

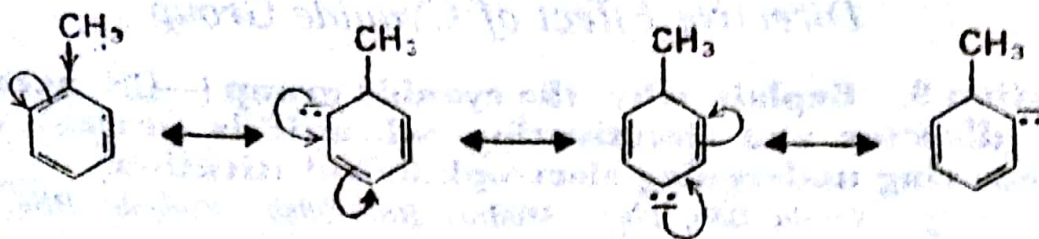
## Directive Effect of Substituents

### Ortho-Para Directors

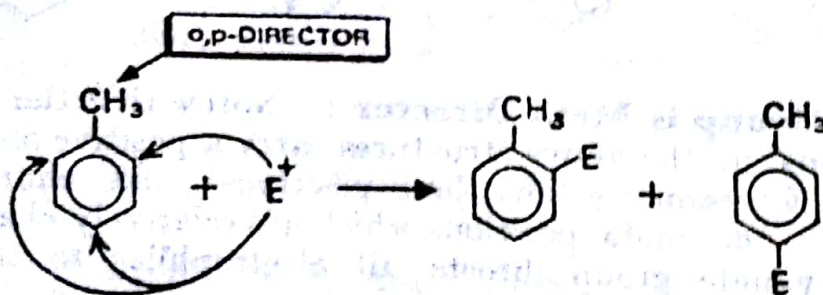
**Question 10.** Explain why the methyl group ( $-\text{CH}_3$ ) acts as an ortho-para director but activating when it is present on a benzene ring undergoing electrophilic substitution.

(Annamalai BSc, 1980 ; Kerala BSc, 1980 ; Bangalore BSc, 1981 ; Udaipur BSc, 1982)

**ANSWER.** Toluene can be represented as a hybrid of the following resonance structures :



**Why  $-\text{CH}_3$  Group is Ortho-Para Director ?** In toluene, the  $+I$  effect of the methyl group initiates the mesomeric effect. Notice that the ortho and para positions in the above resonance structures carry a negative charge. An electrophile ( $\text{E}^+$ ) will attack these positions (Opposite charges attract). Thus, the methyl group directs all electrophiles to the ortho and para positions.



**Why  $-\text{CH}_3$  Group is Activating ?** (Reminder : The  $-\text{CH}_3$  group is activating. This means that toluene undergoes electrophilic substitution faster than benzene). The methyl group donates electrons to the ring by inductive effect. It increases electron density of the ring and makes it more attractive to an incoming electrophile. Thus, the electrophilic substitution is fast as compared to benzene.

**Question 11.** Explain why toluene undergoes...

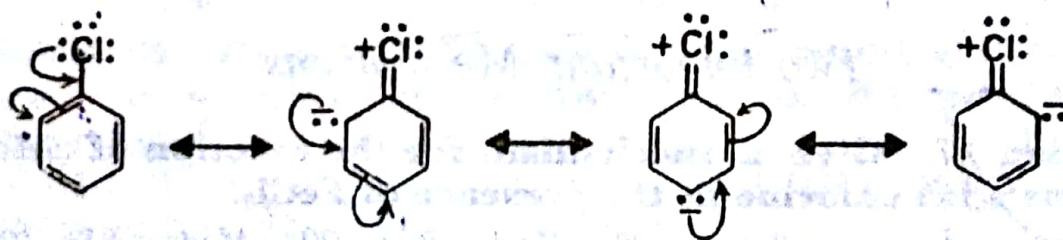


Effect of Halogens

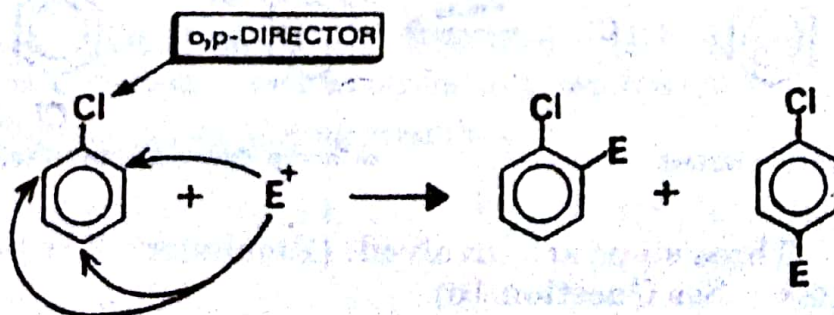
**Question 16.** Explain why the chlorine (or bromine) atom acts as an ortho-para director but deactivating when it is present on a benzene ring undergoing electrophilic substitution.

