CHM 2120 - Assignment 4
ANSWERS

In this assignment:

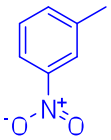
- Drawing and naming aromatic compounds
- Drawing resonance structures involving aromatic compounds
- Distinguishing aromatic from antiaromatic compounds
- Electrophilic aromatic substitution
- Manipulation of products of aromatic substitution
- Acidity/basicity is affected by aromaticity and substituents on aromatic rings
- Synthesis of benzene derivatives

Note: you should be able to draw the mechanism of each electrophilic aromatic substitution rxn in this assignment and clearly justify the formation of the major product(s) if applicable.

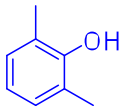
1. Supply a clear structure of:

a) m-dibromobenzene;

b) 3-nitrotoluene;

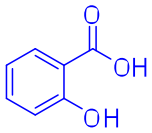


c) 2,6-dimethylphenol;

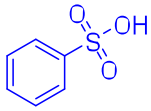


d) 3,3-dichlorocyclopentene;

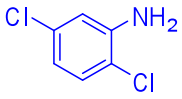
e) o-hydroxybenzoic acid;



f) benzenesulfonic acid;



g) 2,5-dichloroaniline



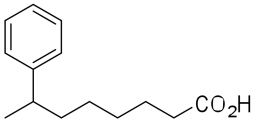
2. Name each of the following compounds using either an acceptable trivial name of the IUPAC nomenclature:

a) 

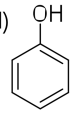
benzene

b) 

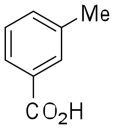
cyclohexane

c) 

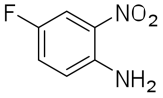
7-phenyloctanoic acid

d) 

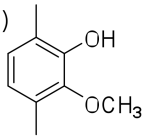
phenol

e) 

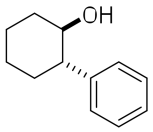
3-methylbenzoic acid OR
m-methylbenzoic acid

f) 

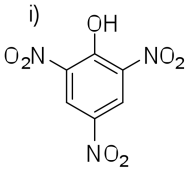
4-fluoro-2-nitroaniline

g) 

3,6-dimethyl-2-methoxyphenol

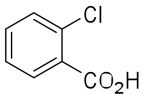
h) 

(1R,2S)-2-phenylcyclohexanol

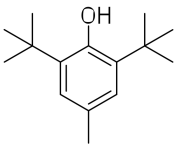
i) 

also known as
picric acid

2,4,6-trinitrophenol

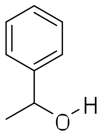
j) 

2-chlorobenzoic acid OR
o-chlorobenzoic acid

k) 

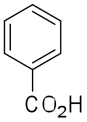
Also known as BHT or
butylated hydroxy toluene.
This helps keep cereal fresh

2,6-di-*tert*-butyl-4-methylphenol

l) 

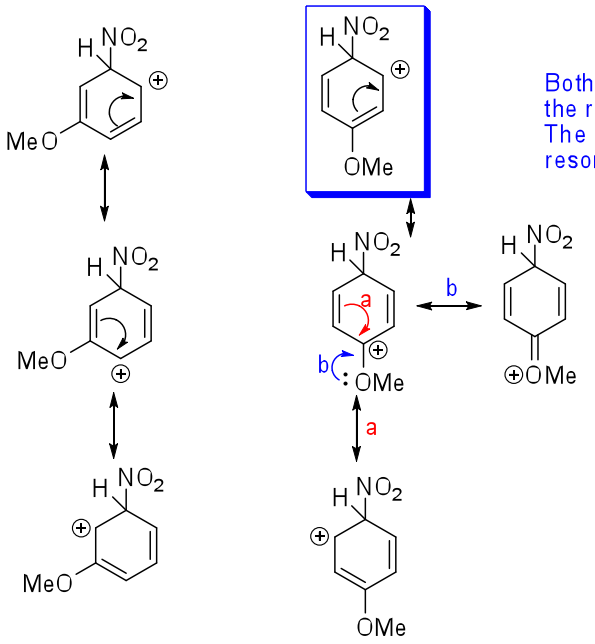
1-phenylethanol

Note: ortho/meta/para nomenclature can only be used when the benzene ring contains exactly2 substituents.

