Organic Chemistry
Electrophilic Aromatic Substitutions
Practice Set

1. (15.1) Give structures and names of the principal products expected from the ring monobromination of each of the following compounds. In each case, tell whether bromination will occur faster or slower that with benzene itself.
   a. acetanilide ($C_6H_5NHCOCH_3$)
   b. iodobenzene
   c. *sec*-butylbenzene
   d. N-methylaniline ($C_6H_5NHCH_3$)
   e. Ethyl benzoate ($C_6H_5COOC_2H_5$)
   f. Acetophenone ($C_6H_5COCH_3$)
   g. ethyl phenyl ether ($C_6H_5OC_2H_5$)
   h. diphenylmethane ($C_6H_5CH_2C_6H_5$)
   i. benzonitrile (C_6H_5CN)
   j. benzotrifluoride ($C_6H_5CF_3$)
   k. biphenyl (C_6H_5- C_6H_5)

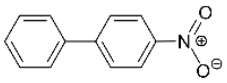
2. (15.2) Give structures and names of the principal organic products expected from ring mononitration of:
   a. *o*-nitrotoluene
   b. *m*-dicbromobenzene
   c. *p*-nitroacetanilide (*p*-$O_2NC_6H_4NHCOCH_3$)
   d. *m*-dinitrobenzene
   e. *m*-cresol (*m*-$CH_3C_6H_4CHO$)
   f. *o*-cresol
   g. *p*-cresol
   h. *m*-nitrotoluene
   i. *p*-xylene (*p*-$C_6H_4(CH_3)_2$)
   j. terephthalic acid (*p*-$C_6H_4(COOH)_2$)
   k. anilinium hydrogen sulfate ($C_6H_5NH_3^+HSO_4$)

3. (15.3) Give structures and names of the principal organic products expected from ring monosulfonation of:
   a. cyclohexylbenzene
   b. nitrobenzene
   c. anisole ($C_6H_5OCH_3$)
   d. benezenesulfonic acid
   e. salicyladehyde (*o*-HOC_6H_4CHO)
   f. *m*-nitrophenol
   g. *o*-fluoroanisole
   h. *o*-nitroacetanilide (o-$O_2NC_6H_4NHCOCH_3$)
   i. *o*-xylene
   j. *m*-xylene
   k. *p*-xylene

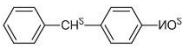
4. (15.4) Arange the following in order of reactivity toward ring nitration, listing by structure the most reactive at the top, the least reactive at the bottom.
   a. benzene, mesitylene (1,3,5-$C_6H_3(CH_3)_3$), toluene, *m*-xylene, *p*-xylene
   b. benzene, bromobenzene, nitrobenzene, toluene
   c. acetanilide ($C_6H_5NHCOCH_3$), acetophenone ($C_6H_5COCH_3$), aniline, benzene
   d. terephthalic acid, toluene, *p*-toluic acid (*p*-$CH_3C_6H_4COOH$), *p*-xylene
   e. chlorobenzene, *p*-chloronitrobenzene, 2,4-dinitrochlorobenzene
   f. 2,4-dintrochlorobenzene, 2-4-dinitrophenol
   g. *m*-dinitrobenzene, 2,4-dinitrotoluene

5. (15.5) For each of the following compounds, indicate which ring you would expect to be attached in nitration, and give structures of the principal products.

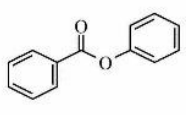
a. b. c.



p-Nitrobiphenyl



m-Nitrodiphenylmethane



Phenyl benzoate

6. (15.15) Outline all steps in the laboratory synthesis of the following compounds from benzene, and/or toluene, using any needed aliphatic or inorganic reagents. Assume that a pure *para* isomer can be separated from an *ortho, para* mixture. (See note at bottom of page)

a. *p*-nitrotoluene
b. *p* -bromonitrobenzene
c. *p* -dichlorobenzene
d. *m*-bromobenzenesulfonic acid
e. *p*-bromobenzenesulfonic acid
f. *p*-bromobenzoic acid
g. *m*-bromobenzoic acid
h. 1,3,5-trinitrobenzene
i. 2-bromo-4-nitrotoluene
j. 2-bromo-4-nitrobenzoic acid
k. 4-bromo-3-nitrobenzoic acid
l. 3,5-dinitrobenzoic acid
m. 4-nitro-1,2-dibromobenzene
n. 2-nitro-1,4-dichlorobenzene

7. (15.16) Outline all steps in the laboratory synthesis of the following compounds, using any needed aliphatic or inorganic reagents. (See note at bottom of page)

a. 4-nitro-2,6-dibromoanisole from anisole ($C_6H_5OCH_3$)
b. 4-bromo-2-nitrobenzoic acid from *o*-nitrotoluene
c. 2,4,6-tribromoaniline from aniline
d. 2,4-dinitroacetanilide from acetanilide ($C_6H_5NHCOCH_3$)
e. 5-nitroisophthalic acid from *m*-xylene
f. 4-nitroisophthalic acid from *m*-xylene
g. 2-nitroterephthalic acid from *p*-xylene (two ways)
h. Explain the preferred method from (g).

About Synthesis

Each synthesis should be the one that gives a reasonably pure product in reasonably good yield.

It is not necessary to complete and balance each equation. Simply draw the structure of the organic compounds, and write on the arrow the necessary reagents and any critical conditions. For example:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br \xrightarrow{CN^-} CH_3CH_2CN$$

At this stage you may be asked to make a particular compound that can readily be bought, or that might better be made by another method: the synthesis of *n*-butane in Problem 17, for example. But if you can work out a way to make *n*-butane from *n*-butyl alcohol, then, when the need arises, you will also know how to make a complicated alkane from a complicated alcohol, and, in fact, how to replace an —OH group by —H in just about any compound you encounter. Furthermore, you will have gained practice in putting together what you have learned about several different kinds of compounds.

Remember: Alkyl halides are *almost never* prepared by direct halogenation of alkanes. *From the standpoint of synthesis in the laboratory, an alkane is a dead-end.*