# MARUDHAR KESARI JAIN COLLEGE FOR WOMEN,VANIYAMBADI
## PG RESEARCH DEPARTMENT OF CHEMISTRY

**CLASS** : II B.Sc CHEMISTRY

**SUBJECT CODE :** FCH31

**SUBJECT NAME :** GENERAL CHEMISTRY-III

**SYLLABUS**

## UNIT-III

Aromaticity - Modern Theory of Aromaticity - Huckel's (4n +2) Rule and Its Simple Applications to Benzenoid and Non- benzenoid Compounds - Electrophilic substitution reactions in Aromatic Compounds - Mechanisms of Nitration, Halogenations, Sulphonation, Friedel-Crafts Acylation and Alkylation - Directive influence - Orientation - Ortho/Para ratio - Nuclear and Side chain Halogenation.

## Aromaticity

In organic chemistry, aromaticity is a property of cyclic, planar structures with a ring of resonance bonds that gives increased stability compared to other geometric or connective arrangements with the same set of atoms. Aromatic molecules are very stable, and do not break apart easily to react with other substances

**Aromaticity** is a characteristic in which any planar system in which there is complete delocalisation of pi electron in the ring,and the system contain 4n+2 pi electrons in the ring is called aromatic.

Example : Benzene, naphthalene, anthracene etc.

## Modern theory of aromaticity

The **modern theory of aromaticity** was given by Erich Huckel in 1931. According to this **theory**, for a compound to exhibit **aromaticity**, it must have the following properties: Delocalization of the π–electrons of the ring system. Planarity of the molecule.

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## Planarity of the molecule.

- To permit sufficient or total delocalization of π–electrons, the ring must be planar toallow cyclic overlap of the p–orbitals.

**Huckel Rule or (4n + 2) Rule:** This rule states that for a compound to exhibit aromatic character, it should have a conjugated, planar cyclic system containing 4n + 2 (where n = 1, 2...) delocalized π– electrons forming a cyclic cloud of delocalized π–electrons above and below the plane of the molecule. This is known as Huckel rule of 4n + 2 π–electrons.

In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has 4n+2 π electrons, it is considered aromatic. This rule would come to be known as Hückel's Rule.

## Four Criteria for Aromaticity

When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has $4n+2$ $\pi$ electrons ($n=0$ or any positive integer)

## Why $4n+2$ $\pi$ Electrons?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons.

This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving all bonding orbitals filled and no anti-bonding orbitals occupied

This gives a total of $4n+2$ $\pi\pi$ electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below. Benzene has 6 $\pi\pi$ electrons.Its first 2 $\pi\pi$ electrons fill the lowest energy orbital, and it has 4 $\pi\pi$ electrons remaining.These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.To apply the $4n+2$ rule, first count the number of $\pi$ electrons in the molecule. Then, set this number equal to $4n+2$ and solve for n. If is 0 or any positive integer (1, 2, 3,...),the rule has been met. For example, benzene has six $\pi\pi$ electrons:

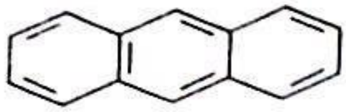
4n+24nn=6=4=1(15.4.1)(15.4.2)(15.4.3)(15.4.1)4n+2=6(15.4.2)4n=4(15.4.3)n=1

For benzene, we find that $n=1$, which is a positive integer, so the rule is met.

## Benzenoid and Non Benzenoid Compounds

Non benzenoid aromatic compound are chemical compounds with conjugated pi-electron system with ring of 5 to 7 carbon atoms.Benzenoid compounds have at least one benzene ring in the molecule whereas non-benzenoid compounds are aromatic compounds with conjugated pi-system but do not benzene ring.

3. **Anthracene**

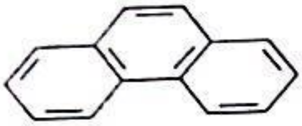


$n = 3$

$(4n + 2)\ \pi = (4 \times 3) + 2$

$= 14\ \pi$ electrons (aromatic)

4. **Phenanthrene**



$n = 3$

$(4n + 2)\ \pi = (4 \times 3) + 2$

$= 14\ \pi$ electrons (aromatic)

Both anthracens and phenanthrene contain 14 π electrons Thus they obey Huckel's rule. Hence it is aromatic.

## 3.2 ELECTROPHILIC SUBSTITUTIONS IN AROMATIC COMPOUNDS

### 3.2.1 Electrophiles

Electrophiles are electron-deficient species. They are either positively charged (or) neutral.

**Examples:** $\overset{\oplus}{NO_2}$ (Nitronium ion), $\overset{\oplus}{NO}$ (Nitrosonium ion)

$Cl^{\oplus}$ (Chloronium ion), $Br^{\oplus}$ (Bromonium ion)

$CH_3 - \overset{\oplus}{CO}$ (Acylium ion)

$BF_3$, $AlCl_3$, $FeCl_3$, $SnCl_4$, $ZnCl_2$ etc.

Electrophiles are attacking reagents in many organic reactions. They seek a centre of high electron density in the substrate molecule.

## 3.2.2 Electrophilic substitution reactions

The displacement of an atom (or) group from benzene (or) aromatic compound by an electron-deficient group (electrophile) is called aromatic electrophilic substitution.

### Mechanism

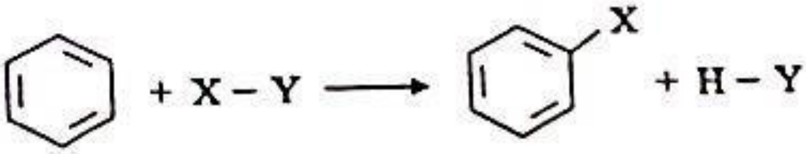
The aromatic electrophilic substitutions proceed in two steps.

