CHEMISTRY 112A FALL 2015

EXAM 1

Answer Key

SEPTEMBER 27, 2016

NAME- WRITE BIG _____

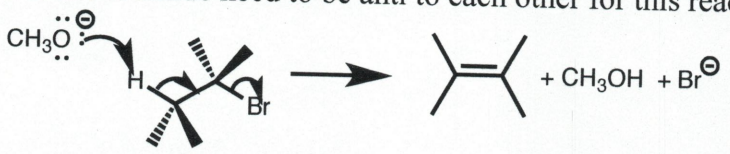
STUDENT ID: _____

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

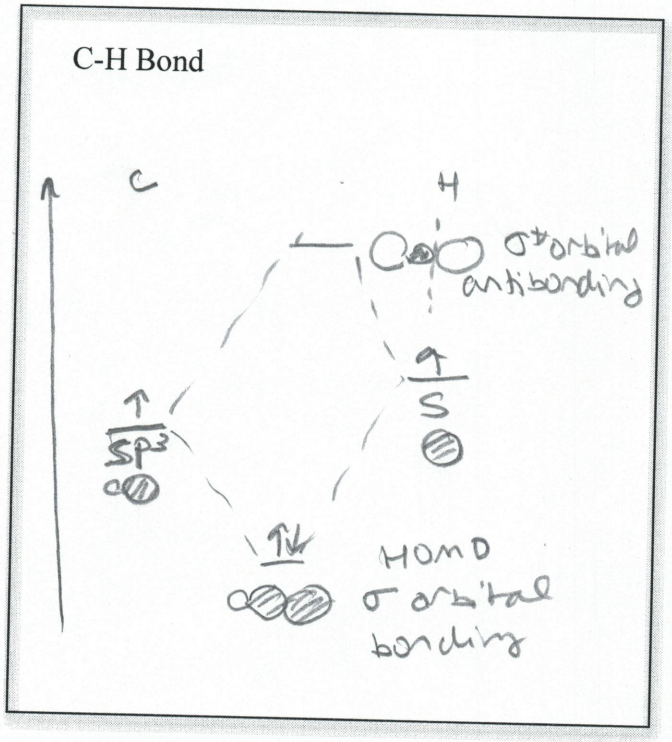
- **You will have 75 minutes in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.**
- **All pages of the exam must be turned in.**
- **No calculators**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

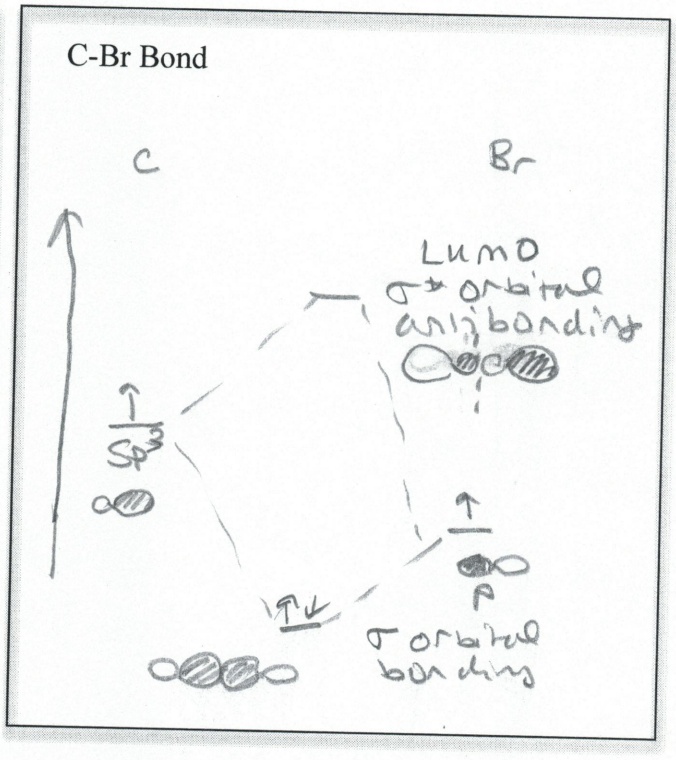
Problem	Points (Maximum)
1	12
2	24
3	15
4	20
5	16
6	8
7	15
8	10
Total	*120*

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.

