Organic Chemistry c3444y

1st Hour Exam

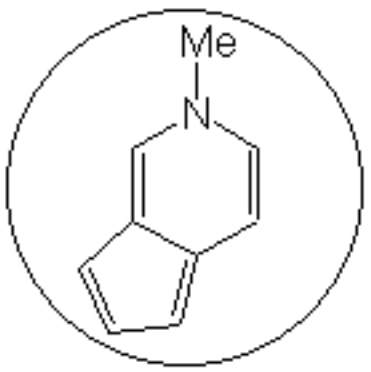
Monday, Feb. 5, 2001

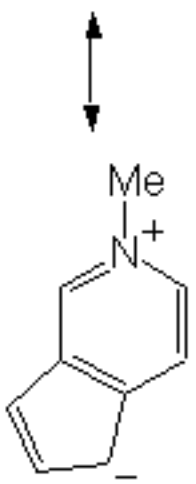
Prof. Leighton

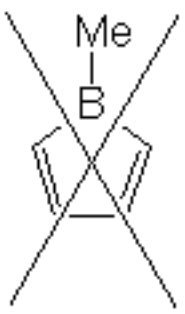
Answer Key

Name: _____

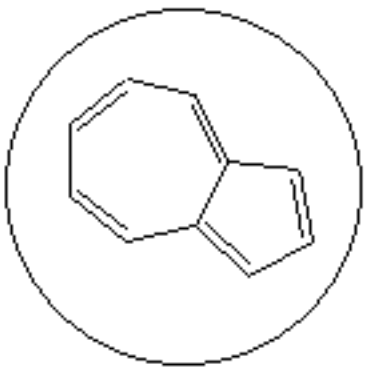
1. a. (10 pts) Consider the following molecules. Put a **circle** around those you would expect to have significant aromatic character, and a big **X** through those that you would expect to have significant antiaromatic character. **Underline** any that you would expect to be simply non-aromatic.

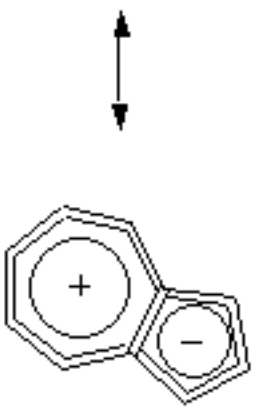


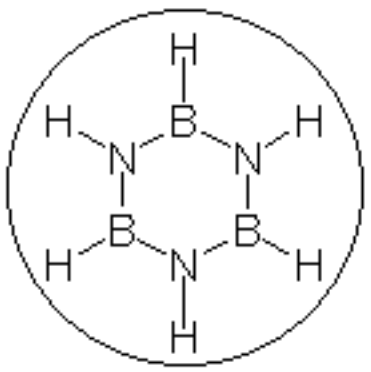




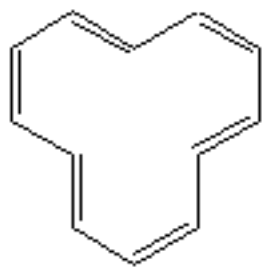
4 pi electrons





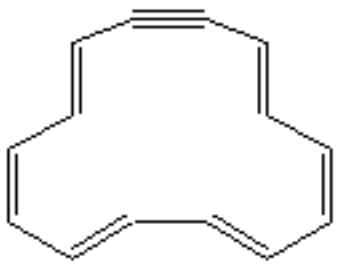


6 pi electrons



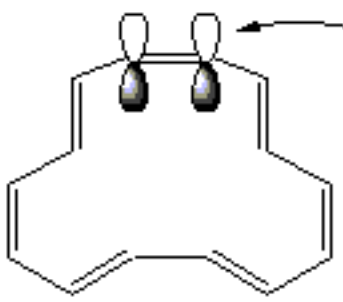
12 pi electrons, but large enough ring to have conformational flexibility. Therefore, it's non-aromatic.

b. (10 pts) Would you expect the illustrated compound to display the properties of an aromatic, antiaromatic, or non-aromatic molecule? Explain briefly and concisely using clear drawings where appropriate. Remember! Orientation matters....



Aromatic!!

