Ortho para meta positions

When substituted benzenes undergo electrophilic attack, groups already on the ring affect both, the rate of the reaction and the site of attack. We say, therefore, that substituent groups affect both **reactivity** and **orientation** in electrophilic aromatic substitutions.

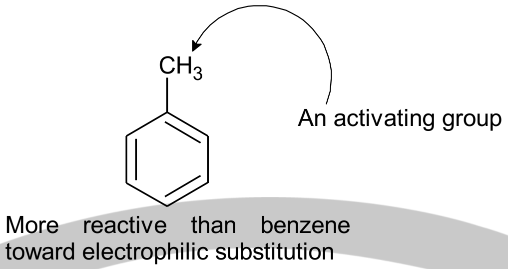
We can divide substituent groups into two classes according to their influence on the reactivity of the ring. Those that cause the ring to be more reactive than benzene itself are called **activating groups.** Those that cause the ring to be less reactive than benzene are called **deactivating groups.**

We also find that we can divide substituent groups into two classes according to the way they influence the orientation of attack by the incoming electrophile. Substituents in one class tend to bring about electrophilic substitution primarily at the positions ***ortho*** and ***para*** to themselves. We call these groups ***ortho - para directors*** because they tend to direct the incoming group into the ortho and para positions. Substituents in the second category tend to direct the incoming electrophile to the ***meta*** position. We call these groups ***meta directors.***

Several examples will illustrate more clearly what we mean by these terms.

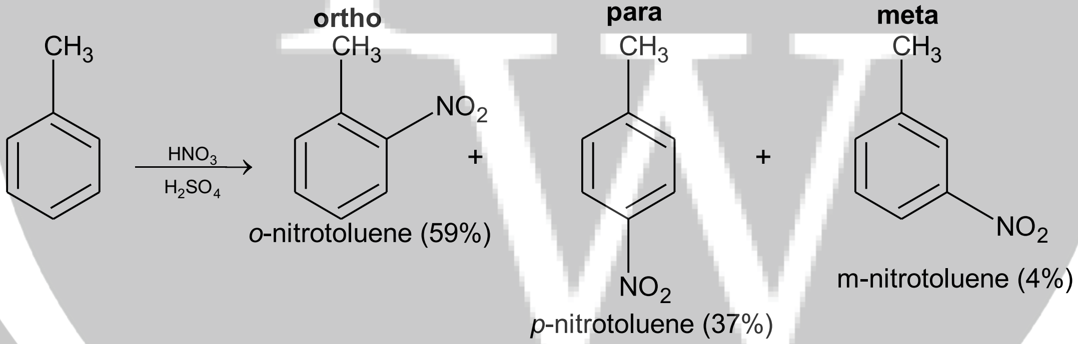
Activating Groups: Ortho - Para Directors

The methyl group is an **activating** group and is **an ortho - para director.** Toluene reacts considerably faster than benzene in all electrophilic substitutions.

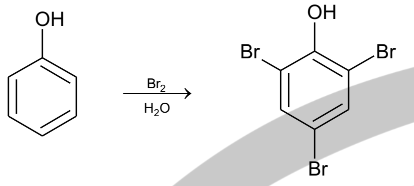


We observe the greater reactivity of toluene in several ways. We find, for example, that with toluene, milder conditions (lower temperatures and lower concentrations of the electrophile) can be used in electrophilic substitutions than with benzene. We also find that under the same conditions, toluene reacts faster than benzene. In nitration, for example, toluene reacts 25 times as fast as benzene.

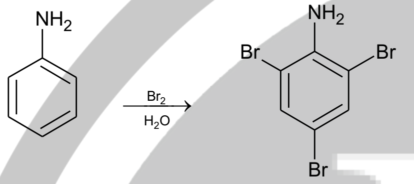
We find, moreover, that when toluene undergoes electrophilic substitution, most of the substitution takes place at its ortho and para positions. When we nitrate toluene with nitric and sulfuric acids, we get mononitrotoluenes in the following relative proportions.



Of the mononitrotoluenes obtained from the reaction, 96% (59% + 37%) has the nitro group at ortho or para position. Only 4% has the nitro group at meta position.Predominant substitution at the ortho and para positions of toluene is not restricted to nitration reactions. The same behavior is observed in halogenation, sulfonation, and so forth.All alkyl groups are activating groups, and they are also ortho – para directors. The methoxy group, CH_3O–, and the acetamido group, CH_3CONH^-, are strong activating groups and both are ortho – para directors.The hydroxyl group and the amino group are very powerful activating groups and are also powerful ortho- para directors. Phenol and aniline react with bromine in water (no catalyst is required) to produce products in which both of the ortho positions and the para position are substituted. These tribromo products are obtained in nearly quantitative yield.



2,4,6-tribromophenol



2,4,6-tribromoaniline

Studies like the ones that we have presented in this section have been done for a number of
other substituted benzenes. The effects of these substituents on reactivity and orientation are included in following Table.

TABLE

Effect of substituents on electrophilic aromatic substitution	
ORTHO - PARA DIRECTORS	***META DIRECTORS***

(Class – I)	***(Class – II)***
Strongly Activating $–NH_2$, $–NHR$, $–NR_2$, $–OH$, $–\ddot{O}:^-$ **Moderately Activating** $–NHCOCH_3$, $–NHCOR$, $–OCH_3$, $–OR$ **Weakly Activating** $– CH_3$, C_2H_5, $– R$, $– CH_2X$, $– C_6H_5$ O **Weakly Deactivating** || $–F:$, $–Cl:$, $–Br:$, $–I:$, $–CHX_2$, $–NO$, $–S– OH$, $–CH = CH – W$, $- CH_2- CH_2- \overset{+}{N}R_3$ W represents electron withdrawing group	**Moderately Deactivating** $–C\equiv N$ $–SO_3H$ $–CO_2H$, $–CO_2R$ $–CHO$, $–COR$ $- CH_2- \overset{+}{N}R_3$ **Strongly Deactivating** $–NO_2$ $–NR_3^+$ $–CF_3$, $–CCl_3$