

# **Aromatic Electrophilic Substitution**

3<sup>rd</sup> Sem  
Lecture – 2  
Paper – CC7

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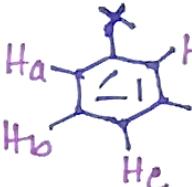
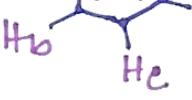
Assistant Professor

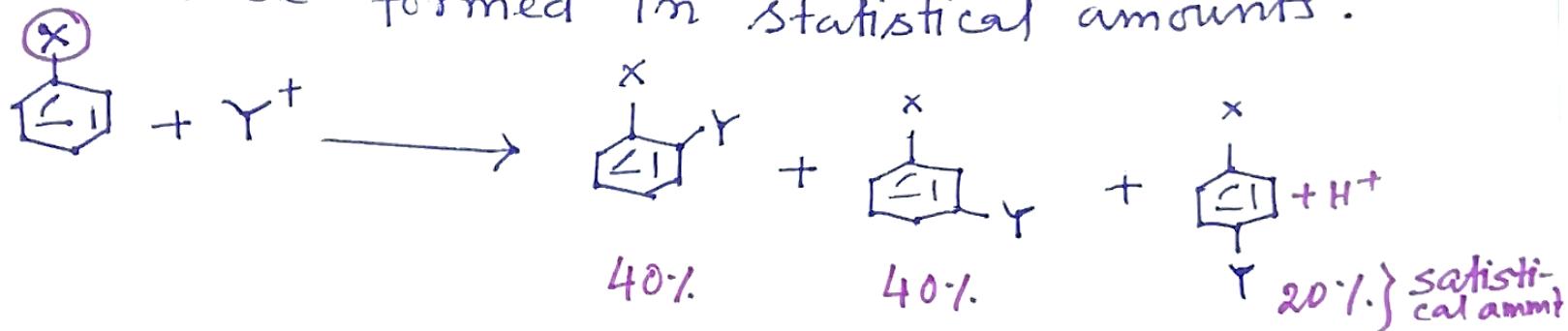
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# Aromatic Electrophilic Substitution

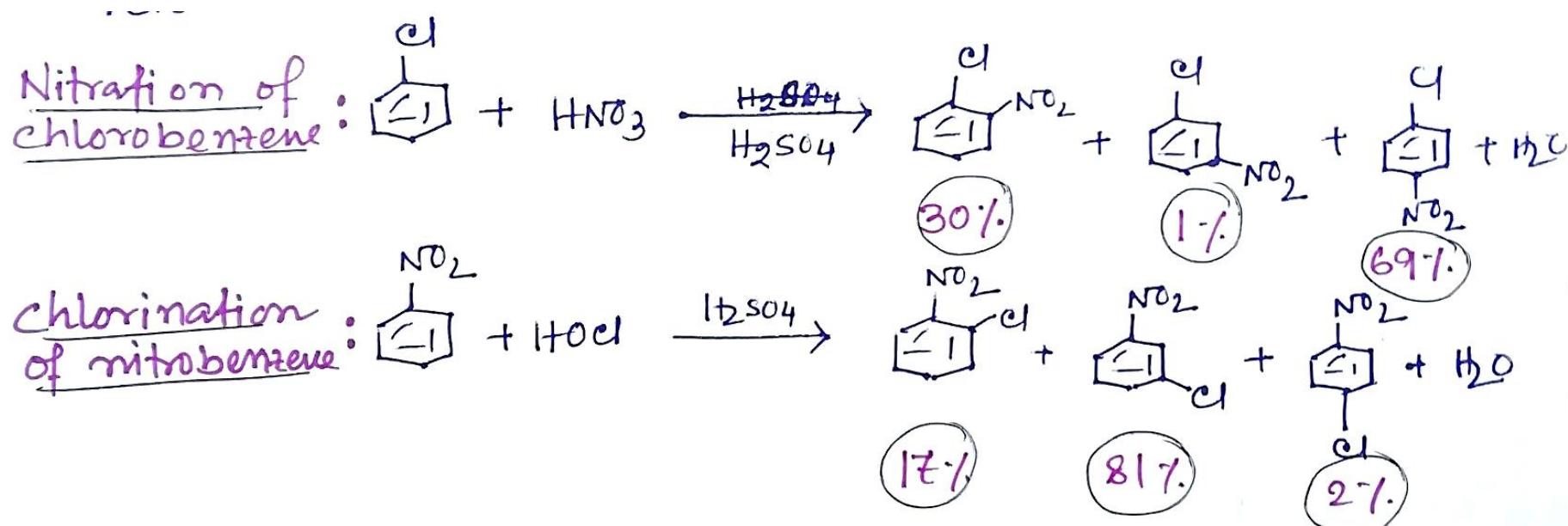
## Effect of substitution Lecture-9 / orientation & Reactivity 1

In mono substituted benzene there are three types of non equivalent protons  . If these H's were replaced with equal case,  the three disubstituted pdts would be formed in statistical amounts.



