**Chemistry 232, Spring 2010**
**Dr. Shaughnessy**
**Exam #1**
**February 2$^{nd}$, 2010**

**Name:___ANSWER KEY____**(print) **CWID:**_____________________

**Honor Pledge**: I promise or affirm that I will not at any time be involved with cheating, plagiarism, fabrication, or misrepresentation while enrolled as a student at The University of Alabama. I have read the Academic Honor Code, which explains disciplinary procedures that will result from the aforementioned. I understand that violation of this code will result in penalties as severe as indefinite suspension from the University.

________________________________(*signature*)

You will have **1 hour and 30 minutes** to complete this exam. When time is called please stop all work and turn in your exam.

Show all work. Partial credit will be given where appropriate.

This exam has **10** pages. Make sure you have all 10 pages, and that they are correctly copied, before starting the exam. The last page is a periodic table

You may use molecular models to help you answer questions on this exam.

You will not need a calculator or any other electronic device to complete this exam.

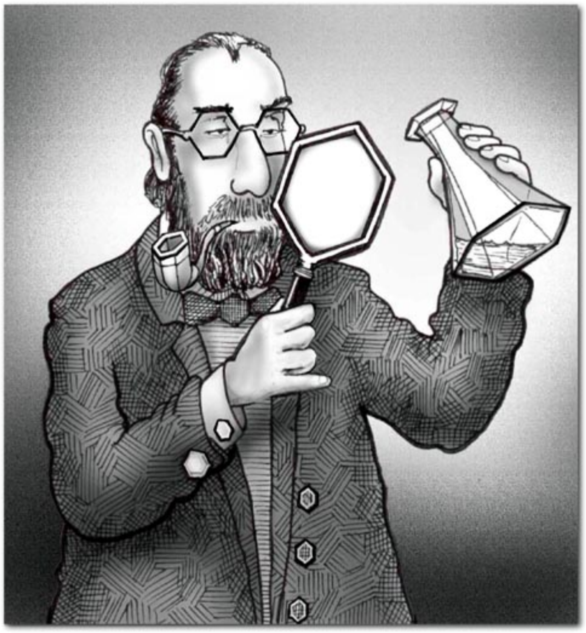
Please put all cell phones (turn off or to silent), ipods, calculators, or other electronic devices away in a book bag.

Your book and all notes should be placed out of sight of yourself and your neighbors before the exam begins.

| Problem | Score |
|---|---|
| 1 | ________ (12) |
| 2 | ________ (20) |
| 3 | ________ (16) |
| 4 | ________ (8) |
| 5 | ________ (16) |
| 6 | ________ (16) |
| 7 | ________ (16) |
| Total | ________ (104) |

The exam is worth 100 points.  There are 4 bonus points built in

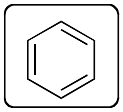
GREAT EVENTS IN CHEMISTRY

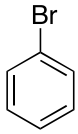


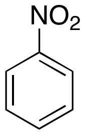
**1865**: Kekulé, moments before his brilliant insight into the structure of benzene.

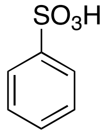
1. For each problem below, circle the **best** answer. In each case, there is only one correct answer (12 points)

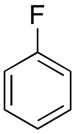
   a. Which benzene ring below would be **most reactive** towards electrophilic aromatic substitution?

[✓ ]

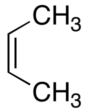


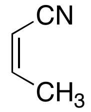


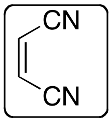


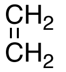


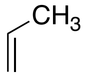
   b. Which alkene would be **most reactive** in a Diels-Alder reaction with 1,3-butadiene.



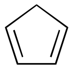


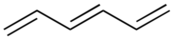
[✓ ]

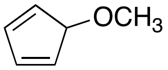


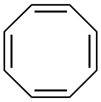


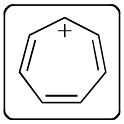
   c. Which compound below would have a peak at the **highest chemical shift** in its $^1$H NMR spectrum?



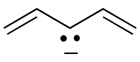


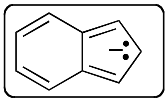


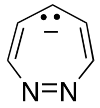


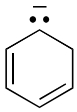
[✓ ]

   d. Which carbanion would be **most stable**?

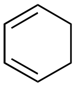


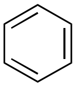
[✓ ]

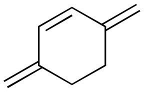


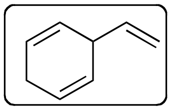


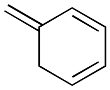
   e. Which compound below would **not absorb** UV light above 200 nm?



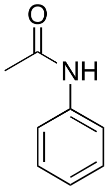


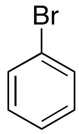


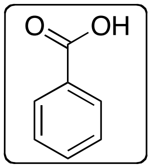
[✓ ]

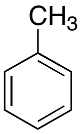


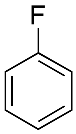
   f. Which compound below would be **chlorinated in the meta position** when reacted with $Cl_2$ and $FeCl_3$.





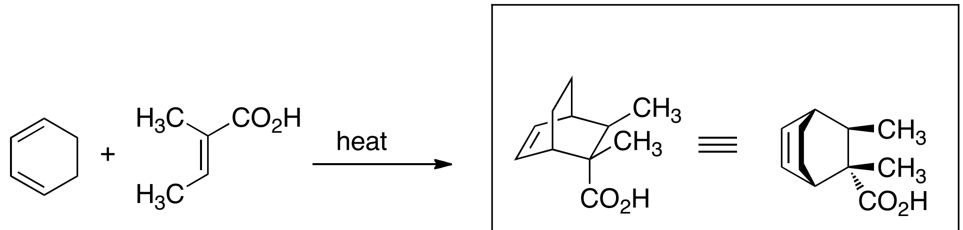
[✓ ]



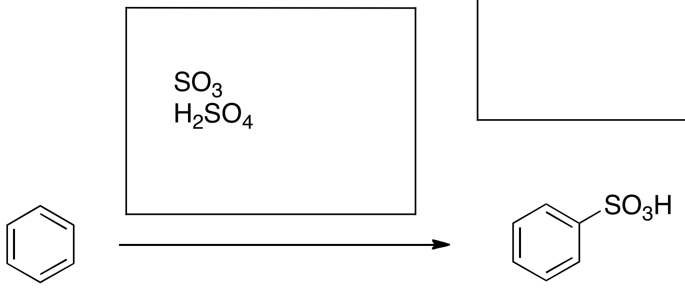


2. For each reaction below, provide the missing starting material(s), reagent(s), or product(s). For reactions in which more than product can be formed, draw each major product. You should not include products formed as minor products, however. You do not need to indicate side products from the reagents used. Where necessary, clearly indicate the stereochemistry of the products obtained or starting materials. (20 points)

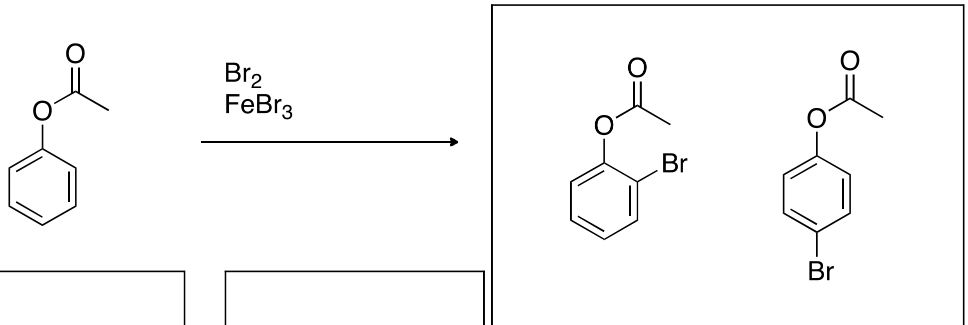
a.



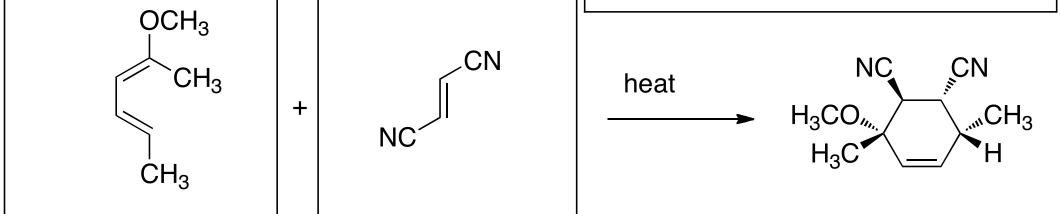
b.



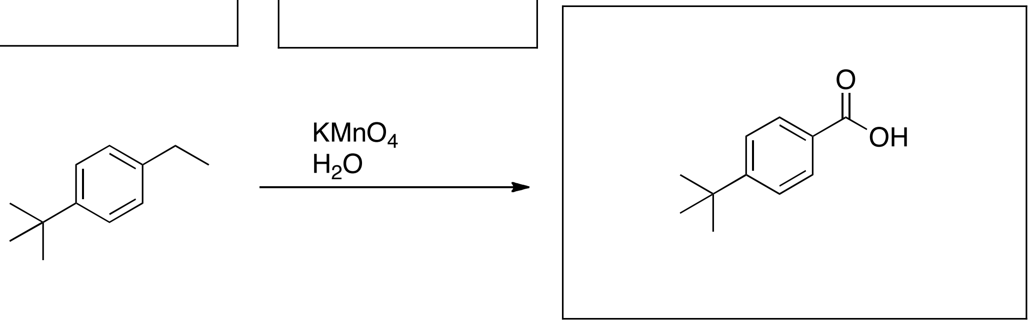
c.



d.

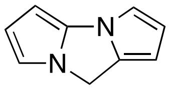


e.



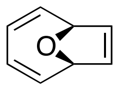
3. Aromaticity (16 points)

a. For each molecule below, determine the total number of π electrons. Classify the molecule is aromatic, anti-aromatic, non-aromatic. You may assume that systems otherwise meeting the Hückel requirements for aromaticity or anti-aromaticity would be flat.



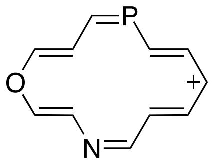
# of π e: 12

Classification: aromatic



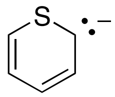
# of π e: 6

Classification: non-aromatic



# of π e: 14

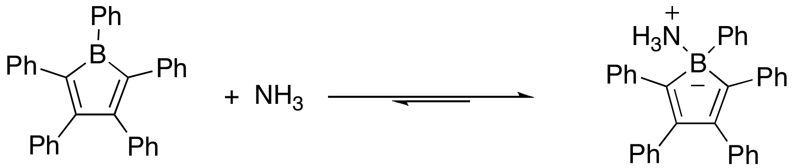
Classification: aromatic



# of π e: 8

Classification: anti-aromatic

b. Boroles, such as pentaphenylborole (**1**), are unstable compounds. Compound **2** is a very strong Lewis acid (i.e. **2** is much more stable than **1**). Briefly explain the low stability of **1** compared to **2**.

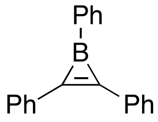


pentaphenylborole (**1**)
Ph = $C_6H_5$

**2**

Borole has 4 π electrons, so it is anti-aromatic. Therefore, it would be particularly unstable. Compound **2** has an $sp^3$ boron center so it is non-aromatic. The non-aromatic structure would be more stable than the anti-aromatic structure.

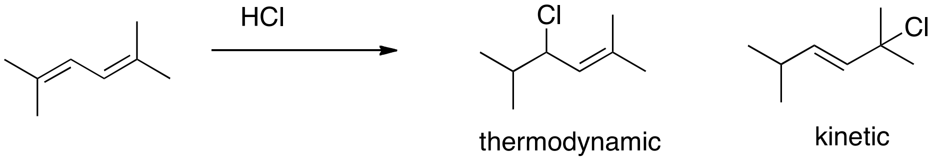
c. Would you expect compound **3** to be more or less stable than **1**. Briefly explain your answer.



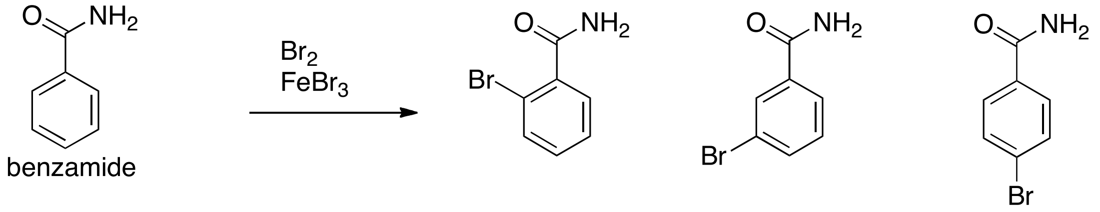
**3**

Compound **3** would be more stable than **1** because it is an aromatic 2 π electron system.

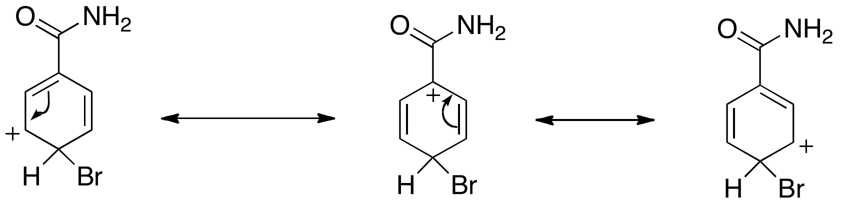
4. Draw the products that would be formed in the reaction below. Label which product would be favored thermodynamically and which one would be favored kinetically. (8 points)



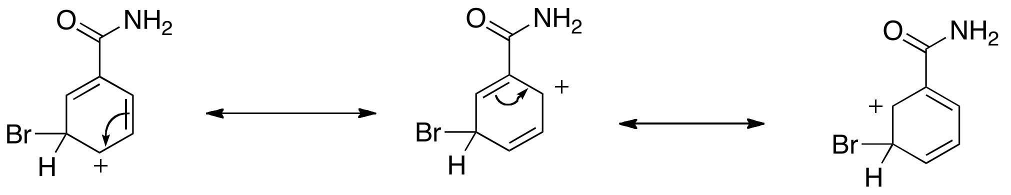
5. Electrophilic bromination of benzamide could potentially lead to *ortho*, *meta*, or *para* products. (16 points)



a. Draw the arenium ion intermediate that would be formed leading to the *para*-product and show all of the other resonance structures for this cation.



b. Draw the arenium ion, including all resonance structures, that would lead to the *meta*-product.

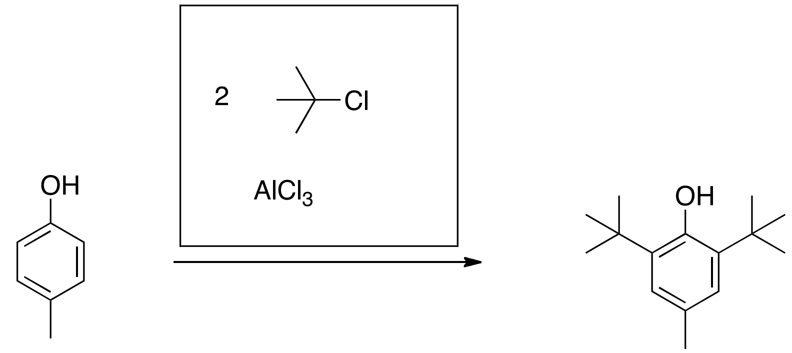


c. Based on your answers to parts (a) and (b), briefly explain whether the major product(s) would be *ortho* and *para* or *meta*.

The *meta* product would be the major product. When the bromine is added para, there is one resonance structure with the positive charge right next to the electron withdrawing carbonyl group. This resonance structure is less stable than the others. In the case meta-substitution, the positive charge is never next to the carbonyl group. Thus, the meta arenium ion is more stable than ortho or para.

