ORTHO, META AND PARA DIRECTING GROUPS

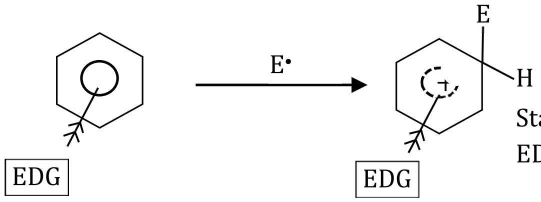
Orientation And Reactivity of Monosubstituted Benzene Ring

When benzene goes through electrophilic aromatic substitution, the first electrophile can attach at any position because all positions are the same. However, when a group is already attached to the ring, this group influences the ring's reactivity and determines how the incoming electrophile will be oriented. There are two main types of substituent groups:

(1) Activating groups
(2) Deactivating groups

Activating groups

Activating groups, also called activators, are those electron-donating groups (like EDG, +M, +I, +H, and the conjugation effect) on the benzene ring. These groups make the s-complex (Adenium ion complex) more stable compared to benzene, contributing to their activator status.

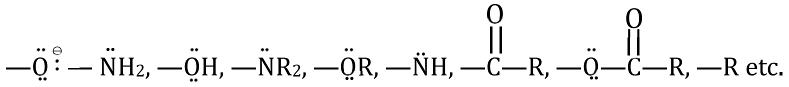


Stabilized adenium ion by EDG (e.g. $\ddot{N}R_2$, –OH, etc.)

EDG increasing electron density in benzene ring

EDG giving more stable σ-complex as compared to that of benzene

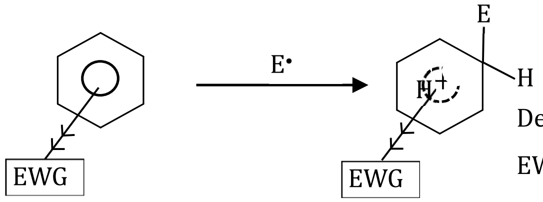
e.g.,



$-\ddot{O}:^{\ominus}$ — $\ddot{N}H_2$, $-\ddot{O}H$, $-\ddot{N}R_2$, $-\ddot{O}R$, $-\ddot{N}H$, $-\overset{\overset{O}{\|}}{C}-R$, $-\ddot{O}-\overset{\overset{O}{\|}}{C}-R$, $-R$ etc.

Deactivating groups

Deactivating groups, also known as deactivators, are electron-drawing groups (like -M and -I effects) on the benzene ring. These groups make the σ - complex (Adenium ion complex) less stable than benzene. As a result, in substituted benzenes where these electron-withdrawing substituents are present, the reactivity towards SE reactions decreases.

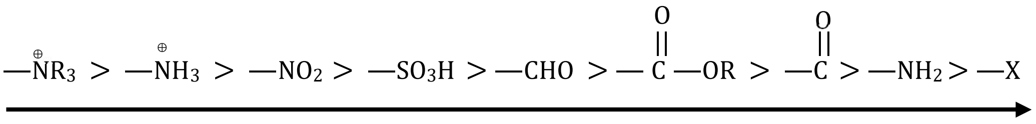


Destabilized Adenium ion by EWG (e.g. $-NO_2$, $-\overset{+}{N}R_3$)

Electron withdrawing group decreases electron density in benzene ring. Hence E^+ attack on electron deficient ring is difficult.

Electron withdrawing group decreases stability of σ -complex

Some deactivating groups are



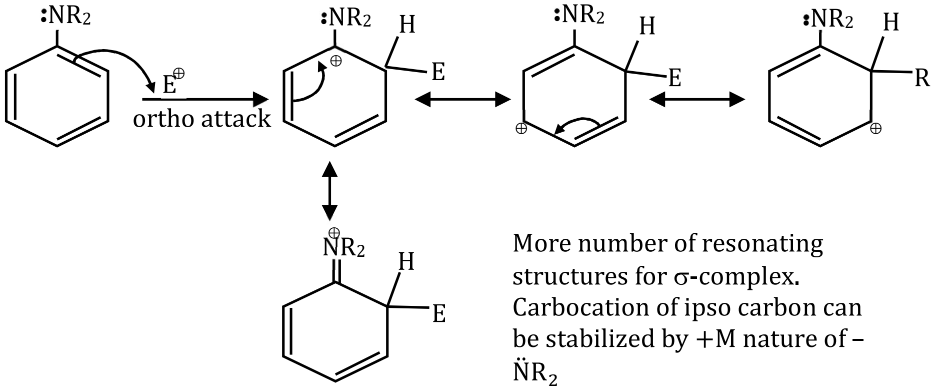
$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_3H > -CHO > -\overset{\overset{O}{\|}}{C}-OR > -\overset{\overset{O}{\|}}{C} > -NH_2 > -X$$

decreasing deactivating power.

Orientation in monosubstituted benzene:

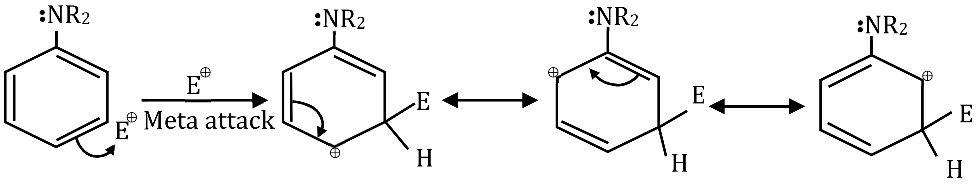
The way a substituent guides the electrophilic substitution reaction in a benzene with one substitution is connected to how stable the σ - complex is when there are attacks at the ortho, meta, or para positions.

For example, the $-\ddot{N}R_2$ group, which is a group where the main atom has a lone pair, acts as an ortho-para director. This means it enhances the stability of the σ - complex formed through attacks at the ortho and para positions.

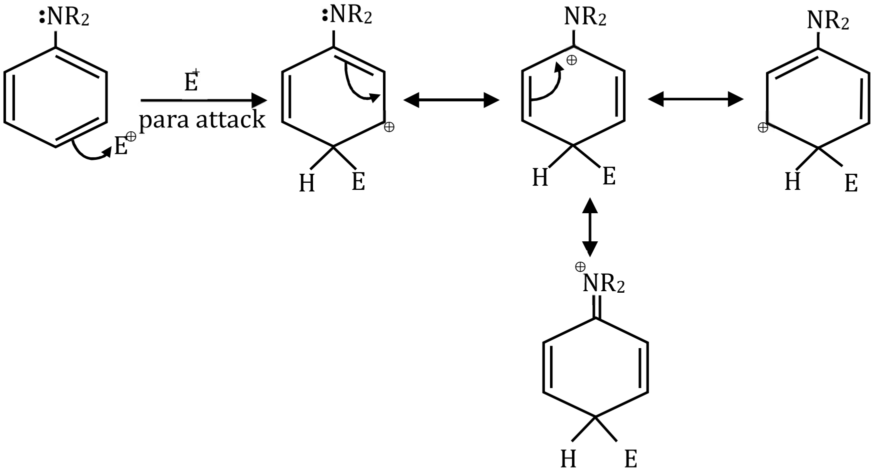


More number of resonating structures for σ-complex. Carbocation of ipso carbon can be stabilized by +M nature of $-\ddot{N}R_2$

More stable σ-complex.



Fewer resonating structures for the σ-complex indicate lower stability. Additionally, there is no carbocation formation at the ipso carbon, which means there is no positive Mesomeric (+M) effect of $-\ddot{N}R_2$.

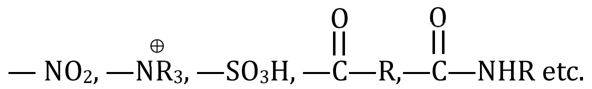


Again, more stable σ-complex through para-attack.

when a group with $-\ddot{N}R_2$ structure is present, it directs the incoming molecules to the ortho and para positions during a reaction. This is because it helps form a more stable structure called a σ-complex when attacked at these positions. As a result, the reaction happens more quickly at the ortho and para positions compared to the meta position.

When the central atom carries a complete positive charge or a partially positive charge, a more stable σ-complex forms through a meta-attack. Consequently, substituents with these characteristics act as meta directors.

e.g.,



$-NO_2, -\overset{\oplus}{N}R_3, -SO_3H, -\overset{O}{\overset{||}{C}}-R, -\overset{O}{\overset{||}{C}}-NHR$ etc.

NOTE

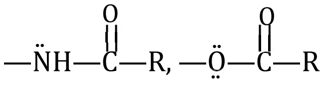
i. Generally, when the central atom has a lone pair, it acts as an ortho-para director and activator. When the central atom has a positive charge or partial positive charge, it serves as a meta director and deactivator.
ii. Halogens direct towards ortho and para positions but deactivate the benzene ring.
iii. Alkyl groups direct towards ortho and para positions because of hyperconjugation.
iv. The –CX group acts as a meta director due to reverse hyperconjugation.

Ortho-Para director
Strongly activating

$-\ddot{\underset{..}{O}}:^{-}, -\ddot{N}H_2, -\ddot{\underset{..}{O}}H$

$-NR_2, -NHR, -OR,$

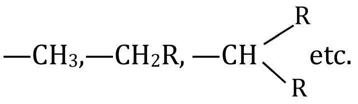
Moderately activating



$-\ddot{N}H-\overset{O}{\overset{||}{C}}-R, -\ddot{\underset{..}{O}}-\overset{O}{\overset{||}{C}}-R$

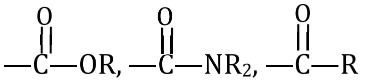
Weakly activating

$-Ar, -R, -CH = CH_2$



$-CH_3, -CH_2R, -CH\langle^{R}_{R}$ etc.

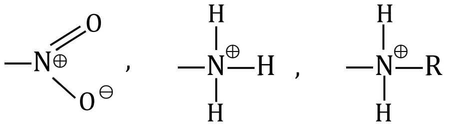
Meta-director
Moderately deactivating



$-\overset{O}{\overset{||}{C}}-OR, -\overset{O}{\overset{||}{C}}-NR_2, -\overset{O}{\overset{||}{C}}-R$

$-CF_3, -CCl_3, -SO_3H, -CHO, -COOH, -COCl$

Strongly deactivating



$-N^{\oplus}(=O)O^{\ominus}, -\overset{\oplus}{N}H_3, -\overset{\oplus}{N}H_2R$

$-CN, -NO_2$

Weakly deactivating

$-F, -Cl, -Br, -I$

When two groups are already present, we analyze the position of a third group by comparing the electron density at the remaining positions.

For instance, in the given compounds, electrophilic substitution will occur at the positions that are indicated.