But actually the above statistical amounts of pdts does not formed.  $\rightarrow$  this is illustrated by following reac<sup>n</sup>.

# Aromatic Electrophilic Substitution



From above two reac<sup>n</sup> we can conclude that the isomer distribution, the rate of the reac<sup>n</sup> are influenced by substituent (here 'x') in monosubstituted benzene. The role played by substituent ('x') is said to exert a directive effect. The substituent groups affect both the reactivity and orientation in electrophilic aromatic substitutions.

# Aromatic Electrophilic Substitution

## Reactivity and Orientation:-

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- ◻ According to reactivities of substituent groups they are classified as —
  - (i) Activating groups :- Those substituents which cause the ring to be more reactive than benzene itself.
  - (ii) Deactivating groups :- those that cause the ring to be less reactive than benzene. ~~are~~
- ◻ According to orientation, substituents groups are divided into two classes.
  - (i) Ortho and Para directing :- A class of substituents tend to bring about  $E^+$  primarily at ortho and para to themselves.
  - (ii) Meta directing :- Other class tend to direct the incoming  $E^+$  to meta position.

# Aromatic Electrophilic Substitution

Activating groups : Ortho - Para directors :-

Strongly activating groups :-  $\text{-NH}_2$ ,  $\text{-NHR}$ ,  $\text{-NR}_2$ ,  $\text{-OH}$ ,  $\text{-O}^-$

Moderately activating groups :-  $\text{-NHCOCH}_3$ ,  $\text{-NHCOR}$ ,  $\text{-OCBz}$ ,  $\text{-OR}$   
 $\text{Ph-Ph}$

Weakly activating groups :-  $\text{-CH}_3$ ,  $\text{-C}_2\text{H}_5$ ,  $\text{-R}$ ,  $\text{-CH}_2\text{H}_5$

Deactivating groups :- Meta directors

Moderately deactivating :-  $\text{-C}\equiv\text{N}$ ,  $\text{-SO}_3\text{H}$ ,  $\text{-COOH}$ ,  $\text{-CO}_2\text{R}$ ,  $\text{-C}_6\text{H}_5$ ,  
 $\text{-COR}$

Strongly deactivating :-  $\text{-NO}_2$ ,  $\text{-NR}_3^+$ ,  $\text{-CF}_3$ ,  $\text{-CD}_3$

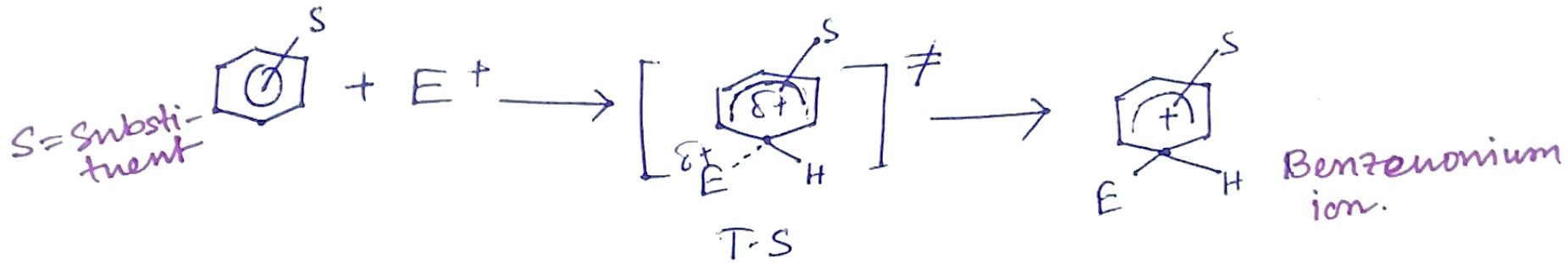
# Aromatic Electrophilic Substitution

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## Theory of reactivity and orientation