(Annamalai BSc, 1980 ; Baroda BSc, 1980 ; Delhi BSc, 1980 ; Himachal BSc, 1980 ; Kurukshetra BSc, 1980 ; Nagpur BSc, 1980 ; Punjabi BSc, 1980 ; Udaipur BSc, 1980 ; Guru Nanak Dev BSc, 1981 ; Punjabi BSc, 1981 ; Udaipur BSc, 1981 ; Calcutta BSc, 1982 ; Jammu BSc, 1982 ; Nagpur BSc, 1982 ; Panjab BSc, 1982)

**ANSWER.** Chlorobenzene can be represented as a hybrid of the following resonance structures :



**Why Cl Atom is Ortho-Para Director ?** Notice that the ortho and para positions in the above structures carry a negative charge. An electrophile ( $E^+$ ) will attack these positions (Opposite charges attract). Thus, the chlorine atom directs all electrophiles to the ortho and para positions.



$\text{CHalogenX} \rightarrow$  undergo mesomeric effect & Inductive effect. Mesomeric effect  $\rightarrow e^-$  releasing & an  $o, p$  directing effect. Directive Effect of Substituents due to resonance or mesomeric effect.

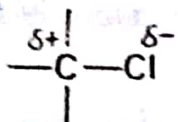
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**Why —Cl Atom is Deactivating?** (Reminder: The —Cl atom is deactivating. This means that chlorobenzene undergoes electrophilic substitution more slowly than benzene). This is because two opposing effects operate simultaneously.

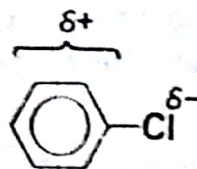
(a) **Mesomeric Effect.** The interaction between the lone pair of electrons on chlorine and the  $\pi$  electrons of the ring places negative charge at the ortho and para positions. See the resonance structures. This effect makes —Cl atom  $o, p$ -director.

(b) **Inductive Effect.** Opposing the mesomeric effect is an inductive effect. Recall, chlorine is more electronegative than carbon. Therefore, the C—Cl bond is polar. The chlorine atom has a small negative charge ( $\delta^-$ ) and the carbon has a small positive charge ( $\delta^+$ ).

$\text{X} \rightarrow$  are deactivating due to Inductive effect (—I)



POLAR CARBON-CHLORINE BOND



POLAR BENZENE-CHLORINE BOND

Because carbon is slightly positive, it will pull electrons away from the ring. The lowering of the electron density in the ring caused by this inductive effect makes chlorobenzene less reactive toward electrophilic substitution than benzene.

Combination of these two effects makes chlorobenzene deactivated overall but with  $o, p$ -directing effect.

**MEMORISE.** Other halogens (—Br, —I, —F) behave in the same way. That is, they are also  $o, p$ -directing but deactivating.

## Two Important Mechanisms



→ ~~the~~ ~~orientation~~

Incoming gr. के लिए

Reactivity

→ A Ring पर attached gr. only

reactivity को ही नहीं but orientation को भी determine करता है.

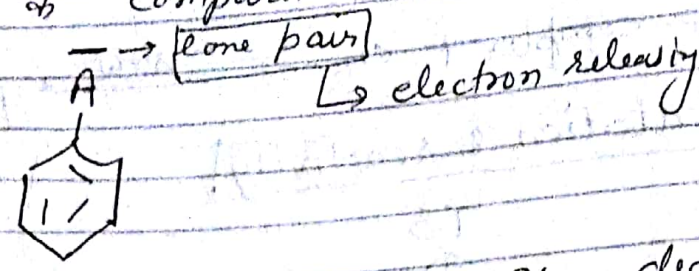
orientation

What position of the ring

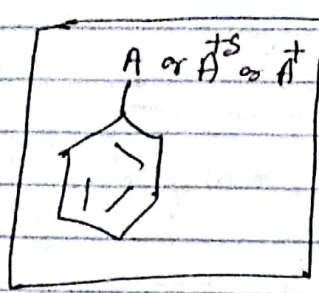
→ Reactivity

How readily the attack

→ Electron releasing gr ring को activate की है, जिसे आगे electrophilic substitution की rate Benzene के comparison में उच्च हो पाती है



↳ while  $e^-$  withdrawing gr decrease की देती है



↳ Other reaction के समय electrophilic substitution की rate depends on the difference b/w the energy of T.S & ground state of the reactants like energy of activation ( $E_{act}$ ). Since the rate determining step of electrophilic aromatic substitution is usually the formation of  $\sigma$ -complex. Ignoring the  $\pi$ -complex.

