CH320N
Spring 2013

Anslyn

April 16th, 2013

Exam 3

Please **PRINT** the first three letters of your **last** name in the three boxes.

K	E	Y

PRINT Name _____ **UT-EID** _____

Only exams written in permanent ink can be submitted for a regrade.
Do not write with a red pen.

Honor Code:

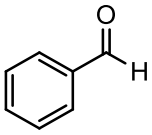
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect towards peers and community.

_____

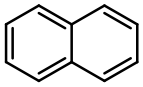
(Your signature)

Page total _____

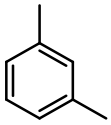
Problem 1. (2 points each) Provide the common name for the following structures. (From class notes.)



benzaldehyde

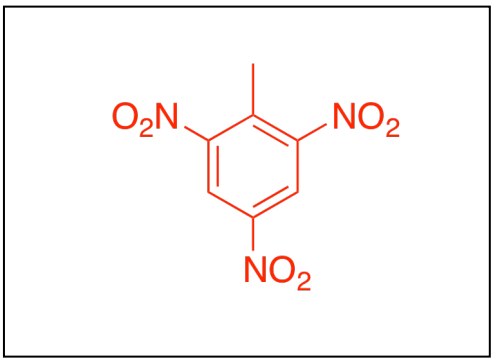


naphthalene

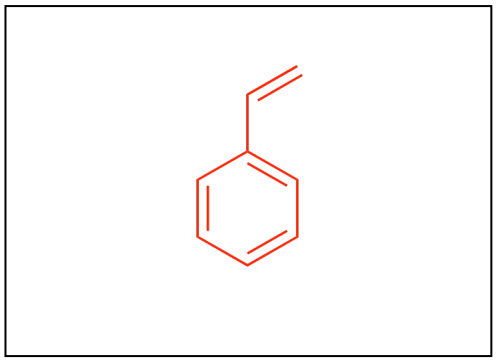


m-xylene

Draw the structure that corresponds to the provided name. (21.9 e and k.)

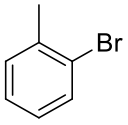


2,4,6-trinitrotoluene

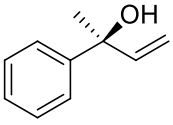


phenylethylene (styrene)

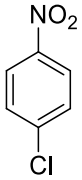
Provide the IUPAC name for the following compounds. (HW 21.8 a, b, and e.)



1-bromo-2-methylbenzene
or 2-bromo-toluene



(S)-2-phenylbut-3-en-2-ol
or (S)-2-phenyl-3-buten-2-ol



1-chloro-4-nitrobenzene
or p-chloro-nitrobenzene

Page total _____

Problem 2. (9 points) Fill in the blanks for the following questions using words from the provided word bank. Words may be used once, more than once, or not at all. (This problem comes from your class notes.)

WORD BANK	
HOMO	LUMO
Absorbed	Reflected
Higher	Lower
Yellow	Violet

Color is the result of a material absorbing particular wavelengths of light that fall in the "visible region" of the electromagnetic spectrum (400-750 nm).

Absorbance transitions involve the absorption of light of a particular energy to promote an electron from the HOMO to the LUMO.

The longer a wavelength of light is, the lower its energy.

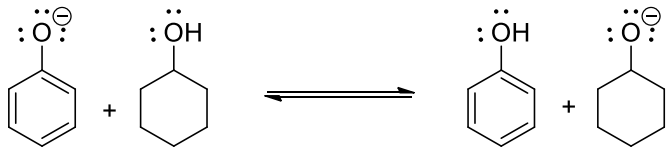
If we see the color ***black*** then all wavelengths of visible light are absorbed and no visible light is reflected.

If we see the color ***white***, then all wavelengths of visible light are reflected and no visible light is absorbed.

Yellow light (575 nm) is the color complement to violet light (465 nm). If a material absorbs photons with a wavelength of 575 nm, its color will appear violet. If a material emits a photon at 465 nm, the light we see will be violet in color.

Page total _____

Problem 3. (12 points) Phenol has a pK_a of 9.95 in H_2O, while cyclohexanol has a pK_a of 16. For the following acid/base reaction:



a) Which is the stronger base, phenoxide or cyclohexanoxide?

Cyclohexanoxide

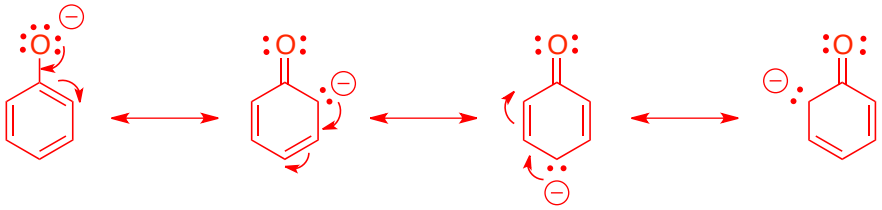
b) Does the equilibrium lie to the left or the right?

Left

c) Estimate the K_{eq} for this reaction.

$K_{eq} = 10^{(10-16)} = 10^{-6}$

d) Draw all of the resonance structures for phenoxide.