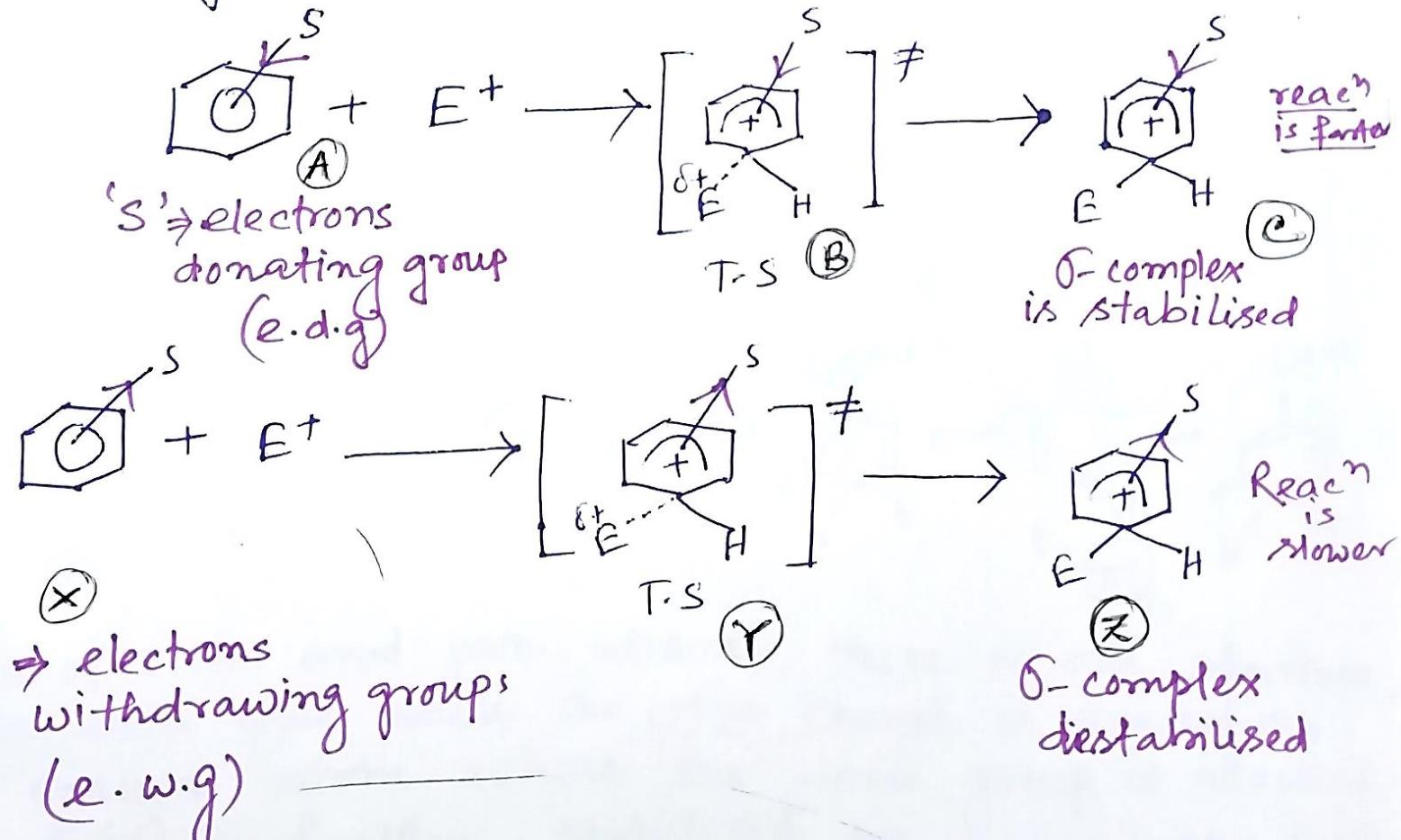
The rate determining step in electrophilic substitutions of substituted benzenes is the step that results in the formation of benzenonium ion. Thus higher the stability of intermediate means higher stability of T-S which lowers the activation energy of the process and speeds up the reac<sup>n</sup>.