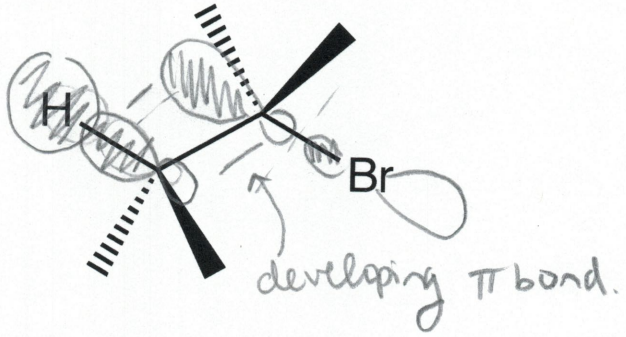


a. In this reaction, the HOMO of the C-H bond interacts with the LUMO of the C-Br bond. Below, draw a molecular orbital diagram for the formation of C-H and C-Br bonds. You do not need to include lone pairs in your diagrams. Sketch and label all orbitals. Label the HOMO of the C-H bond and the LUMO of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

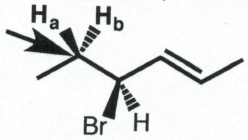




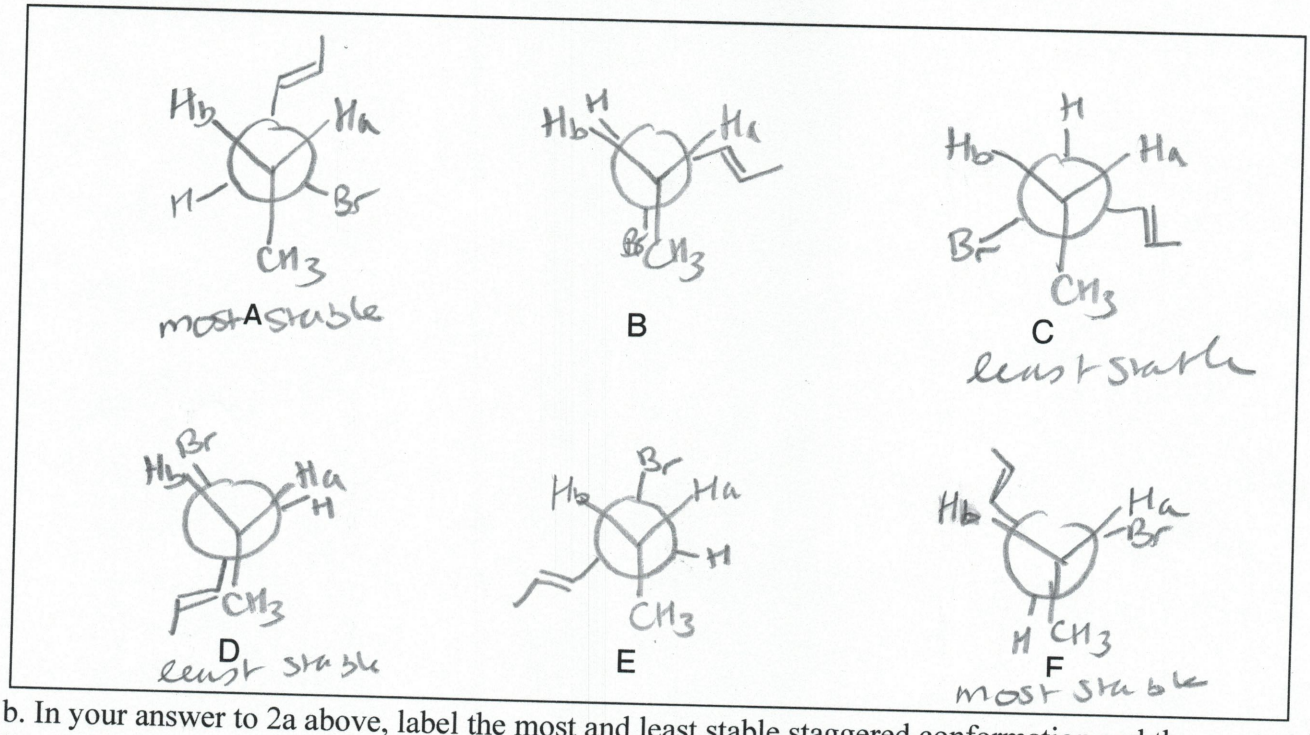
b. Sketch the HOMO of the C-H bond and the LUMO of the C-Br bond on the line drawing below. Indicate the interaction between the two in this reaction.



