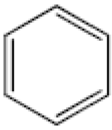
Chapter 6: Arenes “Aromatic Compounds”

6.1. Definition and Aromaticity:

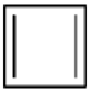
Arenes are unsaturated aromatic hydrocarbons. The term **aromaticity** applies to all compounds that satisfy the criteria established by **Erich Hückel**. According to Hückel's rule, for a compound to be aromatic, it must meet the following conditions:

1. **Be cyclic** (have a ring structure).
2. **Have alternating double bonds** (conjugated π-system).
3. **Follow Hückel’s rule**: The molecule must contain a delocalized π-electron system with **4n + 2 electrons** (where **n = 0, 1, 2, 3...**, an integer). These electrons can come from π-bonds or lone pairs participating in conjugation.

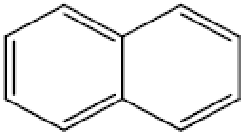


Benzene has 6 π-electrons, satisfying the 4n+2 rule (where n=1)

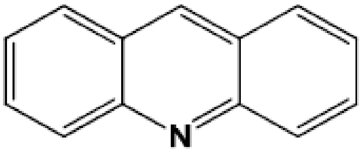
Example:



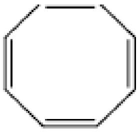
Non-aromatic



Aromatic

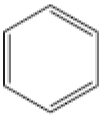


Aromatic

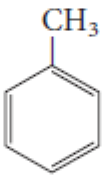


Non-aromatic

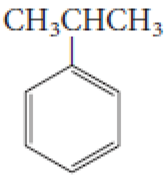
6.2. Nomenclature of Aromatic Compounds :



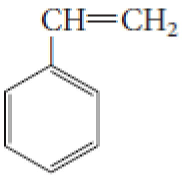
benzene



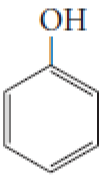
toluene



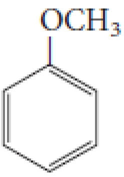
cumene



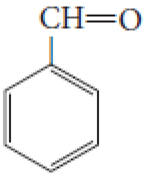
styrene



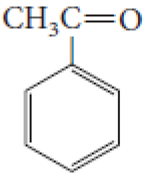
phenol



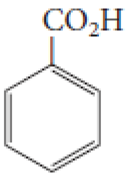
anisole



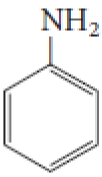
benzaldehyde



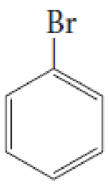
acetophenone



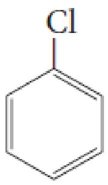
benzoic acid



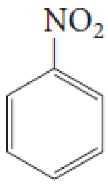
aniline



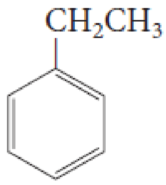
bromobenzene



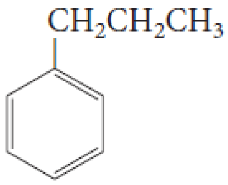
chlorobenzene



nitrobenzene

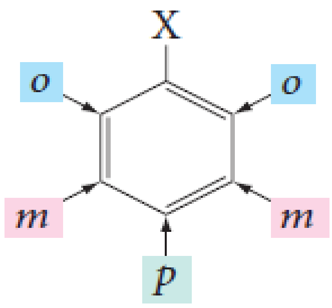


ethylbenzene

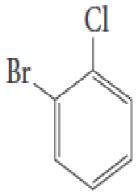


propylbenzene

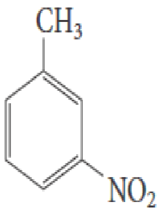
When two substituents are present, three isomeric structures are possible. They are designated by the prefixes ***ortho***-, ***meta***-, and ***para***-, which are usually abbreviated as ***o***-, ***m***-, and ***p***-, respectively.



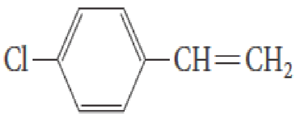
Example:



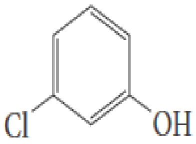
o-bromochlorobenzene
(note alphabetical order)



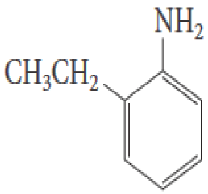
m-nitrotoluene



p-chlorostyrene

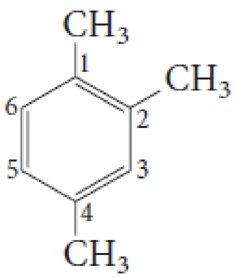


m-chlorophenol

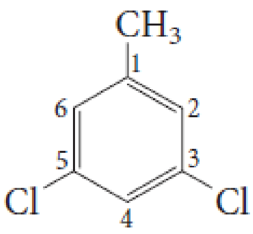


o-ethylaniline

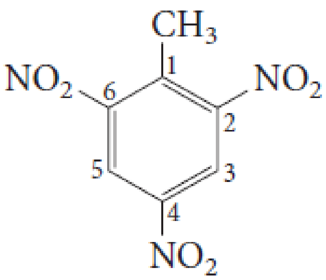
When more than two substituents are present, their positions are designated by numbering the ring.



1,2,4-trimethylbenzene



3,5-dichlorotoluene

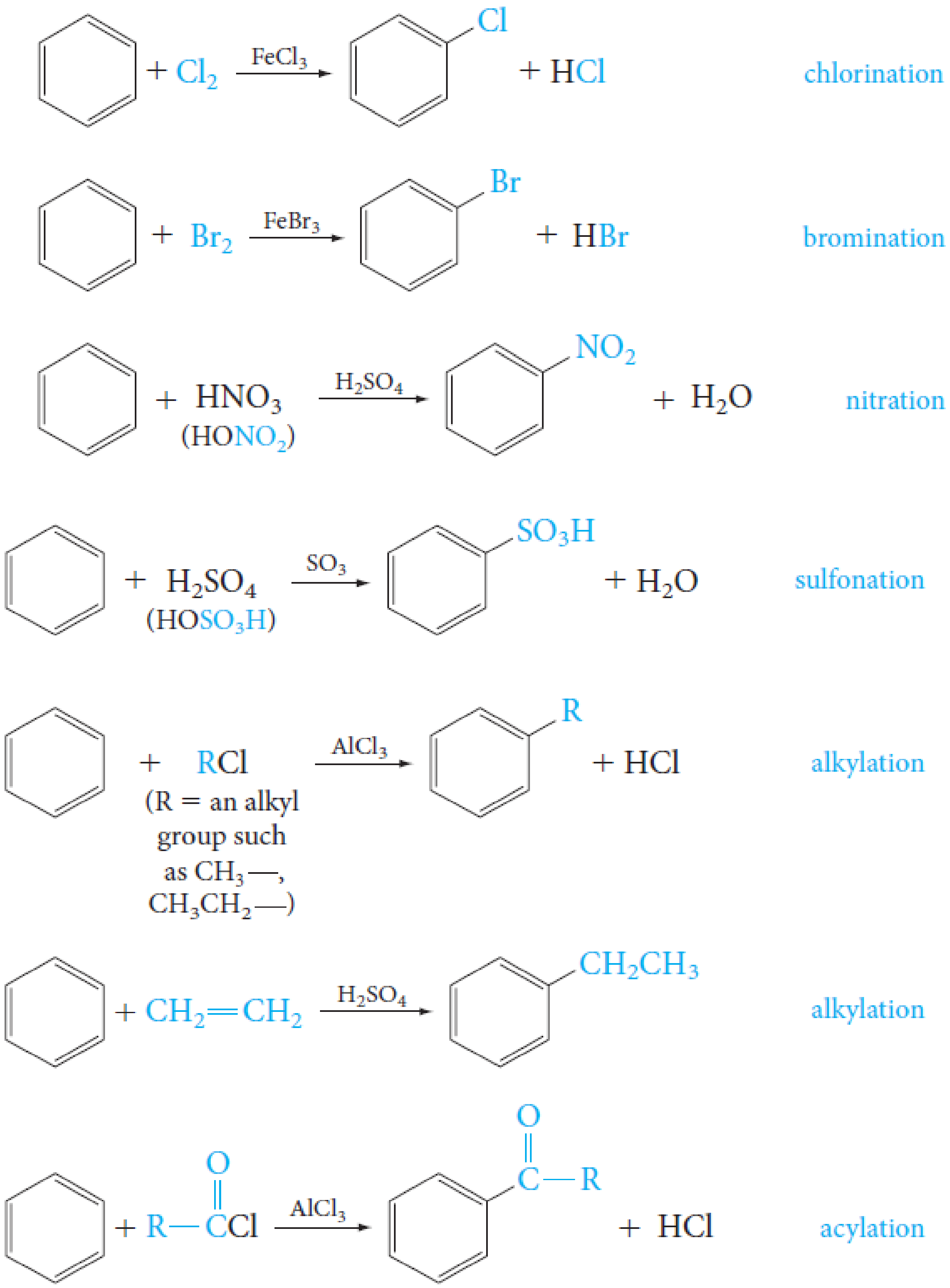


2,4,6-trinitrotoluene
(TNT)

6.3. Reactivity:

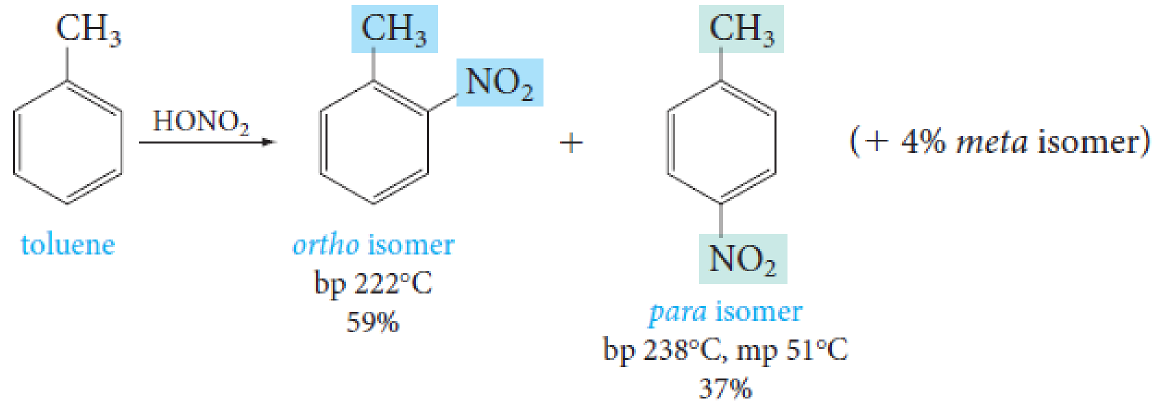
6.3.1. Electrophilic Aromatic Substitution:

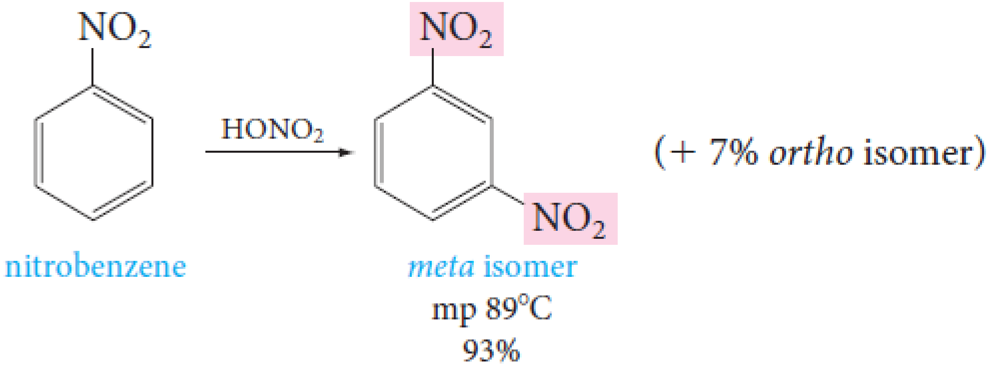
The most common reactions of aromatic compounds involve substitution of other atoms or groups for a ring hydrogen on the aromatic unit. Here are some typical substitution reactions of benzene.



<u>6.3.1.1. Ring-Activating and Ring-Deactivating Substituents: Ortho,Para-Directing and Meta-Directing Groups:</u>

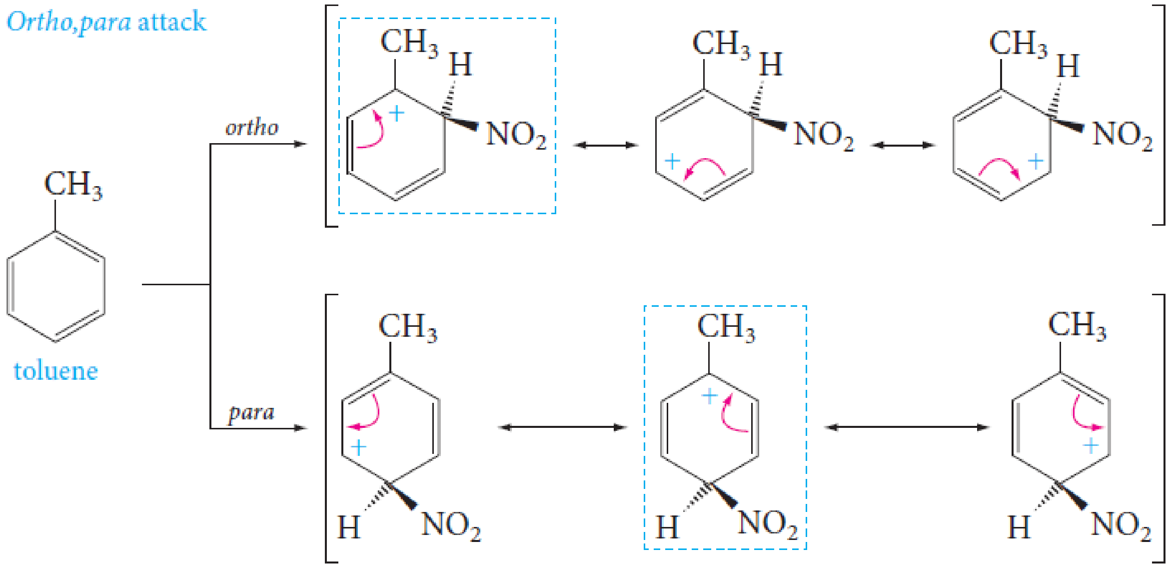
Substituents already present on an aromatic ring determine the position taken by a new substituent. For example, nitration of toluene gives mainly a mixture of o- and p-nitrotoluene.

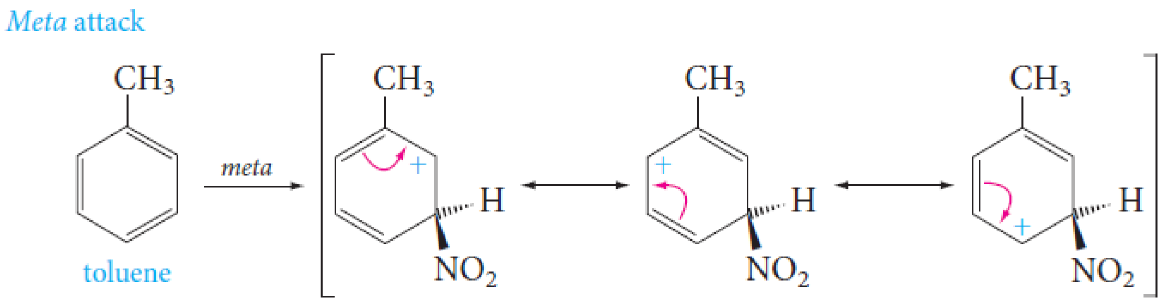




Toluene undergoes mainly *ortho,para* substitution, whereas nitrobenzene undergoes *meta* substitution. In general, groups fall into one of two categories. Certain groups are ***ortho,para* directing**, and others are ***meta* directing**. Table 6.1 lists some of the common groups in each category.

a. *Ortho,Para*-Directing Groups :

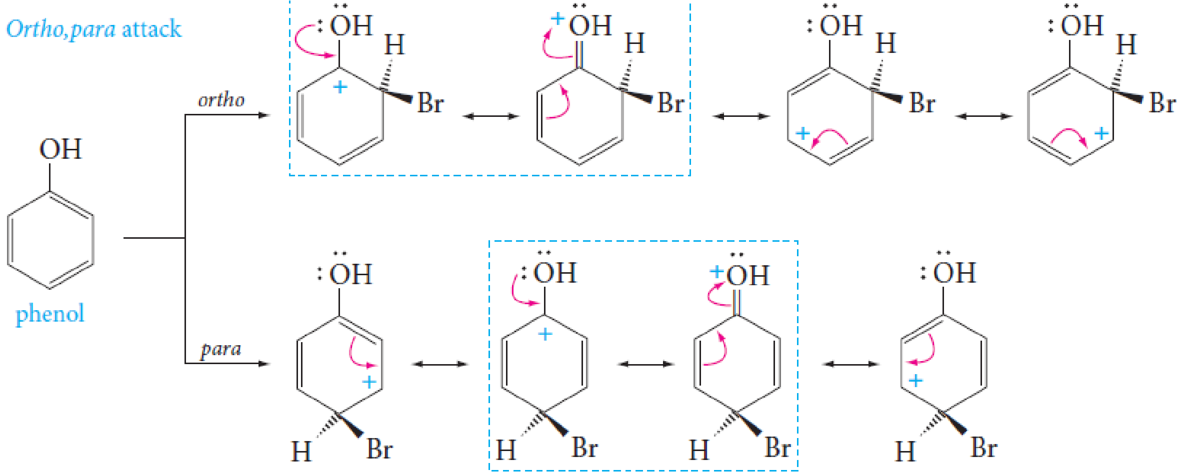


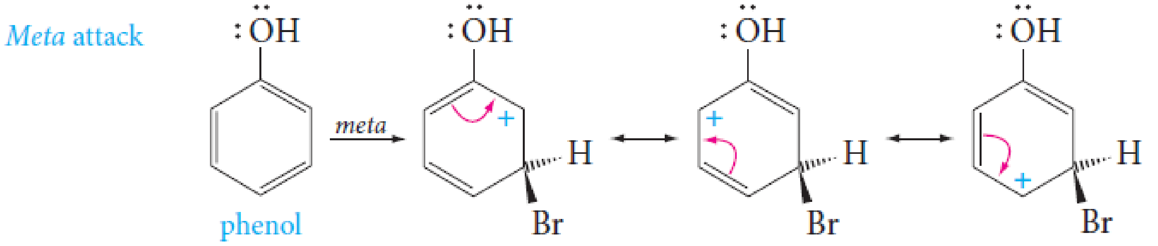


The methyl group is ortho, para directing, so that the reaction can proceed via the most stable carbocation intermediate. Similarly, all other alkyl groups are ortho, para directing.
Consider now the other ortho,para-directing groups listed in Table 6.1. In each of them, the atom attached to the aromatic ring has an unshared electron pair.

$$-\ddot{\underset{\cdot\cdot}{\text{F}}}: \qquad -\ddot{\underset{\cdot\cdot}{\text{O}}}\text{H} \qquad -\ddot{\text{N}}\text{H}_2$$

This unshared electron pair can stabilize an adjacent positive charge. Let us consider, as an example, the bromination of phenol.

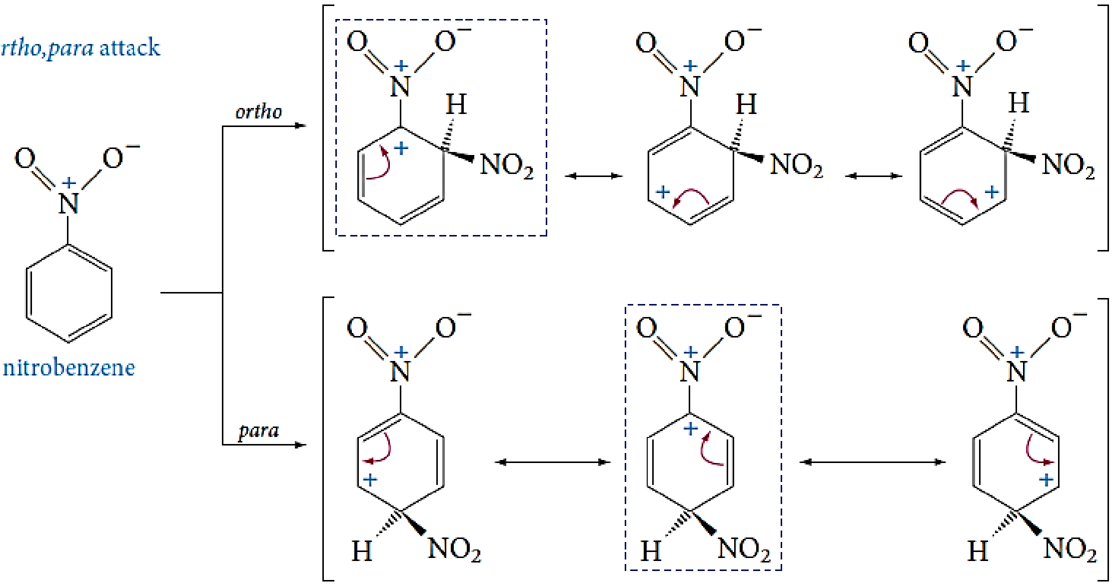




The hydroxyl group is ortho,para directing. We can generalize this observation. All groups with unshared electrons on the atom attached to the ring are ortho,para directing.

***b. Meta*-Directing Groups :**

Ortho,para attack



Meta attack

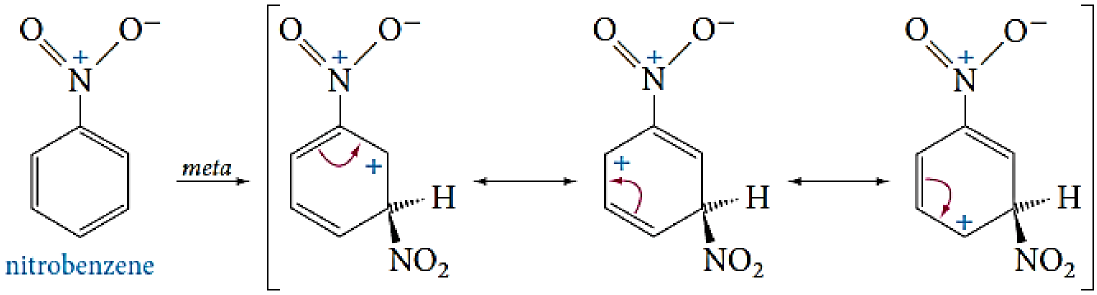
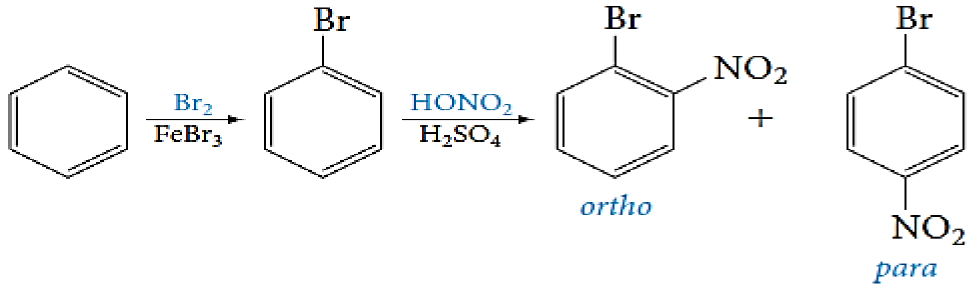


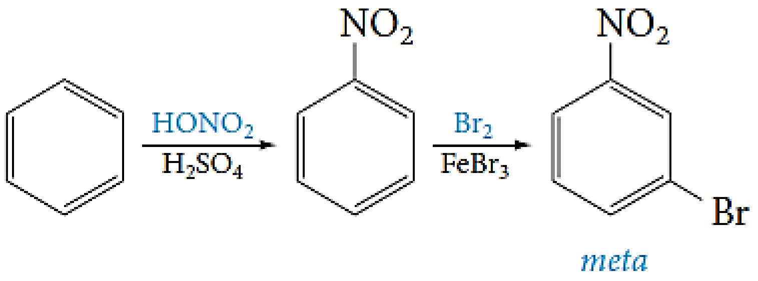
Table 6.1 : Directing and activating effects of common functional groups

Groups are listed in decreasing order of activation

Directing Effect	Effect on Reactivity	Substituent Group	Group Name
Ortho/Para-Directing	Strong Activating	–NH_2, –NHR, –NR_2	Amino
		–OH, –OCH_3, –OR	Hydroxy, Alkoxy
	Moderate Activating	–CH_3, –CH_2CH_3, –R	Alkyl
	Weak Deactivating	–F, –Cl, –Br, –I	Halide
Meta-Directing	Strong Deactivating	–NO_2	Nitro
		–C≡N	Cyano
		–SO_3H	Sulfonic acid
	Moderate Deactivating	–C(=O)R, –COOH	Acyl, Carboxy
		–COOR	Carbalkoxy
		–$CONH_2$	Carboxamide

The Importance of Directing Effects in Synthesis:





6.3.2. Addition reaction:

6.3.2. 1. Hydrogenation:

C_6H_6 (benzene) + 3 H_2 → C_6H_{12} (cyclohexane)

6.3.2. 2. Halogen Addition :

$$C_6H_6 + 3\,Cl_2 \text{ (or } Br_2) \xrightarrow{UV} C_6H_6Cl_6$$

6.3.2. 3. Oxydation:

The side chain of an alkylbenzene is highly susceptible to oxidation by common oxidizing agents (dilute HNO_3, $KMnO_4$, $K_2Cr_2O_7$, CrO_3…), regardless of its structure or length.