We can write the E<sup>+</sup> subtn reac<sup>n</sup> as follows

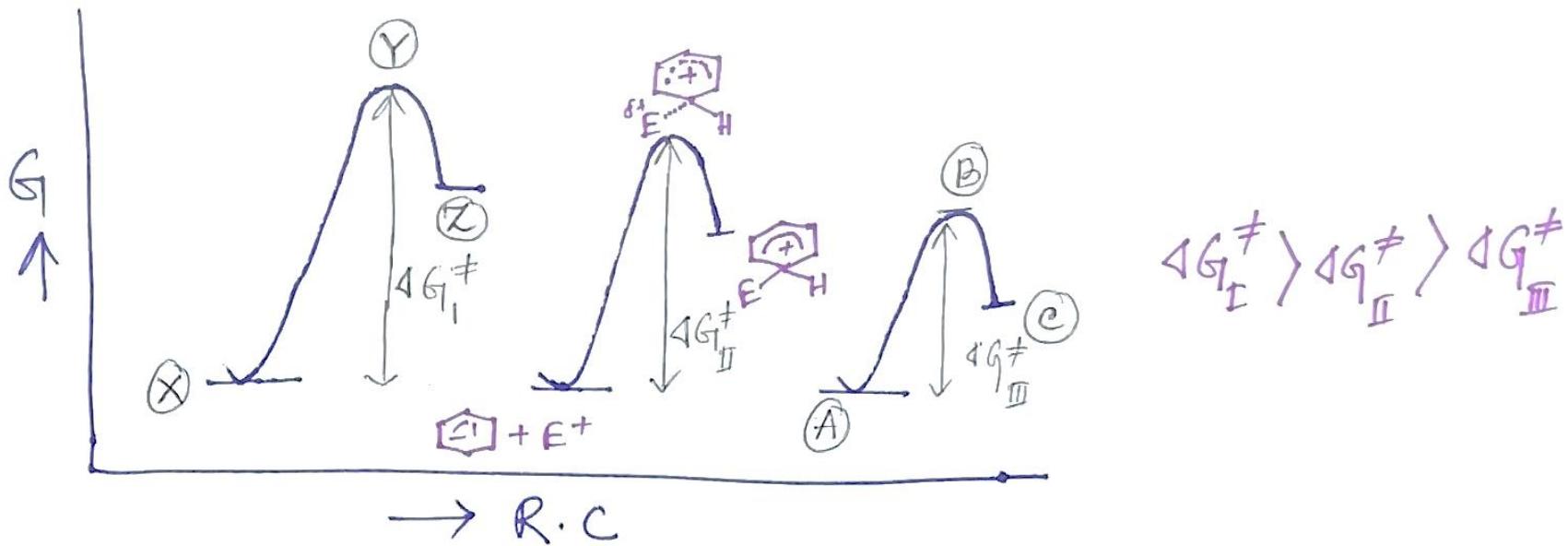


# Aromatic Electrophilic Substitution

The relative rates of the reac<sup>n</sup> depend on whether S is e<sup>-</sup> withdrawal or e<sup>-</sup>-releasing. If 'S' is e.w.g, the reac<sup>n</sup> is slower than that of benzene and if 'S' is e.d.g, then the reac<sup>n</sup> occurs faster than benzene.



# Aromatic Electrophilic Substitution



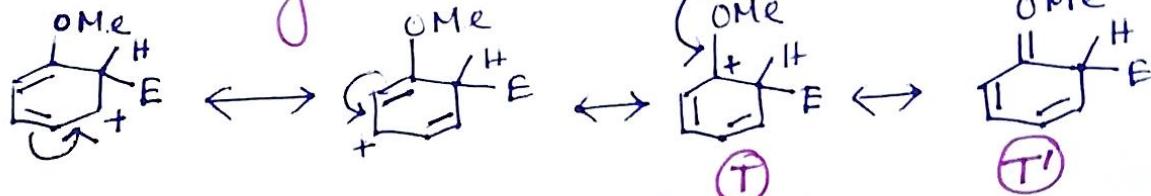
## ■ Theory of orientation :-

The orientation of the substituents can be explained by considering the relative stability of  $\sigma$ -complexes during attack at ortho, meta and para positions.

