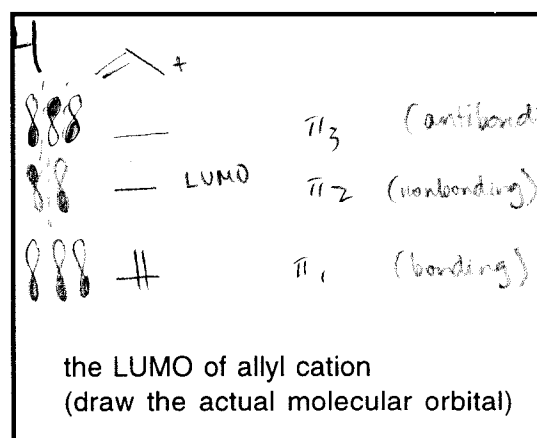
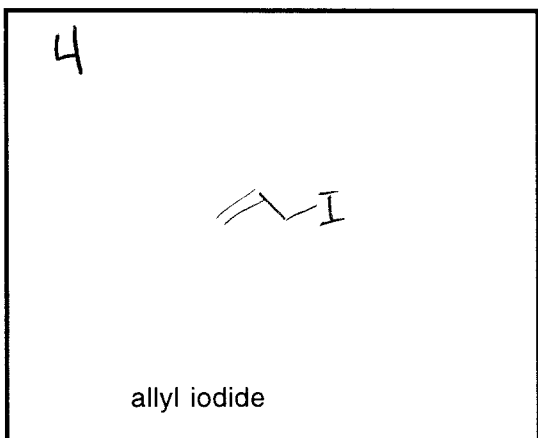
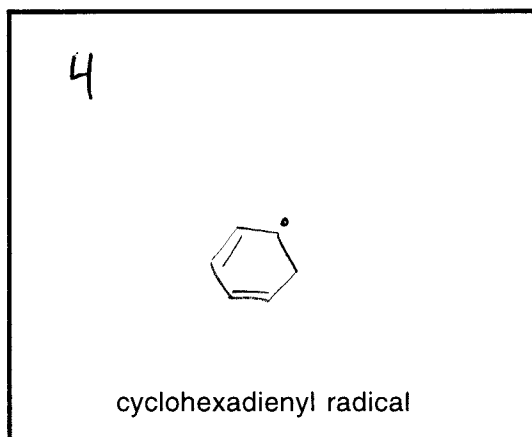
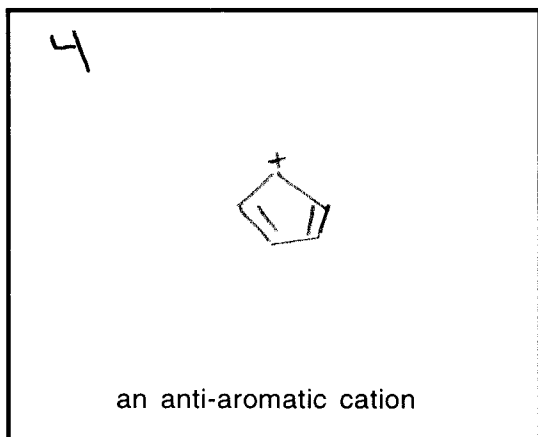
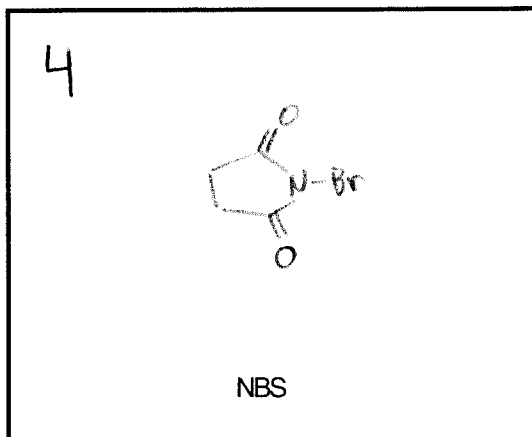
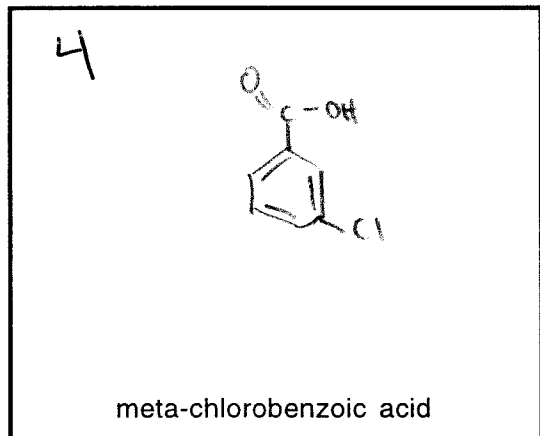
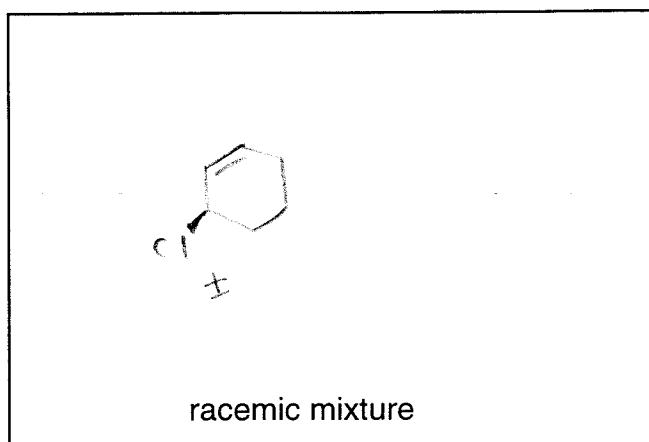
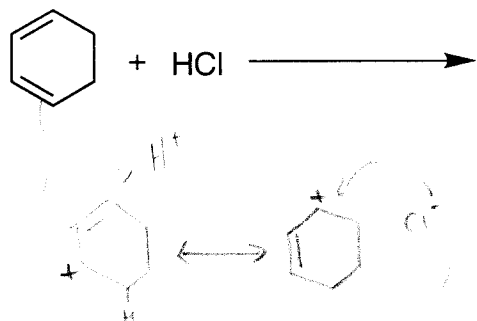