### I-Step

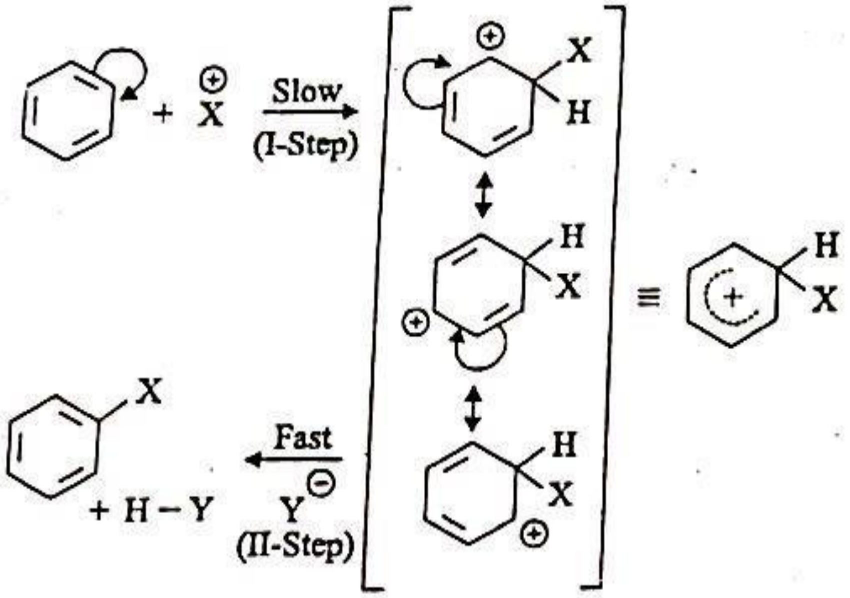
In the first step (called the rate-determine step), the electrophile attacks the π-electrons of the benzene ring forming an intermediate carbonium ion. This intermediate carbonium ion is called by various names – Wheeland intermediate, σ-complex, aronium cation etc. This carbonium ion is stabilized by resonance.

### II-Step

The second step is a fast step in which a proton is released from the intermediate carbonium ion by an anionic species to form the substituted product.



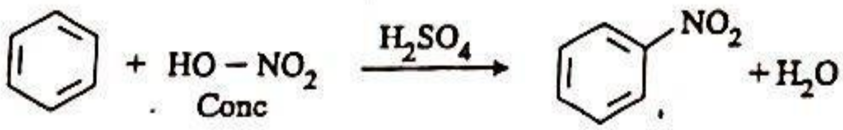
$$X-Y \longrightarrow \overset{\oplus}{X} + \overset{\ominus}{Y}$$



### 3.2.3 Nitration

Substitution of one hydrogen atom of the benzene ring (or aromatic ring) by a nitro group is called nitration.

When benzene is heated with a mixture of conc. $HNO_3$ and conc $H_2SO_4$, nitrobenzene is formed.



**Mechanism**

Nitration is an electrophilic substitution. The attacking electrophile is nitronium ($NO_2^{\oplus}$) ion. This fact has been confirmed by Raman spectrum and cryoscopic studies.

Nitronium ion is formed by the reaction between $HNO_3$ and $H_2SO_4$.

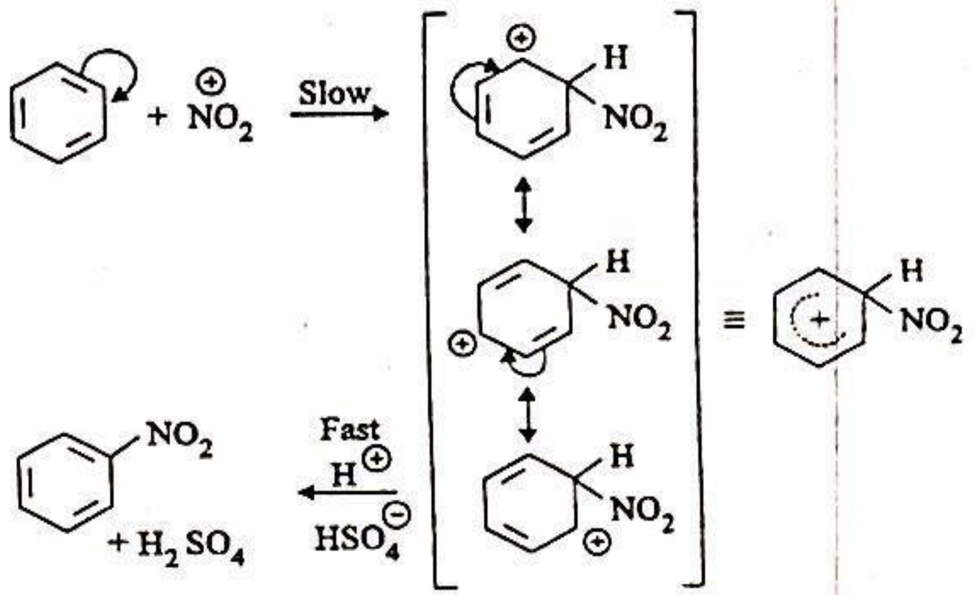
$$HNO_3 + 2H_2SO_4 \rightleftharpoons \overset{\oplus}{H_3O} + \overset{\oplus}{NO_2} + 2HSO_4^{\ominus}$$

**Step 1**

This nitronium ion attacks the π electron in benzene ring and gives an intermediate carbonium ion. This carbonium ion is stabilized by resonance. It is a slow process.