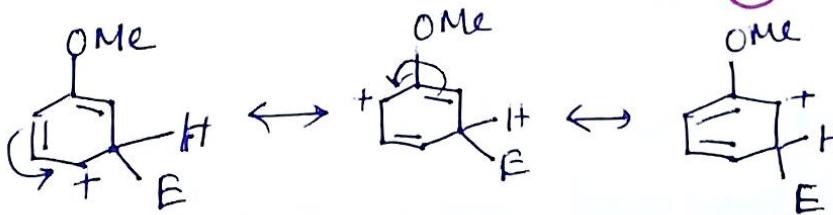
# Aromatic Electrophilic Substitution

When electron donating substituent is present :-

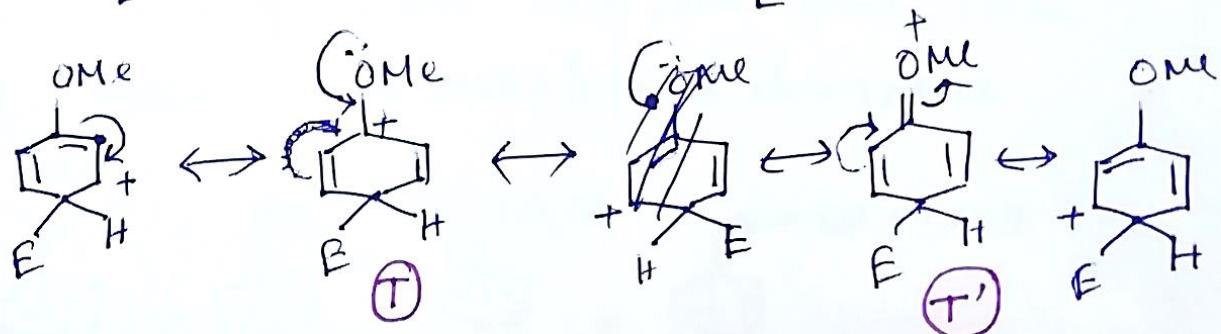
Ortho attack :-



meta attack :-



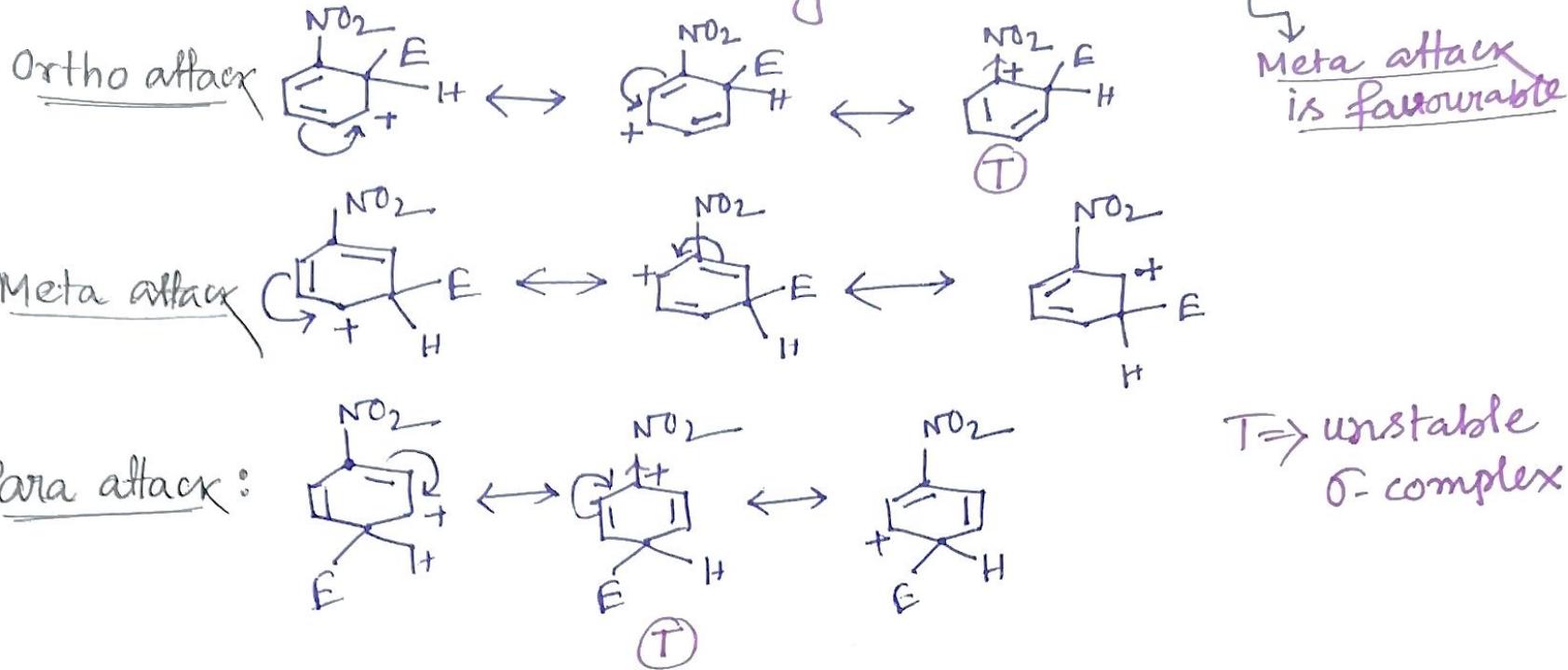
para attack :-



In case of ortho and para attack, there is one structure ( $T$ ) in each case where the (+)ve charge is located on that carbon atom where the  $-\text{OMe}$  group is attached. Such str. ( $T$ ) is further stabilised by e.d.g.  $-\text{OMe}$  ( $T'$ ). Such stabilisation is absent when  $\text{E}^+$  attacks on meta carbon.

