

CHEMISTRY 112A FALL 2014

EXAM 1

SEPTEMBER 30, 2014

NAME- WRITE BIG _____

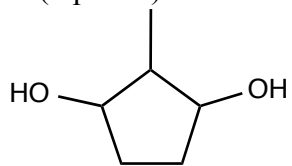
STUDENT ID: _____

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

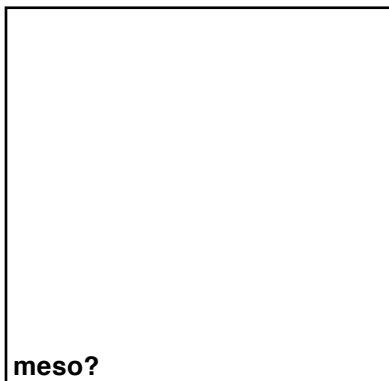
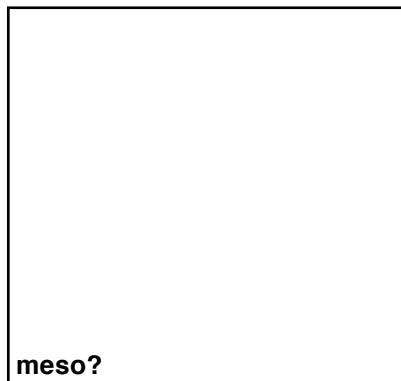
- You will have 75 minutes in which to work.
- **BE NEAT!** Non-legible structure drawings will not be graded.
- Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.
- All pages of the exam must be turned in.
- No calculators
- Molecular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

Problem	Points (Maximum)
1	8
2	15
3	29
4	25
5	7
6	8
7	8
<i>Total</i>	<i>100</i>

1. (8 points) Consider the molecule below:



- a. i) Draw two **chiral** configurational stereoisomers of this molecule.
ii) Indicate whether these two molecules are enantiomers or diastereomers.
iii) Label any **meso** compounds 'meso'.

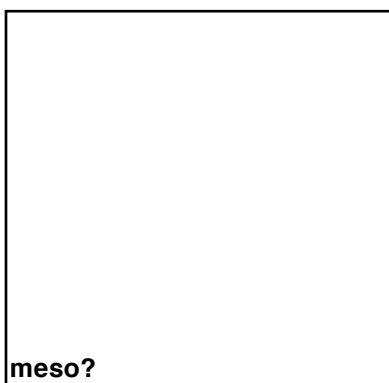
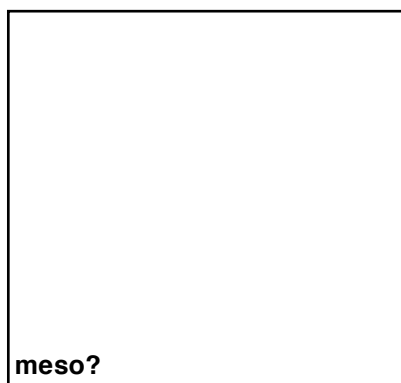


Circle correct relationship:

enantiomers

diastereomers

- b. i) Draw two **achiral** configurational stereoisomers of this molecule.
ii) Indicate whether these two molecules are enantiomers or diastereomers.
iii) Label any **meso** compounds 'meso'.



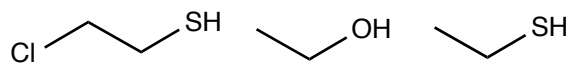
Circle correct relationship:

enantiomers

diastereomers

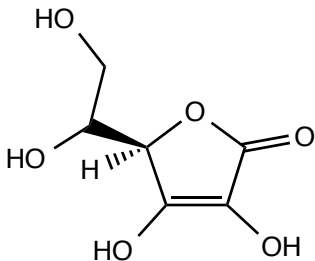
2. (15 points) The following questions ask you about acids and bases.

a. Place the following three molecules in order of increasing acidity. Explain why you put them in this order.