**Step 2**

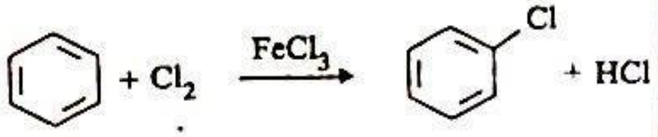
Next step is the fast step here $HSO_4^-$ attracts $H^+$ ion from benzene ring and forms nitrobenzene.



### 3.2.4 Halogenation

Displacement of one hydrogen atom of the benzene ring by a halogen atom is known as halogenation.

In the presence of halogen-carrier (like $FeCl_3$), benzene reacts with $Cl_2$ (or) $Br_2$ to form chlorobenzene (or) bromobenzene.

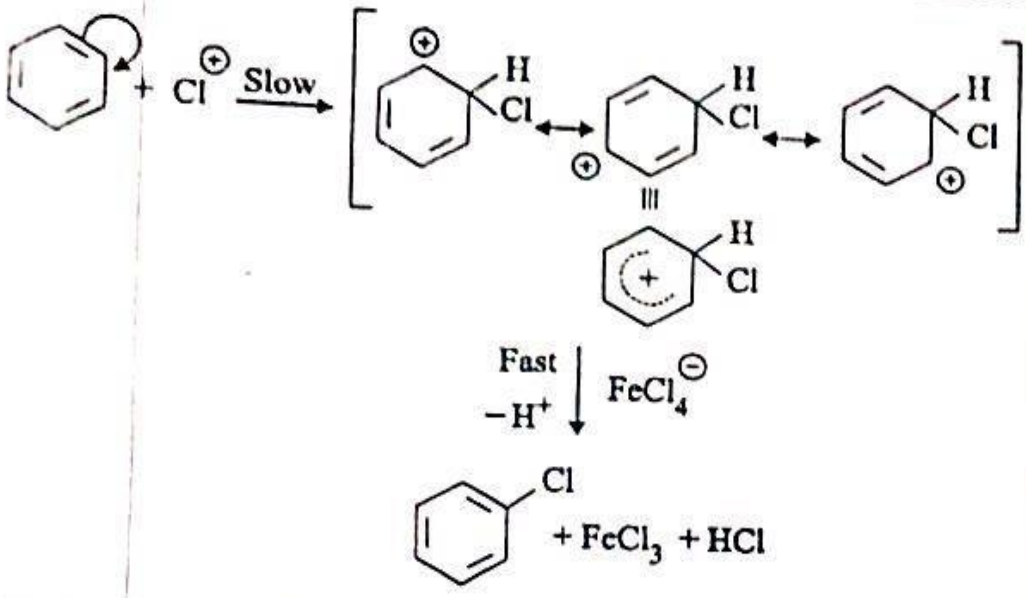


$FeCl_3$, $FeBr_3$, Fe, $ZnCl_2$, $AlCl_3$ are halogen carriers.

**Mechanism**

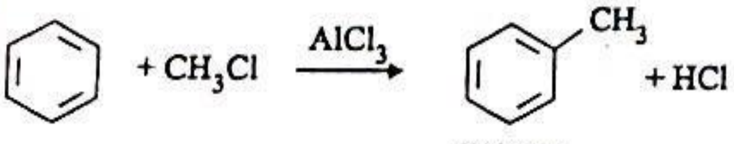
Halogenation is an electrophilic substitution. The attacking electrophile is halonium ion ($Cl^+$ or $Br^+$).

$$:\ddot{Cl}-:\ddot{Cl}: + FeCl_3 \longrightarrow FeCl_4^{\ominus} + Cl^{\oplus}$$



## 3.2.5 Friedel - Craft's alkylation

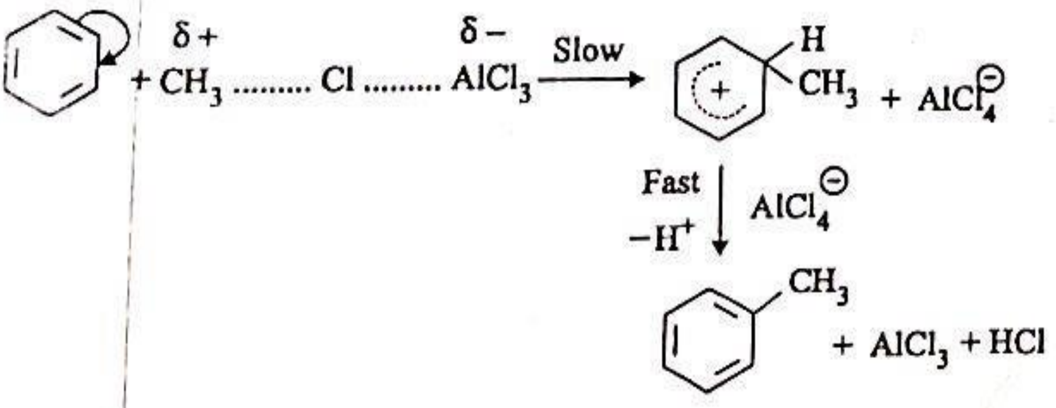
Benzene reacts with an alkyl halide in the presence of anhydrous $AlCl_3$ to form alkylbenzene. This reaction is known as Friedel - Craft's alkylation.