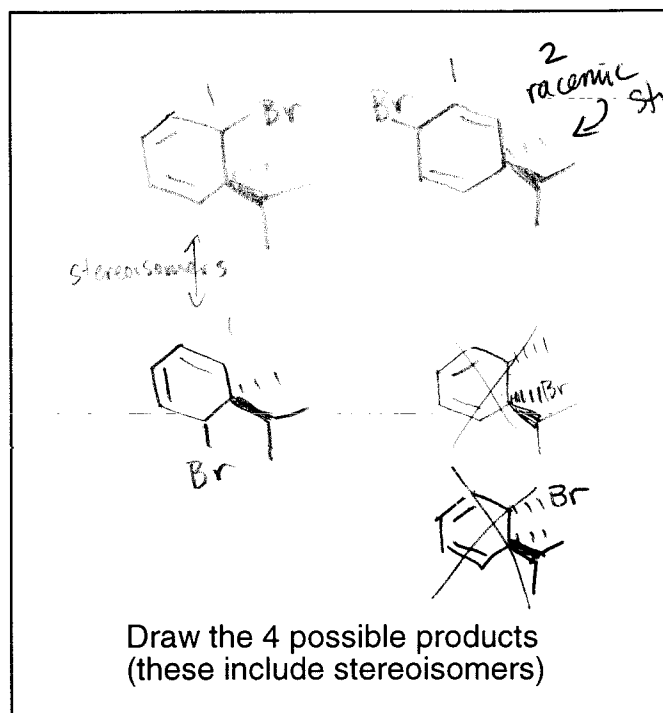
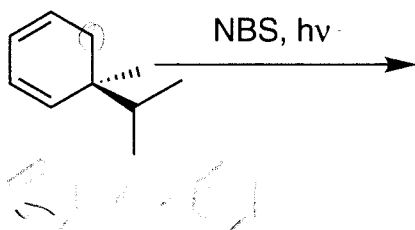
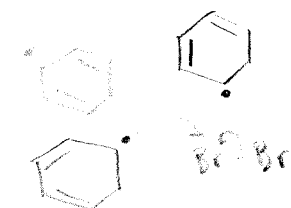
1. Provide one (and only one) real example for each of the following terms or, write a structure for a given chemical name (24 pts).



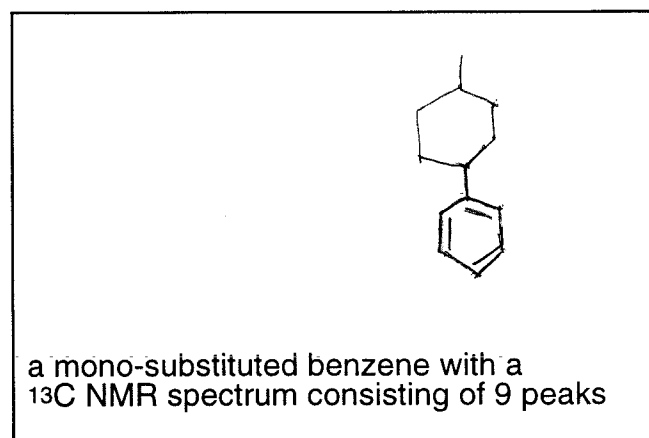
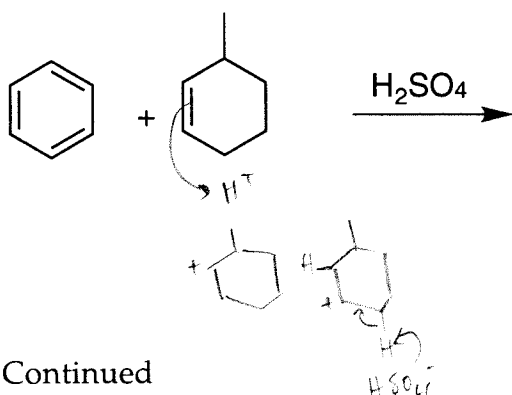
2. Predict the product(s) from the following reactions. (32 pts)



2

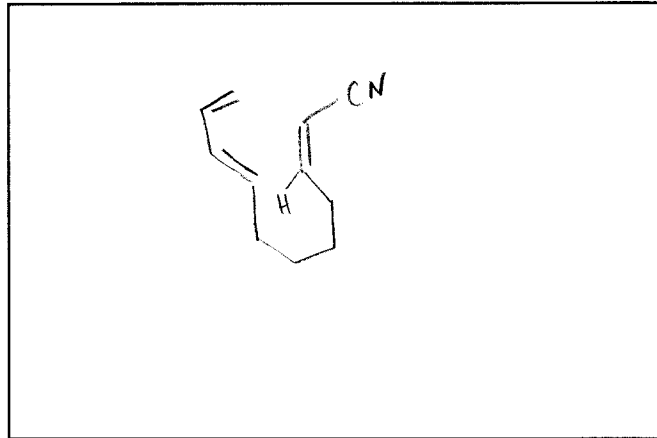
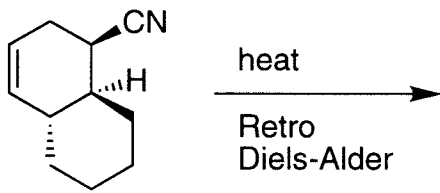


