# CHEMISTRY 12A FALL 2020

**EXAM 1**

**17 September 2020**

**Name:** _____

**Student ID:** _____

*As a member of the UC Berkeley community, I act with honesty, integrity, and respect for others. This exam represents my own original work.*

**Please sign:** _____

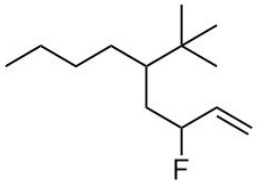
- You have 80 minutes to complete this exam. Gradescope will not accept submissions after the 80-minute mark, so please submit your exam before this point, even if you are not done.
- Only answers located within or very close to the answer boxes will be graded.
- You may refer to your notes, the textbook, the answer guide, and any documents that have been uploaded to the 2020 Chem 12A bCourses website. You may use molecular models. You may not consult any website, or collaborate or consult with any other person.

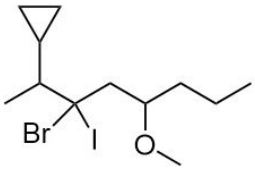
**This exam consists of seven questions spread over ten pages. If you are printing the exam, please make sure the pages are in the correct order when you scan your completed exam. The pages are numbered in the bottom right corner.**

**Good luck!!!**

**1. (8 points) Nomenclature**

a. Please name each of the following molecules.



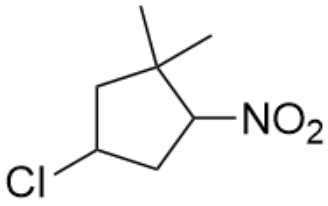
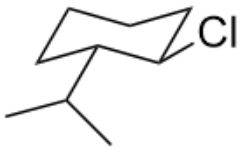




| | |
|---|---|
| 5-(*tert*-butyl)-3-fluorononon-1-ene<br>or:<br>5-(1,1-dimethylethyl)-3-fluorononon-1-ene | 3-bromo-2-cyclopropyl-3-iodo-5-methoxyoctane |

b. Draw the structure associated with each name.

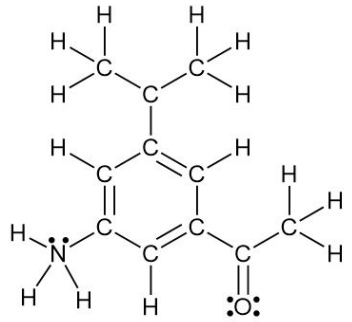
4-chloro-1,1-dimethyl-2-nitrocyclopentane

*trans*-1-chloro-2-isopropylcyclohexane
**(Please draw a chair conformation)**

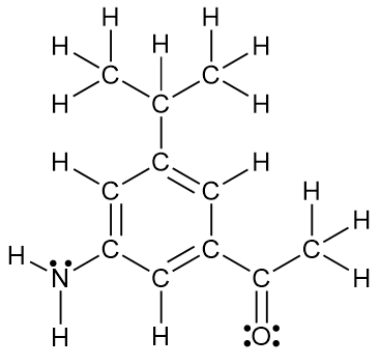
| | |
|---|---|
|  |  <br>or many other options as long as the chlorine and isopropyl groups are trans |

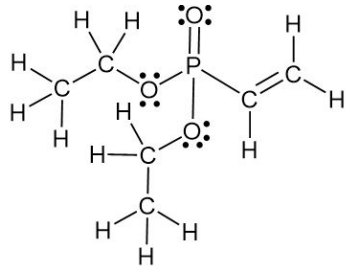
**2. (12 points) Lewis Structures**

a. Determine whether the following Lewis structures are valid. If the structure is not valid, draw a correct version in the box. The correct Lewis structure(s) will carry no formal charges.