Toluene

**Mechanism**

$$CH_3-\ddot{\underset{..}{Cl}}: + AlCl_3 \longrightarrow \overset{\delta+}{CH_3}\,\cdots\cdots\, Cl \,\cdots\cdots\, \overset{\delta-}{AlCl_3}$$



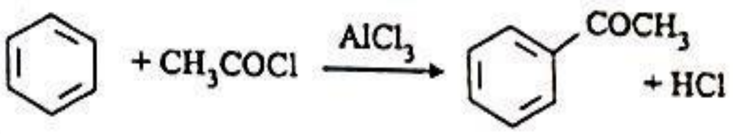
**Draw back**

Friedel - Craft's alkylation suffers from the following drawbacks:

1. Polyalkylation
2. Isomerisation
3. Formation of rearranged products
4. Disproportionation

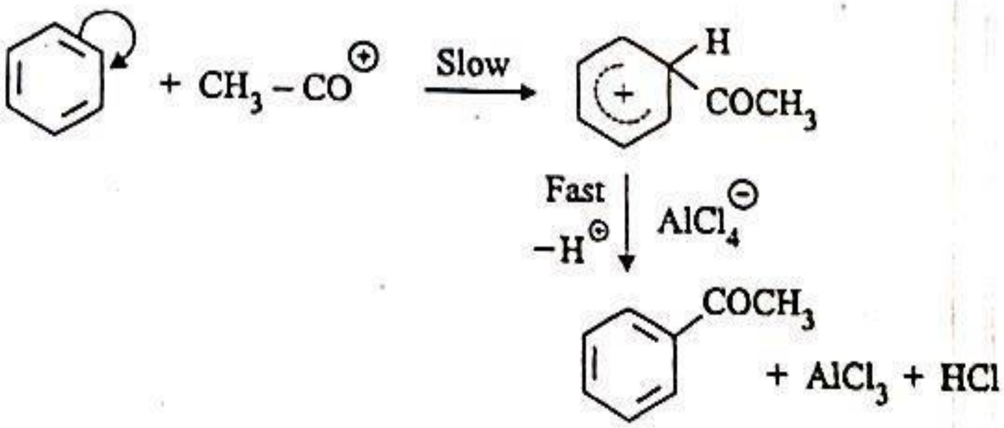
### 3.2.6 Friedel - Crafts acylation

Benzene reacts with an acid chloride in the presence of anhydrous $AlCl_3$ to form a ketone. This reaction is known as Friedel-Crafts acylation.



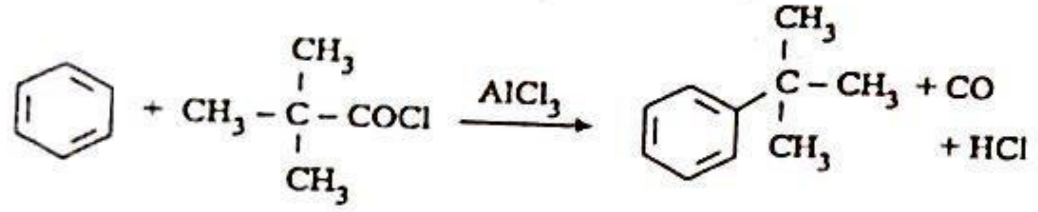
**Mechanism**

$$CH_3-COCl + AlCl_3 \longrightarrow CH_3-\overset{\oplus}{C}O + AlCl_3^{\ominus}$$

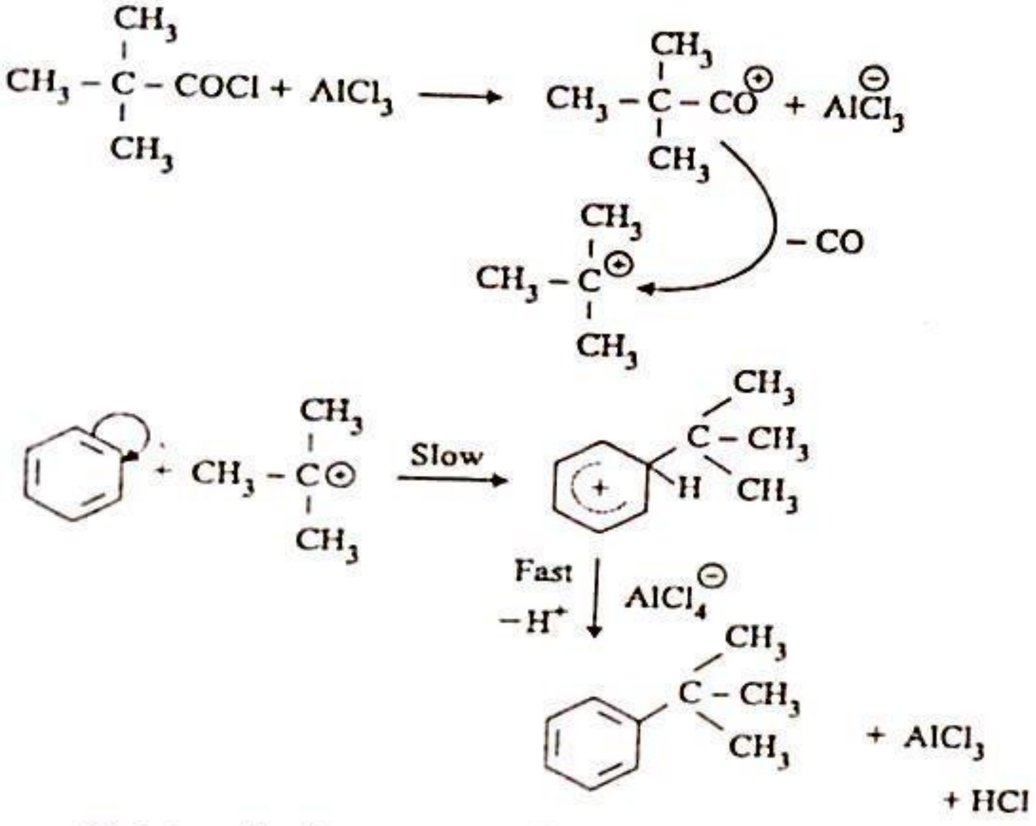


Friedel - Crafts acylation reaction is conducted in solvents like $CS_2$, $C_6H_5NO_2$ etc. Excess of catalyst is used in this reaction. The product forms a complex with the catalyst. Hence polyacylation does not take place.