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

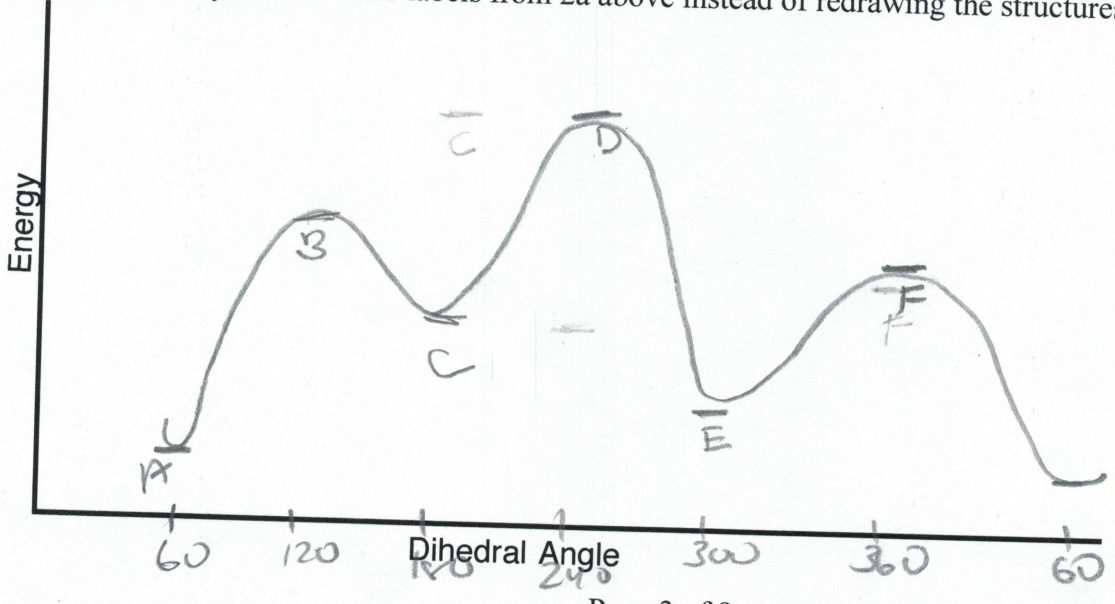


a. Draw Newman projections looking down the indicated arrow. Rotate around the bond to draw all the staggered and eclipsed conformations for a total of 6 conformations. Draw each structure above one of the letter labels A-F.

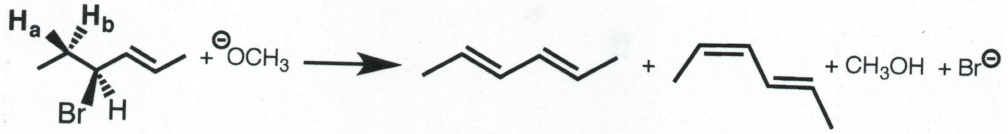


b. In your answer to 2a above, label the most and least stable staggered conformation and the most and least stable eclipsed conformation **Hint**: The group with the double bond is bigger than Br, but smaller than methyl.

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.