3

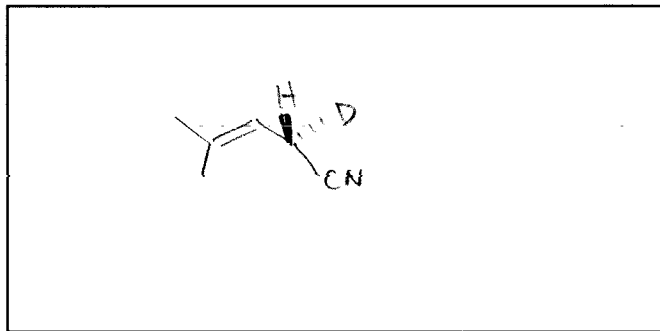
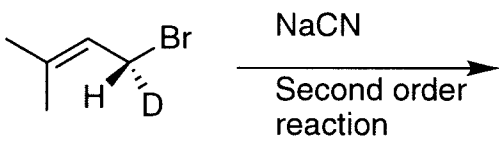


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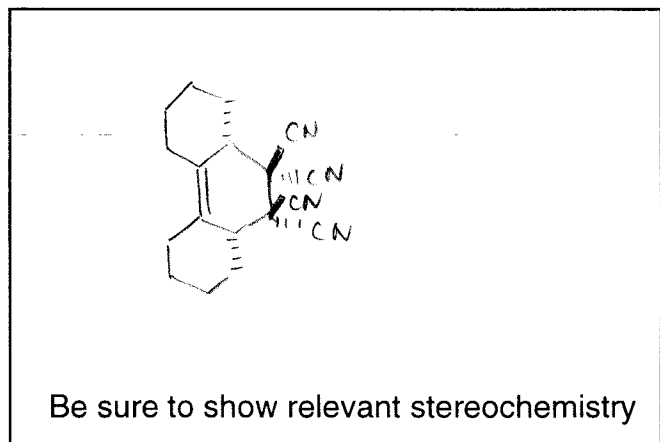
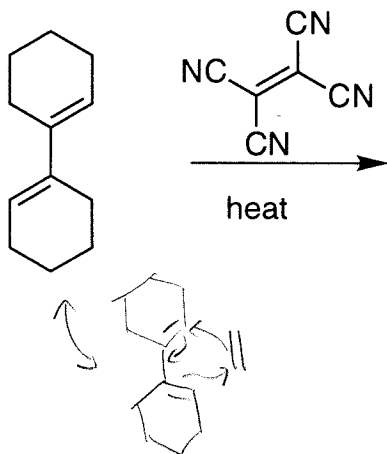
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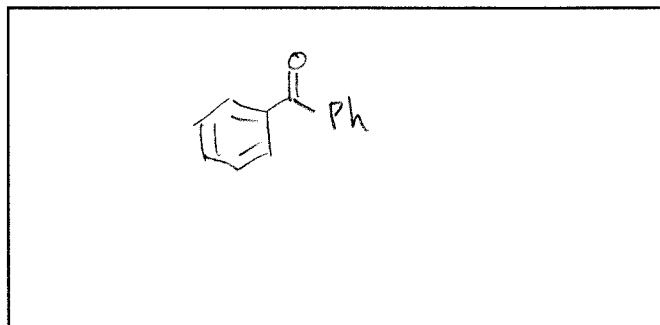
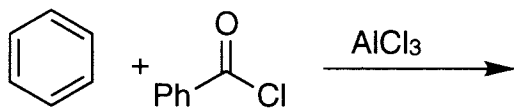
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4