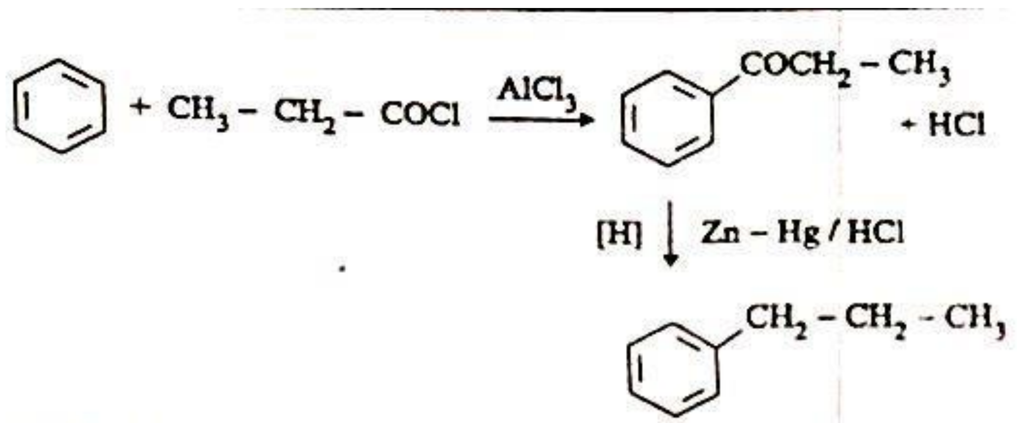
Rearranged products are not formed in Friedel-crafts acylation. But when the $-COCl$ group is attached to a highly branched carbon atom, alkylation takes place instead o acylation.



**Mechanism**



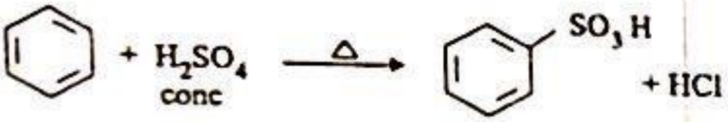
Certain alkylbenzenes, which cannot be prepared by direct alkylation, can be prepared by Friedel-crafts acylation followed by reduction.



### 3.2.7 Sulphonation

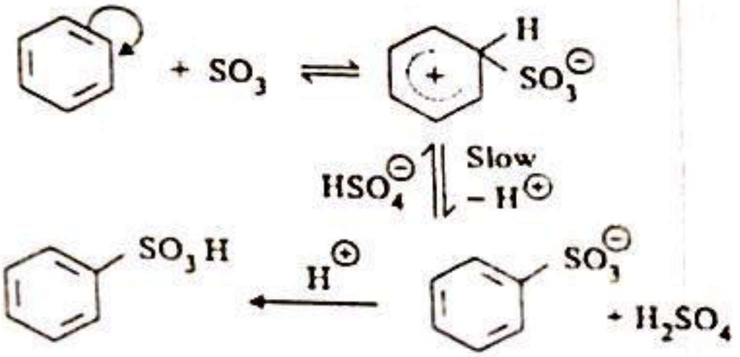
Displacement of one hydrogen atom of the benzene ring by a sulphonic $(-SO_3H)$ group is known as sulphonation

When benzene is heated with conc. $H_2SO_4$, benzene sulphonic acid is formed.



**Mechanism**

$$2H_2SO_4 \rightleftharpoons \overset{\oplus}{H_3O} + SO_3 + HSO_4^{\ominus}$$



Sulphonation differs from other electrophilic substitution reactions in the following aspects:

1. The attacking electrophile in sulphonation is $SO_3$ which is neutral. But in other electrophilic substitutions, the electrophile is positively charged.
2. All the steps are reversible. Hence desulphonation can be effected easily.
3. Proton loss takes place in the slow step, i.e., the rate determining step.

## 3.3 ORIENTING EFFECT IN SUBSTITUTED BENZENES (or) DIRECTIVE INFLUENCE

It is a well known fact that in the preparation of disubstituted benzenes, the group already present in the benzene ring has two important effects.

(i) It governs the reactivity of the nucleus towards further electrophilic substitution.

(ii) It determines the relative position for the new entrant (or) substituent.

### 3.3.1 Classification of substituents (groups)

On the basis of electron-donating (or) attracting properties, all the groups have been divided into two classes.

**1. o-p,- Directing groups**

These groups direct the incoming group primarily to o- and p- positions with respect to themselves. The presence of these groups, except halogens, enhances further electrophilic substitution in the benzene nucleus. Hence they are also known as Activating groups.