*Benzoic acid is: 

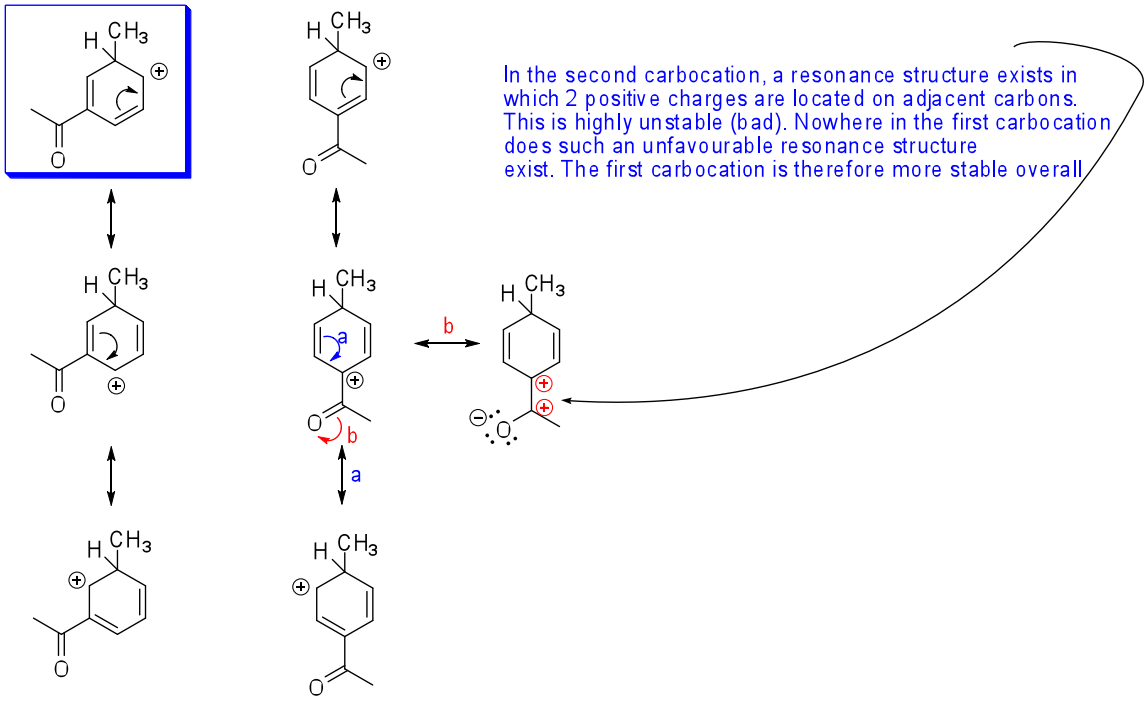
3. Which of the following carbocations in each pair is most stable? Part of your answer should include showing the relevant resonance structures.

a.

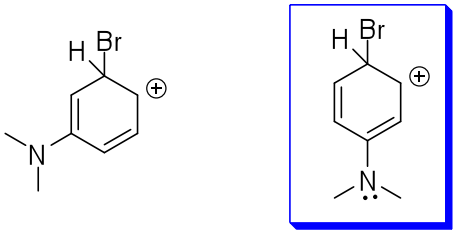


Both compounds are stabilized by resonance within the ring (2 additional resonance structures each). The second carbocation is additionally stabilized by resonance with the methoxy group.

b.

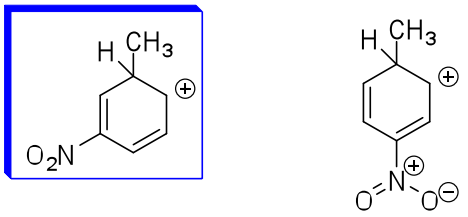


c.



Same explanation as in part A.

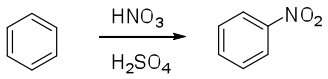
d.