If we just count pi electrons, we will count 16, which is a non-Huckel number, and we would conclude that the compound should be antiaromatic. But we must remember the structure of alkynes: They are composed of two pi bonds, which are orthogonal to eachother. In this case, only one of those pi bonds will be aligned or oriented properly for overlap with the other double bonds. The other is orthogonal, and therefore, cannot interact. So we only count 2 electrons for the alkyne. This gives 14 overall, which is a Huckel number.

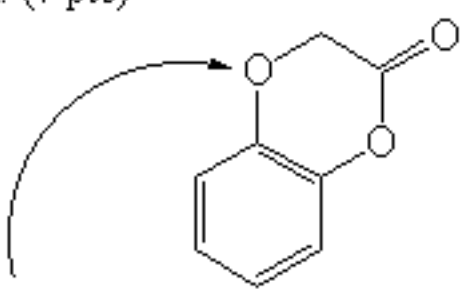


Orthogonal pi bond that does not interact with the pi system of the ring. These orbitals are in the plane of the ring, and are orthogonal to all the other p orbitals in the system.

Name: _____

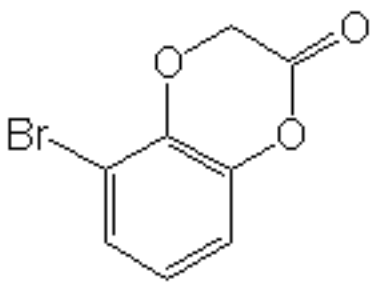
2. Predict the major product, if any, of the following reactions:

a. (7 pts)

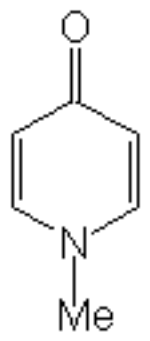


Strongest activator

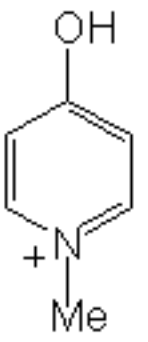
$$\xrightarrow[\text{2. } Br_2,\ FeBr_3]{\text{1. } SO_3, H_2SO_4} \xrightarrow[\text{3. } H_3O^+]{}$$



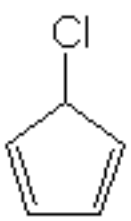
b. (7 pts)



$$\xrightarrow{H^+}$$



c. (6 pts)



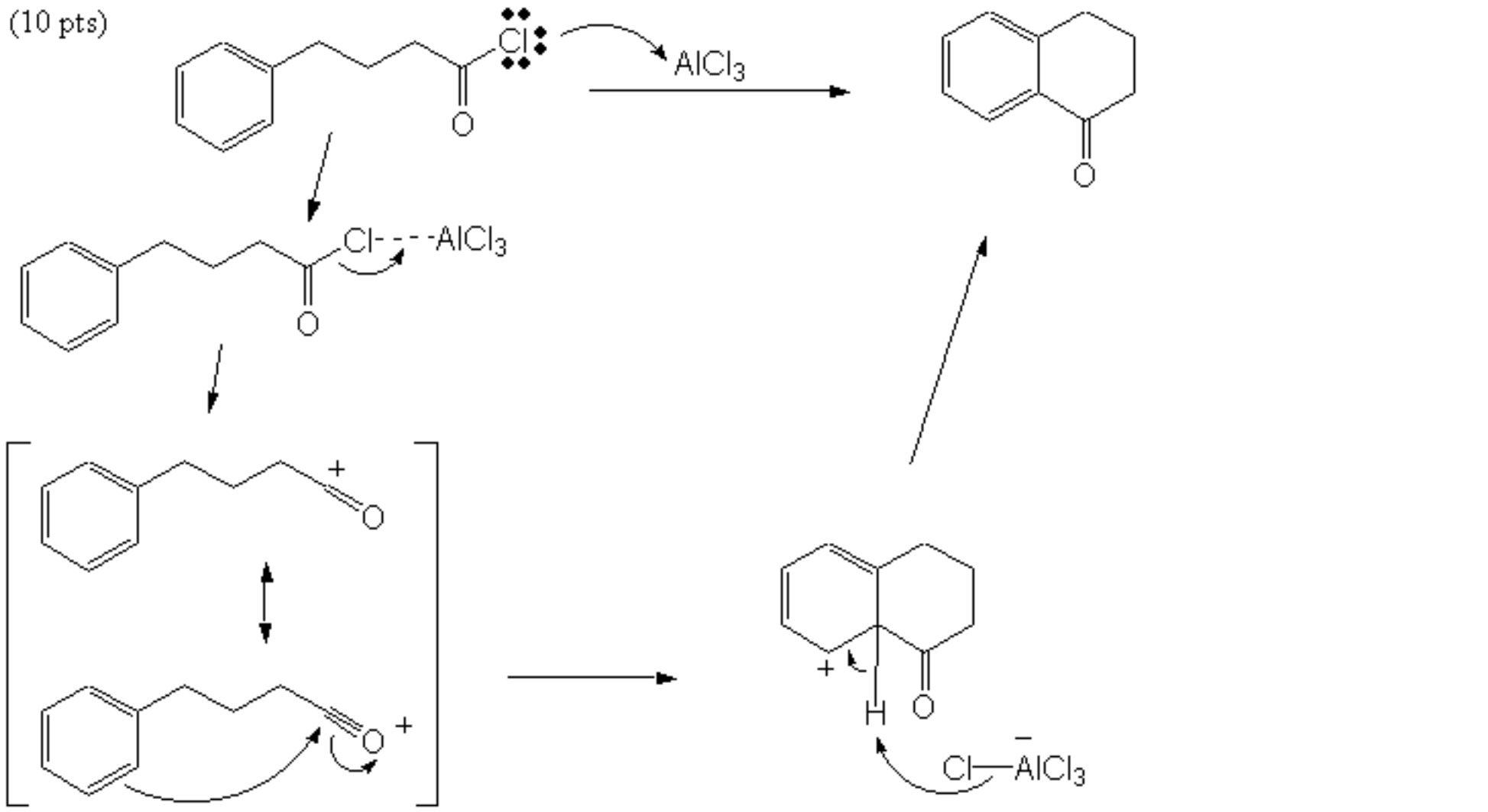
$$\xrightarrow[\text{(Abstracts } Cl^-)]{SbCl_5}$$