4

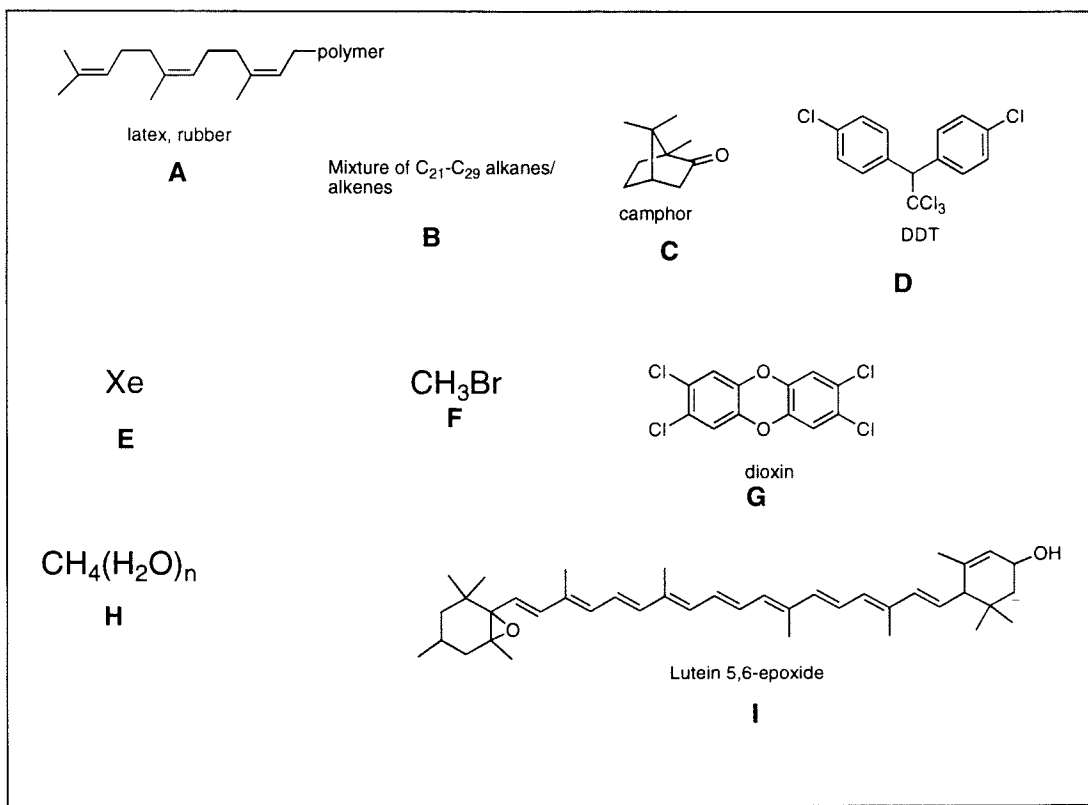


4

16

3. Match the molecules shown below with the statements (18 pts).

- a. This very toxic compound can probably be found in your local compost pile. G 2
- b. Flammable "snow balls". H 2
- c. Fragrant smelling shipwrecks. C 2
- d. After you hear about this molecule, strawberries never taste quite the same. F 2
- e. The newest space fuel. E 2
- f. "Hey, stop stealing my abscisic acid!" said the host to the guest. "I can't help it!" said the guest. "I have no more neoxanthin." I 2
- g. "Rats! Fooled again!" said the male bee to the orchid. B 2
- h. The Mayan's put bouncing balls made out of this molecule through hoops using no hands or feet! I wonder if Shaq could do that. A 2
- i. A molecule tied to both the Endangered Species Act and malaria. D 2

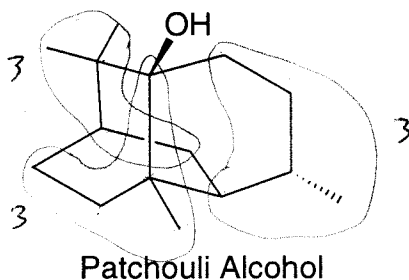


18

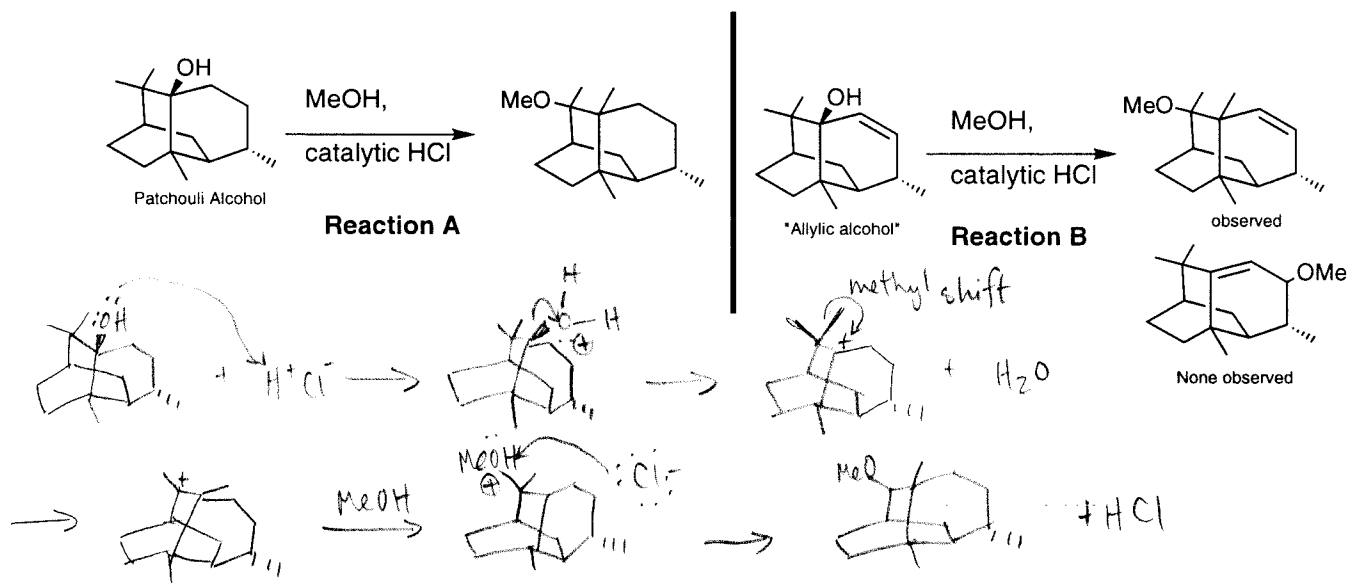
4. (42 pts)

A. Patchouli alcohol is the terpene primarily responsible for the smell of patchouli oil, famous for its use in perfumes. What type of terpene is this? (mono, di, etc.): sesquiterpene 2

B. Circle the isoprene units in patchouli alcohol. Be sure to include all carbons of a given isoprene unit in each circle.



C. S_N1 solvolysis of patchouli alcohol and its allylic alcohol analog proceed at approximately the same rates, each leading to similar products. Provide a rational arrow pushing mechanism for Reaction A shown below.



10

D. Allylic alcohols normally undergo S_N1 solvolysis reactions faster than non-allylic analogs. They also lead to products such as the one that was not observed in Reaction B. Briefly explain why neither of these generalizations are true in this case.

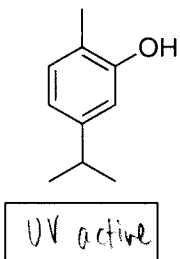
The allylic resonance that produces the product not observed leads to a secondary carbocation that is less stable than the tertiary carbocation produced as an intermediate if the methyl shift occurs. In addition, this lack of allylic resonance activity is the reason why reaction B proceeds as quickly as reaction A: the double bond provides no additional stabilizing force.

10

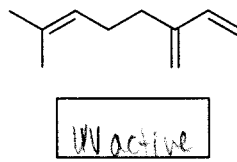
E. Hexane extracts of a maple leaf at peak fall foliage were applied to a TLC plate and the plate was developed. The six compounds shown below were identified from these extracts.

- ◆ Two of these compounds showed up on the plate as orange/red spots without any type of visualization other than ones eyes. Label these compounds as VISIBLE.
- ◆ Two of these compounds were not visible on the plate until it was placed under an UV lamp. At this point they showed up as dark spots on a green fluorescent background. Label these UV ACTIVE.
- ◆ The remaining two compounds were not visible to the eye or under an UV lamp. Label these UV INACTIVE.
- ◆ How would one visualize the UV INACTIVE compounds? Circle the one that applies:

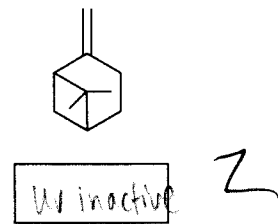
Iodine DNPH Purpald ~~X-rays~~



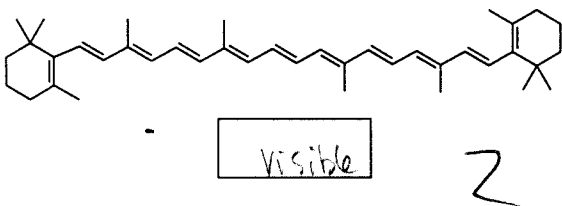
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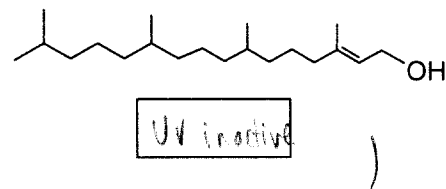
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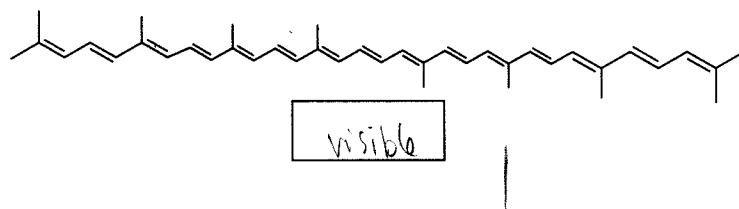
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2