# Aromatic Electrophilic Substitution

When electron withdrawing substituent is present :-

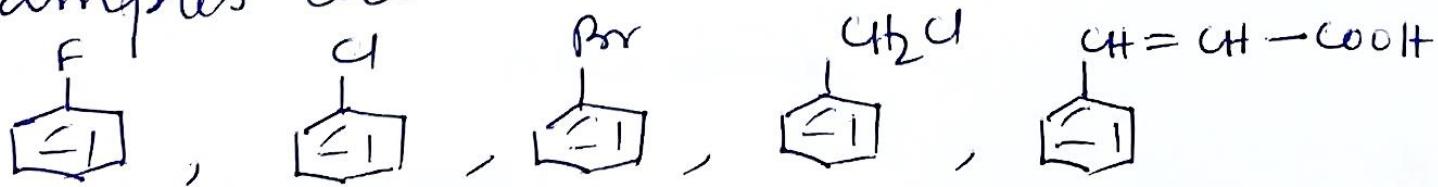


In this case, during ortho, para attack  $\textcircled{T}$  str. is formed in each case which is unstable bcz (+) ve charge is located on the carbon atom to which electron withdrawing group ( $-\text{NO}_2$ ) is attached. Such case is absent for meta attack.

# Aromatic Electrophilic Substitution

## ■ Deactivating Ortho - Para directors :-

HaloBenzene, benzylchloride and cinnamic acid react more slowly than benzene but form ortho and para - di. substituted benzene examples are

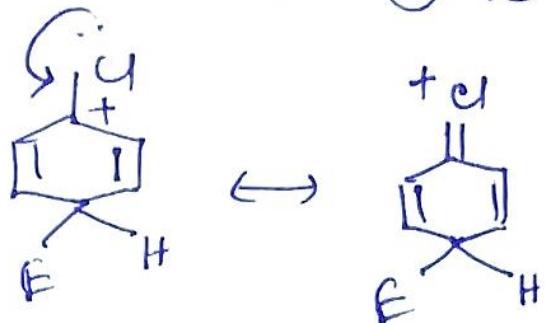


This anomalous phenomenon can be explained by considering Inductive effect and Resonance effects of halogens or other substituents. These groups withdraw e<sup>-</sup>s by -I effect and thereby deactivate the ring ring towards E<sup>+</sup> attack.

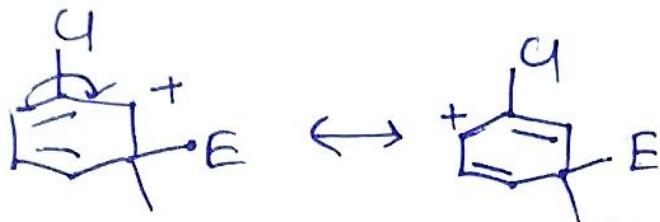
# Aromatic Electrophilic Substitution

On the other hand halogens are capable of sharing the  $e^-$  pairs with the aromatic ring and can accommodate a  $\oplus$  ve charge.