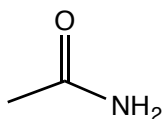
most acidic	Explanation
least acidic	

b. Circle the most acidic hydroxyl (OH) group in ascorbic acid, which is drawn below. Why is that OH most acidic? Include a drawing of the chemical structure of the anion in your answer.

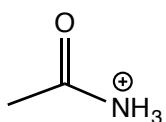


Explanation:

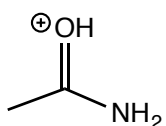
c. Consider the molecule below:



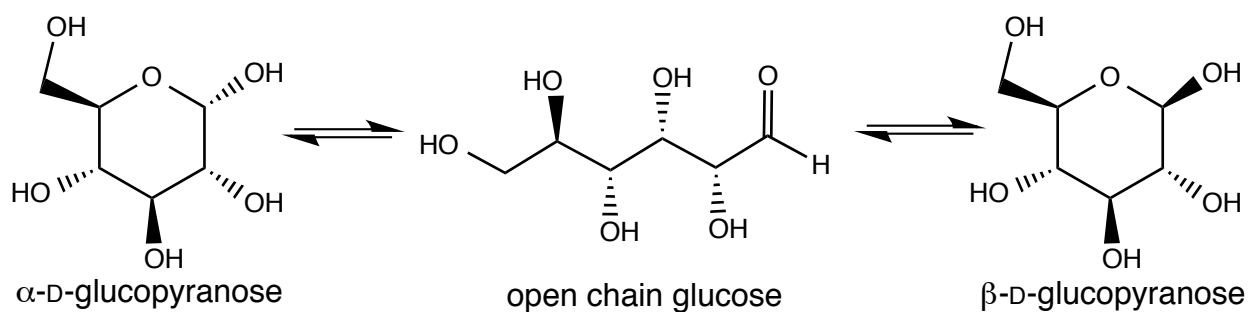
i) There are two possible sites of protonation: oxygen or nitrogen. What would be the primary rationale for protonation on nitrogen to form the molecule shown below?



ii) In fact the molecule is protonated on oxygen to form the molecule drawn below. Explain why this is the site of protonation. Include any drawings that help explain your reasoning.



3. (29 points) D-Glucose in solution equilibrates between the three structures shown below.

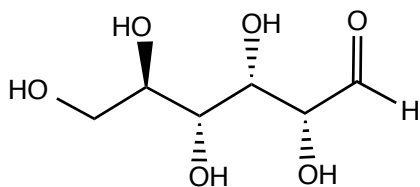


a. What are the isomeric relationships between the different forms of glucose: different compounds, identical compounds, constitutional isomers, diastereomers, or enantiomers.

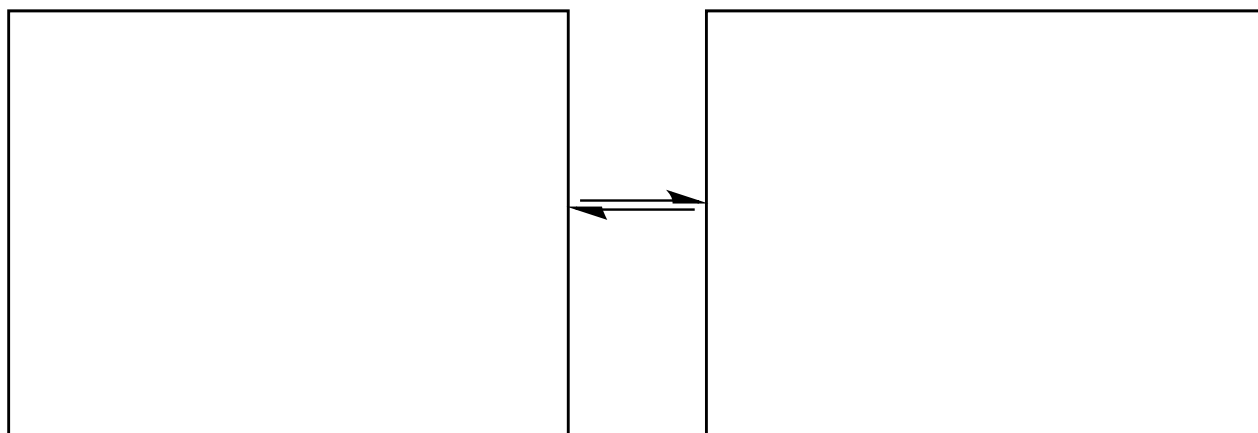
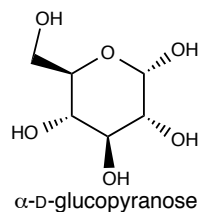
i) α -D-glucopyranose and β -D-glucopyranose are