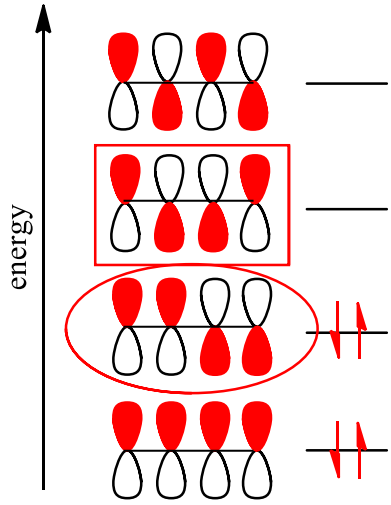


e) Use these resonance structures to rationalize the stabilities of the conjugate bases and explain the relative acidities of phenol and cyclohexanol. Write no more than two sentences.

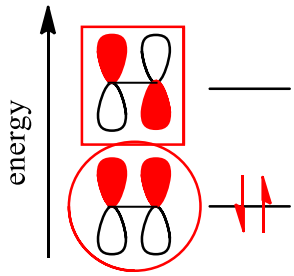
Phenoxide is stabilized by resonance, but cyclohexanoxide has no resonance structures. Thus, phenoxide is more stable than cyclohexanoxide and phenol is more acidic.

Problem 4. (16 points) This problem comes from your class notes.

a) For the π systems of butadiene and ethylene shown below:
   1) Fill in the phasing of the molecular orbitals for both molecules (i.e., shade the lobes appropriately).
   2) Using the spaces provided to the right of the molecular orbital cartoons, fill the orbitals with the π electrons for the two molecules.
   3) Put a **CIRCLE** around the HOMO of each molecule.
   4) Put a **BOX** around the LUMO of each molecule.



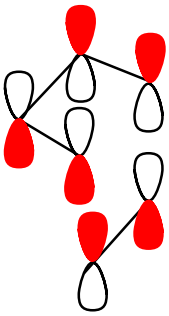
butadiene



ethylene

b) From your answer above, fill in the HOMO of butadiene and the LUMO of ethylene in the diagram below to show a [4+2] cycloaddition (i.e., Diels-Alder reaction):

butadiene
(HOMO)



ethylene
(LUMO)

c) Finally, explain in one sentence why this reaction is allowed:

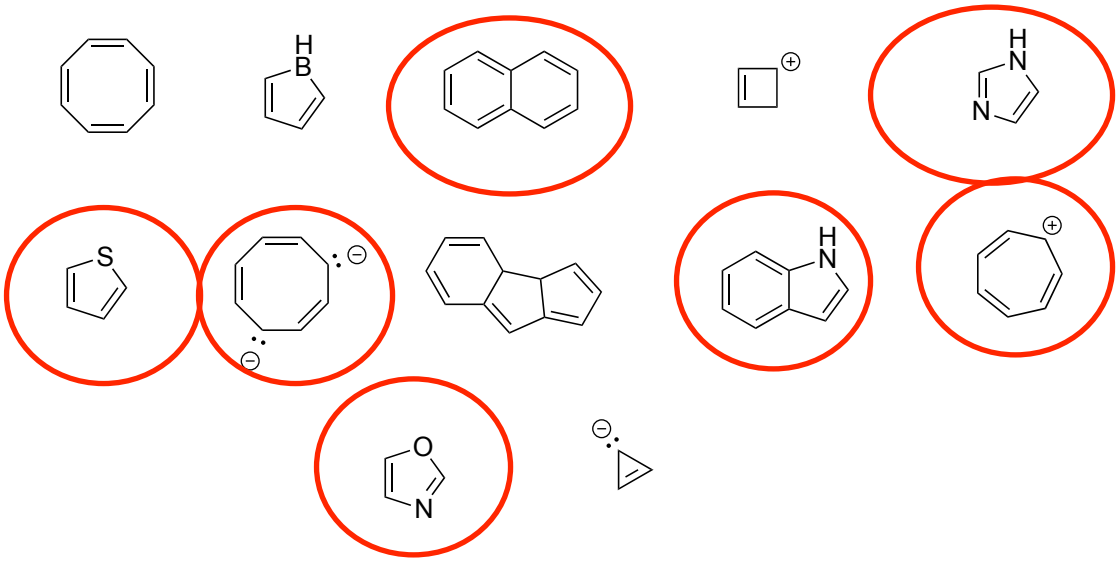
The phasing of the HOMO of butadiene and the LUMO of ethylene matches.

Problem 5. (27 points)