Circle:
Valid Lewis Structure? Yes **No**

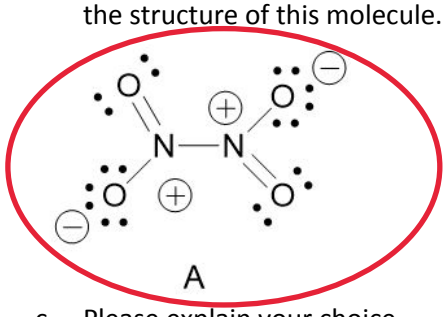




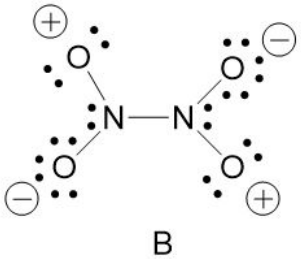
Circle:
Valid Lewis Structure? **Yes** No

N/A, already valid

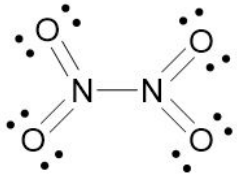
b. Consider the three Lewis structures below. **Circle the one** that you believe contributes most to the structure of this molecule.



A



B



C

c. Please explain your choice.

Structure A is the only one with full octets on every atom. In structure B, the oxygens with positive formal charges have less than full octets. In structure C, there are five bonds to each nitrogen, violating the octet rule.

d. What is the molecular geometry about nitrogen in structures A and B? **Circle your choice.**

| | | | | | |
|---|---|---|---|---|---|
| **Structure A** | Bent | Linear | Tetrahedral | Trigonal Planar | Trigonal Pyramidal |
| **Structure B** | Bent | Linear | Tetrahedral | Trigonal Planar | Trigonal Pyramidal |

**we'll also accept tetrahedral for B**

**3. (18 points) Resonance**

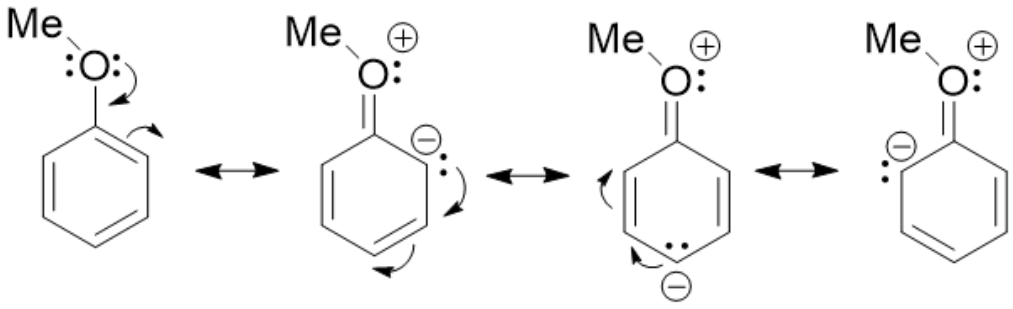
While we have often used resonance to compare the relative *stability* of two different molecules, we can also use resonance to compare their relative *reactivity*. Consider the two molecules below:


A B

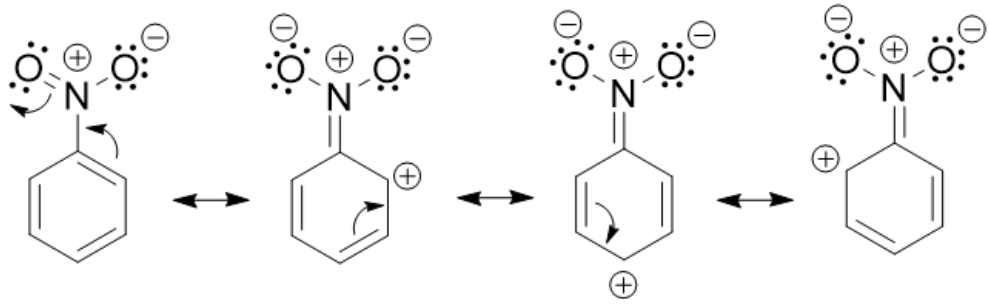
a. (4 pts) Draw all lone pairs and identify all non-zero formal charges on each of the structures above.

b. (6 pts) For each molecule, draw all resonance structures that involve the substituent and do not increase the number of formal charges on the molecule by more than 2. For example, if the original structure has one formal charge, none of your resonance structures should have more than three formal charges.