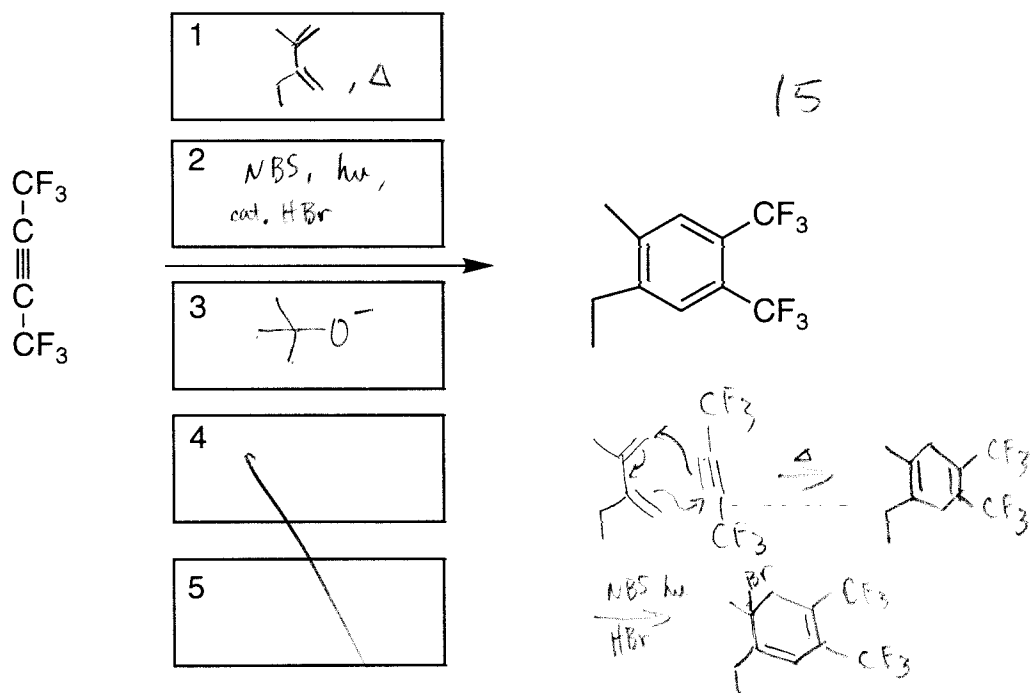
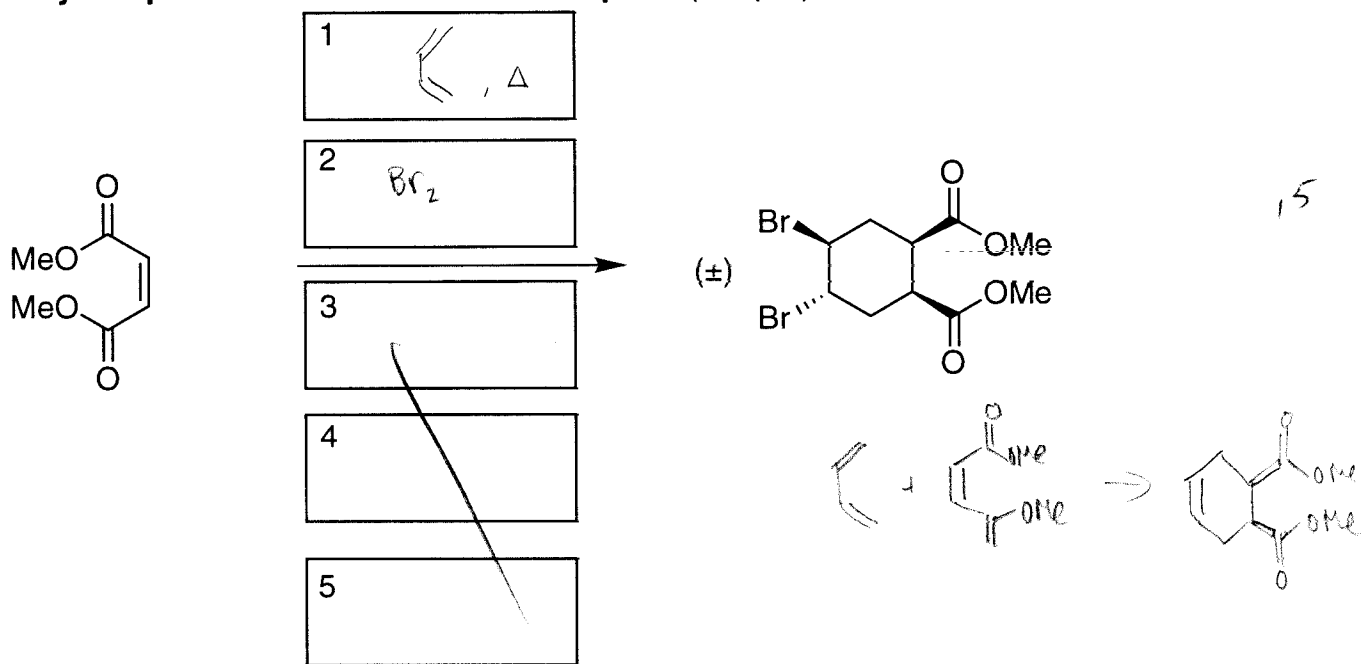


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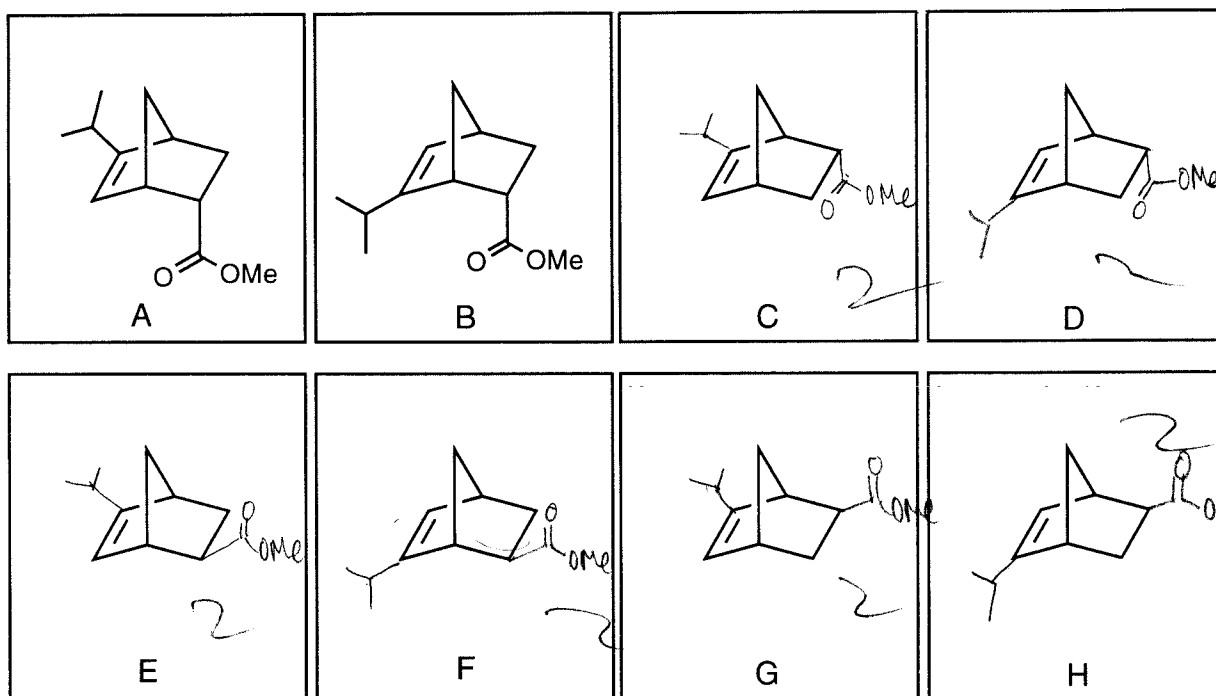
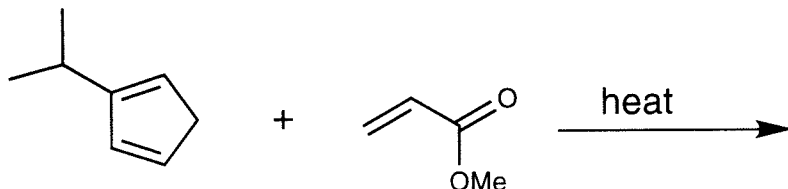
1