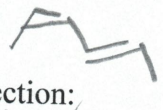


d. When the alkene at the beginning of this problem undergoes an E2 elimination reaction, two diene products are formed.

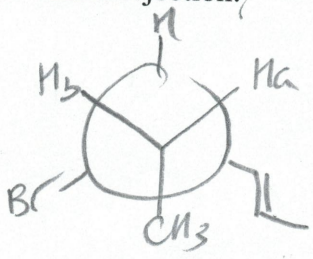


Which hydrogen (Ha or Hb) is deprotonated to form each diene? Remember, in the E2 reaction, the proton and halide are anti to each other. To answer this question:
i. Redraw the relevant Newman projections below with Ha and Hb indicated
ii. Draw the diene product formed.
Iii Circle whether Ha or Hb was deprotonated

Product:



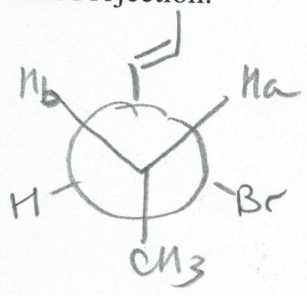
Newman Projection:



Circle: **Ha** or **Hb** was deprotonated

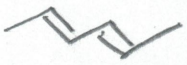
Product:

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.

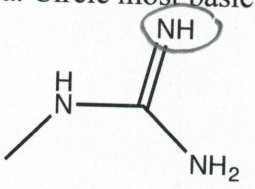


(1) Conformation of alkene to form this structure is most stable, which will result in higher concentration of this conformation and fast

(2) All trans alkene product more stable because trans has less steric destabilization than cis double bond.

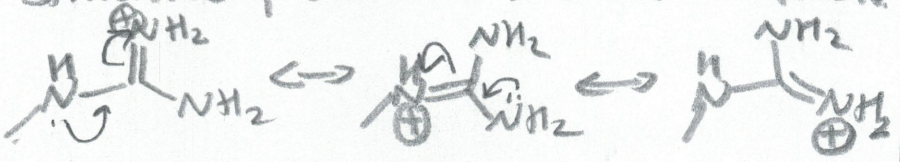
3.(15 points) Indicate the most acidic or basic atom in the following molecules. Explain your choice in the box provided. If your explanation includes resonance structures, draw the most relevant resonance structures.

a. Circle most basic N

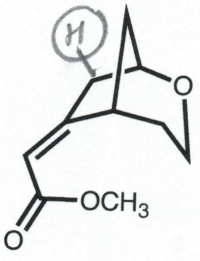


Explanation:

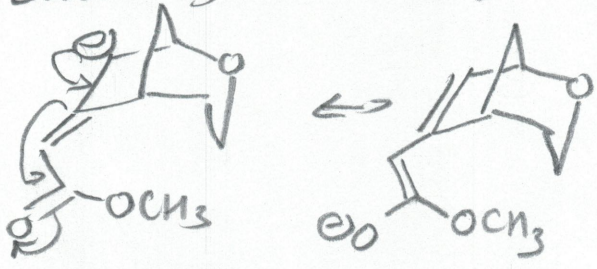
Conjugate acid is stabilized by resonance when protonated on this N. There is no resonance stabilization of structures protonated on the other two N.



b. Draw in and circle most acidic H

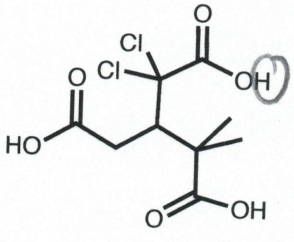


Explanation: Anion is stabilized by resonance that spreads negative charge to (an) electronegative oxygen.