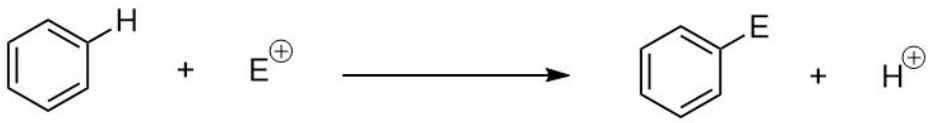
**Molecule A:**




**Molecule B:**



c. (3 pts) Now consider the reaction shown below:

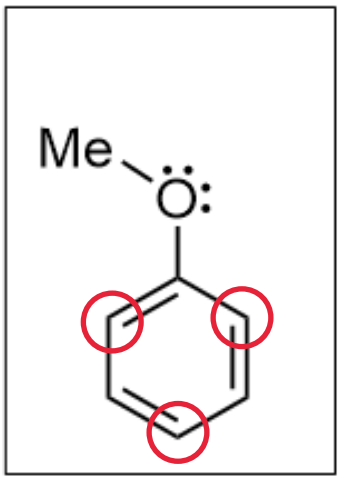



Although we haven't seen this reaction before, we can predict the relative reactivity of **molecules A and B** by considering the resonance structures you drew in part (b). Based on these resonance structures, predict which of these two molecules will more readily react with $E^+$, a generic positively charged molecule.

**Circle your choice:** **Molecule A** **Molecule B**

d. (3 pts) Modify the structure in the box below so it matches the molecule you have chosen (**Molecule A** or **B**), then **circle the positions on the ring** that are most likely to react with E+.

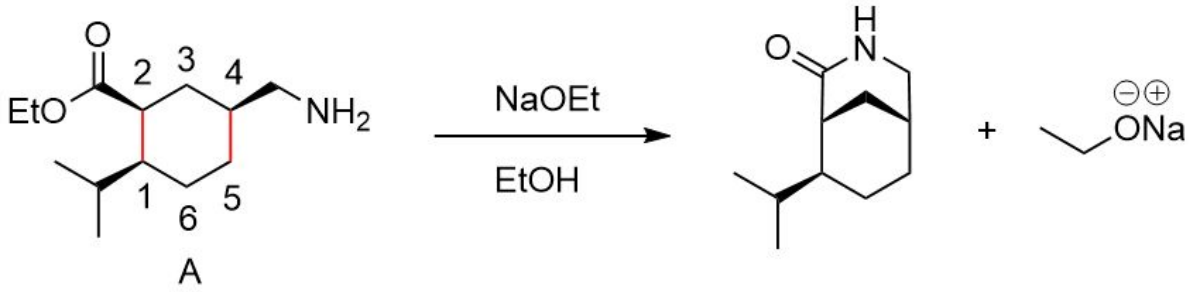
e. (2 pts) In the box, explain why you chose **Molecule A or B** in Part (c) and the positions circled in part (d).




Since the reaction occurs with a positively charged species, we expect that a negative charge will attack. As seen from the two resonance structures, the methoxy group pushes electrons into the ring, increasing the minus charge, while the nitro group pulls electrons out, causing it to be less negative. Based on these structures, we predict molecule A to react more readily with E+. From the resonance structures, we can see that the minus charge is more localized on the ortho/para positions, so those will be the most likely to react.

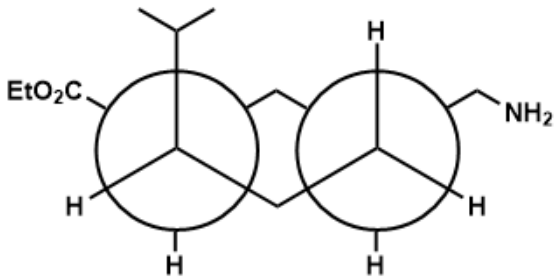
**4. (18 points) Conformational Analysis**

Consider the following reaction, in which an amine and ester react to form an amide.