5. Provide the reagents (you do not have to make reagents as a separate step) and any other organic compounds necessary to synthesize the indicated product from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require fewer than five steps.** (30 pts)

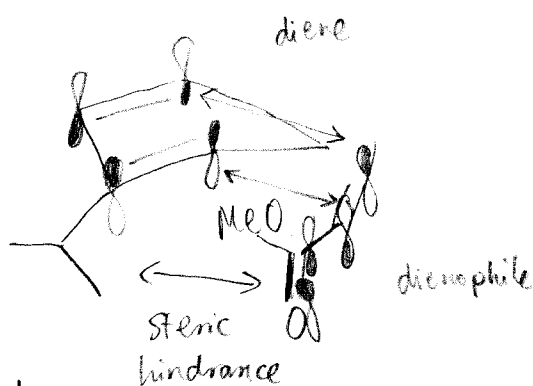


6. (54 pts)

- A. There are eight possible products for the following Diels-Alder reaction shown below. On the frameworks below, add in the appropriate substituents. Note: two compounds are already drawn for you.



- B. The ratio of (\pm) A to (\pm) B in this reaction is 5:1. Rationalize this ratio using words AND any representation of the transition states you wish to draw.



The incoming dienophile has a large carbonyl group in the "endo" slot that will interfere with the isopropyl group at the position shown (product B); the process is thus less favorable than A.

Continued

/ 20

- C. The pyrrole anion is shown below. Is this an aromatic compound? Yes
Justify your answer by stating all of Huckel's rules AND by drawing the π -Energy level diagram for this molecule. Be sure to fill in the electrons on your diagram.

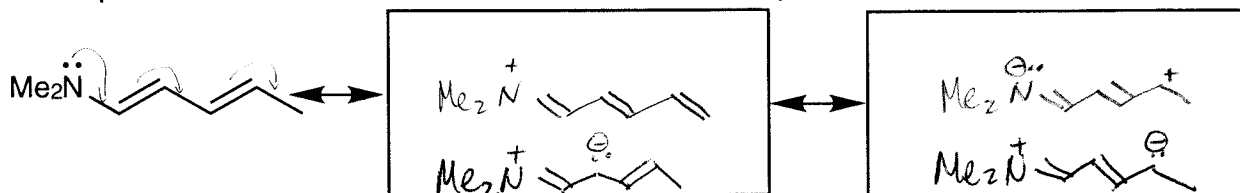


over 4p levels?

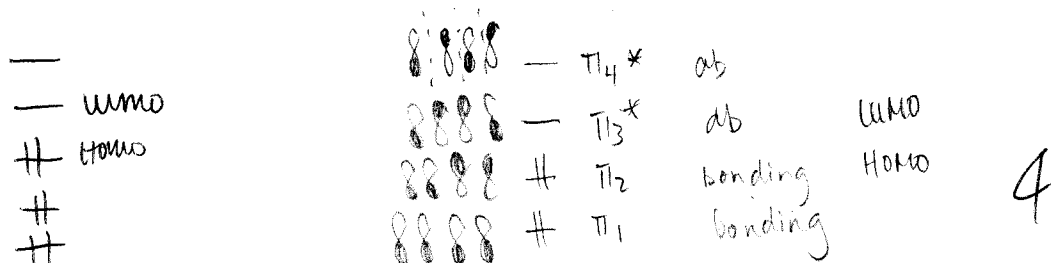
1. planar Yes
2. cyclic Yes
3. $(4n+2)\pi e^-$ Yes
 (one set of lone pairs resides in a p orbital; the other one is in an sp^2 orbital)
4. All C atoms have p orbitals (complete conjugation) Yes

6

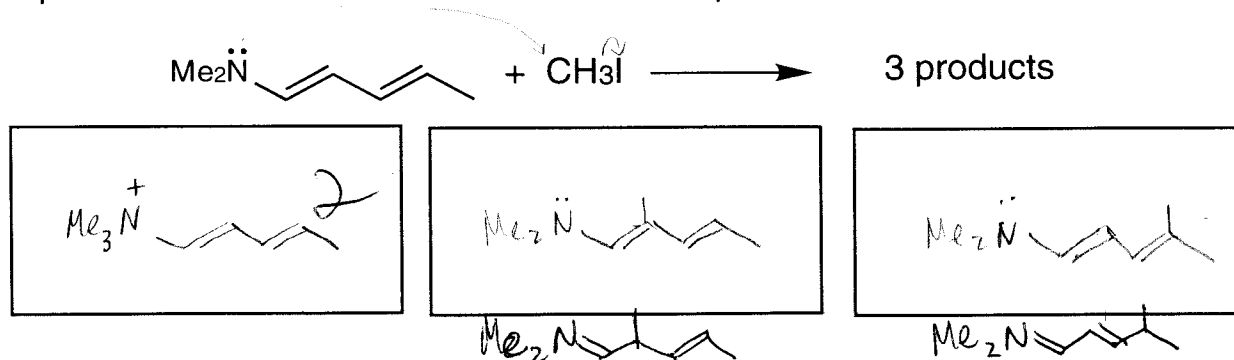
- D. The compound shown below is known as an enamine. Show two other important resonance structures of this compound.



- E. Draw the π -energy level diagram for this molecule. Fill in the electrons and label the HOMO and LUMO.



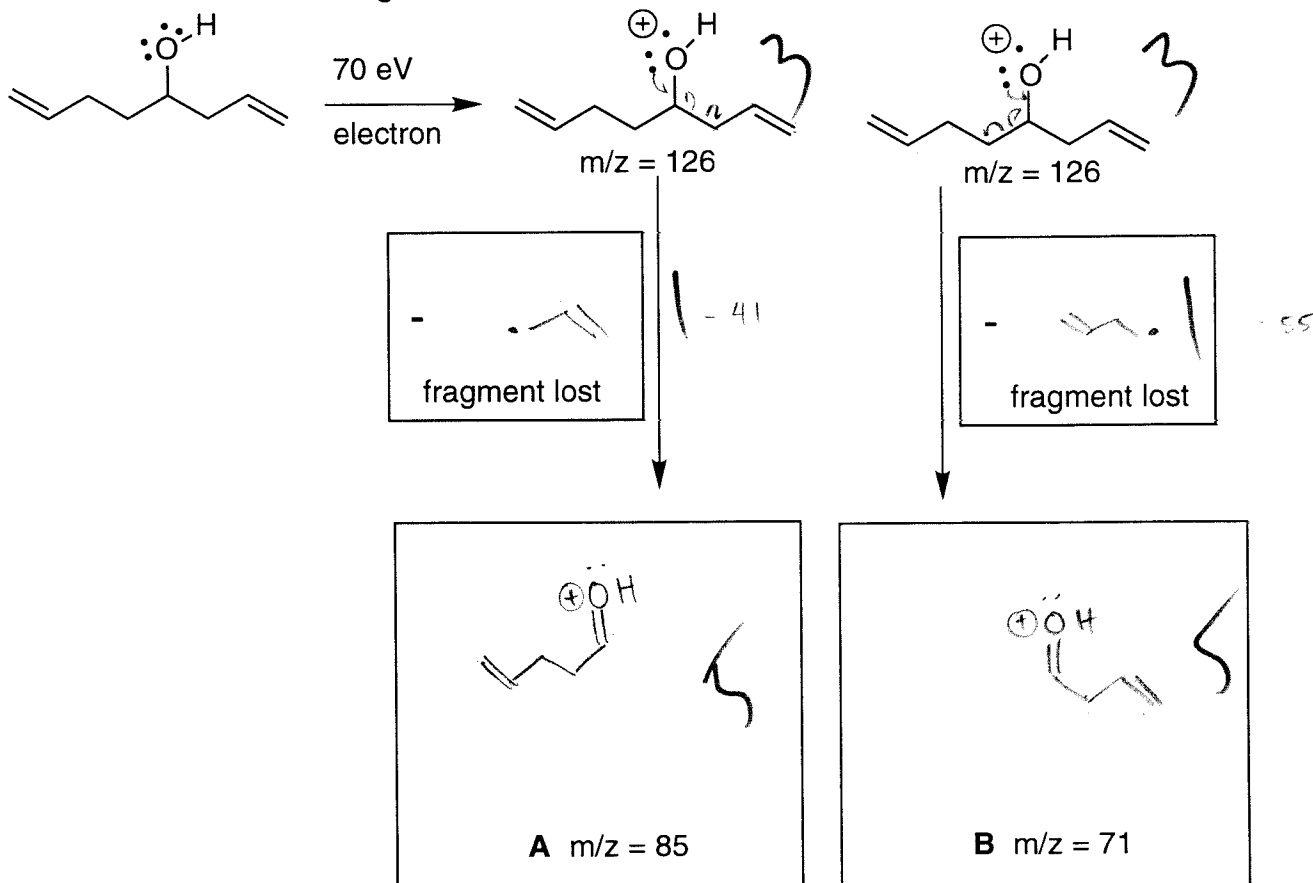
- F. This enamine can react with methyl iodide to give three possible products. Draw the structures of these products.



12

7. (25 pts)

- A. An EI mass spectrum of the alcohol shown below was obtained. Two of the ions observed (identified as m/z) are shown in the boxes below. Draw rational arrow pushing mechanisms leading to these ions. BE SURE TO SHOW ALL NON-BONDING ELECTRONS AND INDICATE WHERE THE CHARGE OF THE ION IS LOCALIZED. In the boxes next to the arrows, show the structure of the fragment that was lost.



- B. Would you expect the ratio of ion A to ion B to be? Circle one:

A>B B>A A=B

Briefly justify your answer:

The radical lost to form ion A is an allylic radical, more stable than the butenyl radical of B. There is resonance for $\cdot\text{CH}_2\text{CH}=\text{CH}_2$ but not for $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$.

125