**Examples**

Some important o-, p- directing groups are:

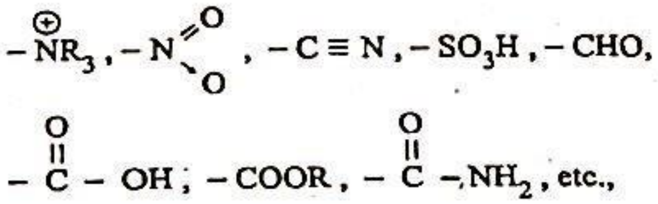
$-\ddot{N}H_2 , -\ddot{N}R_2 , -\underset{\cdot\cdot}{\ddot{O}}H , -\underset{\cdot\cdot}{\ddot{O}}R , -NH-COR , -R$ , Halogens, etc.,

**2. m-Directing groups**

These groups direct the new entrant primarily to meta positions with respect to themselves. The presence of these groups hinder further electrophilic substitution. Therefore they are also known as deactivating groups.

**Examples**

Some examples are



$$-\overset{\oplus}{N}R_3\,,\ -N\overset{\nearrow O}{\underset{\searrow O}{}}\,,\ -C\equiv N\,,\ -SO_3H\,,\ -CHO,$$

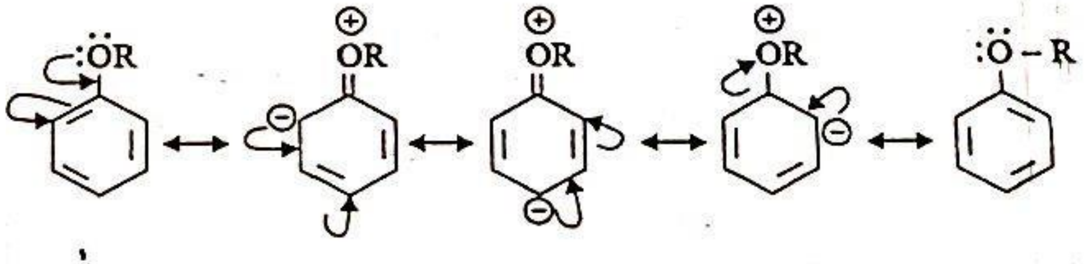
$$-\overset{O}{\overset{\|}{C}}-OH\,;\ -COOR\,,\ -\overset{O}{\overset{\|}{C}}-NH_2\,,\ \text{etc.,}$$

## 3.3.2 Effect of Ortho and para directing groups in aromatic compounds

These groups enhance the electron density at o- and p-positions of the benzene nucleus, thus facilitating attack by positively charged (or) electron-deficient groups (electrophiles) at these positions. A property common to all these groups is that the atom adjacent to the nucleus (key atom) has atleast one lone pair of electrons. A conspicuous exception is alkyl group. Thus,

$$-\ddot{\underset{\cdot\cdot}{Cl}}:\,,\ -\ddot{\underset{\cdot\cdot}{O}}H\,,\ -\dot{N}H_2\,,\ -\dot{N}HR\,,\ -\dot{N}R_2\,,\ -\ddot{\underset{\cdot\cdot}{O}}R,\ \text{etc}$$

Due to the presence of lone pair of electrons on these groups, mesomeric effect is set in the molecule enhancing electron densities at o- and p- positions.



Thus, $C_6H_5\ddot{\underset{..}{O}}R$ is a resonance hybrid of five structure.

Due to +M effect, the molecule has a small negative charge at o- and p- positions. The electron densities at o- and p-positions are further increased by +E effect brought into play at the demand of the attacking agent.

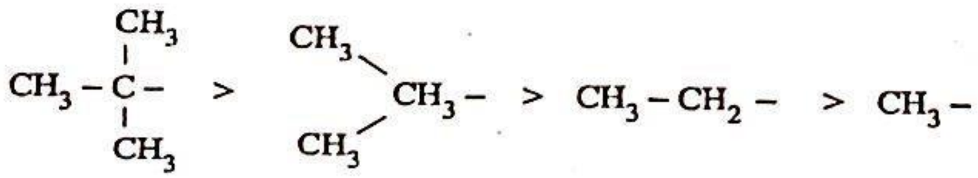
It must be remembered that mesomeric effect is a permanent effect and electromeric effect is a temporary effect. They never oppose each other, rather reinforce each other. The sum of both these effects (+M and E) is known as Tautomeric (+T) (or) conjugative effect. Thus it can be said that o-, p-substitution is due to +T effect.

## Effect of different groups in o and p position

### 1. Effect of alkyl groups

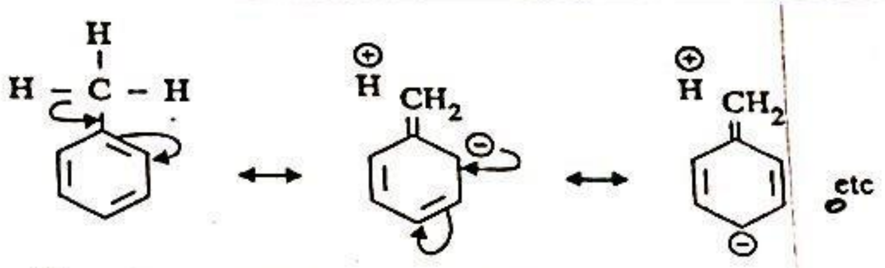
It is well known that alkyl groups are o-, p- directing. Alkyl groups do not contain lone pair of electrons. Hence no mesomeric effect can operate in the molecule. Alkyl groups are strong electron donating due to +I effect. This increases the electron density at o- and p- positions and thus facilitate electrophilic substitution at these positions.

If inductive effect alone is responsible for o- and p-directing influence of the alkyl groups, it should be in the following order:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}- \;>\; \begin{array}{l}CH_3\diagdown\\ \qquad CH_3-\\ CH_3\diagup\end{array} \;>\; CH_3-CH_2- \;>\; CH_3-$$

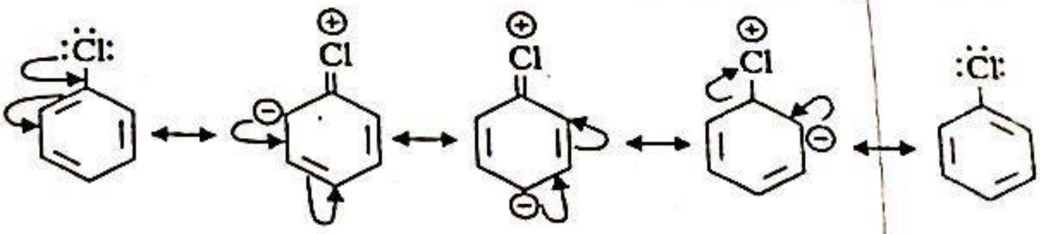
But in a number of cases, the order is reverse. The anomaly can be explained on the basis of hyper-conjugation which is greatest for methyl group.



Thus it can be summarised that o-, p- directing power of methyl group is due to inductive and hyperconjugative effects.

## 2. Effect of halogens

Halogens contain lone pair of electrons and thus resonance can be set in the molecule. Due to + M effect, the electron densities are increased at ortho and para positions.



But, at the same time, chlorine exerts strong − I effect which reduces the electron-density at o- and p- positions. Since − I > + M, the ring is deactivated. Hence further electrophilic substitution in chlorobenzene is difficult.

However, electromeric effect is brought into play at the time of reaction. The combined effect (+ T) becomes mor powerful than − I effect.

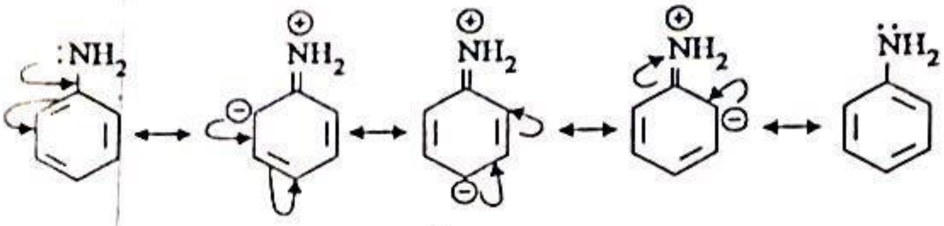
$$+T > -I$$

The o- and p- positions are raised in electron densit Although chlorine atom is o-, p- directing, it deactivates tl ring. Hence it is more difficult to carry out the substitution chlorobenzene than in benzene.

### 3. Effect of $-\ddot{N}H_2$ group

When the reactions of aniline are carried out in aqueous solution, main products are o- and p- isomers. In aniline, both + M and − I effects are operating but they oppose each other. Actually + M effect predominates over − I effect.

$$+M > -I$$

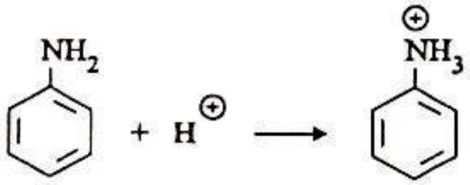


Thus, + M effect of $-\ddot{N}H_2$ group activates the benzene ring and increases the electron density at o- and p- positions. Further electromeric effect operating at the time of attack by the electrophile causes an additional increase in electron density at o- and p- positions.

$$+M \text{ and } +E = +T$$

$$+T > -I$$

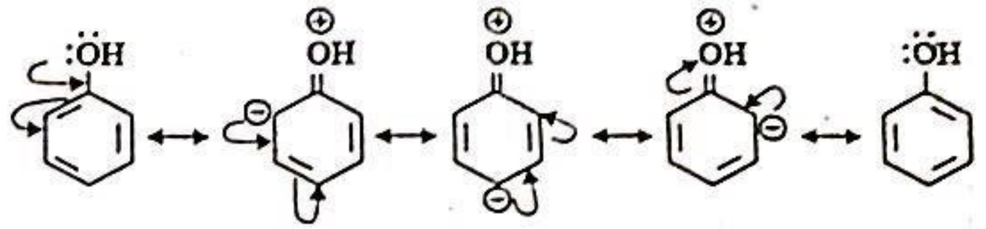
If the reactions of aniline are carried out in the presence of strong acids, mainly meta product is obtained. The simple reason is that in strongly acidic solutions, aniline takes up a proton and forms anilinium ion.



Due to the presence of positive charge on the nitrogen atom, its electron-attracting power (− I effect) is increased and thus electron-density is immensely decreased at the o- and p-positions. Secondly, due to protonation there can be no longer any +M effect. Hence it gives mainly the meta substituted product.

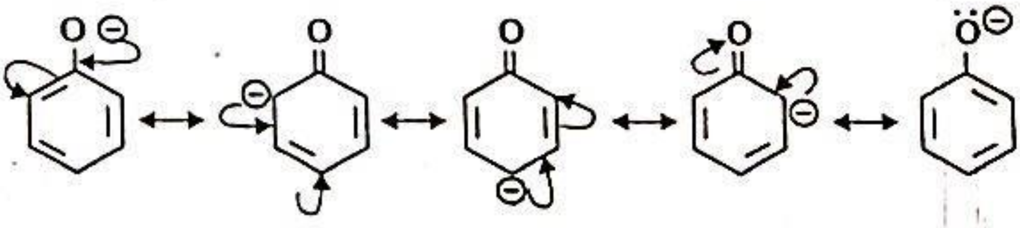
## 4. Effect of phenolic and phenoxide groups

In phenol +M effect and −I effect oppose each other. Since +M > −I, the group activates the ring towards further electrophilic substitution. Due to +M effect, the electron-density at o- and p- positions increases.