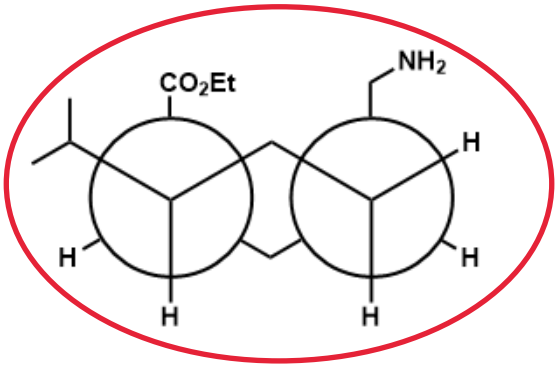



a. (4 pts) Looking down the 1-2 and 5-4 bonds, draw Newman projections for the two conformational isomers of compound A using the templates below.

**Conformer #1**

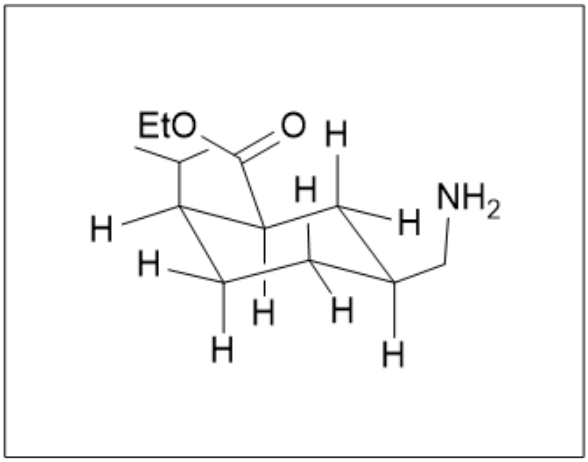



**Conformer #2**

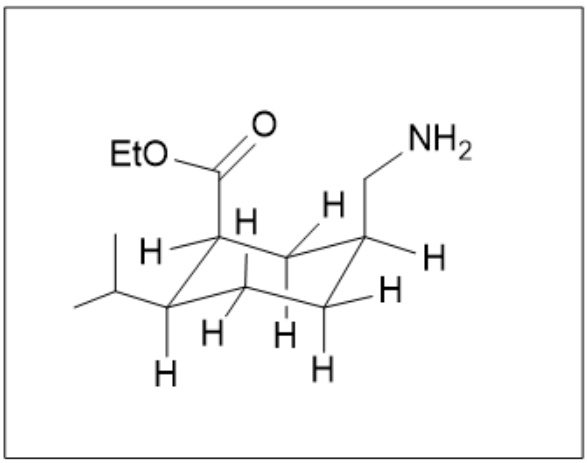



b. (4 pts) Draw chair structures that correspond to the Newman projections drawn in part (a).

Draw the chair corresponding to **Conformer #1.**




Draw the chair corresponding to **Conformer #2.**




c. (2 pts) For this reaction to occur, the ester and amine must be close enough to one another for the bond to form. **Circle the conformer (Conformer #1 or Conformer #2)** that best allows the reaction to proceed.

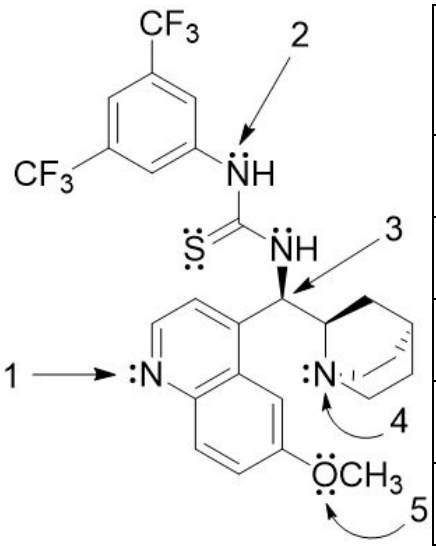
d. (4 pts) Which conformer drawn above **(Conformer #1 or Conformer #2)** is lower in energy? Why?

Conformer #1 is lower in energy due to fewer gauche and 1,3-diaxial interactions, minimizing steric strain. Conformer #1 has one bulky group in an axial position and two bulky groups in equatorial positions. This results in two gauche interactions. Conformer #2, on the other hand, has two bulky groups in axial positions and one bulky group in an equatorial position, resulting in three gauche interactions.

e. (4 pts) Based on your answers to parts c and d, would you expect this reaction to readily occur? Why?

I would not expect this reaction to readily occur due its reliance upon a thermodynamically unfavorable conformation.

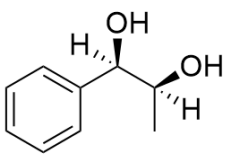
**5. (10 points) Hybridization.** This thiourea molecule is a catalyst for a stereoselective Friedel-Crafts alkylation reaction. Fill in the table to show the correct hybridization state of each atom listed and what type of orbital contains the indicated lone pairs.

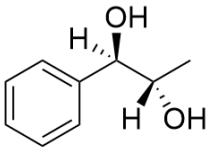



| | Atomic Hybridization | First Lone Pair Orbital | Second Lone Pair Orbital |
|---|---|---|---|
| **Nitrogen 1** | $sp^2$ | $sp^2$ | |
| **Nitrogen 2** | $sp^2$ | p | |
| **Carbon 3** | $sp^3$ | | |
| **Nitrogen 4** | $sp^3$ | $sp^3$ | |
| **Oxygen 5** | $sp^2$ | p | $sp^2$ |

**6. (16 points) Isomerism**

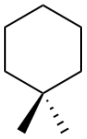
a. Determine if the following pairs of molecules are configurational isomers, conformational isomers, constitutional isomers, or identical. **Circle your choice.**

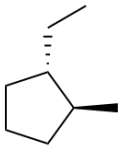


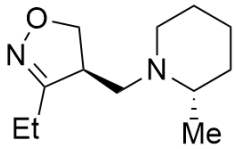



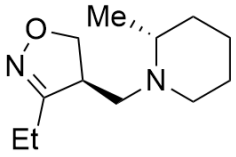



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Circle:** | Configurational | **Conformational** | | **Circle:** | Configurational | Conformational | |
| | Constitutional | Identical | | | Constitutional | **Identical** | |



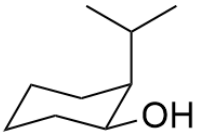


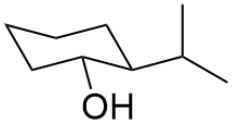



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Circle:** | Configurational | Conformational | | **Circle:** | **Configurational** | Conformational | |
| | **Constitutional** | Identical | | | Constitutional | Identical | |

b. Label the following 1,2-disubstituted cyclohexane isomers as cis or trans.



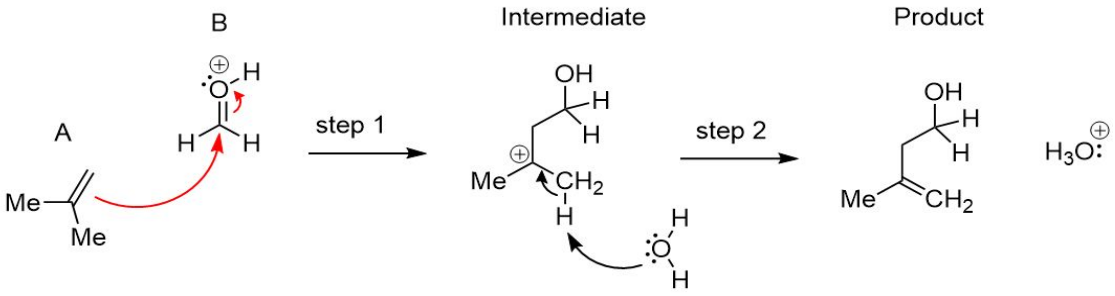

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Circle:** | **cis** | trans | | **Circle:** | cis | **trans** | |

