Chem. 310N, Spring 2008, Prof. Krische

Midterm Exam III

Name (Last, First):_____

Problem

1. (12 points)_____

2. (6 points)_____

3. (6 points)_____

4. (24 points)_____

5. (12 points)_____

6. (12 points)_____

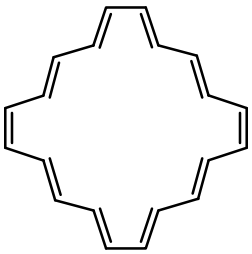
7. (12 points)_____

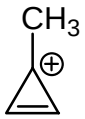
8. (7 points)_____

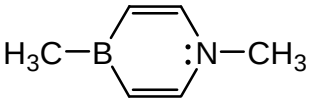
9. (9 points)_____

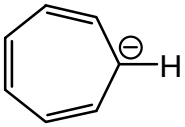
Total Points:_____/100

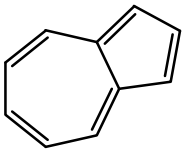
1. (12 points) Some of the following compounds are aromatic, whereas others are "antiaromatic" (or would be if all carbons were co-planar). Write "aromatic" or "antiaromatic" as appropriate under each of these structures.

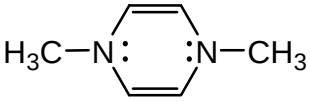






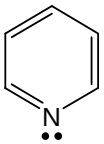


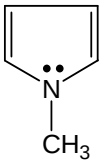




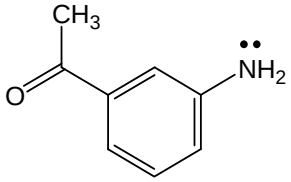
2. (6 points) For the following pairs of compounds, the circle the compound that is more basic. **Hint**: Consider both aromaticity and resonance effects.

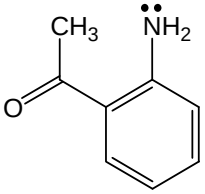
A.





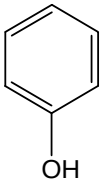
B.

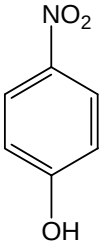




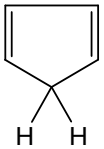
3. (6 points) For the following pairs of compounds, the circle the compound that is more acidic. **Hint**: Consider both aromaticity and resonance effects.

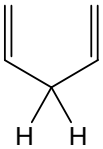
A.





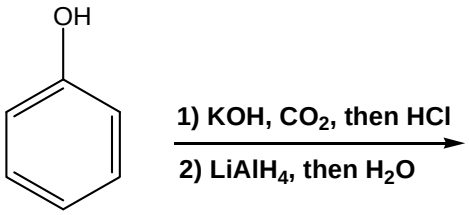
B.



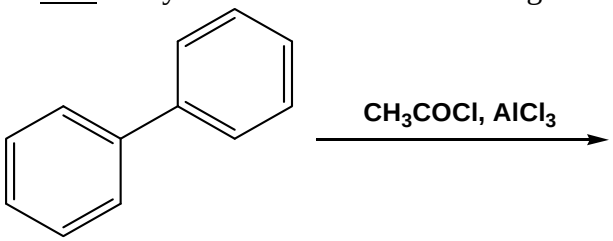


4. (24 points) Draw the major product that is formed when the indicated starting materials are subjected to the following transformations.

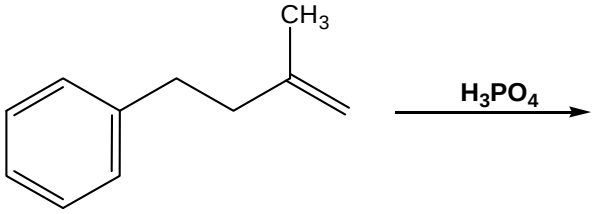
A.



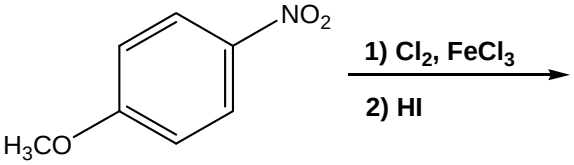
B. Hint: Only one of the two benzene rings undergos reaction.



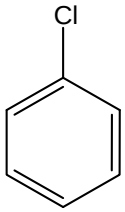
C.



D.



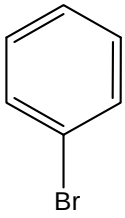
E.



1) KOH, H_20, 200 ^oC

2) H_3CBr, KOH

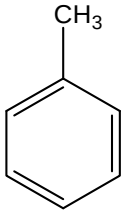
F.



1) Mg, Et_2O, 0 ^oC

2) $H_2C{=}O$, Then H_2O

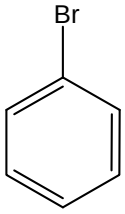
G.



1) $K_2Cr_2O_7$, H_2SO_4, H_2O

2) CH_3OH, HCl (cat.)
Dean-Stark Trap
Benzene, Reflux

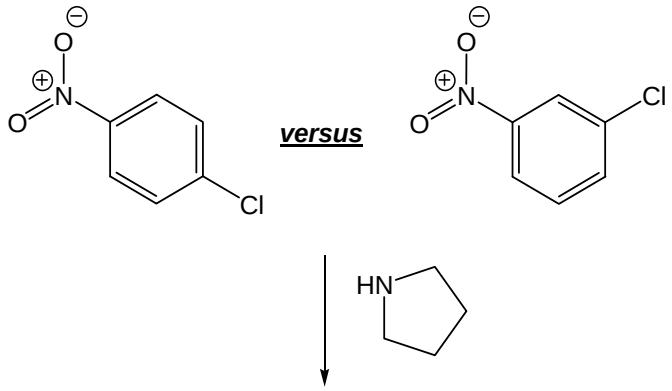
H.



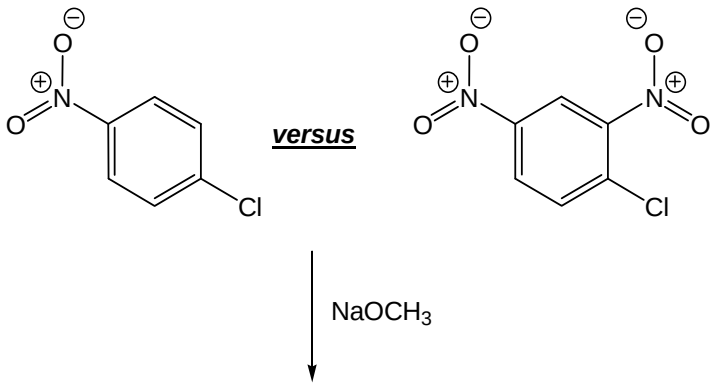
HNO_3, H_2SO_4

5. (12 points) For the following pairs of compounds, circle the compound that reacts faster in nucleophilic aromatic substitution (NAS) through an addition-elimination mechanism. For the faster reacting compound only, draw the product of its reaction with the indicated nucleophile.

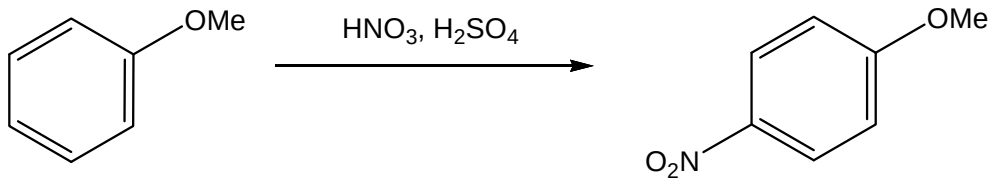
A.



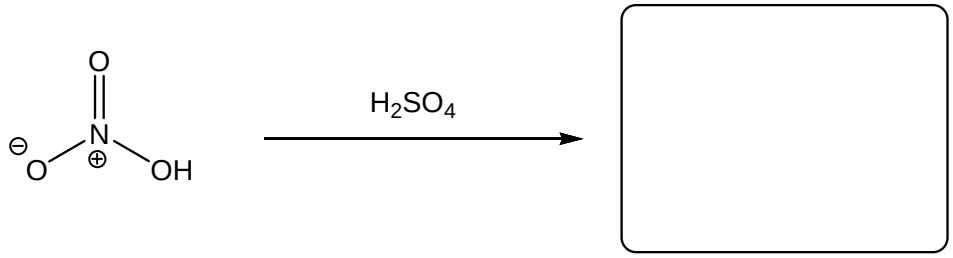
B.



6. (12 Points) Consider the nitration of anisole.



A. This electrophilic aromatic substitution reaction is initiated by conversion of nitric acid to the "active electrophile." Provide a stepwise mechanism accounting for formation of the "active electrophile." Use the arrow pushing formalism to interconvert intermediates draw all lone pair electrons, any formal charges, and all important resonance structures.

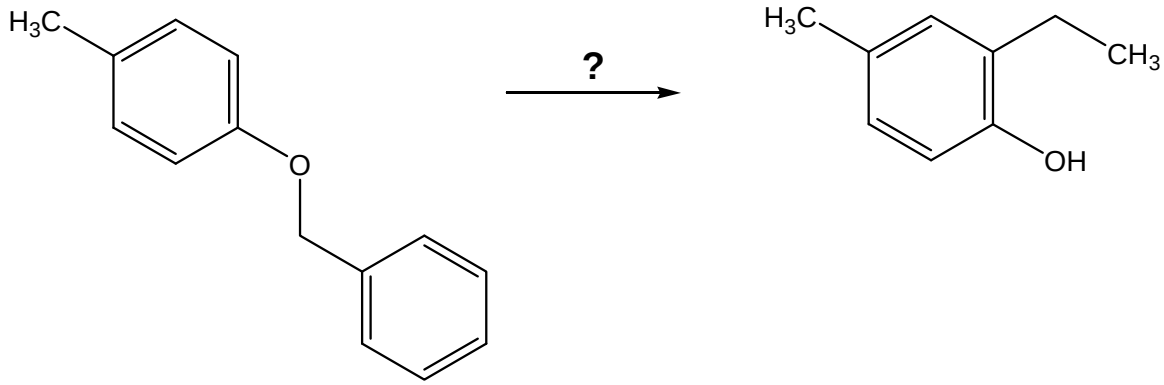


"Active Electrophile"

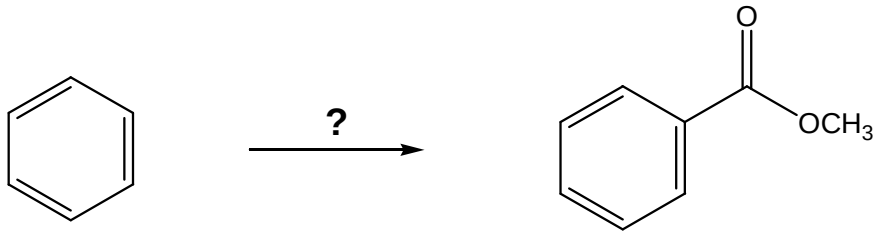
B. The “active electrophile” reacts with anisole at the *para* position. Provide a stepwise mechanism accounting for formation of the para-product. Use the arrow pushing formalism to interconvert intermediates draw all lone pair electrons, any formal charges, and all important resonance structures.

7. (12 points) Devise a synthetic route to accomplish the following transformations. Clearly number each step of your proposed sequence. (Hint: Try to work backwards. Each synthesis can be accomplished in as few as 2-3 steps, though longer routes are possible).

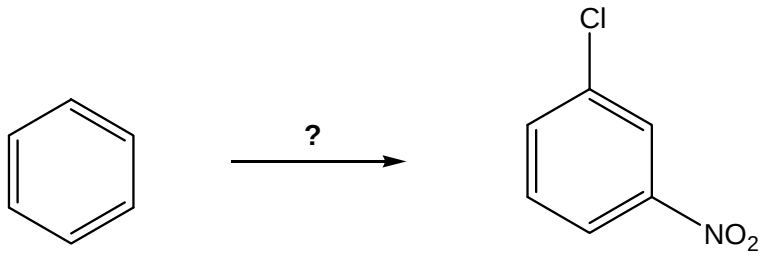
A.



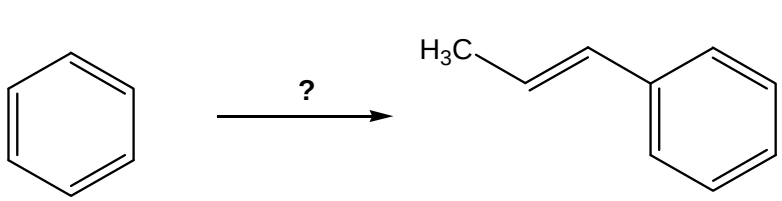
B.



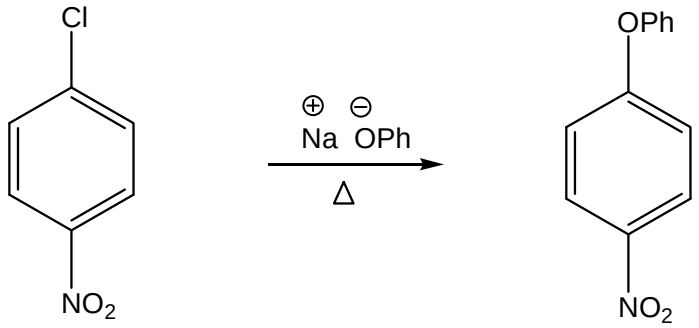
C.



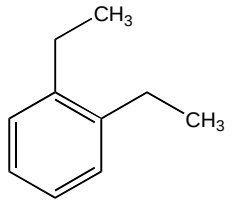
D.



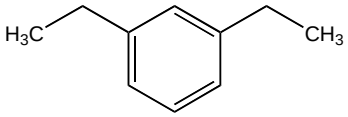
8. (7 points) Nucleophilic aromatic substitution (NAS) reactions will work with electron deficient aromatic systems. The following example of NAS will provide a mixed aromatic ether. Provide a mechanism for the following reaction. For each intermediate, draw all lone pair electrons, any formal charges, and all important resonance structures. Use the arrow pushing formalism to interconvert intermediates.



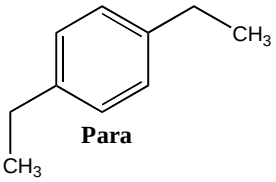
9. (9 points) Assign the following ^{13}C NMR spectra by clearly circling the appropriate isomer designation (Hint: consider symmetry). The small triplet at 77 ppm is $CDCl_3$, your NMR solvent).



Ortho

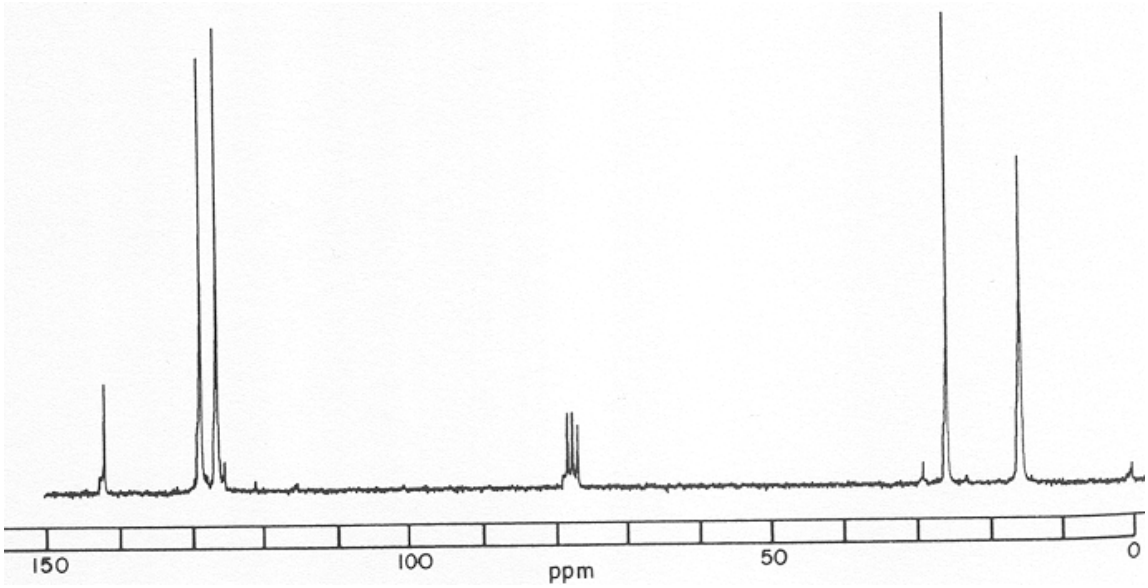


Meta

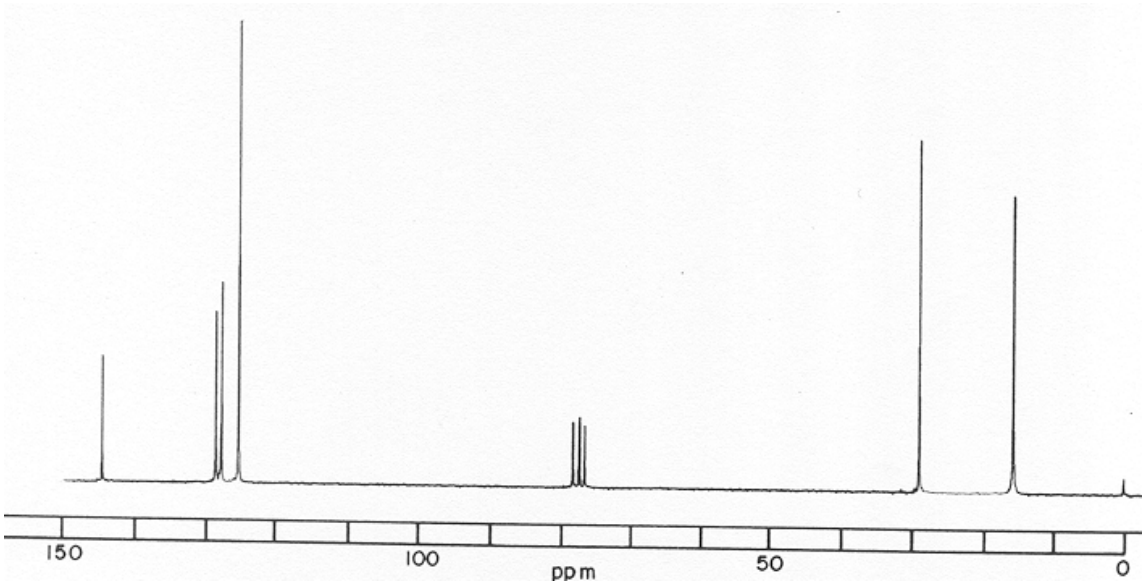


Para

A. Circle Correct Assignment: **Ortho-**….or….**Meta-**….or….**Para-**



B. Circle Correct Assignment: **Ortho-**….or….**Meta-**….or….**Para-**



C. Circle Correct Assignment: **Ortho-**….or….**Meta-**….or….**Para-**