## Chemistry 12A Fall 2018

## EXAM 1

## September 25, 2018

## Name- WRITE BIG

Student ID: $\qquad$
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: $\qquad$

- 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 <br> Maximum) |
| :---: | :---: |
| $\mathbf{1}$ | 8 |
| $\mathbf{2}$ | 14 |
| $\mathbf{3}$ | 18 |
| $\mathbf{4}$ | 20 |
| $\mathbf{5}$ | 9 |
| $\mathbf{6}$ | 6 |
| $\mathbf{7}$ | 15 |
| $\mathbf{8}$ | 14 |
| $\mathbf{9}$ | 16 |
| Total | $\mathbf{1 2 0}$ |

1. (8 points) Nomenclature questions:
a. Draw the molecule that the name represents.
( $2 S, 4 S$ )-1,2,4,5-tetrabromopentane

b. Name the following molecule, including stereochemistry.


2. (14 points) Consider the two carbocations shown below


a. Draw the resonance structures of the molecule on the left. Use arrows to show the flow of electrons.

b. Draw the resonance structures of the molecule on the right. Use arrows to show the flow of electrons.

c. Which molecule is more stable? Explain your answer.
3. (18 points) You are planning to run the reaction below to synthesize this cyclic amide.


In order for this reaction to proceed rapidly, the $\mathrm{NH}_{2}$ and the $\mathrm{C}=\mathrm{O}$ need to be close to each other (gauche). You are trying to decide between the following two stereoisomers to use as a starting material.

a. What is the relationship between stereoisomers $\mathbf{1}$ and $\mathbf{2}$ ?
$\square$
b. Draw Newman projections of $\mathbf{1}$ looking down the bond indicated with the arrow. Draw the three staggered conformations and identify the most stable conformer. Note: $\mathrm{CH}_{3}, \mathrm{NH}_{2}$, and $\mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{OCH}_{3}$ are of similar size and are about twice as large as OCH3.

c. Draw Newman projections of $\mathbf{2}$ looking down the bond indicated with the arrow. Draw the three staggered conformations and identify the most stable conformer. Note: $\mathrm{CH}_{3}, \mathrm{NH}_{2}$, and $\mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{OCH}_{3}$ are of similar size and are about twice as large as $\mathrm{OCH}_{3}$.

d. Considering the stability of the staggered conformations you determined in part $b$ and $c$, which stereoisomer is the best choice for this reaction? Remember that the $\mathrm{NH}_{2}$ and the $\mathrm{C}=\mathrm{O}$ need to be close to each other (gauche) for this reaction to proceed. Explain your answer briefly.
$\square$
4. (20 points) Consider the series of molecules below.
a. Identify the hybridization and lone pair orbital for the indicated atoms. If there are no lone pairs, write N/A.
i.




Hybridization of



Type of orbital for lone pair on indicated carbon

ii.





Hybridization of nitrogen



Type of orbital for lone pair on nitrogen $\square$
$\square$

$\square$
c. Rank the following sets of molecules by the property indicated. Explain your ranking and include relevant structures in your explanation.
i. Basicity

1.


2


3


4

Rank Basicity by putting compound numbers in the boxes


Give an explanation for each compound's position in the ranking. Include relevant structures in your explanation.

| Compound | Explanation |
| :---: | :---: |
| 1 |  |
| 2 |  |
| 2 |  |
| 3 |  |
| 4 |  |
|  |  |

ii. Acidity

1

2

3

4

Rank Acidity by putting compound numbers in the boxes


Give an explanation for each compound's position in the ranking. Include relevant structures in your explanation.

| Compound | Explanation |
| :---: | :---: |
| 1 |  |
| 1 |  |
| 2 |  |
| 3 |  |
| 4 |  |
|  |  |

5. (9 points) Consider the pairs of molecules below and identify them as chiral, achiral and/or meso. Indicate whether the molecules are constitutional isomers, enantiomers, diastereomers, identical or different molecules that are not isomers.
a.

$\left.\begin{array}{|cc|}\hline \text { Circle: chiral achiral } \\ \text { meso }\end{array} \begin{array}{c}\text { chiral achiral } \\ \text { meso }\end{array}\right]$
b.



| Circle one: constitutional isomers enantiomers diateromers |
| :---: |
| identicaldifferent molecules |


| Circle: chiral achiral | chiral achiral |
| :---: | :---: |
| meso | meso |

c.


| Circle one: constitutional isomers <br> identical <br> different molecules |
| :---: |


| Circle: chiral achiral | chiral achiral <br> meso |
| :---: | :---: |

6. (6 points) Consider the molecule below.

a. Fill in R or S for the indicated chiral centers in the structure above.
b. You recently completed a synthesis of this molecule. You are concerned that you may have a mixture of enantiomers. The specific rotation of the pure compound is $60^{\circ}$. If your isolated compound has a specific rotation of $54^{\circ}$, what is the ratio of the desired molecule to its enantiomer? Show your work.
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. (14 points) Alkenes can undergo addition of boranes as part of the hydroboration reaction, as shown below. The B-H bond is broken and the double bond system forms a bond with the boron all in one step as shown with the arrows.


a. Draw a molecular orbital diagram of the $\mathrm{C}=\mathrm{C}$ bond. Sketch and label all orbitals and label the LUMO and HOMO.
$\square$
b. What is the hybridization of boron in $\mathrm{BH}_{3}$ ? Sketch the geometry of $\mathrm{BH}_{3}$. The lowest unoccupied orbital on boron is the empty p orbital. Sketch this orbital on your drawing of $\mathrm{BH}_{3}$ below.
$\square$
c. In this reaction, the LUMO of $\mathrm{BH}_{3}$ interacts with the HOMO of the $\mathrm{C}=\mathrm{C}$ bond. On a line drawing of the molecules, sketch the HOMO of the $\mathrm{C}=\mathrm{C}$ bond interacting with the LUMO of $\mathrm{BH}_{3}$.

9. (16 points) The reaction of B-H bonds with alkenes from problem 8 occurs in one step, and therefore, both new bonds ( $\mathrm{C}-\mathrm{H}$ and $\mathrm{C}-\mathrm{B}$ ) will be formed on the same side of the molecule. When the boron is substituted with large alkyl groups it will bond to the less substituted carbon of the alkene. Therefore, in the following reaction, there are two possible products.

a. Draw both chair conformations compound 3. Draw in all hydrogens on the cyclohexane ring.
b. Draw both chair conformations of compound 4. Draw in all hydrogens on the cyclohexane ring.
$\square$
c. Which product is more stable? Explain your answer.
