Aromatic Substitution Problem Set #2

Due in lecture on 2/12/2003
no late homeworks accepted
Only the additional problems need to be turned in.

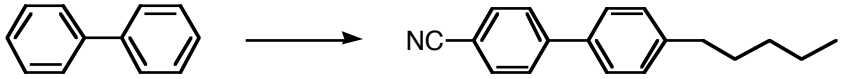
❖ Read Chapter 16 and section 24.8.

Excercises:

❖ McMurry 5th Ed Problems: 16.3, 16.4, 16.5, 16.7, 16.8, 16.9, 16.10, 16.22, 16.23, 16.27, 16.28, 16.33, 16.39, 16.41, 16.54, 16.60. I know this is alot of problems but it really is helpful to practice these reactions.

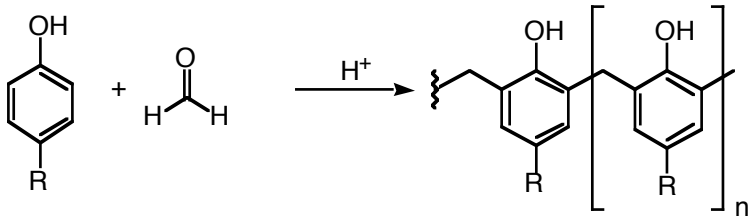
❖ Additions Problems:

(1) Shown below is a molecule called **K15**, a liquid crystalline compound found in the LCDs of inexpensive calculators and wrist watches. Devise an efficient synthesis of **K15** that employees *two* electrophilic aromatic substitutions.



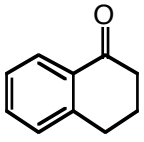
K15

(2) Shown below is a polymerization reaction discovered in 1906 by L. H. Baekeland to make extremely hard and brittle plastics—"Bakelite Plastics"—the black ones used in portable radios. (a) Draw a mechanism for its formation. (b) Give a reason why phenols are commonly used in these reactions.

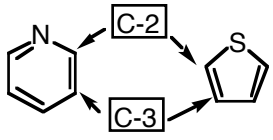


Bakelite Plastics

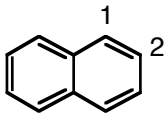
(3) Synthesize the compound below using electrophilic aromatic subsitution with benzene as your starting material.



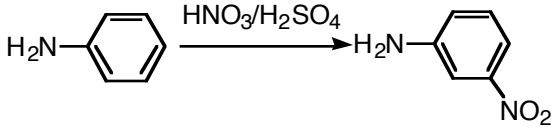
(4) Write out the mechanisms for addition of electrophiles to both C-2 and C-3 in the heterocycles. Draw all the resonance forms for the cationic intermediates. Use these structures to predict the regiochemistry of electrophilic substitution for both heterocycles.



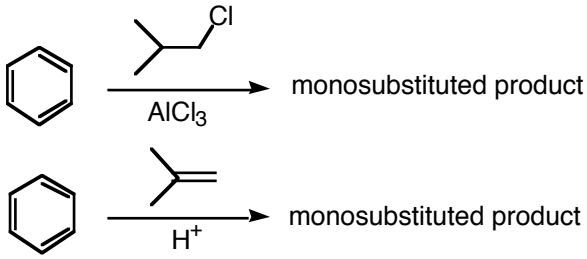
(5) Through resonance structures explain why bromination and nitration occur at the 1-position in naphalene. Now explain why Friedel Crafts acylation occurs at the 2 position.



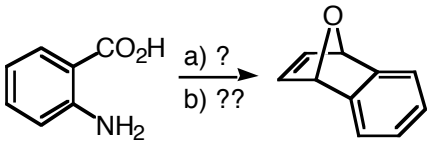
(6) The amino group is listed as one of the strongest o,p-directing groups. Explain why if standard nitration conditions are used a poor yield of the m-nitroaniline results.



(7) Predict the product for each of the two reactions shown below. Write a mechanism for their formation.



(8) Shown below is anthranilic acid, a constituent of elephant dung, fill in the missing reagents to produce the compound shown on the right.



(9) Would you consider <u>benzyne</u> to be anti-aromatic due to its 8π electrons? Explain.

(10) What is "A"? Write a mechanism for its formation.