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Directing Effect of Substituents in Monosubstituted Benzene

When a monosubstituted benzene is subjected to further substitution, all the three possible disubstituted products are not formed in equal amounts but, either ortho and para products or meta product is formed predominantly.

In fact, the disubstituted product formed by further substitution of monosubstituted benzene depends upon the nature of the substituent already attached to the benzene ring, but not on the nature of the entering group. Thus, the substituent already present in the benzene ring directs the new incoming group to a definite position of the benzene ring. This behaviour of the substituents is called the directive influence or directing effect of the substituents.

Directing effect may be of following two types-

(1) Ortho-Para directing Effect- There are certain atoms or groups which direct the new incoming group to either ortho or para position of benzene ring. These groups are called ortho-para directing groups and this effect is called ortho-para directing effect.

Ortho-para directing effect can be explained by taking the example of the directing effect of phenolic group ($-OH$ group) of Phenol. In fact, Phenol is the resonance hybrid of following five resonating structures-

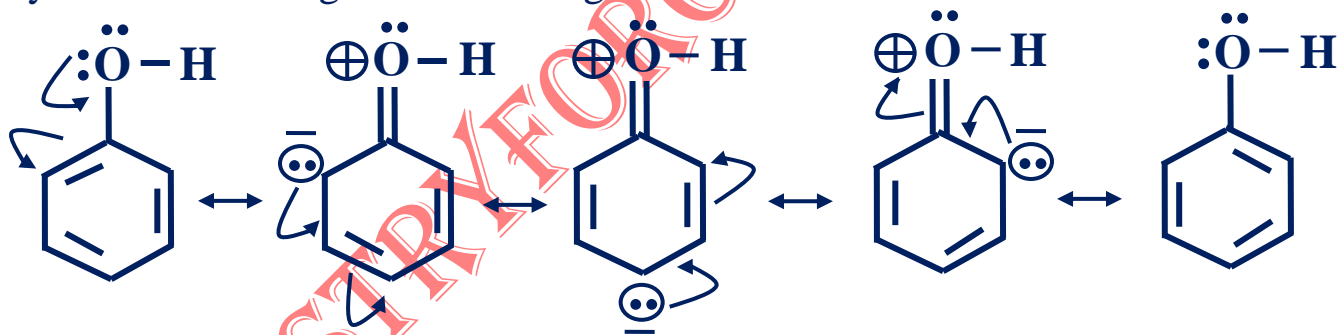


Fig.- Resonance in Phenol

It is clear that, due to electron releasing effect (+M effect) of $-OH$ group, the electron density gets increased on ortho and para positions as compared to meta position of the benzene ring. Hence, electrophiles preferably attack on these positions and therefore, the further substitution occurs mainly on these positions. Here, $-I$ effect of $-OH$ group also operates and it slightly reduces the electron density on ortho and para positions of the benzene ring. However, there is overall increase of electron density on these positions of the benzene ring.

Some important atoms and groups having ortho-para directing effect are listed here-



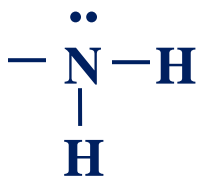
Halogen atom



Alcoholic group



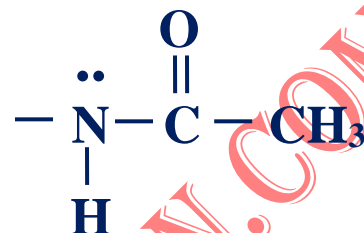
Alcoxy group



1^oAmine group



2^oAmine group



Acid amide group

It is clear that, atoms or groups having ortho-para directing effect, in general contain at least one lone pair of electrons on key atom to which they release to the benzene ring (+M effect). Alkyl groups (e.g. $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc.) are its exception where, key atom does not contain lone pair of electrons but they show ortho-para directing effect due to hyperconjugation.

Ortho-para directing groups increase electron density in benzene ring and therefore, they activate the benzene ring for the attack of an electrophile. Thus, they increase the reactivity of ring for electrophilic substitution reactions and act like ring activators for the electrophilic substitution reactions.

For an exception, halogen atoms of haloarenes, though ortho-para directing, are moderately deactivating for electrophilic substitution reactions. In fact, due to strong -I effect of halogen atoms, overall electron density in benzene ring gets decreased and therefore, further substitution becomes somewhat difficult. However, due to resonance, the electron density on ortho and para positions in haloarenes is greater than that at the meta position. Hence, they are also ortho-para directing in nature. Resonance in chlorobenzene can be represented as under-

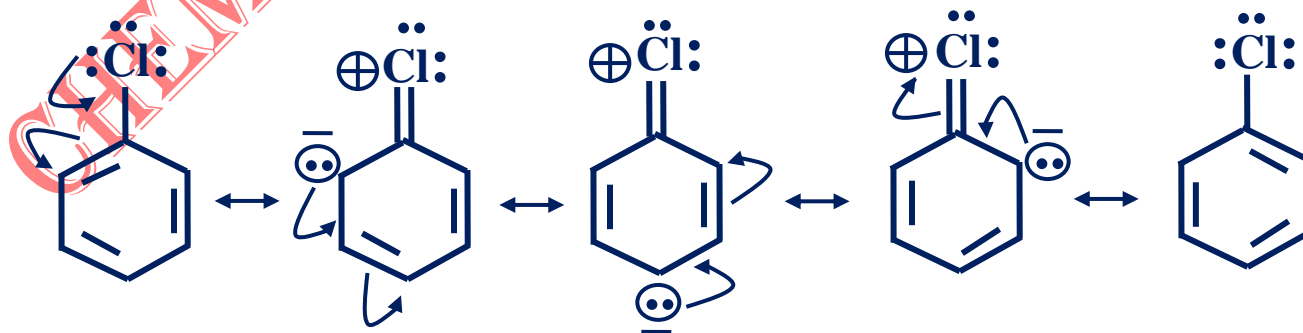


Fig.- Resonance in Chlorobenzene

(2)Meta directing Effect- There are certain groups which direct the new incoming group on meta position of the benzene ring. These groups are called meta directing groups and this effect is called meta directing effect.

Meta directing effect can be explained by taking the example of the directing effect of aldehyde group (-CHO group) of benzaldehyde. In fact, benzaldehyde is the resonance hybrid of following five resonating structures-

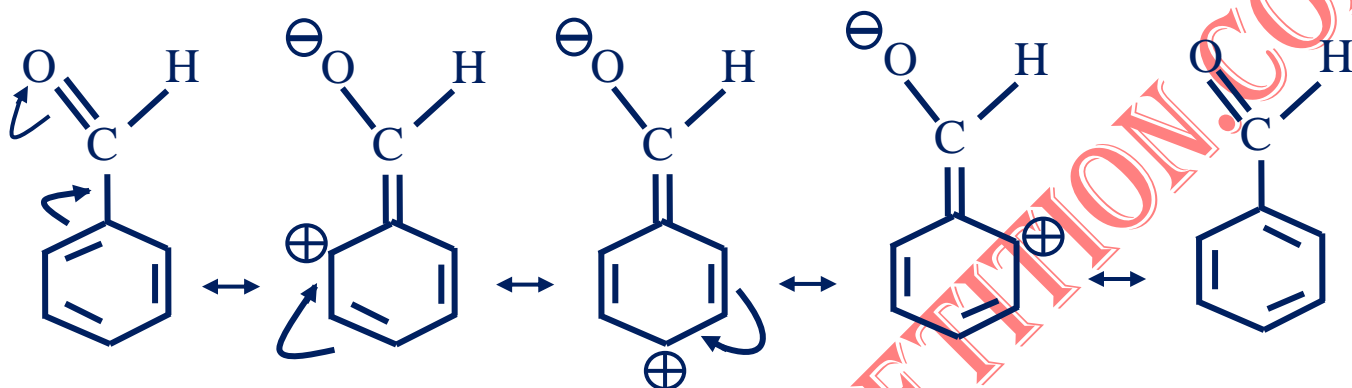
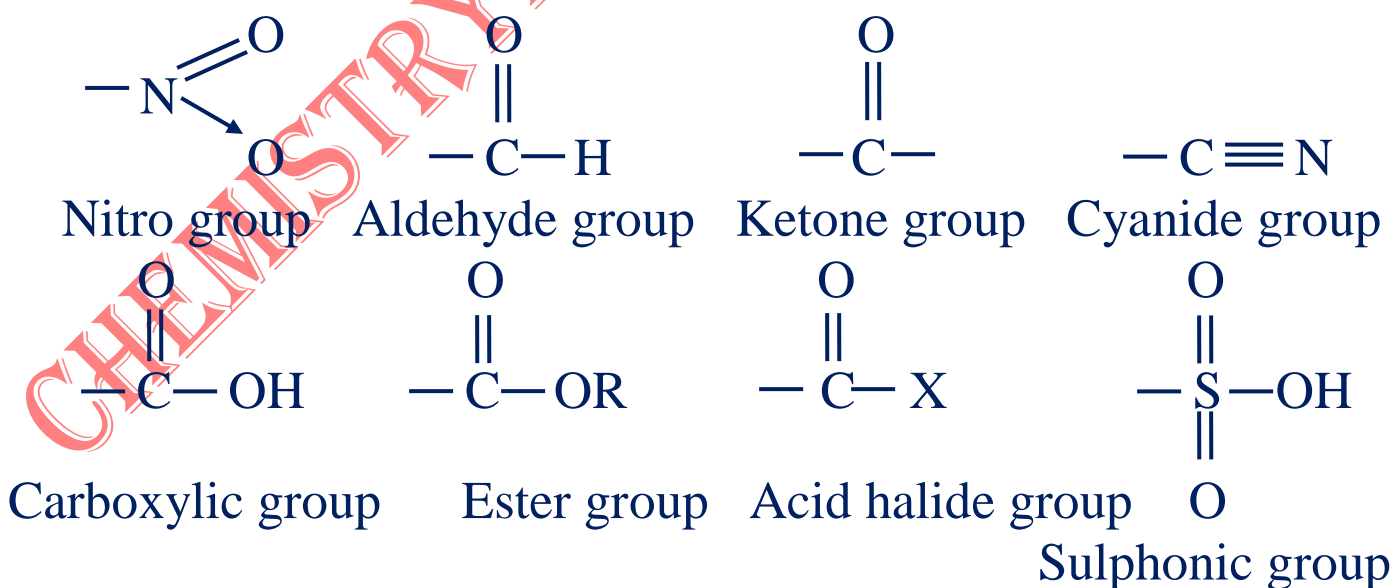


Fig.- Resonance in Benzaldehyde

It is clear that, due to electron withdrawing effect (-M effect) of -CHO group, the electron density gets decreased on ortho and para positions as compared to meta position of the benzene ring. Hence, electrophiles preferably attack on meta position and therefore, the further substitution occurs mainly on meta position.

Some important groups having -M effect are listed here-



It is clear that, the groups having meta directing effect contain a multiple bond between two polyvalent atoms of different electronegativities, which acts like electron sink.

Meta directing groups decrease electron density in benzene ring and therefore, they deactivate the benzene ring for the attack of an electrophile. Thus, they decrease the reactivity of ring for electrophilic substitution reactions and act like ring deactivators for the electrophilic substitution reactions.

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