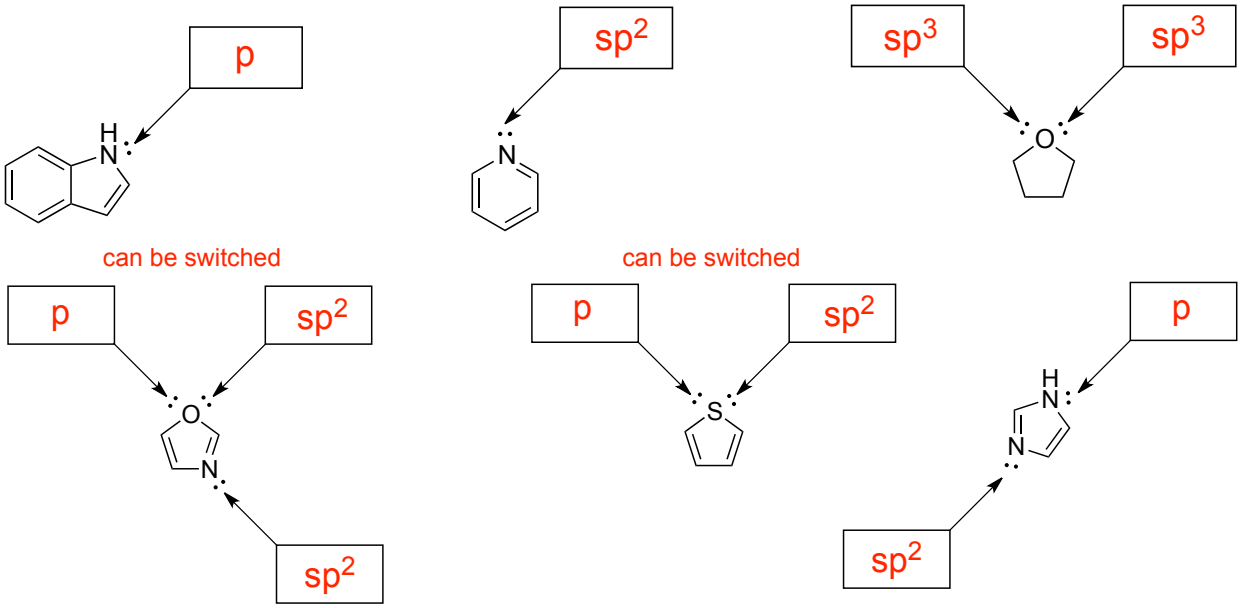
a) List Hückel's four criteria for aromaticity:

1. Cyclic (in a ring)
2. Planar
3. 4n + 2 π electrons
4. All atoms have p orbitals or all atoms are sp^2 hybridized

b) **CIRCLE** the molecules below that are aromatic according to Hückel's criteria:

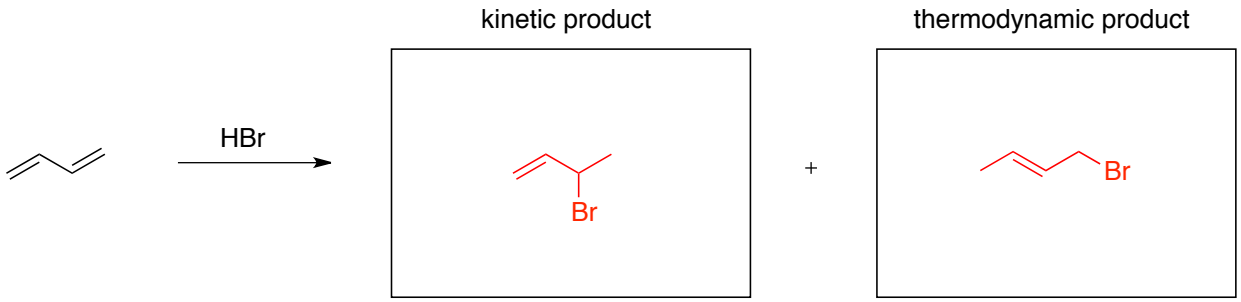


c) Identify the orbital that the indicated lone pair resides in.

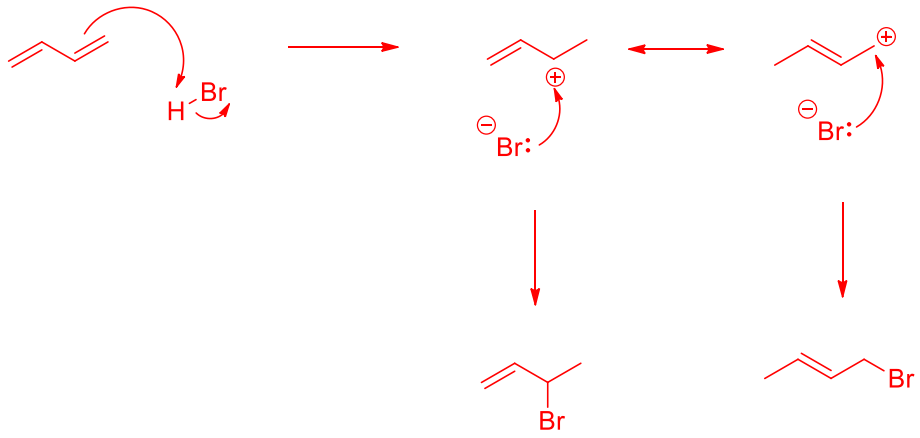


Problem 6. (36 points) This problem is all about the addition of HBr to butadiene. (From class notes.)