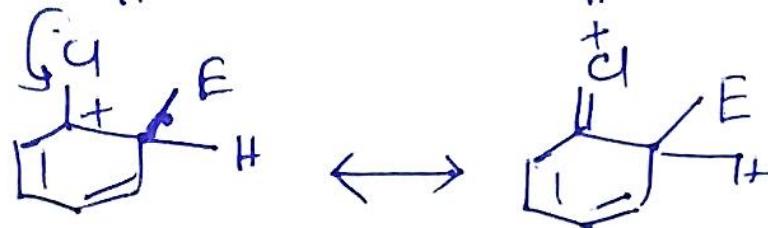
p-attack



m-attack

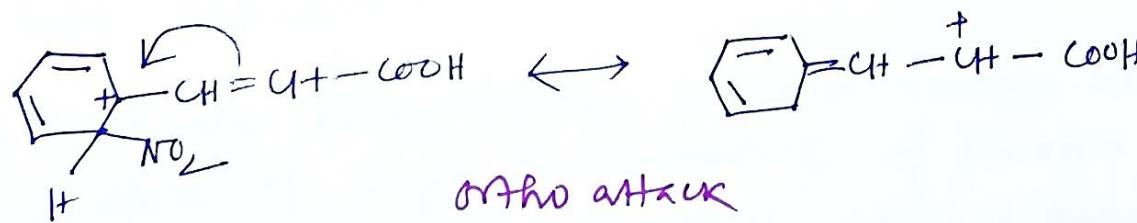
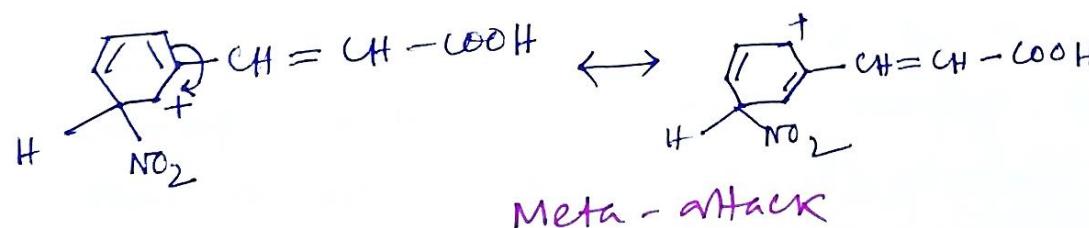
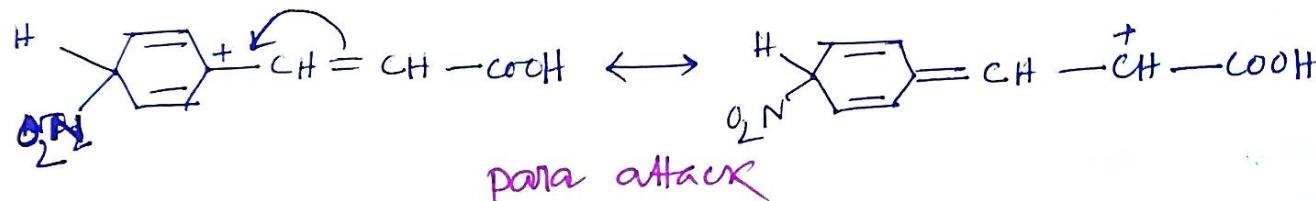


o-attack

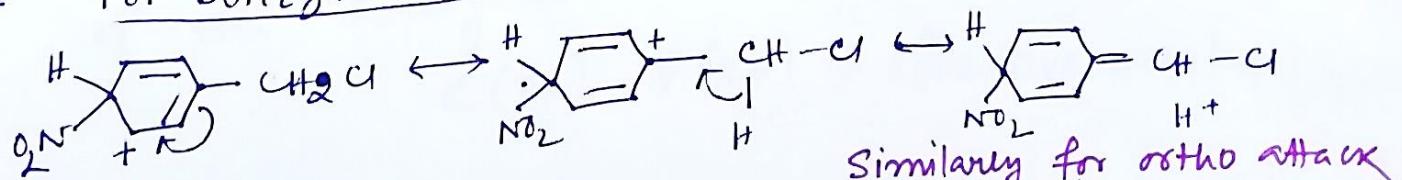


# Aromatic Electrophilic Substitution

For cinnamic acid in nitration :-



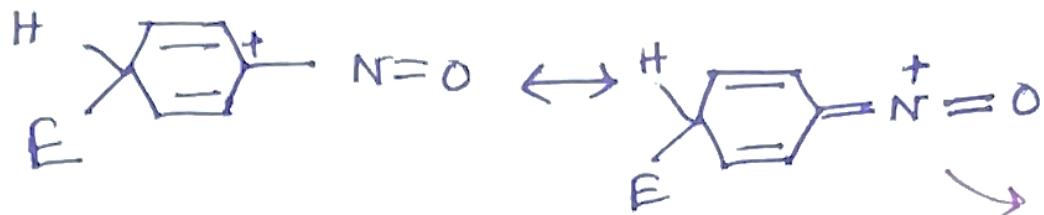
\*\* For benzyl chloride :-



Hence the hyperconjugation with the methyl C-H bonds stabilised the  $\text{O}^+ \text{P}^-$  benzoniun ion.

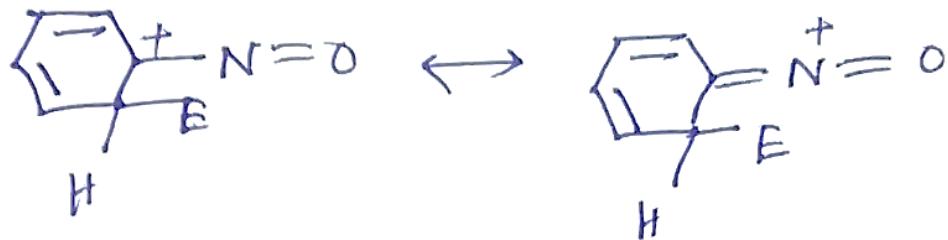
# Aromatic Electrophilic Substitution

Similarly  $-NO$  (nitroso group) behaves like halogen.



Similarly for ortho attack

Stable  $\sigma$  complex as all atoms have fulfilled octet.