6. Butylated hydroxytoluene (BHT) is commonly used as a food preservative. (16 points)

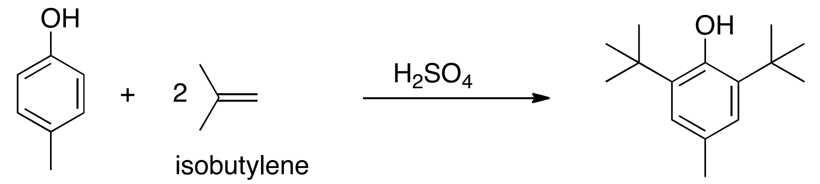
   a. Provide the missing reagent in the synthesis of BHT starting from *p*-cresol using one of the reactions we have discussed.



*p*-Cresol

BHT

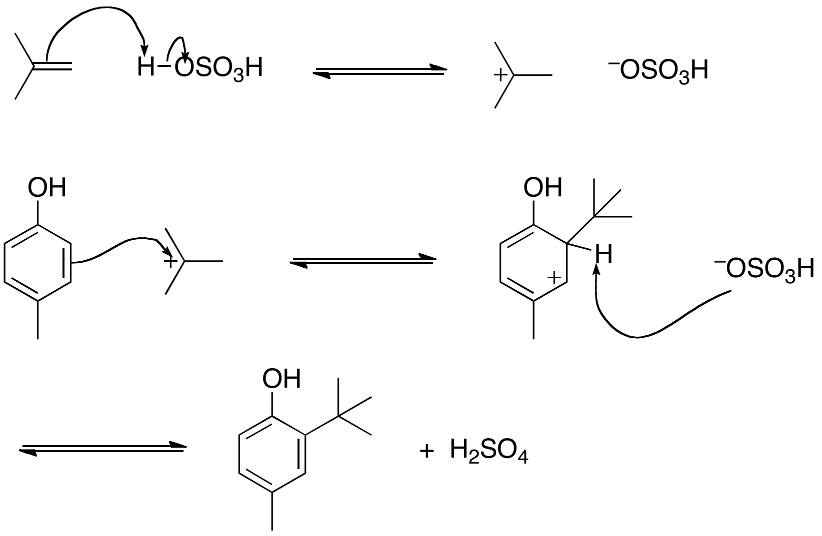
   b. Industrially BHT is made by reacting *p*-cresol with isobutylene in the presence of a strong acid (i.e. $H_2SO_4$), which is a cheaper process than the reaction in part a. Draw a complete electron pushing mechanism for the addition of one *tert*-butyl group to *p*-cresol under these conditions. You only need to show addition of **one *tert*-butyl group.**



*p*-Cresol

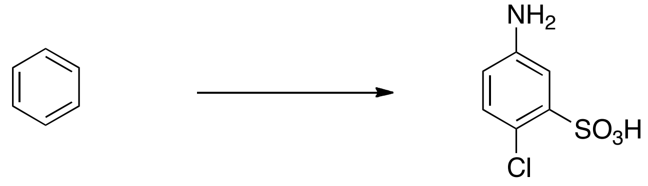
isobutylene

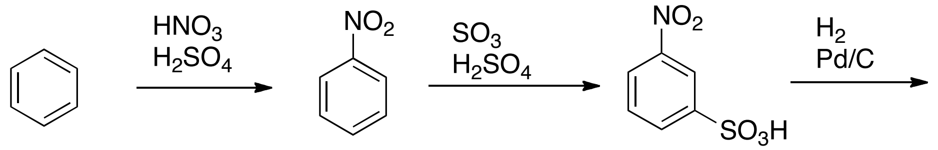
BHT

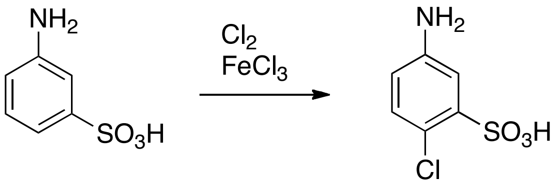


7. Starting from the indicated molecule, provide an efficient synthesis of the desired product. An efficient synthesis should give the desired product as the major product in each step. Where necessary, assume that you can separate *ortho* and *para* isomers. In addition to the indicated starting material, you may use any other necessary reagents. (16 points)

a.







Other possibilities:
1) Chlorinate, 2) nitrate, 3) sulfonate 4) reduce nitro

1) Sulfonate, 2) nitrate, 3) reduce nitro, 4) chlorinate

b.