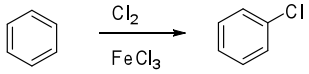
Same explanation as in part b. The nitro group is a strong electron-withdrawing group.

4. Show how you would synthesize each of the following monosubsituted benzenes:

a. Nitrobenzene

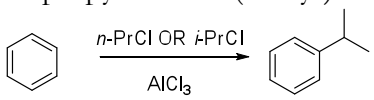


b. Chlorobenzene

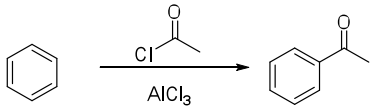


c. Methylbenzene (toluene)

d. Isopropylbenzene (2 ways)

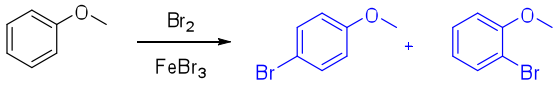


e. Acetylbenzene (acetophenone)



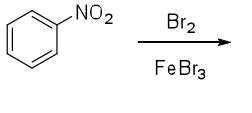
5. Give the product expected or reagents required for each of the following reactions. Clearly justify the formation of the major product.
Note: you could be asked on the test to support your answer with a mechanism and any relevant resonance structures as shown in class.

a)



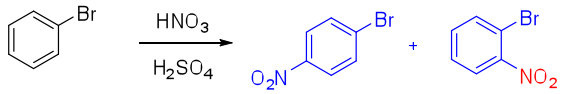
OMe is an *o,p*-director

b)



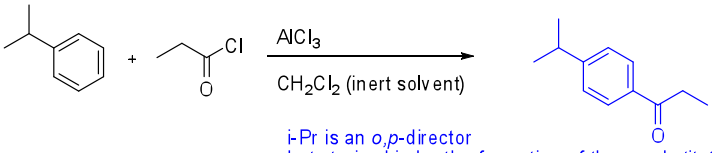
NO_2 is a *m*-director

c)



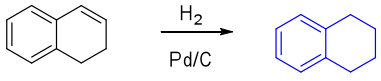
Br is an *o,p*-director (even though it's a deactivating group)

d)

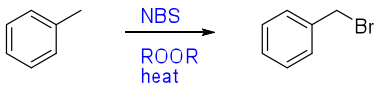


i-Pr is an *o,p*-director but sterics hinder the formation of the *o*-substituted product

e)

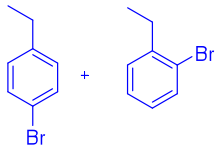


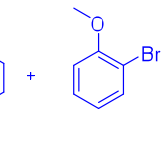
f)

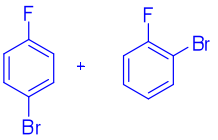


just like an allylic bromination, but this is a benzylic bromination instead

6. Give the major product(s) that would be obtained when each of the following compounds is subjected to Br_2 and $FeBr_3$:

a. Ethylbenzene → 

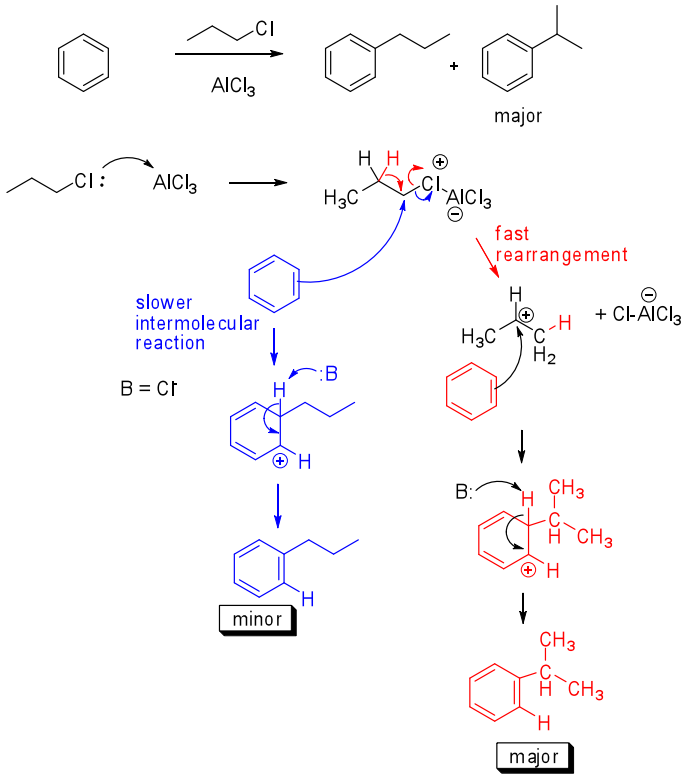
b. Anisole → 

c. Fluorobenzene → 

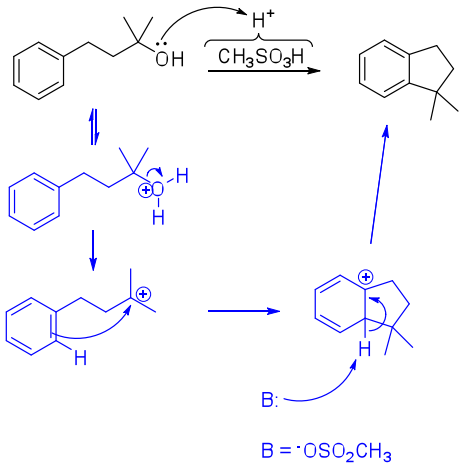
d. Benzoic acid → 

e. Nitrobenzene → 

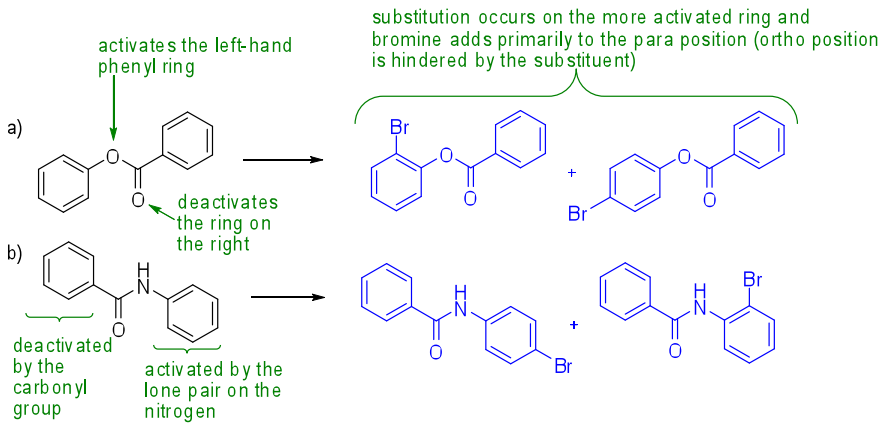
7. When benzene is reacted with 1-chloropropane and aluminum trichloride, a mixture of n-propylbenzene and isopropylbenzene is obtained. Explain by drawing the mechanism for the reaction.



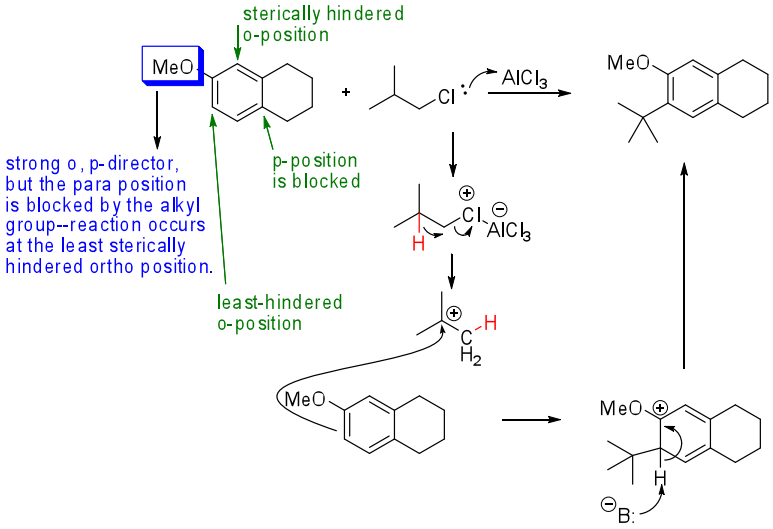
8. Draw a mechanism for the following transformation:



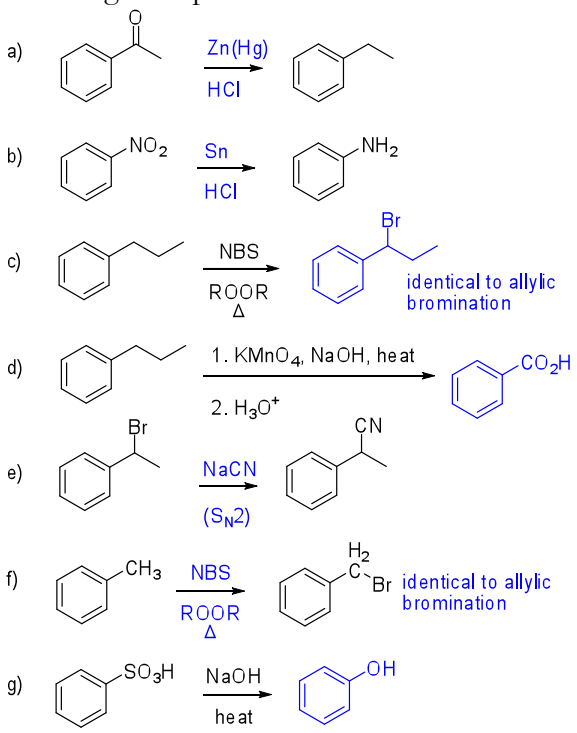
9. What is the monobromination product expected from the reaction of the following molecules with Br_2 and $FeBr_3$?



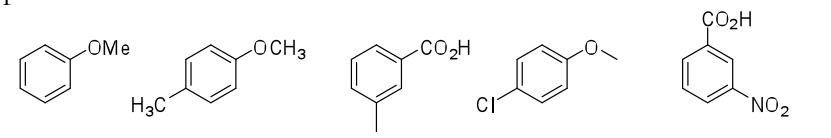
10. Explain the regioselectivity of following transformation by drawing the mechanism for the formation of the indicated product.
Note: This question required that the regioselectivity (where the substituent is added) be explained, as well as the formation of the *tert*-butyl substituent via rearrangement.



11. Once substituted benzenes have been synthesized (by electrophilic aromatic substitution reactions or other methods), they can be modified to generate new products. Identify either the required reagents or the expected products in the following examples.



12. Which of the following aromatics would react most rapidly and which would react most slowly with $Br_2/FeBr_3$? Justify your answer and predict the structure of the major product.



1 SAG

1 SAG
+1 WAG

fastest reaction

1 WAG
+1 SDG

1 SAG
+1 WDG

2 SDG's

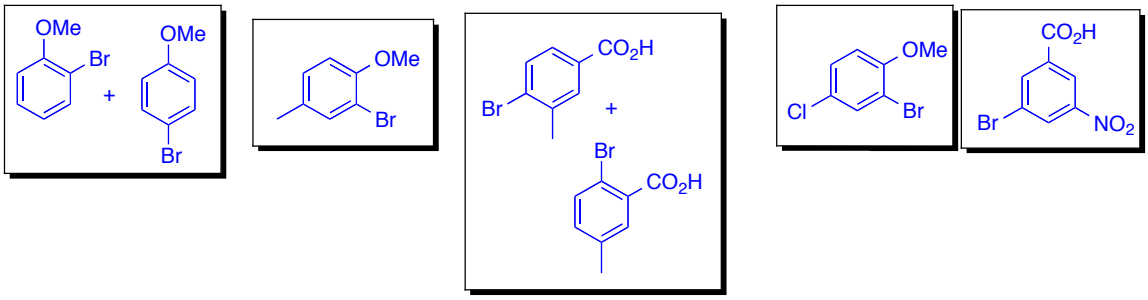
slowest reaction

Ranking: 2 1 4 3 5
(not required in this case)

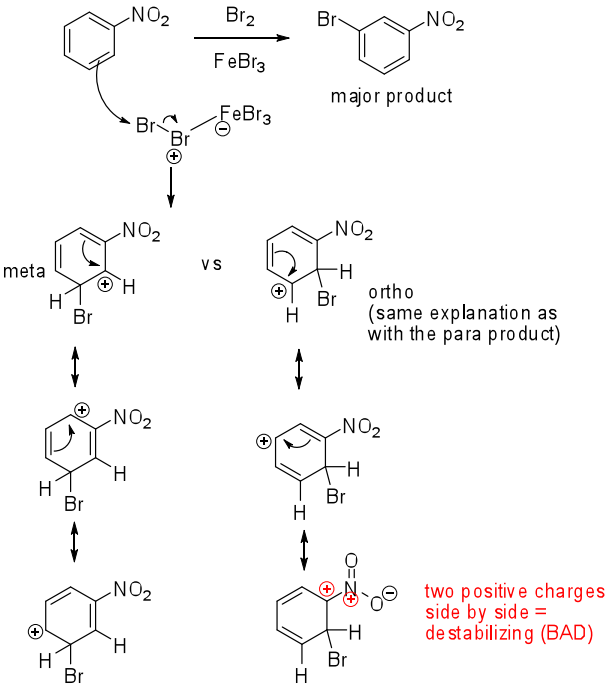
SAG = strong activating group
WAG = weak activating group

SDG = strong deactivating group
WDG = weak deactivating group

The more activating groups, the faster the reaction.
The more deactivating groups, the slower the reaction.
"Strong" groups have a greater effect than "weak" groups.

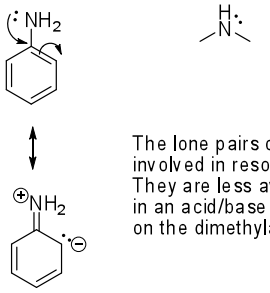


13. Consider the reaction of nitrobenzene with $Br_2/FeBr_3$. Why is the meta product the major product of this reaction?



positive charge is never directly adjacent to the NO_2 group = better, more stable ∴ the transition state of this r.d.s. (leading to the meta intermediate) is lower in energy than those leading to the o and p-intermediates and therefore this intermediate forms faster. This gives the meta product as the major one.

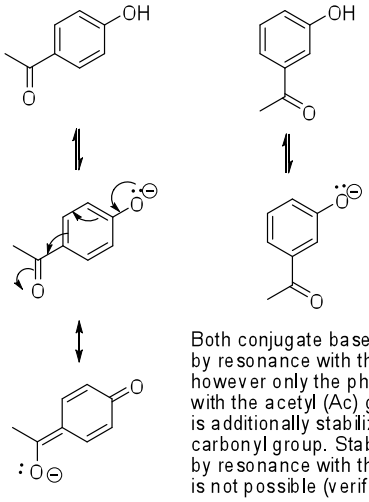
14. Aniline is much less basic than dimethylamine. Why?



The lone pairs on the N in the aniline are involved in resonance with the ring. They are less available to react in an acid/base reaction than those on the dimethylamine (no resonance).

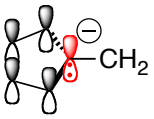
15. Which of the following phenols is most acidic? Why?

Both acids are phenols--can't use pKa differences and so a comparison of bases must be made. DRAW both the conjugate bases of the phenols BEFORE doing the explanation.



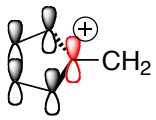
Both conjugate bases are stabilized by resonance with the aromatic ring, however only the phenoxide (c.b. of the phenol) with the acetyl (Ac) group in the para position is additionally stabilized by resonance with the carbonyl group. Stabilization of the negative charge by resonance with the carbonyl group in the meta position is not possible (verify this by drawing resonance structures).

16. Why are two of the following ions aromatic and one is not?



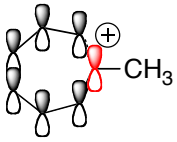
- Ring is planar
- All ring atoms are sp^2
- 6 π electrons; n=1 by the 4n+2 rule

Aromatic



- Ring is planar
- All ring atoms are sp^2
- 4 π electrons; n=1 by the 4n rule

Anti-Aromatic



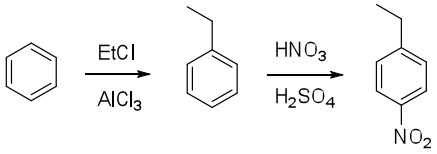
- Ring is planar
- All ring atoms are sp^2
- 6 π electrons; n=1 by the 4n+2 rule

Aromatic

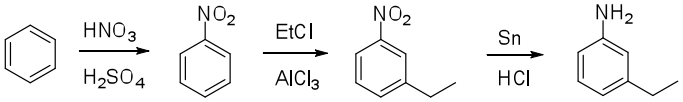
17. Propose a synthesis of each of the following disubstituted benzenes starting with benzene and any other reagents that are necessary to complete the task. Your proposal should give the desired product as the major product.

Note: The order of reactions is important in order to obtain the correct substitution pattern.

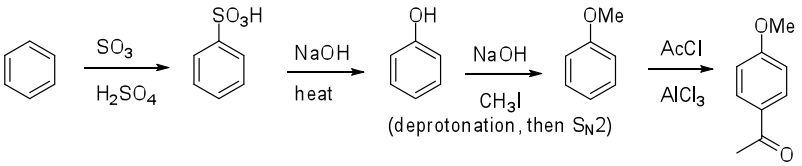
a. 1-ethyl-4-nitrobenzene



b. 1-amino-3-ethylbenzene (m-ethylaniline)

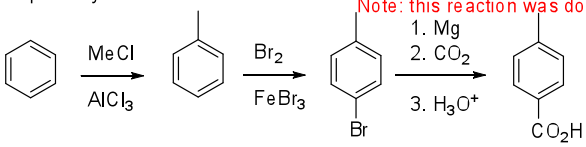


c. 1-acetyl-4-methoxybenzene (p-acetylanisole)

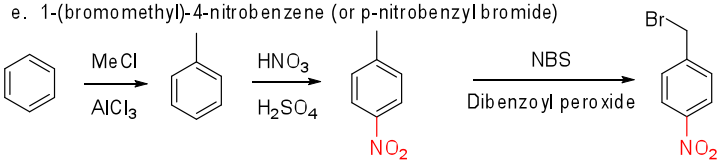


d. p-Methylbenzoic acid

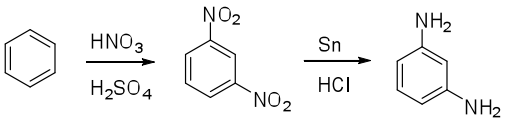
Grignard reaction-to be covered later in the course
Note: this reaction was done in the CHM 1321 lab.



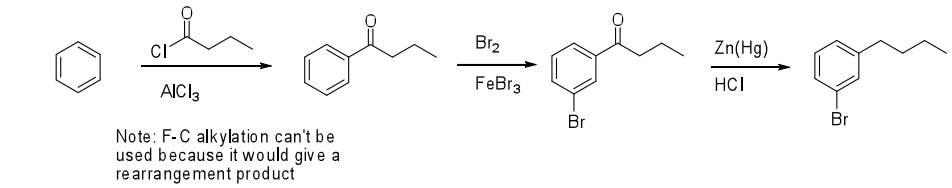
e. 1-(bromomethyl)-4-nitrobenzene (or p-nitrobenzyl bromide)



f. 1,3-diaminobenzene

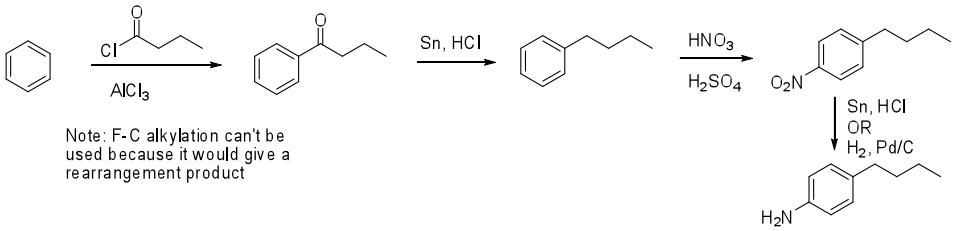


g.



Note: F-C alkylation can't be used because it would give a rearrangement product

h.

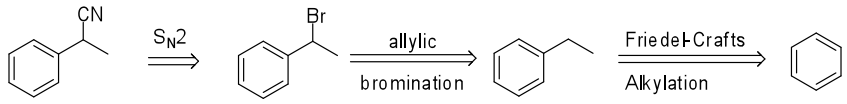


Note: F-C alkylation can't be used because it would give a rearrangement product

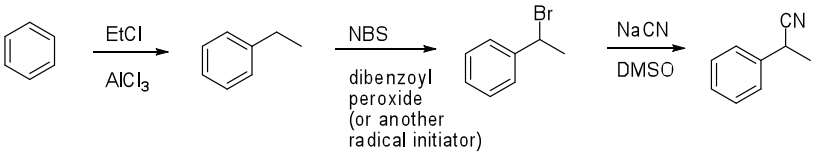
18. Propose a synthesis of each of the following molecules starting with benzene and using any other reagents that are necessary to complete the task. Your proposal should give the desired product as the major product and a retrosynthetic analysis should be included

Retrosynthesis:

a)

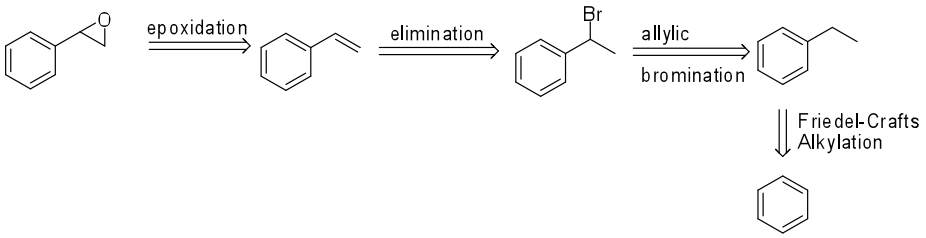


Synthesis (show the actual reagents that you would use)

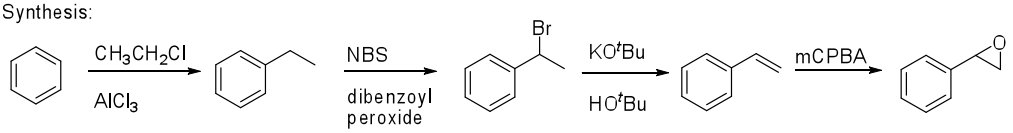


Retrosynthesis:

b)

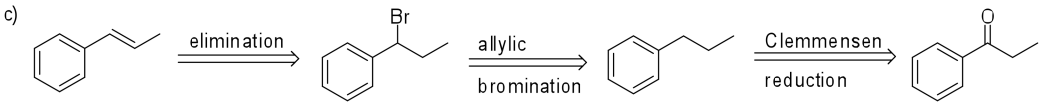


Synthesis:

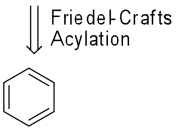


c)

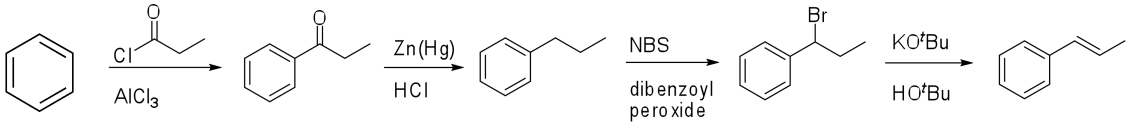
Retrosynthesis:



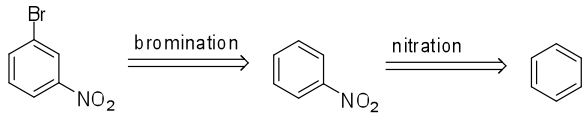
Note: Two steps are required to install the *n*-propyl substituent. Friedel-Crafts alkylation would not successfully give the *n*-propylbenzene product--why?



Synthesis:



d) Retrosynthesis:



Synthesis: