CHEMISTRY 12A FALL 2019

EXAM 1

OCTOBER 3, 2019

NAME- WRITE BIG _____

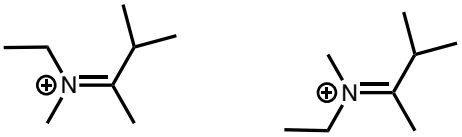
STUDENT ID: _____

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	17
2	23
3	20
4	8
5	23
6	21
7	8
Total	***120***

1. (17 points) Consider the two molecules below. They are called iminium ions.



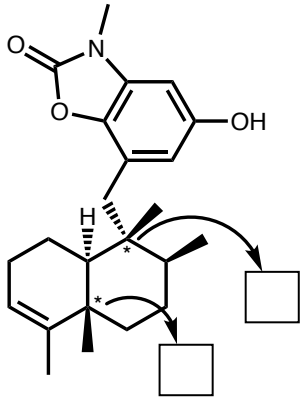
a. Assign E and Z to each

b. Which is more stable? Explain your answer.

c. Which would you expect to have a larger (more negative) heat of combustion?

d. Draw a molecular orbital diagram of the N=C bond in an iminium ion.
Sketch and label all hybrid atomic and molecular orbitals and label the LUMO and HOMO.

2. (23 points) The natural product below was recently isolated from marine sponges, and is known as Cinerol G.



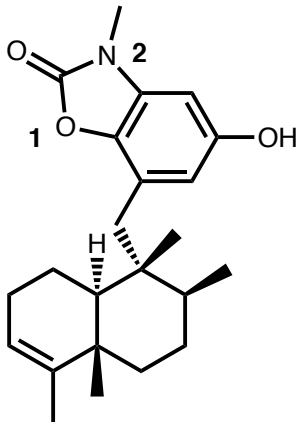
a. Draw in partial charges for each carbon-heteroatom bond on Cinerol G.

b. Label the starred carbons as R or S in the boxes provide.

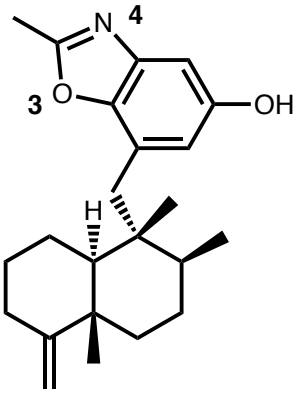
c. The specific rotation of pure Cinerol G is 16°. A chemist isolates a sample, expecting Cinerol G, and finds that the specific rotation is 1.6°. What is the % ee of the mixture? Show your work.

d. What is the ratio of Cinerol G to its enantiomer? Show your work.

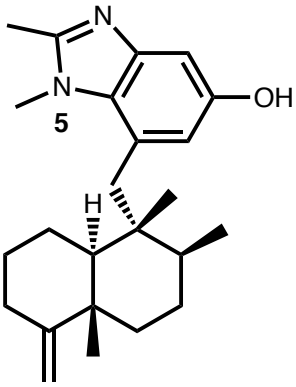
e. Two other forms of Cinerol are found in nature. All three Cinerols are shown below. Fill in the table for the hybridization and lone pair orbitals of the indicated atoms.



Cinerol G



Cinerol E

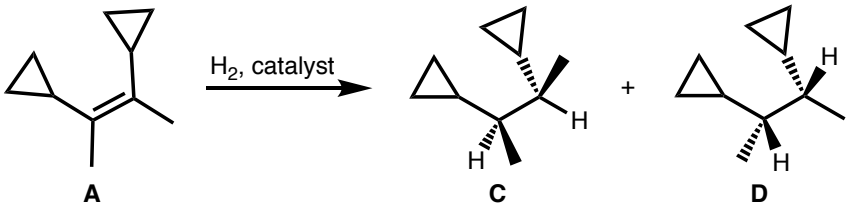


Cinerol A

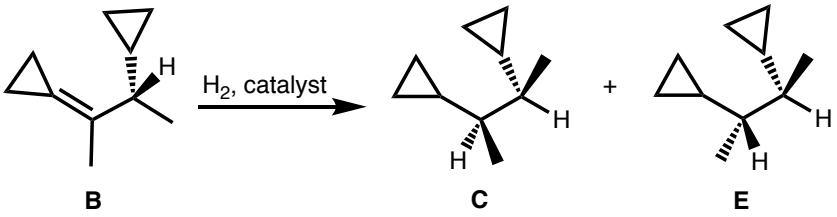
	Oxygen **1**	Nitrogen **2**	Oxygen **3**	Nitrogen **4**	Nitrogen **5**
Atomic hybridization					
1st Lone pair orbital					
2nd Lone pair orbital (oxygen only)					

f. Which of the Cinerols in part e is most basic? Draw the protonated molecule and explain your selection. If resonance is a part of your explanation, draw the relevant resonance structures. You do not need to draw the entire structure in your resonance structures. You may abbreviate the parts of the molecule that are not participating in resonance as 'R'.

3. (20 points) Consider the two reactions below.



A C D



B C E

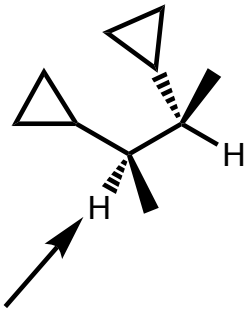
a. Is alkene **A** or **B** more stable? Explain your answer.