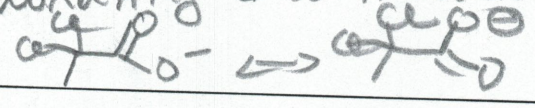


Cannot be H at bridgehead because no double bonds at bridgehead due to angle strain

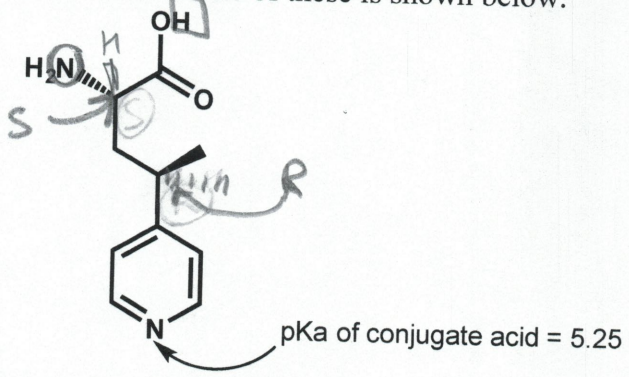
c. Most acidic H



Explanation: Anion stabilized by resonance The two Cl are closest to this $\ominus O$ ← withdraw negative charge to stabilize base. In contrast the two methyl groups next to the bottom acid are e⁻ donating & will destabilize base.



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.



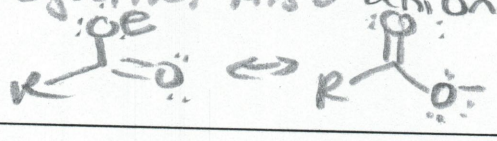
a. Assign all stereocenters as R or S.

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

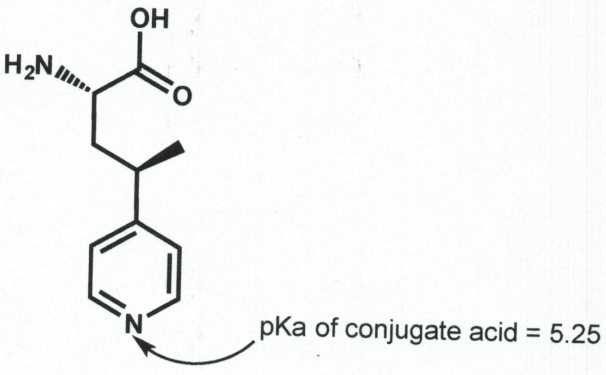
N more basic than oxygen because less electronegative
sp^3 N more basic than sp^2 N because more s character stabilizes electron density.
pka of RNH_2 ~ 10

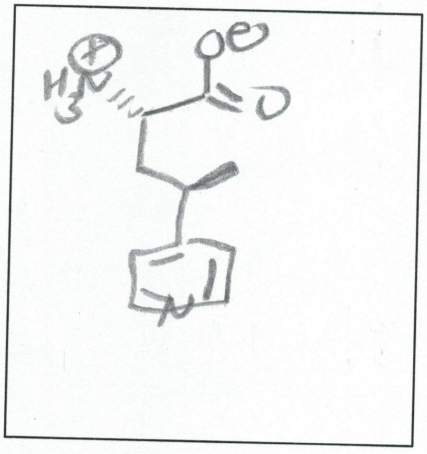
c. Put a square around the most acidic hydrogen in this molecule. Explain this hydrogen is most acidic.

Negative charge more stable on O than N because O more electronegative. Also anion is resonance stabilized:



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

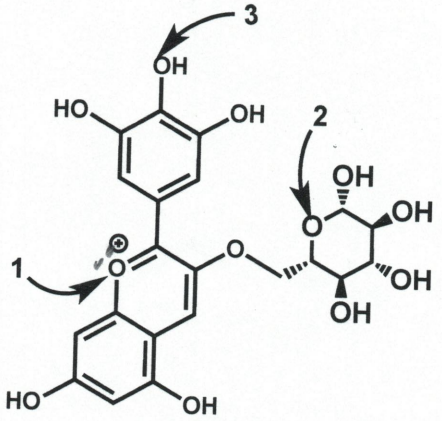




e. After synthesizing the compound you find that it is a mixture of enantiomers. From optical rotation, you determine the %ee is 90%. What is the ratio of the desired product to the enantiomer?