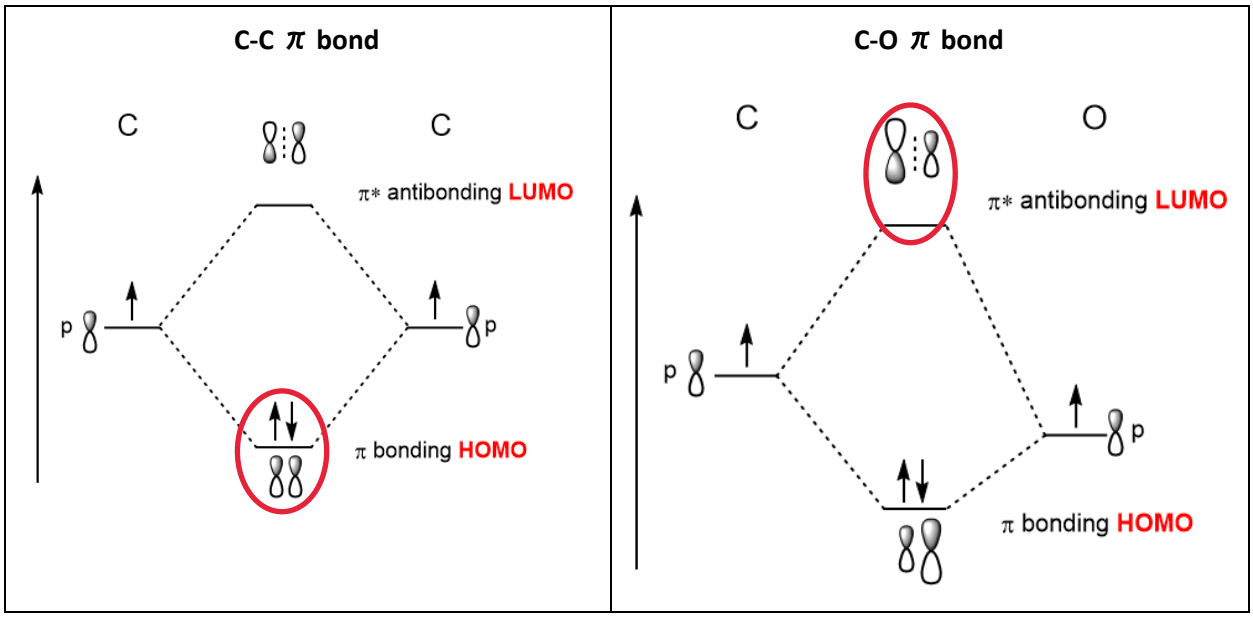
Are these configurational isomers, conformational isomers, constitutional isomers, or identical? **Circle your choice.**

| | | | | |
|---|---|---|---|---|
| **Circle:** | **Configurational** | Conformational | Constitutional | Identical |

**7. (18 points) Molecular Orbital Theory**

a. Draw molecular orbital diagrams for the C-C pi bond of molecule A and the C-O pi bond of molecule B, which react according to the scheme below. Sketch and label all orbitals and the HOMO and LUMO in each diagram.




b. Using the MO diagrams drawn in part A, identify (with a circle) which orbitals are involved in the reaction that takes place in step 1.

c. In the box below, describe how the occupancy of each one circled changes as bonds form and break.

The C–C π (HOMO) donates a pair of electrons into the C–O π* (LUMO). Therefore, the occupancy of the C–C π changes from 2 electrons to 0 electrons and the occupancy of the C–O π* changes from 0 electrons to 2 electrons.

d. Describe in one or two sentences how and why the C-C and C-O pi bonds break in this step. Consider bond orders.

Each π bond breaks because the net bond order is left at 0. As the electron pair leaves C–C π , there are no electrons in the bonding orbital, leaving the bond order at 0. As the C–O π bond breaks, C–O π* is populated with an electron pair, leaving the bond order (# antibonding electrons minus # bonding electrons) at 0.