No Reaction

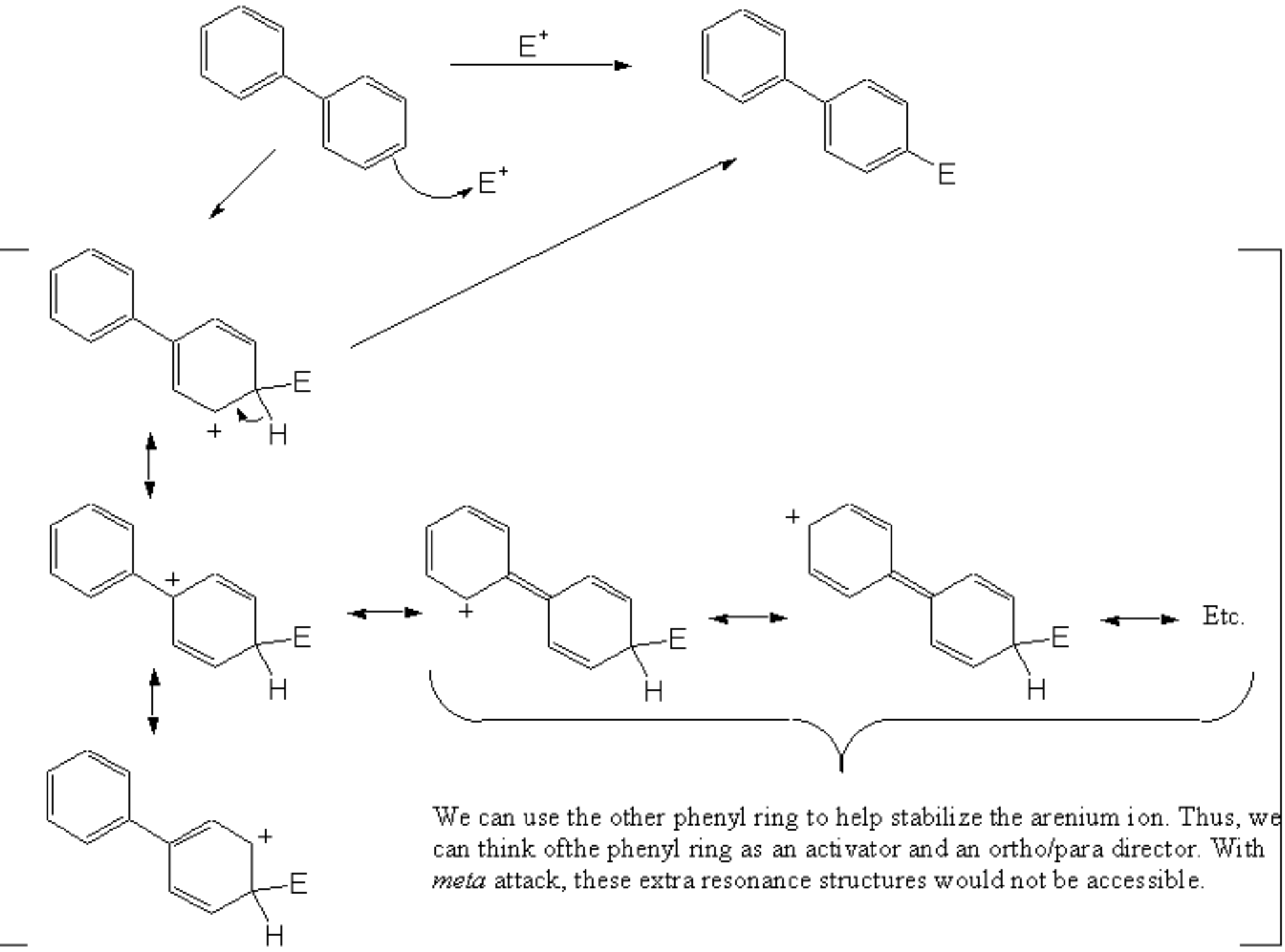
Name: _____

3. Provide detailed mechanisms for the following transformations:

a. (10 pts)



