated. You may use the letter labels from 2a above instead of redrawing the structures.



d. When the alkene at the beginning of this problem undergoes an E2 elimination reaction, two diene products are formed.



Which hydrogen (Ha or Hb) is deprotonated to form each diene? Remember, in the E2 reaction, the proton and halide are anti to each other. To answer this question:

i. Redraw the relevant Newman projections below with Ha and Hb indicated

ii. Draw the diene product formed.

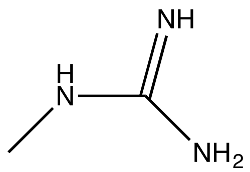
Iii Circle whether Ha or Hb was deprotonated

Product: Newman Projection: **Circle**: **Ha** or **Hb** was deprotonated	Product: Newman Projection: **Circle**: **Ha** or **Hb** was deprotonated

e. Which diene do you expect to be the major product of the reaction? Explain your answer.

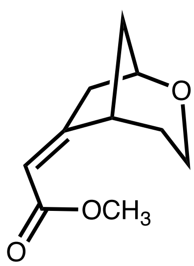
3. (15 points) Indicate the most acidic or basic atom in the following molecules. Explain your choice in the box provided. If your explanation includes resonance structures, draw the most relevant resonance structures.

a. Circle most basic N



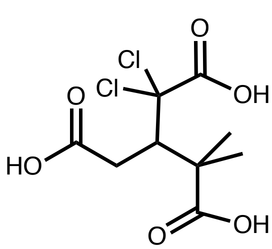
Explanation:

b. Draw in and circle most acidic H



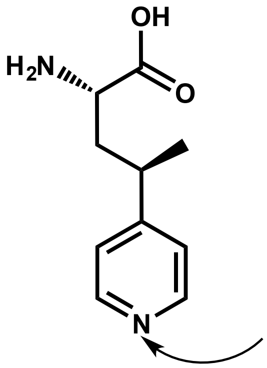
Explanation:

c. Circle most acidic H



Explanation:

4. (20 points) Recent advances in synthetic biology have called for the design and synthesis of artificial amino acids. One of these is shown below.



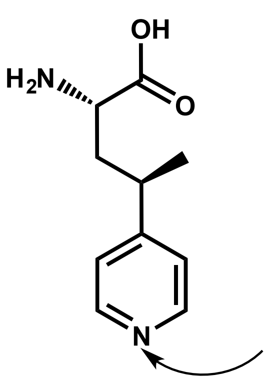
pKa of conjugate acid = 5.25

a. Assign all stereocenters as R or S.

b. Circle the most basic atom in this molecule. Explain why this atom is most basic.

c. Put a square around the most acidic hydrogen in this molecule. Explain this hydrogen is most acidic.

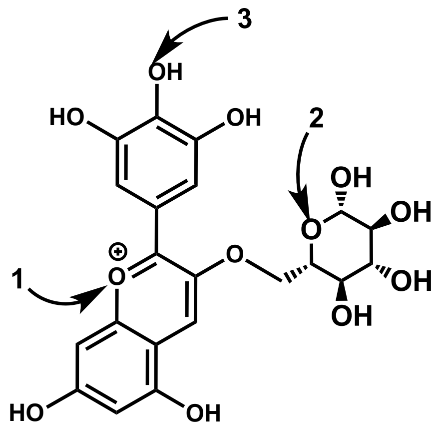
d. Based on your knowledge of the pK_a's of the functional groups in this molecule, draw the structure of the molecule at pH 7.



pKa of conjugate acid = 5.25

e. After synthesizing the compound you find that it is a mixture of enantiomers. From optical rotation, you determine the %ee is 90% of the desired product. What is the ratio of the desired product to the enantiomer?

5. (16 points) Petunidin-3-glucoside is an interesting charged and highly colored molecule. It is a member of the anthocyanin class of molecules that is responsible for the red-purple color seen in fall leaves.



a. Determine the hybridization of the atom and lone pair of the **numbered oxygens** above.

	1		2		3
oxygen		oxygen		oxygen	
lone pair		lone pair		lone pair	

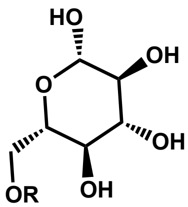
b. All known anthocyanins contain multiple OH groups on benzene rings. Draw a resonance structure involving the OH group numbered **3** in the structure above to explain how the OH group stabilizes this molecule. You do not need to redraw the entire molecule, just the portion that supports your argument.

c. Petunidin-3-glucoside contains a glucose molecule on the right side of the molecule drawn at the beginning of this problem. The structure of this glucose is drawn again below.

i. Draw both chair conformations of glucose. Draw in all of the hydrogens on the rings.

ii. Indicate which conformation is more stable

iii. Explain your answer to ii.



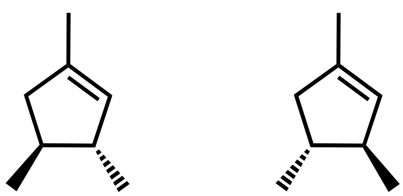
glucose

Chair conformations:

Explanation:

6. (8 points) Consider the pairs of molecules below and identify them as chiral, achiral, or meso. Indicate whether the molecules are constitutional isomers, enantiomers, diastereomers, identical, or different molecules.

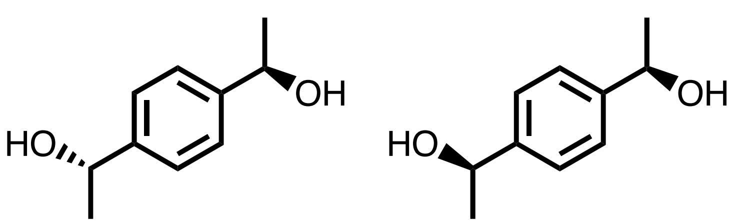
a.



Chiral, Achiral, or Meso? ____________ ____________

Relationship between molecules? ____________

b.

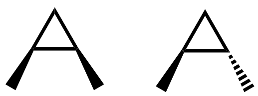


Chiral, Achiral, or Meso? ____________ ____________

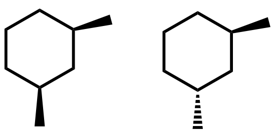
Relationship between molecules? ____________

7. (15 points) Consider the pairs of molecules shown below. Circle the molecule that is the most stable in each pair. Describe the factors that destabilize one compared to the other in the box provided.

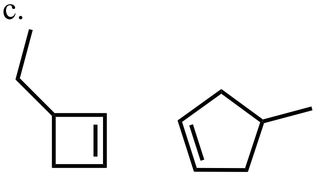
a.



b.



c.



8. (10 points) Nomenclature questions:

a. Draw the molecule that the name represents: (*E*)-4-ethyl-3-methylhept-3-ene

b. Name the following molecule, including stereochemistry: