Organic Chemistry 2 Name:___Bernie Madoff_____
First Examination
February 27, 2009
Prof. Malachowski

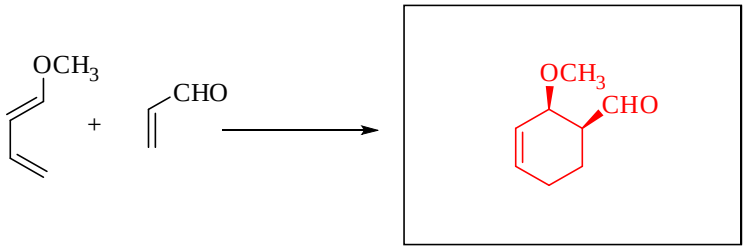
The examination has six questions on four pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex , then you may need to rethink the question. Keep in mind the intended examination topics.

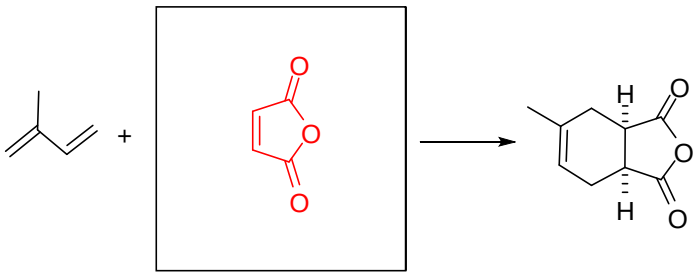
In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include lone pairs of electrons and formal charges when appropriate.

1. Provide the necessary information, product(s), reagents or starting materials, to complete the following reactions. (3 pts. per question)

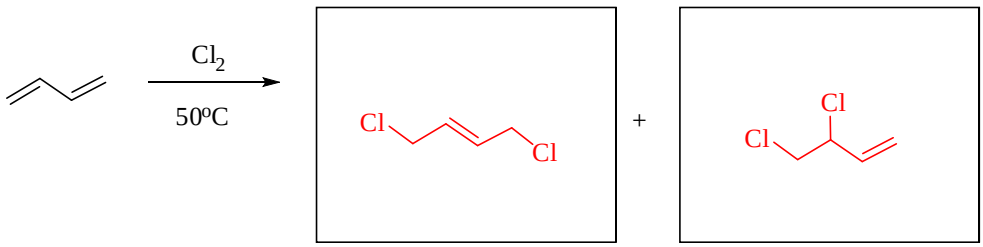
a)



b)



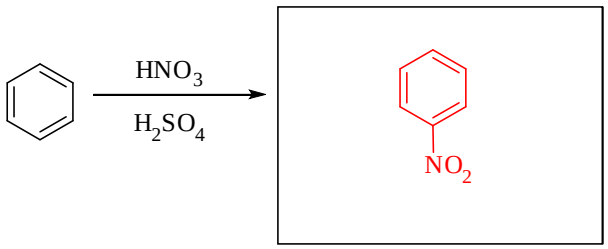
c)



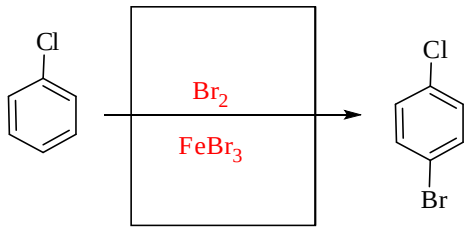
major product

minor product

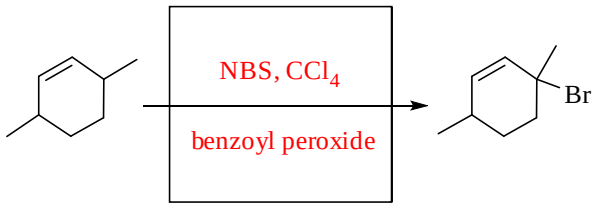
d)



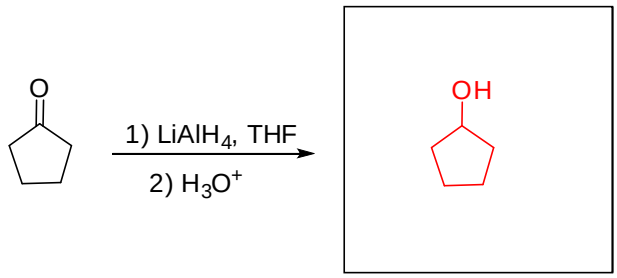
e)



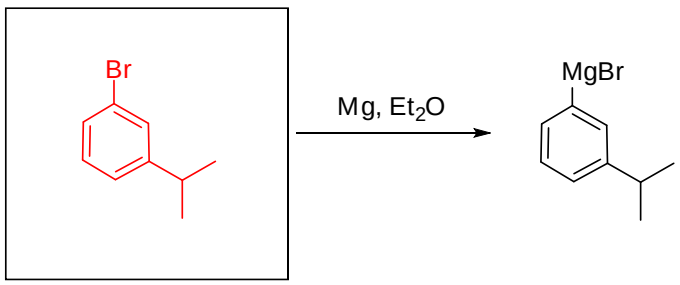
f)



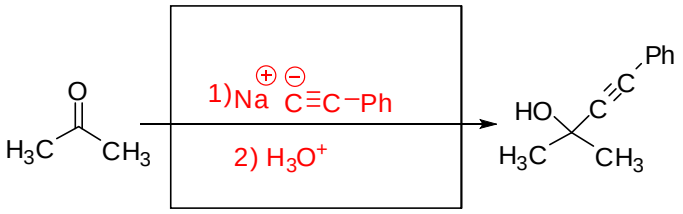
g)



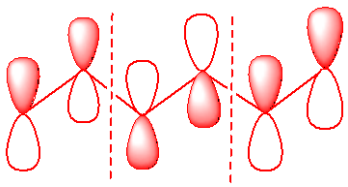
h)



i)



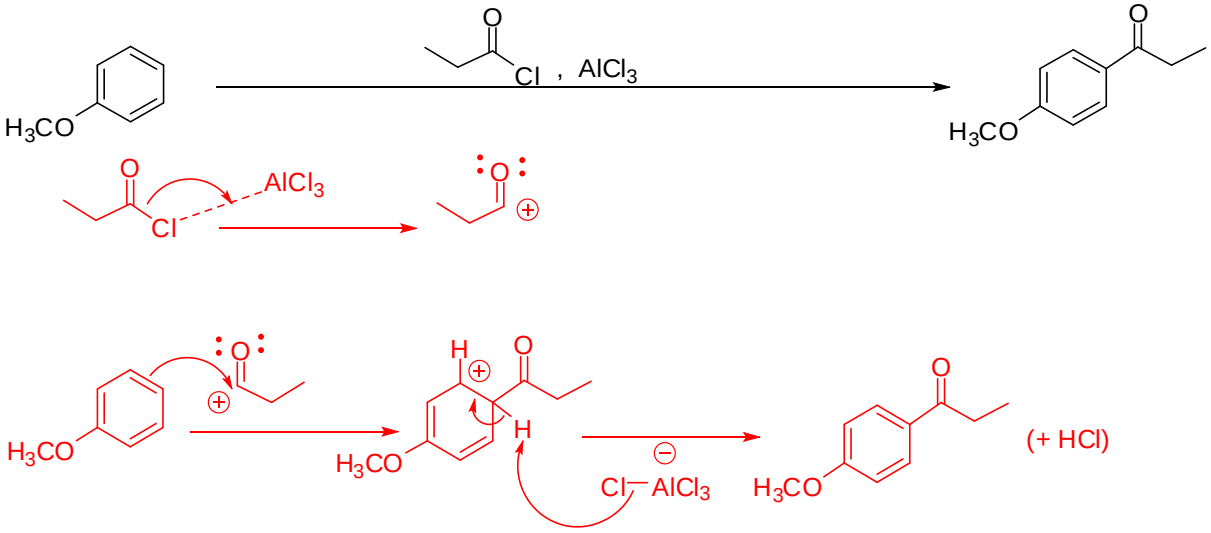
2. Draw the HOMO for 1,3,5-hexatriene. (4 pts.)



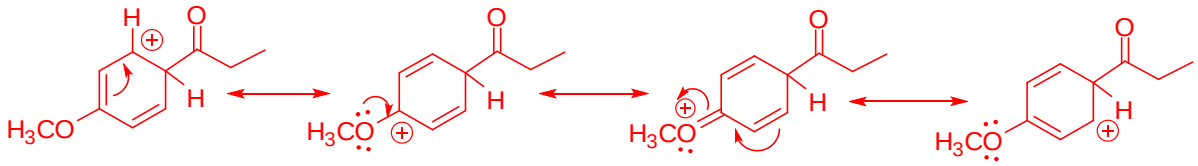
1,3,5-hexatriene→ $H_2C=CH-CH=CH-CH=CH_2$, therefore HOMO is:

/31 pts.

3. Provide the necessary information about the reaction shown below.
a) Draw the mechanism of the reaction. You do NOT need to include resonance structures here. You should include all formal charges and curved electron flow arrows. (8 pts.)



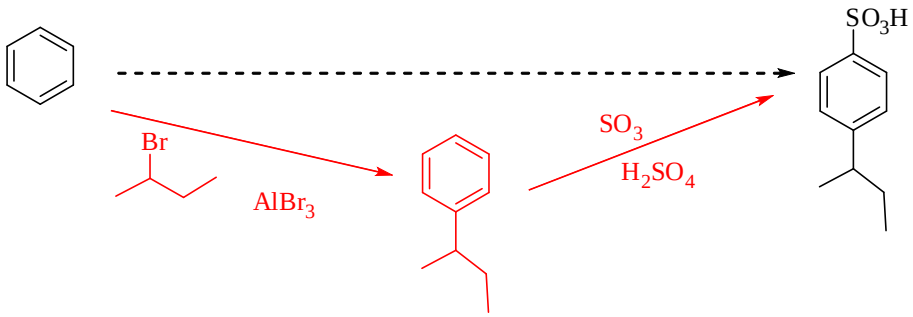
b) Show the important resonance contributors of the key ring intermediate in the reaction. Be sure to include formal charges and curved electron flow arrows to indicate all electron movement. (8 pts.)



c) What's the name of this reaction? (2 pts.) Friedel-Crafts acylation

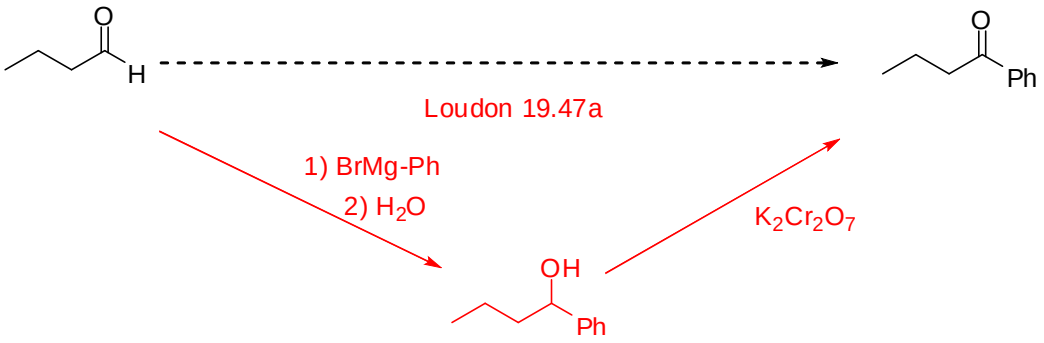
d) What's the common name of the starting material (NOT the reagents)? (2 pts.) anisole

4. Suggest a synthesis to take the starting material on the left to the product on the right. This will require more than one step. You may use any inorganic reagent and any organic reagent of six carbons or less. (7 pts. each)
a)



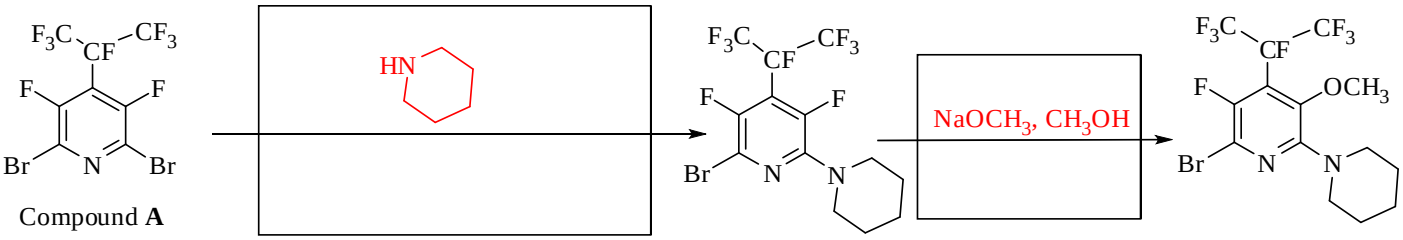
/27 pts.

b)



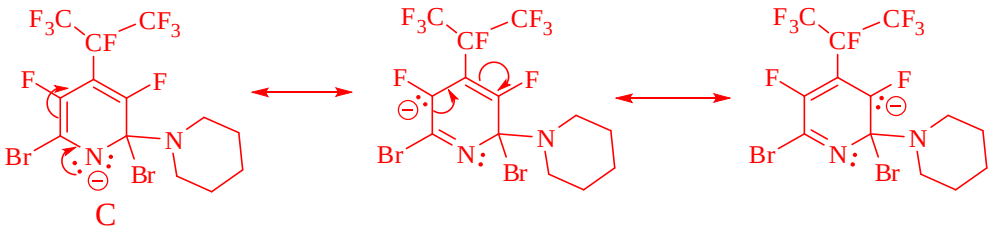
5. A report in a chemistry journal discussed the use of highly fluorinated heterocyclic aromatic compounds in organic synthesis. Fluorinated organic compounds have many applications and consequently, methods to synthesize complex fluorinated compounds are considered valuable. The article showed the following nucleophilic aromatic substitution reactions on a pyridine derivative, compound **A**. Use your knowledge of nucleophilic aromatic substitution reactions with benzene derivatives to answer the following questions.

a) Provide the necessary reagents to complete the following reactions. (3 pts. each)



Compound **A**

b) Draw the three important resonance contributors of the Meisenheimer complex that forms in the first reaction of part a. Be sure to include all formal charges and curved electron flow arrows indicating the electron movement from one structure to the next. (6 pts.)



C

c) One of your Meisenheimer complexes has special stabilization that is seen in pyridine derivatives like compound **A**, but not in benzene derivatives with identical substituents. Write a "C" next to the structure that shows why pyridine Meisenheimer complexes can be more stable than benzene Meisenheimer complexes and briefly describe below why this structure is more stable than an analogous benzene compound. (3 pts.)

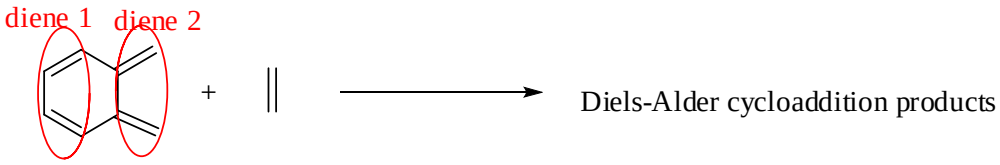
The formal negative charge is on the nitrogen atom. Since nitrogen is more electronegative than carbon, this is more stable than if the atom were a carbon and the ring was benzene.

d) The other two Meisenheimer complexes you have drawn are also stabilized carbanions. Briefly describe what stabilizes these anions. (Hint: You only need to provide one answer, because both are stabilized for primarily the same reason.) (2 pts.)

Both are stabilized by an electronegative fluorine atom attached to the carbon with the lone pair of electrons and negative formal charge. The fluorine will have a strong polar effect that will stabilize this carbanion.

/24 pts.

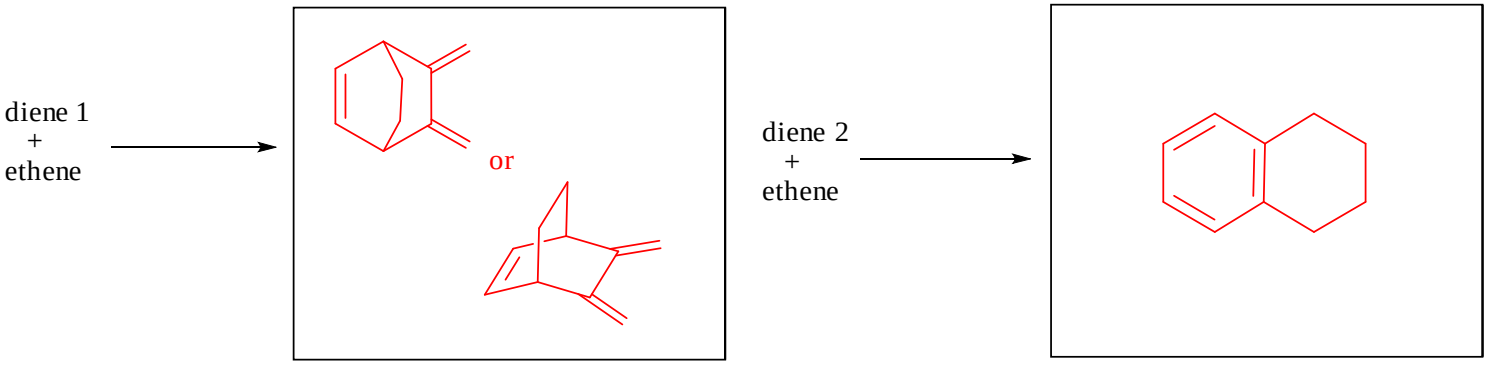
6. A computational study of the following Diels-Alder reaction was recently reported in the organic chemistry literature.



a) There are actually two possible Diels-Alder products from the reaction because there are two conjugated dienes that could react. Circle the two possible dienes and write "diene 1" and "diene 2" next to them. (4 pts.)

b) In the box labeled **Diels-Alder product 1** below, show the product that results from the Diels-Alder reaction of ethene with the diene you have identified as diene 1. (3 pts.)

c) In the box labeled **Diels-Alder product 2** below, show the product that results from the Diels-Alder reaction of ethene with the diene you have identified as diene 2. (3 pts.)

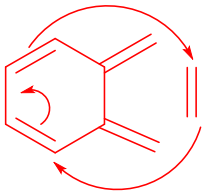


Diels-Alder product 1

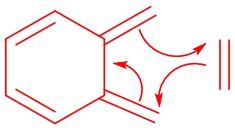
Diels-Alder product 2

d) Choose one of your reactions and draw the mechanism of the reaction in the space below. (3 pts.)

mechanism for diene 1:



mechanism for diene 2:



The authors actually only studied one of these products because one Diels-Alder reaction yields an extremely stable cycloaddition product.

e) Which one of your products is an extremely stable molecule? (Circle one, 2 pts.)

Diels-Alder product 1 or **[Diels-Alder product 2]**

f) Why is the product you selected so stable? (3 pts.)

Diels-Alder product 2 has an aromatic ring while Diels-Alder product 1 only has one conjugated diene.

/18 pts.