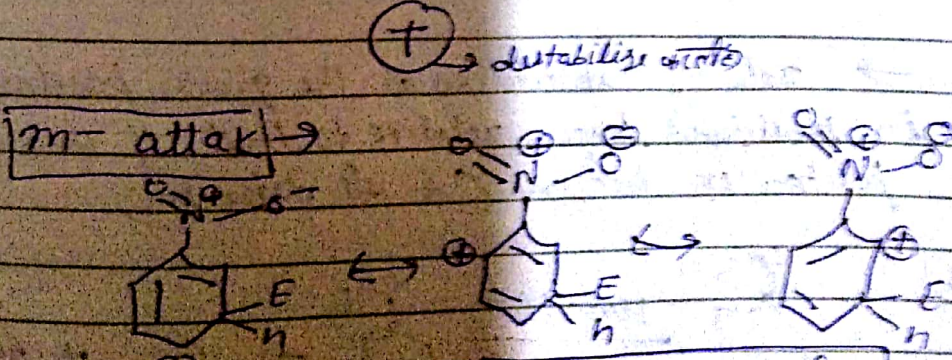
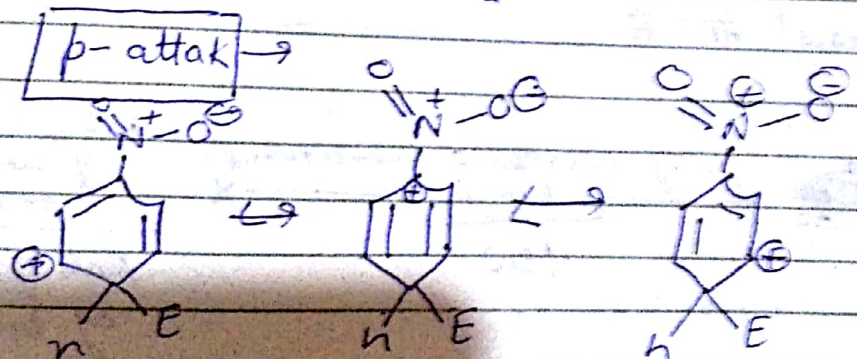
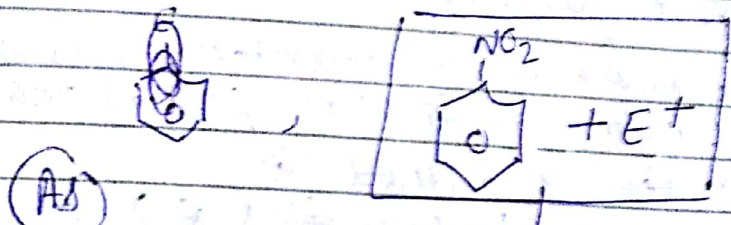
↳ o, p, & m-position पर substitution की rate reactant & T.S ( $E_{act}$ ) के बीच energy-barrier की height पर depend करती है। यहाँ कोई भी factor, substituent के कारण  $E_{act}$  को कम कर देता है तो substitution की rate बढ़ जाती है & attack के लिए 'favoured' orientation (position) वह होगा जिसका  $E_{act}$  को lowest कर देता है।



→ दोनों effect यदि same direction में हों तो Reinforce यदि opposite में हों तो Oppose करते हैं

↳ So electron donating substituent (Inductive effect or resonance effect), electrophile को stabilize करते हैं जो +vely charged  $\sigma$ -complex को बना देते हैं। So rate of reaction को बढ़ा देते हैं।

↳ while  $e^-$  withdrawing ग्रुप की तरह  $\sigma$ -complex को destabilize करते हैं +ve charge को Intensified करते हैं जिससे rate of reaction कम हो जाती है।



→ T like  $\Delta$  में  $\sigma$  complex  
 ↳ So m-attack का



O-attack → 1 st

→ orientation in other ring system

→ Activating power →

$-OH, -NR_2, O^{\ominus}, -NH_2 > -OR > OCOR > NHCOCH_3 > C_6H_5 > H$

→ Quantitative treatment