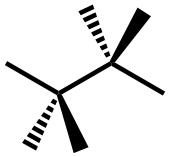
b. Which of these 3 product molecules (**C**, **D**, and **E**) are chiral?

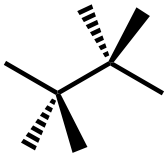
c. Are **C** and **D** constitutional isomers, enantiomers, diastereomers or identical?

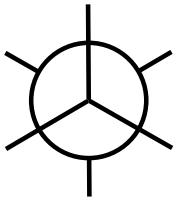
d. Are **C** and **E** constitutional isomers, enantiomers, diastereomers or identical?

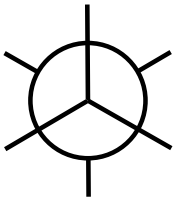
e. i. Draw a Newman projection of the molecule **C** below looking down the bond indicated with the arrow using the template above 'Conformation A'.
ii. Using the remaining 4 templates, draw Newman projections and line drawings of the other two staggered conformations.
iii. What is the order of stability of these conformations. Explain your answer.

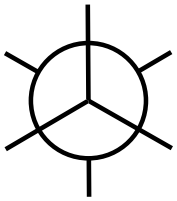












Conformation A

Conformation B

Conformation C

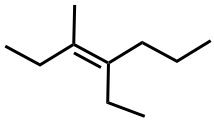
Explanation

4. (8 points) Nomenclature.

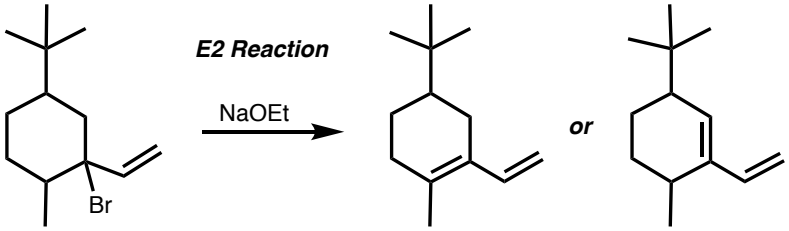
a. Draw the molecule that the name represents.

(3*R*,4*R*)-3,4-dichloro-1,1,2,2-tetramethylcyclobutane

b. Name the following molecule, including stereochemistry.

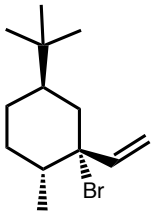


5. (23 points) You plan to run the following E2 reaction.

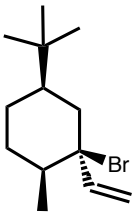


a. You know that E2 reactions form the more stable alkene. Therefore, you expect that product **1** will be the major product. Why is **1** more stable than **2**?

You are choosing between the following two isomeric molecules to do this reaction.



3



4

b. Are **3** and **4** constitutional isomers, enantiomers, diastereomers or identical?

c. For isomers **3** and **4**:
i. Draw both chair conformations. Draw in all hydrogens on the cyclohexane ring.
ii. Indicate which is more stable and explain your selection.
iii. Circle the H's (if any) that are anti to the Br in each conformation you draw.

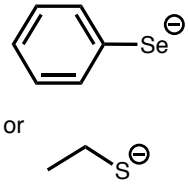
Isomer 3

Isomer 4

d. Keeping in mind that the H and Br are required to be anti to each other to form the alkene product **1** in the E2 reaction. Which stereoisomer should you use for this reaction? Justify your choice.

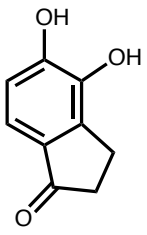
6. (21 points) Answer the following questions regarding acidity and basicity below. Explain your answers in the boxes provided. If resonance is involved in your explanation, draw the relevant resonance structures.

a. Circle the strongest **base**.



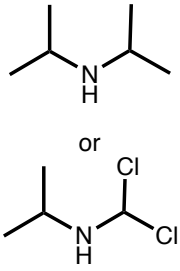
Explanation

b. Circle the most **acidic** hydrogen.



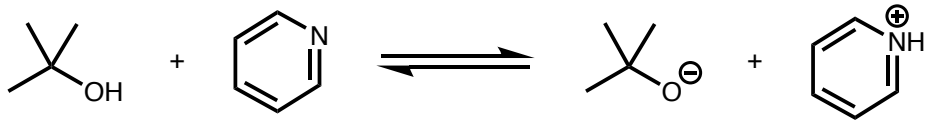
Explanation

c. Circle the strongest **acid**



Explanation

d. Consider the following equilibrium.



approximate pK_a

approximate pK_a

i. Fill in all lone pairs.
ii. Fill in approximate pK_a values in the boxes.
iii. Will the products or starting materials be favored in this equilibrium? Explain your answer.

7. (8 points) Consider the molecule below.
i. Draw in all lone pairs.
ii. Draw reasonable resonance structures. The atoms in all resonance structures have full octets. Do not draw structures with more than two formal charges.
iii. Use arrows to show the flow of electrons from one resonance structure to the other.
iv. Identify the most important contributor to the resonance structures and explain your answer.