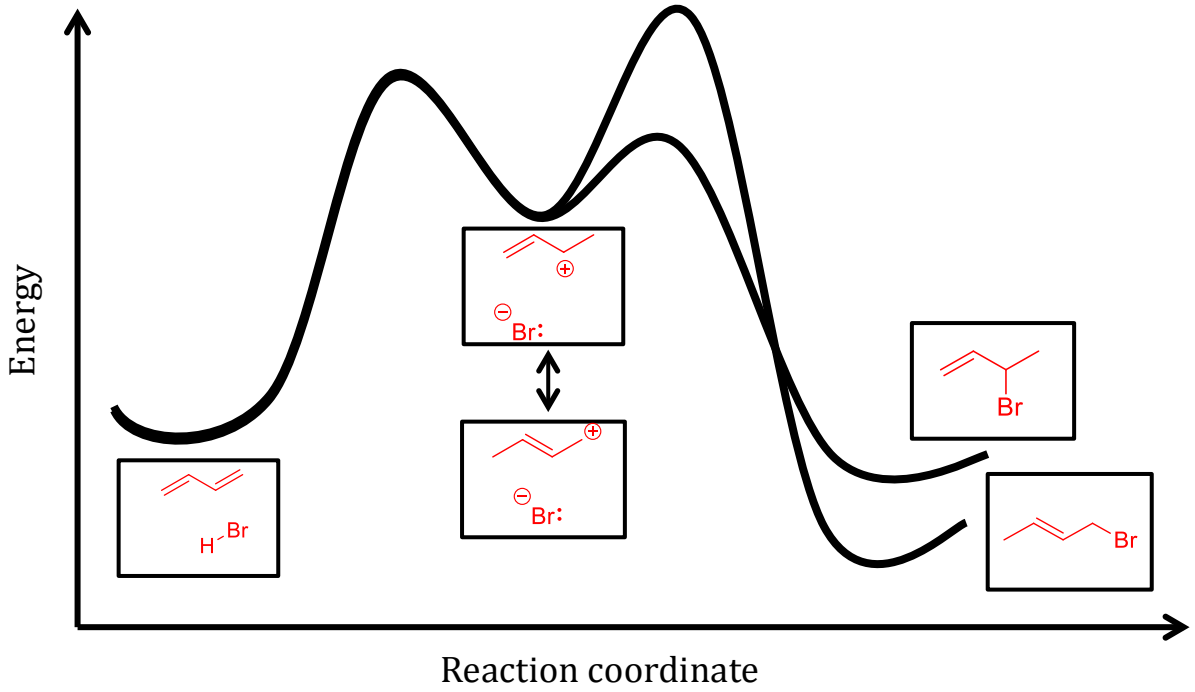
a) Draw the kinetic product and thermodynamic product:



b) Draw the mechanism for the formation of the kinetic and thermodynamic products with all arrow pushing. Show all lone pairs, formal charges, and resonance structures.



c) On the diagram given below, fill in the boxes with the correct structures for the reactants, intermediates, and products.



d) Circle the correct answer to the following questions.

1. Which product results from 1,4-addition of HBr to butadiene?
   a. Kinetic product
   b. Thermodynamic product
   c. Both
   d. Neither

2. Which product is formed more rapidly?
   a. Kinetic product
   b. Thermodynamic product
   c. They're formed at the same speed

3. Which product results in the more substituted double bond?
   a. Kinetic product
   b. Thermodynamic product
   c. They both have the same substitution on the double bond

4. Which product is more sterically congested?
   a. Kinetic product
   b. Thermodynamic product
   c. They are equally sterically congested

5. Which product is favored at high temperatures?
   a. Kinetic product
   b. Thermodynamic product
   c. Neither product is favored over the other at high temperatures

6. Which product has a lower barrier to formation?
   a. Kinetic product
   b. Thermodynamic product
   c. They have the same barrier to formation

7. Which product is more stable?
   a. Kinetic product
   b. Thermodynamic product
   c. Neither product is more stable than the other

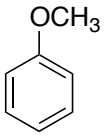
e) What kind of isomers are the kinetic product and thermodynamic product?

Constitutional isomers or regioisomers

f) By looking at the resonance structures of the intermediate carbocation, give a hypothesis as to why the kinetic product is formed the fastest. Explain in two sentences or less.

The resonance structure with the secondary carbocation contributes more to the overall structure than the resonance structure with the primary carbocation because the secondary carbocation is more stable. Thus there is a greater partial positive charge on the internal carbon and bromide is more likely to attack at this position.

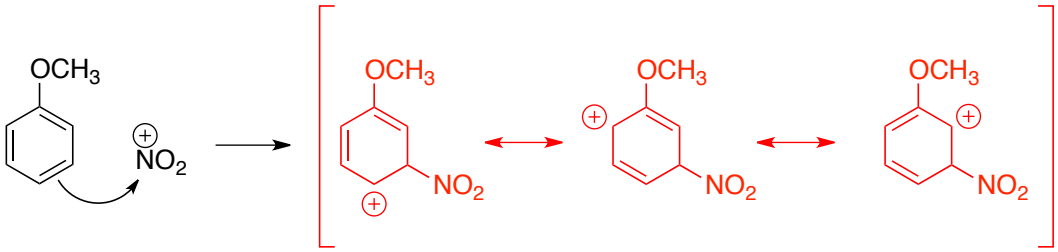
Problem 7. (36 points) This problem comes from your class notes.