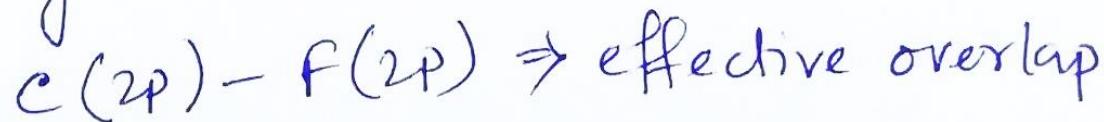
# Aromatic Electrophilic Substitution

## Points to be noted :-

- (1) Though oxygen is more electronegative than  $-Cl$ ,  $-Br$  yet  $-OH$  gr. is an activating group, whereas halogens are deactivating grs. This can be explained by considering relative stability of benzenonium ion by resonance stns. involving a group  $Z$  ( $Z \Rightarrow -NH_2, -OH, -F, -Cl, -Br, -I$ ) that is directly attached to benzene ring in which  $Z$  donates an  $e^-$  pair. If  $Z = -OH, -NH_2$ , these resonance stns. is stabilised by the  $2p(c)$  and  $2p(O\text{ or }N)$  overlap which is favourable overlap. But for halogens ( $-Cl, -Br, -I$ ) this is  $2p(c) - 3p(-Cl, -Br, -I)$  overlap which is less effective.

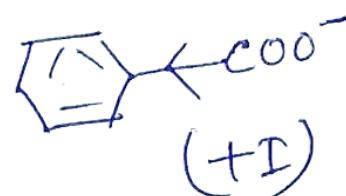
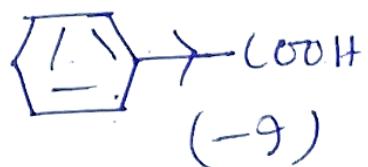
# Aromatic Electrophilic Substitution

\* Similarly Fluorobenzene is most reactive halobenzene in spite of high electronegativity of fluorine atom, and -F is most powerful ortho & para director of the halogens.



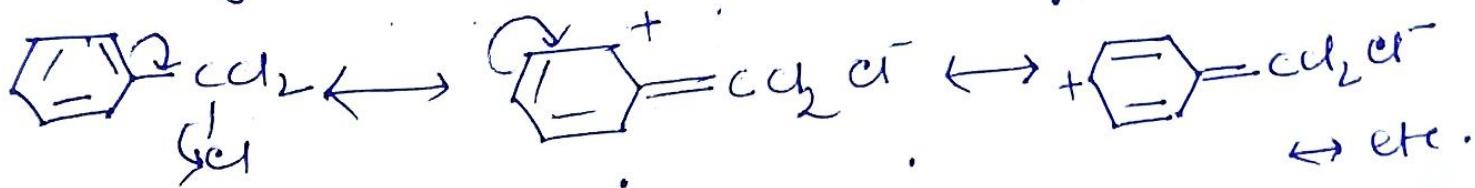
(2)

-COOH gr. m- orienting, but  $-COO^-$  ion is O+P orienting. Bcz -ve charge on each oxygen atom giving the  $-COO^-$  ion electron repelling properties (+I effect) in contrast to the  $-COOH$  group which is electron attracting (-I)

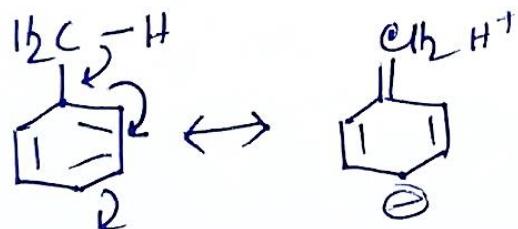


# Aromatic Electrophilic Substitution

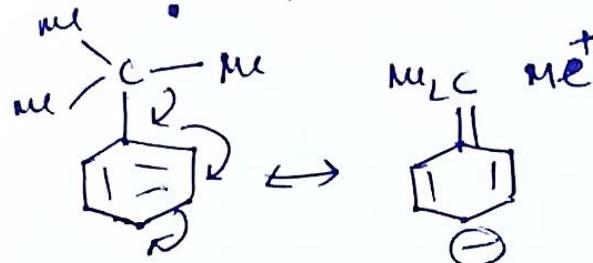
- ③  $-C\bar{C}l_2$  gr. is  $m$ -directing, explained by hyperconjugation.



- ③ In toluene  $-C\bar{C}l_2$  gr. is better e- donor than that of  $-CMe_3$  gr.



toluene is more reactive



less important bcz.  
c-c hyperconjugation  
is less important than  
C-H