ii) α -D-glucopyranose and open chain glucose are

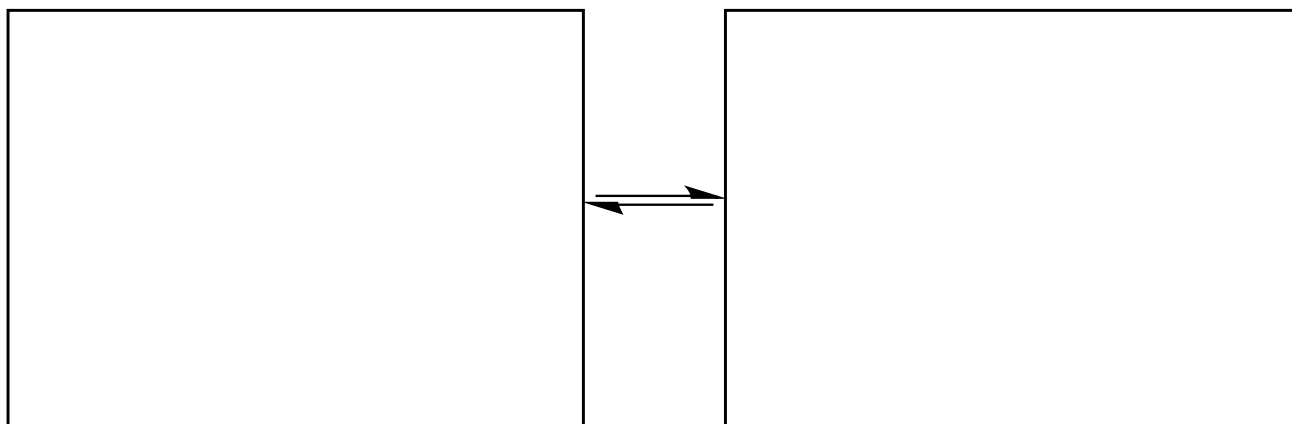
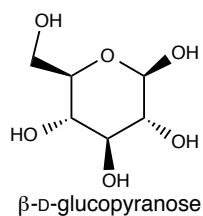
b. Assign all of the stereocenters in the open chain glucose as *R* or *S*.



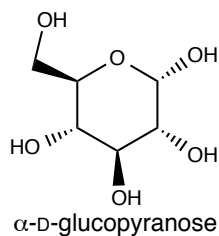
c. Draw the two chair conformations of α -D-glucopyranose. Include **all** the hydrogens on the ring in your drawings. **Circle** the most stable conformation.



d. Draw the two chair conformations of β -D-glucopyranose. Include **all** the hydrogens on the ring in your drawings. **Circle** the most stable conformation.



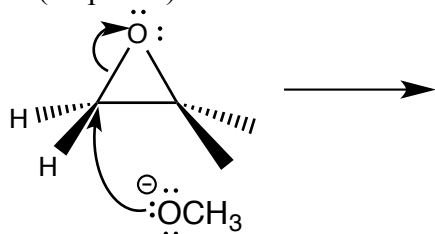
e. Draw the enantiomer of α -D-glucopyranose. You do not need to draw it in chair conformation.