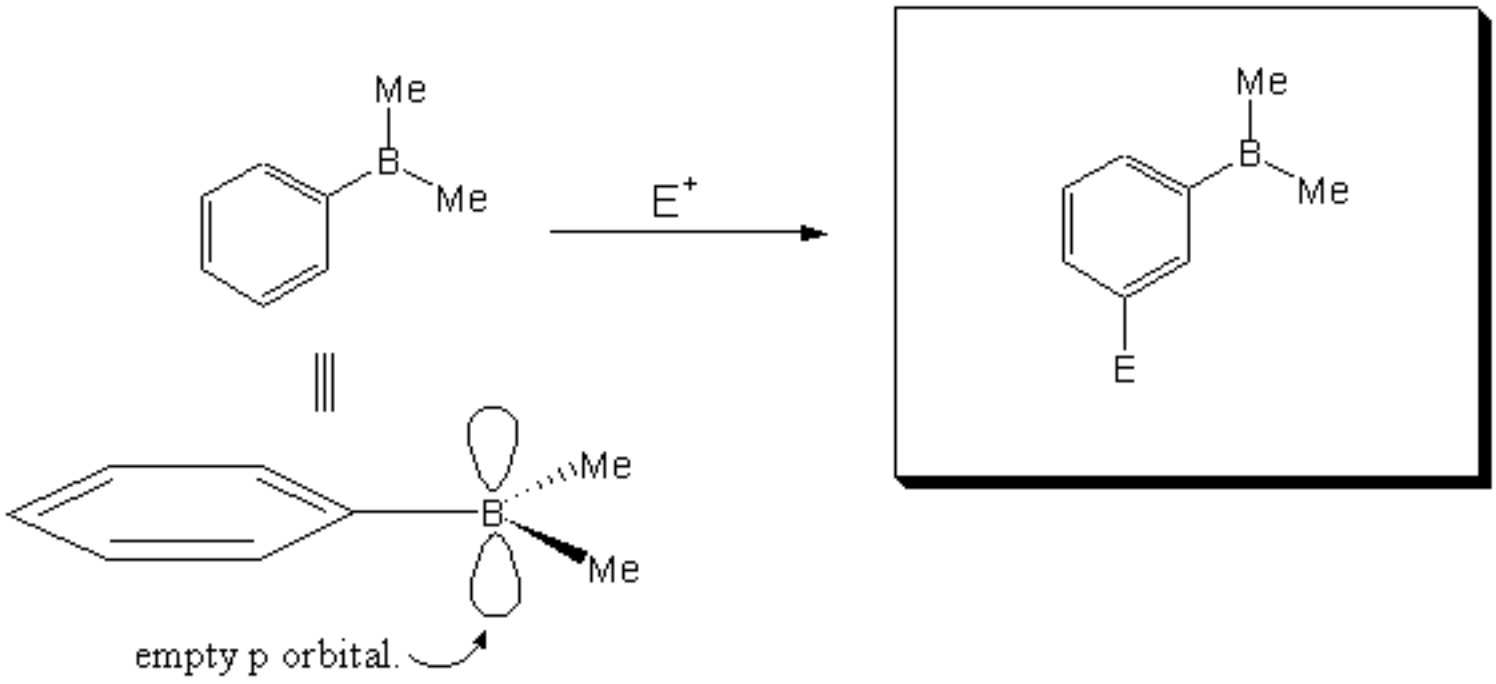
b. (10 pts) For this one, you must also explain with clear drawings why the *para* isomer is the major product.



We can use the other phenyl ring to help stabilize the arenium ion. Thus, we can think ofthe phenyl ring as an activator and an ortho/para director. With *meta* attack, these extra resonance structures would not be accessible.

Name: _____

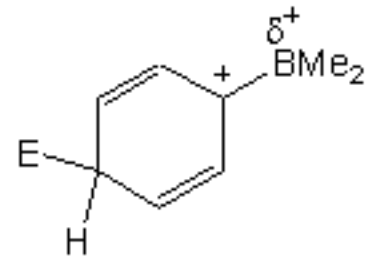
4. a. (10 pts) Predict the major product of the following reaction. Would you expect the BMe_2 group to be an activator or a deactivator? A meta director, or an ortho/para director? Justify your answer with clear drawings.



empty p orbital.

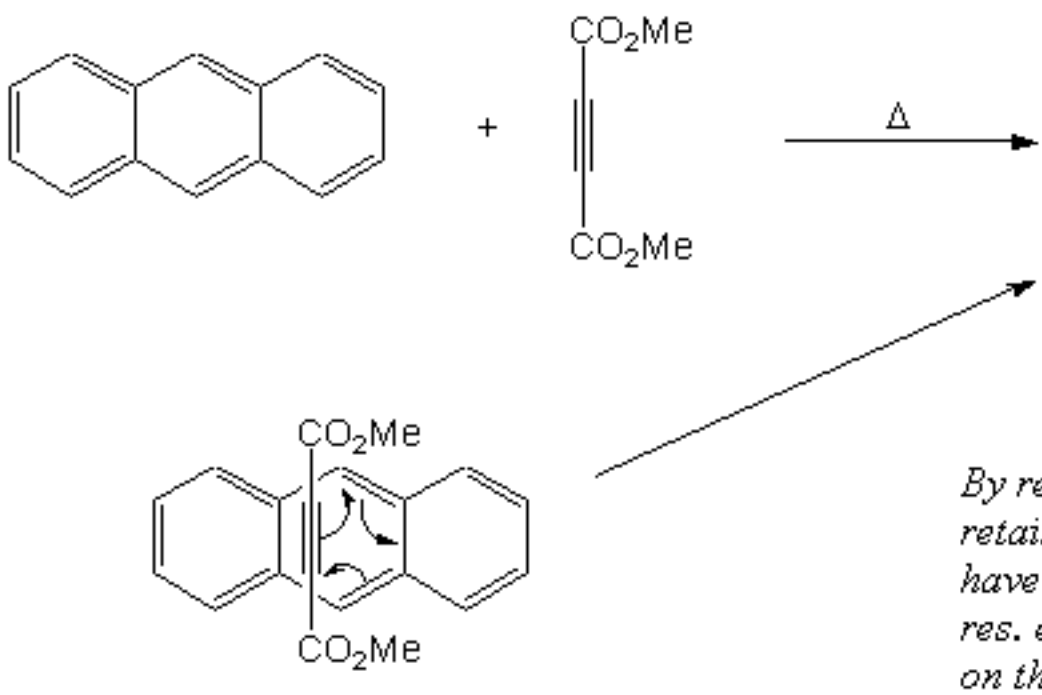
BMe_2 should be an electron withdrawing group, and therefore both a deactivator and a *meta*-director.

If the reaction went *para*, we would generate the following unstable resonance structure:



By reacting at the *meta* position, the system avoids any such unstable resonance structure.

b. (10 pts) It is well-known that anthracene can act as a diene in Diels-Alder reactions. Your task is to decide *where* on the anthracene the reaction takes place. Show the product of this Diels-Alder reaction, and explain why the reaction takes place at that position of the anthracene.



By reacting accross the middle ring, we retain two benzene rings in the product. We have thus lost (84-2(36)) or 12 kcal/mol in res. energy. Reaction at any other position on the anthracene would result in the loss of substantially more resonance energy.

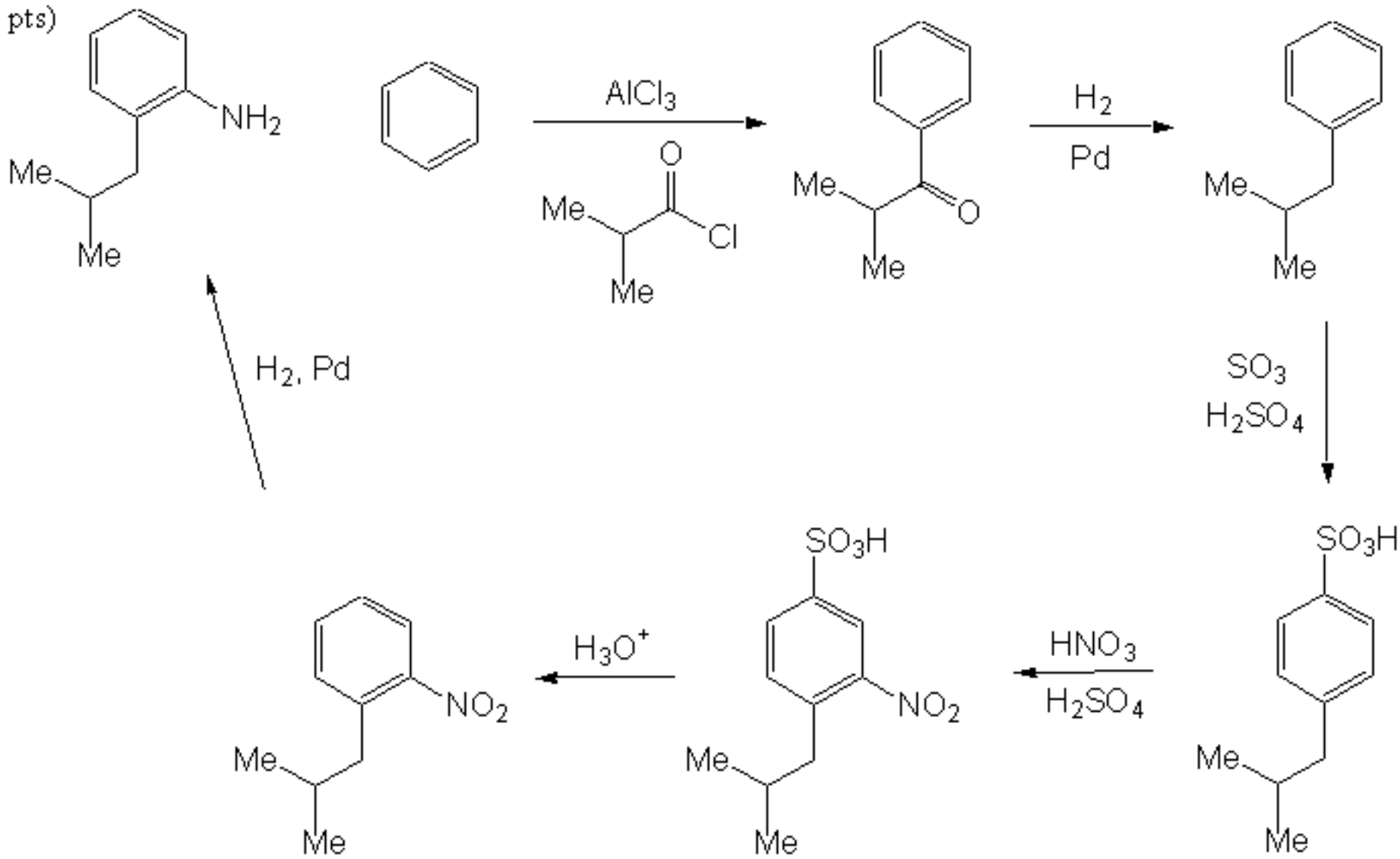
Resonance Energy

Benzene	= 36 kcal/mol
Naphthalene	= 61 kcal/mol
Anthracene	= 84 kcal/mol

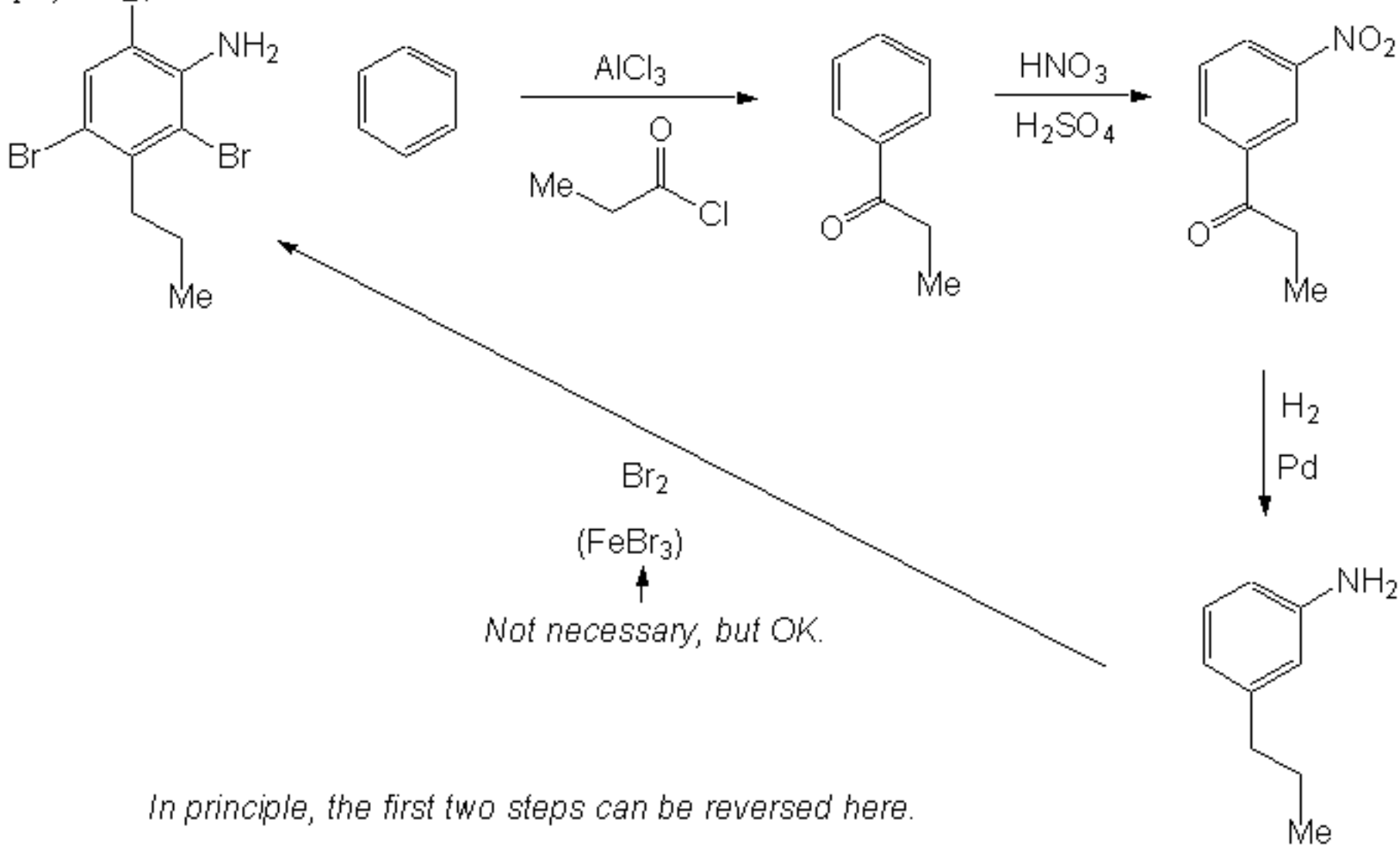
Name: _____

5. Propose syntheses of the following compounds from benzene and any other reagents you need.

a. (10 pts)



b. (10 pts) Br



Not necessary, but OK.

In principle, the first two steps can be reversed here.