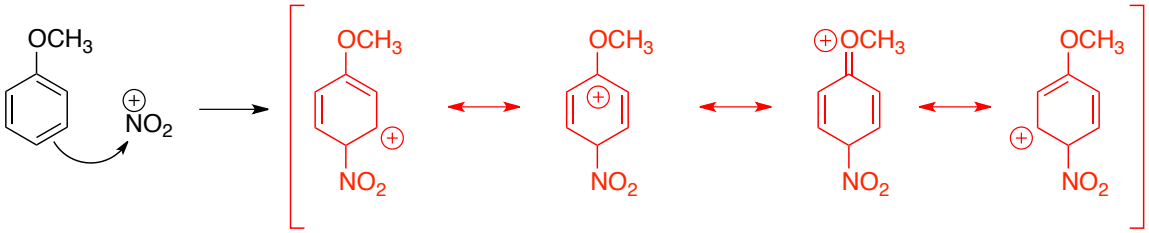
a) Is the methoxy group on the molecule shown above electron-withdrawing or electron-donating during electrophilic aromatic substitution?

Electron-donating

b) Show all resonance structures for the intermediate that forms as a result of **meta** attack:



c) Show all resonance structures for the intermediate that forms as a result of **para** attack:



d) Based on your answers to parts (b) and (c), which product – meta or para – will be favored? Explain this preference in two sentences or less.

Para.
The intermediate that results from para attack has an additional resonance structure in which the methoxy oxygen donates electron density to the neighboring carbon, which has a partial positive charge. This additional resonance structure stabilizes the intermediate, and thus this intermediate is favored over that of the meta attack.

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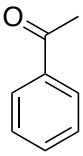
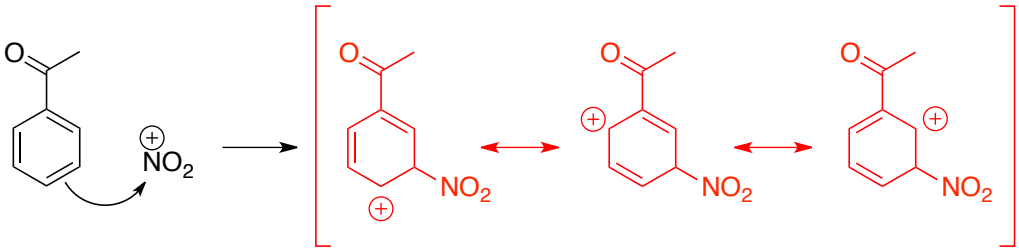


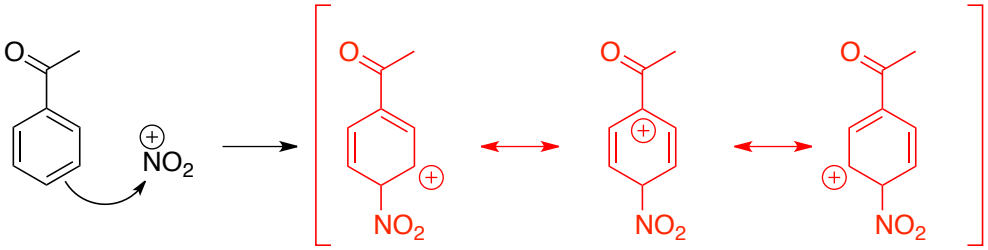
e) Is the acetyl group on the molecule shown above electron-withdrawing or electron-donating during electrophilic aromatic substitution?

Electron-withdrawing

f) Show all resonance structures for the intermediate that forms as a result of **meta** attack:



g) Show all resonance structures for the intermediate that forms as a result of **para** attack:

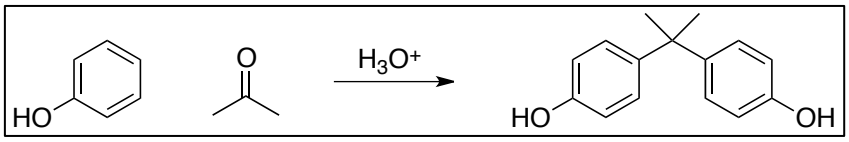


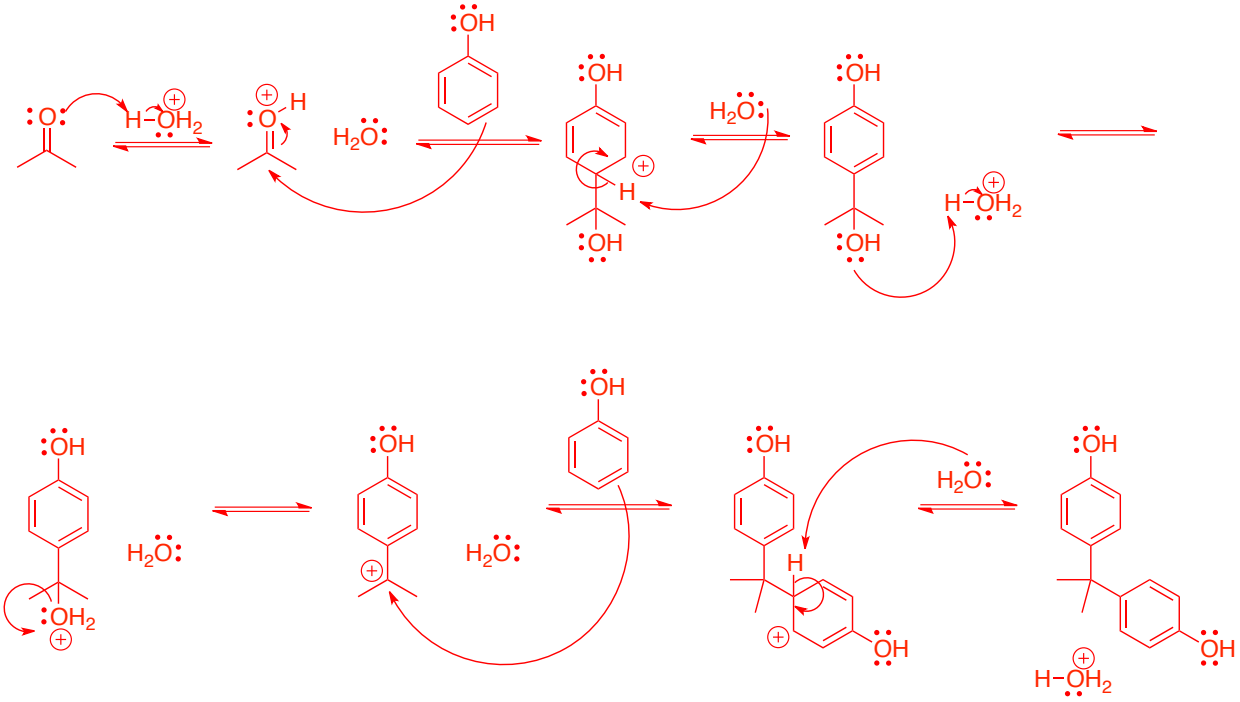
h) Based on your answers to parts (f) and (g), which product – meta or para – will be favored? Explain this preference in two sentences or less.

Meta.

The intermediate that results from para attack has an unfavorable resonance structure in which there is a positive charge adjacent to the carbonyl carbon, which also has a partial positive charge. This causes electrostatic repulsion, which destabilizes the intermediate, and thus the intermediate that results from meta attack is favored.

Problem 8. (31 points) Write the mechanism for the formation of bisphenol A shown below. Draw all arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all products for each step. (This problem is from HW 22.22.)





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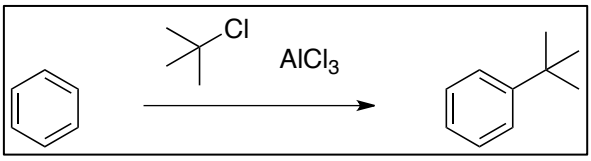
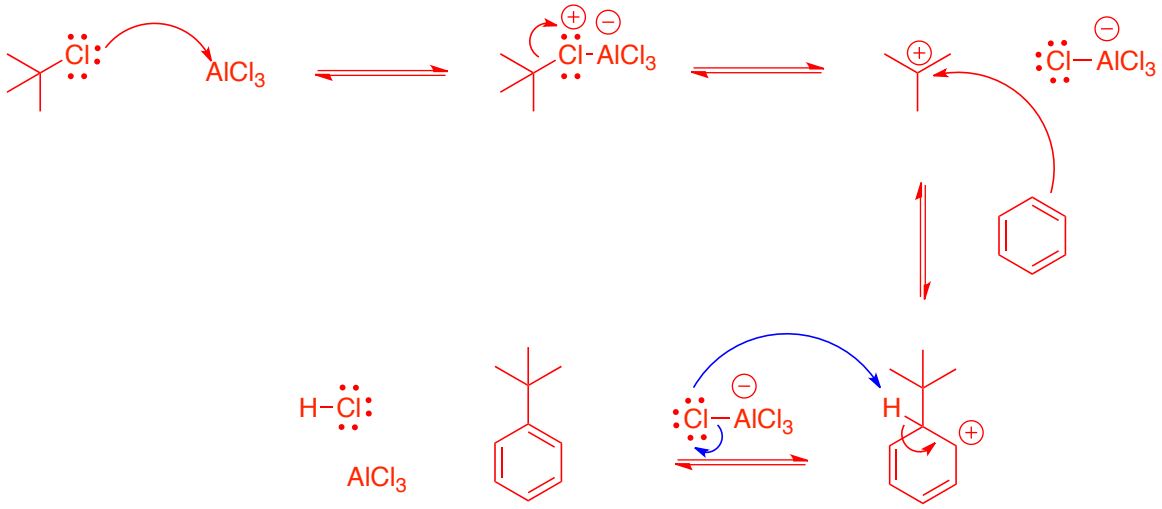
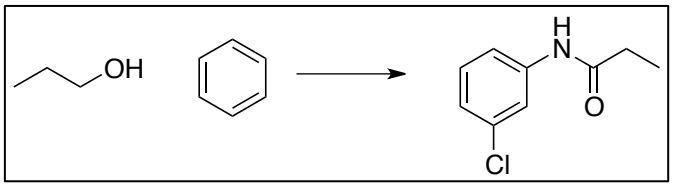
Problem 9. (13 points) Write the mechanism for Friedel-Crafts alkylation. Draw all arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all products for each step. (This problem is from your class notes.)