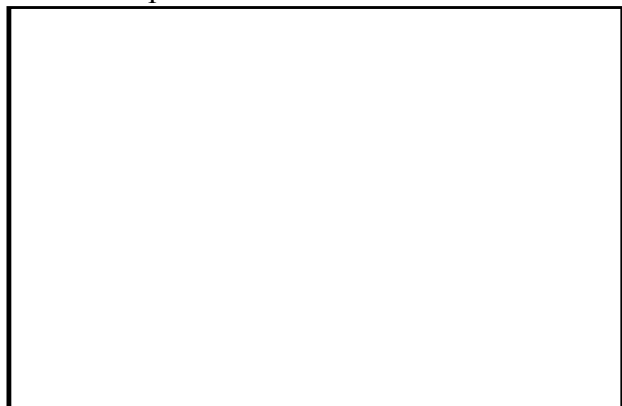
f. The specific rotation $[\alpha]$ of pure α -D-glucopyranose is 112° . What is the specific rotation $[\alpha]$ of a mixture that is 25% α -D-glucopyranose and 75% the enantiomer of α -D-glucopyranose? Assume that conditions are used such that α -D-glucopyranose does not equilibrate with the open chain form or β -D-glucopyranose. Show your work.



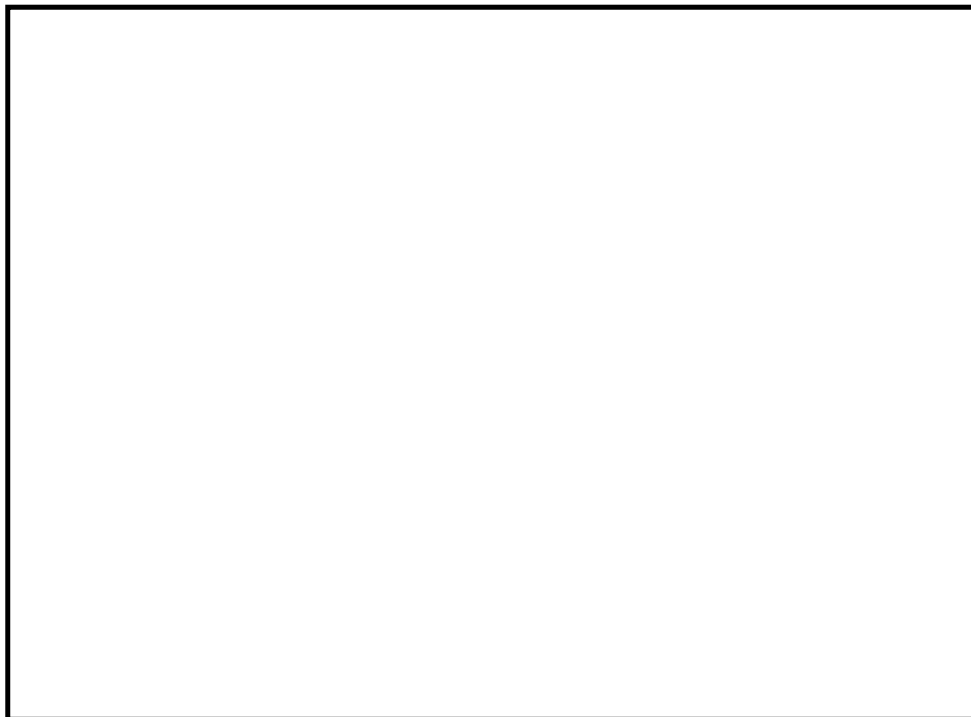
4. (25 points) Consider the reaction below:



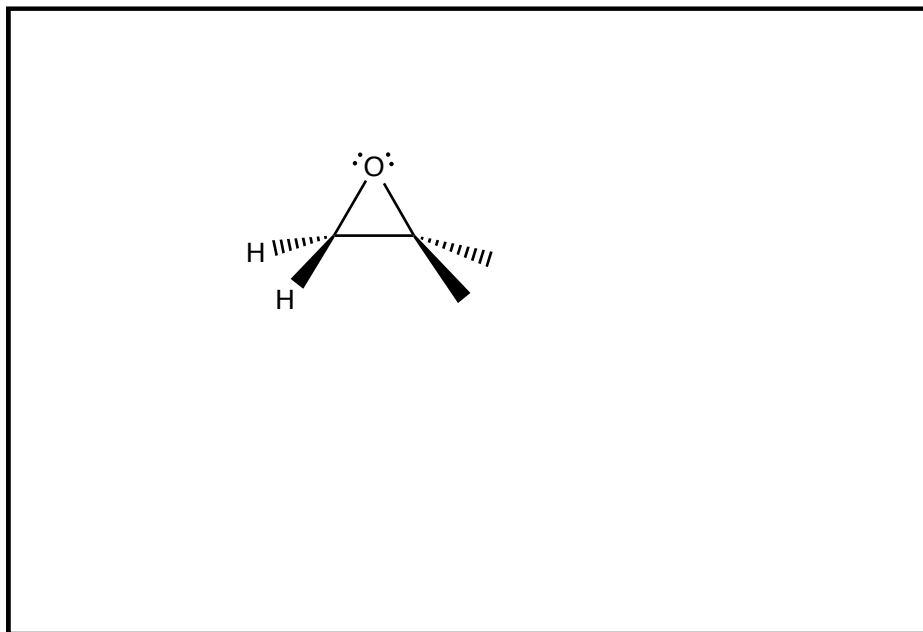
a. Draw the product of the reaction.



b. Draw a molecular orbital diagram of the reactive C-O bond in the 3-membered ring containing oxygen (called an epoxide). Label and sketch all orbitals. Identify the HOMO and LUMO. You do not need to include lone pairs in this diagram. Assume oxygen is hybridized.

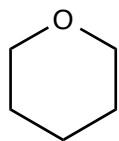


c. A lone pair on oxygen reacts with the LUMO of the C-O bond of the epoxide to initiate this reaction. Sketch the interaction of the lone pair of ${}^{-}\text{OCH}_3$ with the LUMO of the C-O bond on the molecule below. Assume oxygen is hybridized in ${}^{-}\text{OCH}_3$.

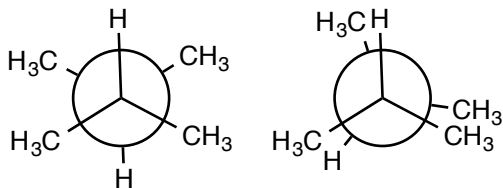


d. Notice that the OCH_3^- reacts with the carbon with two hydrogens, rather than the carbon with two methyl groups. Propose an explanation for this observation.

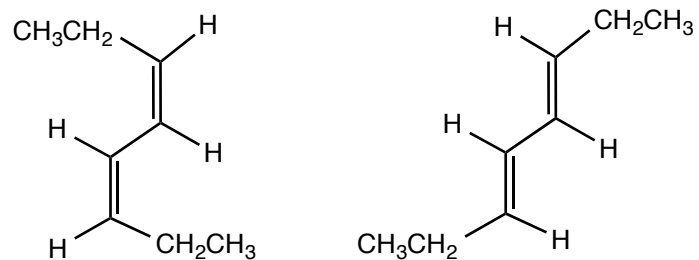
e. The following molecule does not undergo this reaction. Explain why the molecule below is much less reactive than the epoxide.



5. (7 points) Consider the two conformations shown below. Explain which conformation is more stable. Include in your answer the different types of strain that contribute to destabilizing each conformation.



6. (8 points) Consider the two molecules below:



a. Which of the two molecules above is more stable and why.

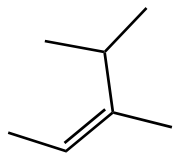
Explanation:

b. Do the two molecules interconvert at room temperature? Explain your answer.

Explanation:

7. (8 points) Name the following molecules:

a.



b.