90% ee → 90% desired product
10% racemic: 5% desired 5% enantiomer
so 95% desired product 5% enantiomer

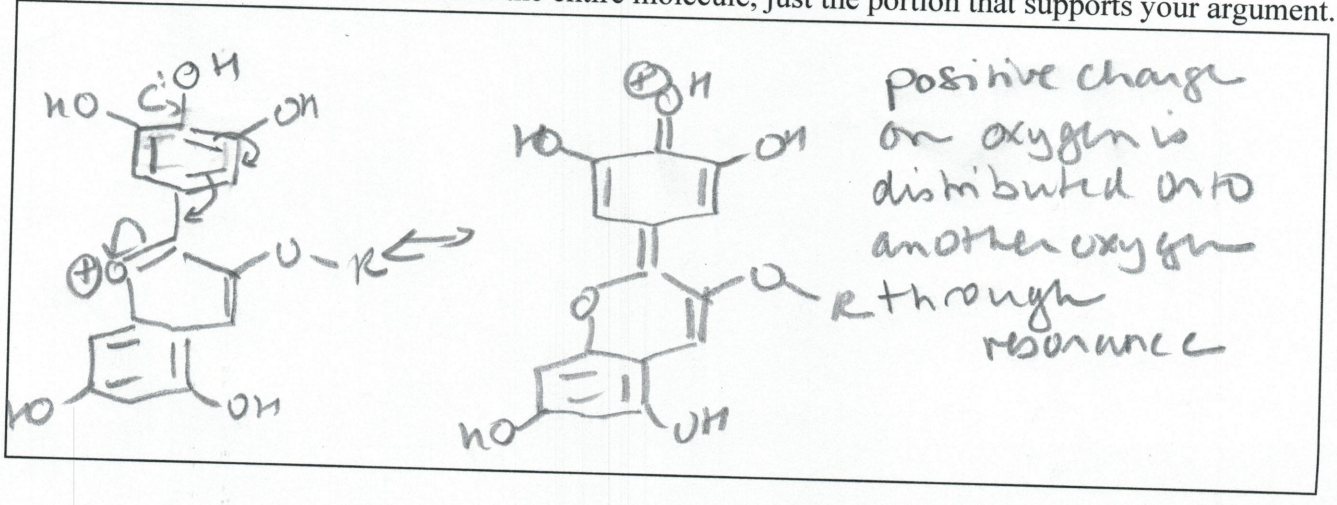
5. (16 points) Petunidin-3-glucoside is an interesting charged and highly colored molecule. It is a member of the anthocyanin class of molecules that is responsible for the red-purple color seen in fall leaves.



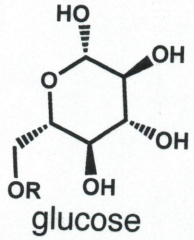
a. Determine the hybridization of the atom and lone pair of the **numbered oxygens** above.

	1	2	3
oxygen	sp^2	sp^3	sp^2
lone pair	sp^2 (4 p)	sp^3 + sp^3	p + sp^2

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.

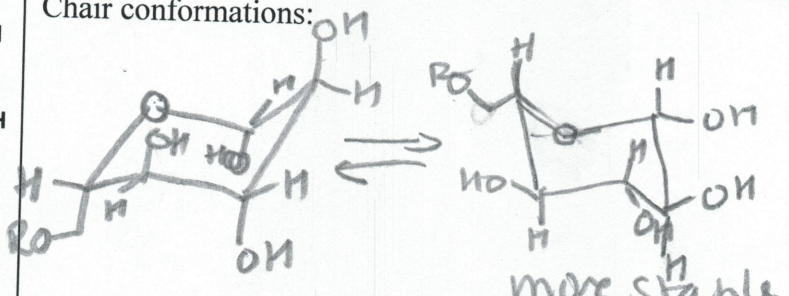


c. Petunidin-3-glucoside contains a glucose molecule on the right side of the molecule drawn at the beginning of this problem. The structure of this glucose is drawn again below.
i. Draw both chair conformations of glucose. Draw in all of the hydrogens on the rings.
ii. Indicate which conformation is more stable
iii. Explain your answer to ii.