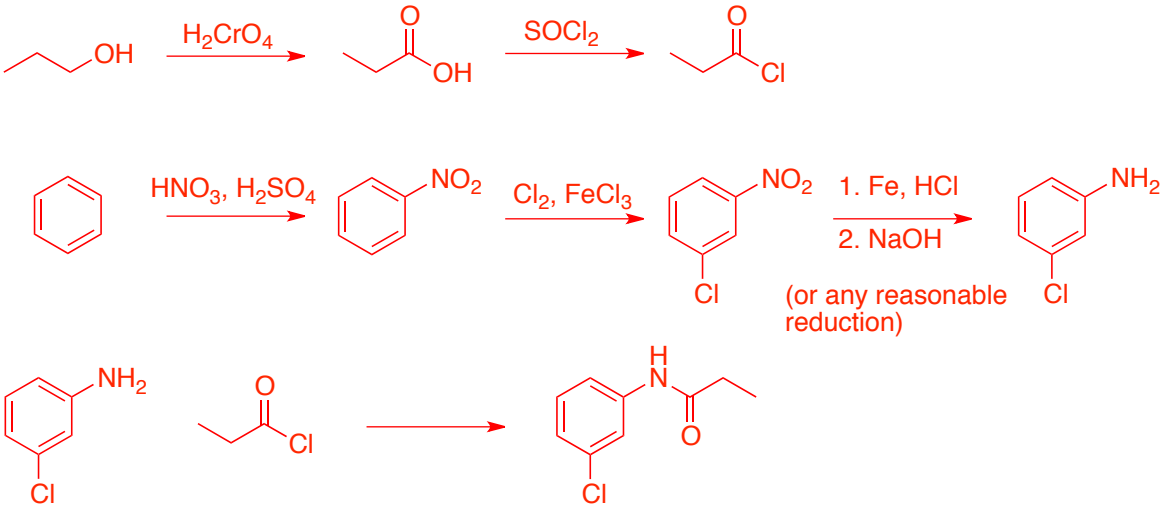




The two arrows shown in blue are not necessary for full credit. As Dr. Anslyn said in class, it is not well understood how this deprotonation step occurs. For this reason, we accept answers that simply show departure of the proton and the resulting final products.

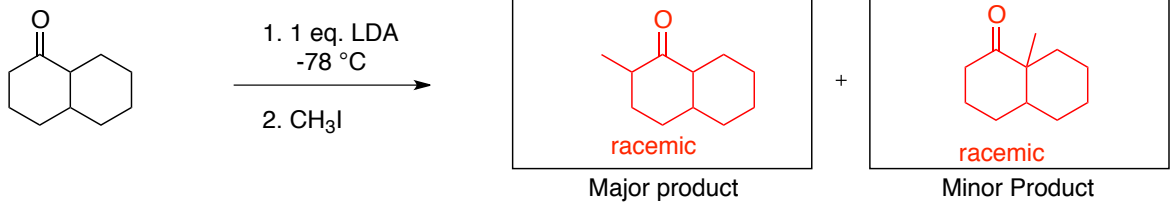
Problem 10. (16 points) Using the following starting materials as your only source of all **carbon atoms**, show how to synthesize the given product. Show all reagents and steps, and show all molecules synthesized along the way. (This problem is from HW 22.37 b.)



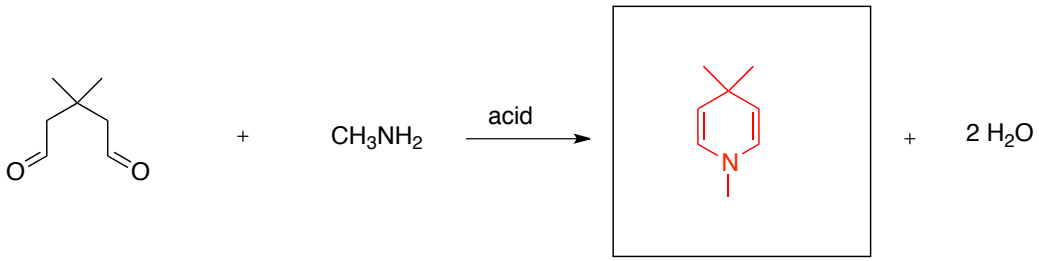


Problem 11. (3 points per box) Fill in the boxes with the appropriate reactant, reagent, or product to achieve the following transformations. Some boxes require more than one step. If a transformation produces a racemic mixture, write "racemic".

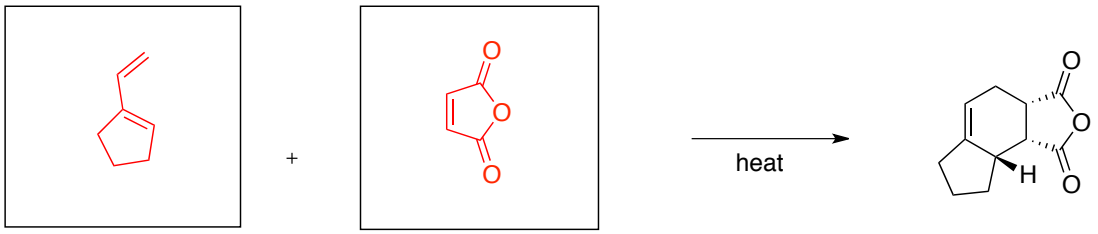
a)



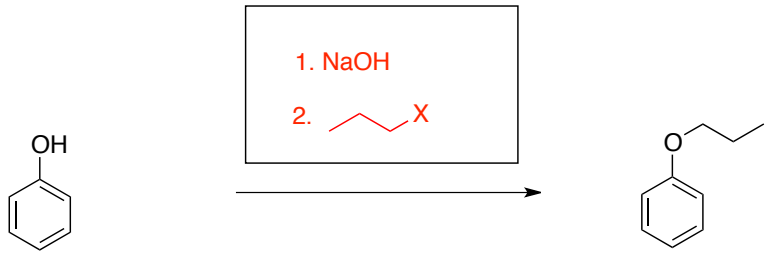
b) From Homework 19.43



c) From Homework 20.38



d)



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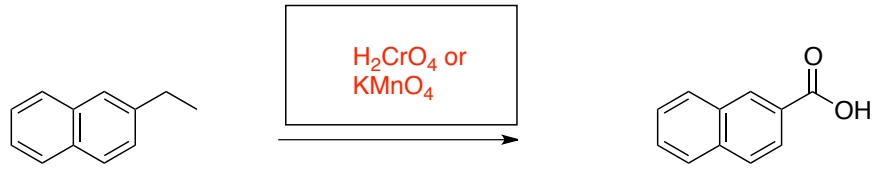
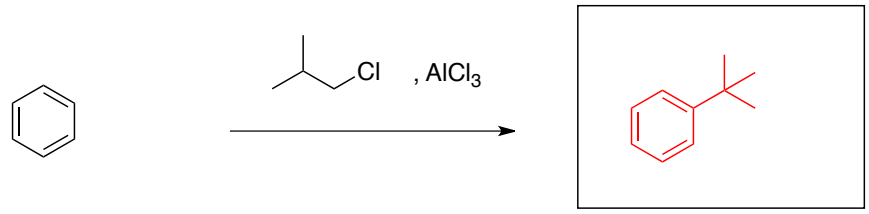
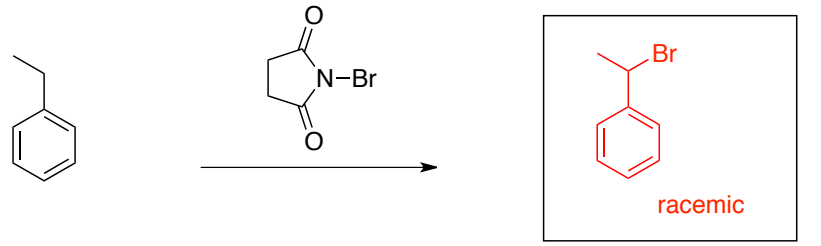
e)



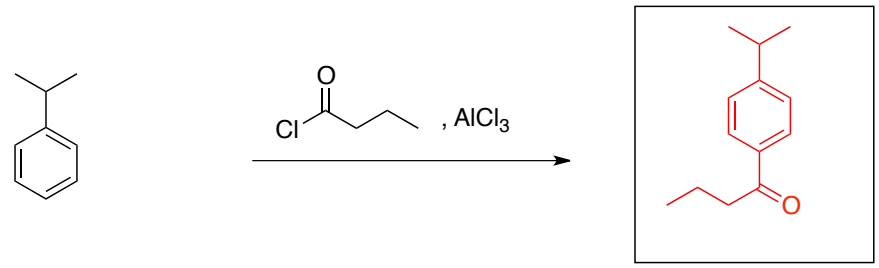
f)



g)

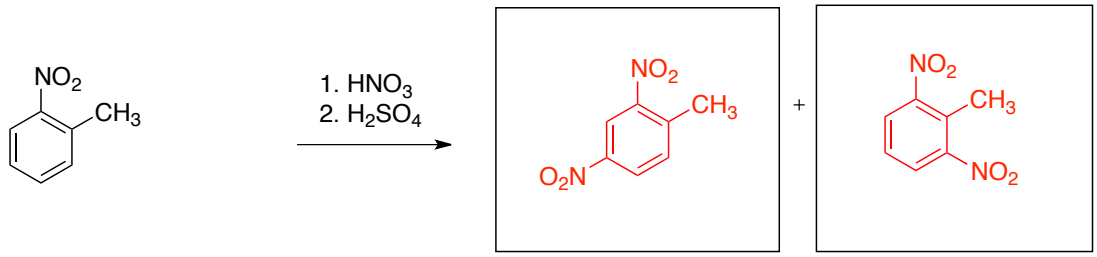


h)



The ortho product was also accepted for full credit.

i) From Homework 22.15b



Bonus Question. (3 points) What is Dr. Anslyn's favorite movie?

The Wizard of Oz

Anslyn CH320N
Spring 2013

Exam 3

April 16th, 2013

Exam Score

Page	Earned Points	Total Points
3		16
4		9
5		12
6		16
7		27
8		13
9		11
10		12
11		19
12		17
13		31
14		13
15		16
16		18
17		18
Bonus		3
Total		248
%		
T-Score		