glucose

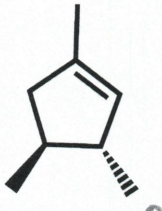
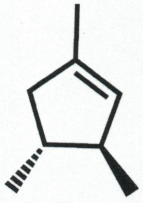
Chair conformations:



more stable

Explanation:
All groups are equatorial in more stable conformation
This minimizes destabilizing steric interactions

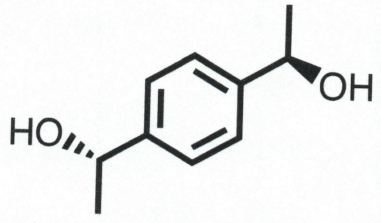
6. (8 points)Consider the pairs of molecules below and identify them as chiral, achiral, or meso. Indicate whether the molecules are constitutional isomers, enantiomers, diastereomers, identical, or different molecules.
a.

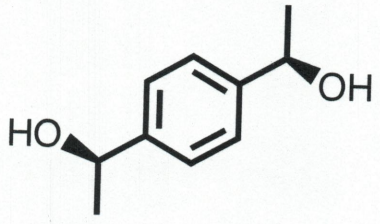



Chiral, Achiral, or Meso? Chiral Chiral

Relationship between molecules? enantiomers

b.



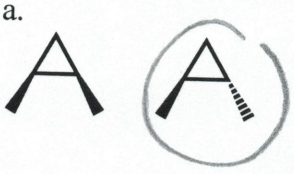


Chiral, Achiral, or Meso? meso Chiral

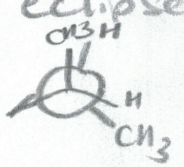
Relationship between molecules? diastereomers

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.

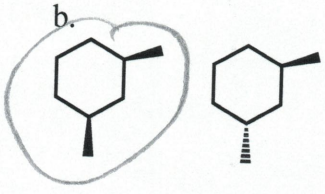
a.

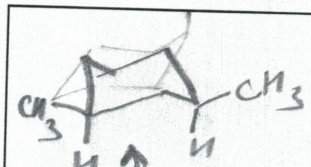


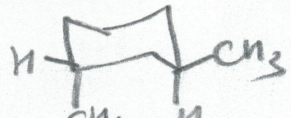
The groups on these two carbons are eclipsed. There are destabilizing steric interactions between the two Me groups when they are eclipsed with each other

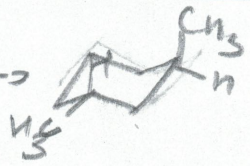


b.



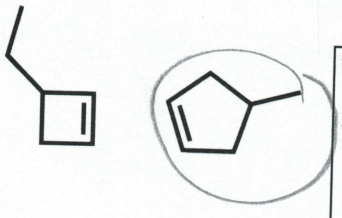






more stable - all equatorial - fewer steric interactions

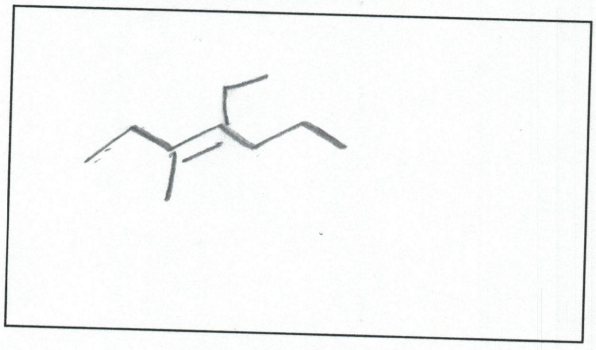
c.



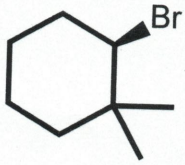
This molecule has less bond angle & torsional strain because of the larger bond angles of the 5-membered ring

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:



(R)-2-bromo-1,1-dimethylcyclohexane