Further electromeric effect (+E) operating at the time of attack causes a further increase in the electron-density at o- and p- positions. Thus +T > −I. Hence $-\ddot{\underset{..}{O}}H$ group directs the new entrant to o- and p- positions.

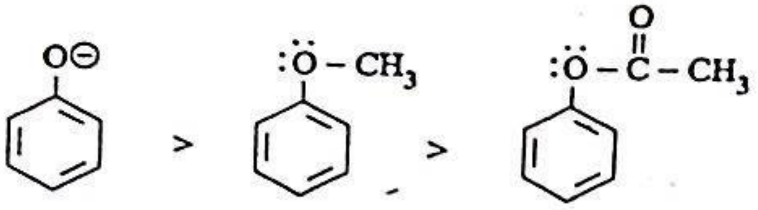
In the presence of strong alkali, phenol forms $C_6H_5ONa$ which easily ionises into phenoxide ion. The phenoxide ion is o-, p- directing due to all the three effects viz., +M, +E and +I.



## 5. Effect of protected −OH and −NH₂ groups

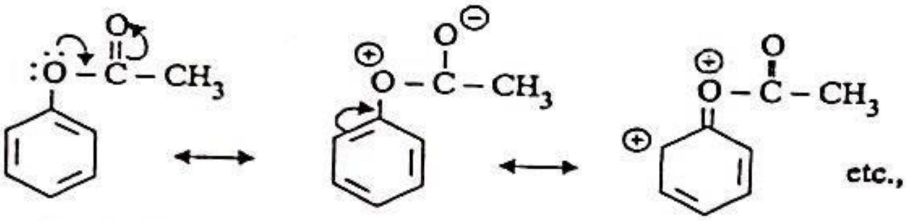
It has been found that the order of substitution of three derivatives of phenol is

The maximum ease for o-, p- directing substitution in phenoxide ion may be accounted for by that it contains a



negatively charged oxygen atom with its three unshared electron pairs. Flow of electrons is facilitated towards the ring, i.e., +M, +E and +I effects operate while in methoxy group and acetyl group, only two lone pairs of electrons are present. Hence they are less prone to electrophilic attack.

In acetyl group the phenomenon of resonance occurs and this further diminishes the availability of electrons to the ring and hence though acetoxy group is o-, p- directing, its activating power is feebler than methoxy and exceedingly lesser than phenoxide ion.

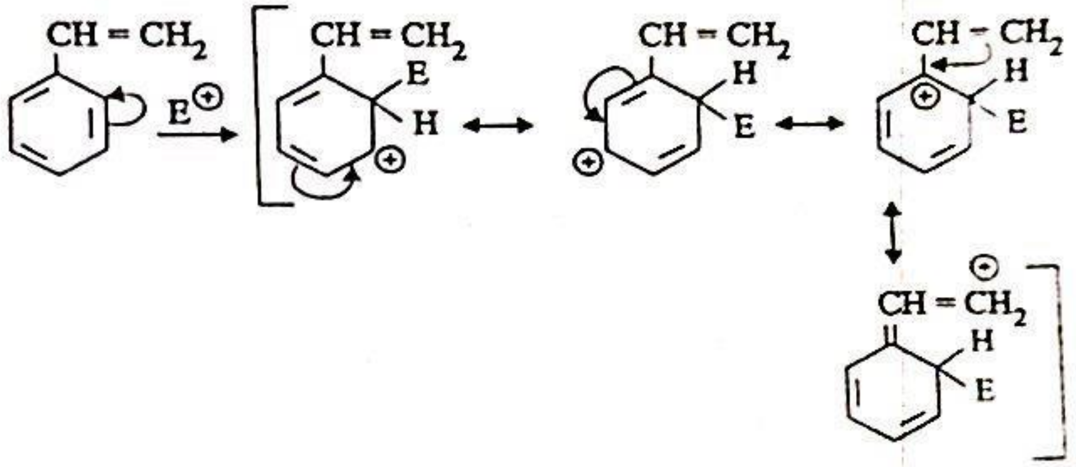


Similarly the introduction of acetyl group in amino group of aniline deactivates aniline molecule. This too can be accounted for by resonance.

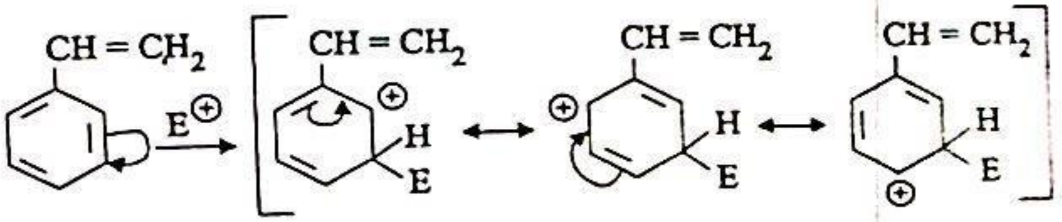
## 6. Effect of vinyl and substituted vinyl groups

The vinyl and $-CH=CH-COOH$ groups are expected to substitute in meta position due to inductive and electromeric effects. But actually both the groups are o-, p- directing. This is explained on the basis of transition states. The carbonium ions (transition states) formed as a result of attack at o- and p- positions are more stable than that formed by attack at meta position.

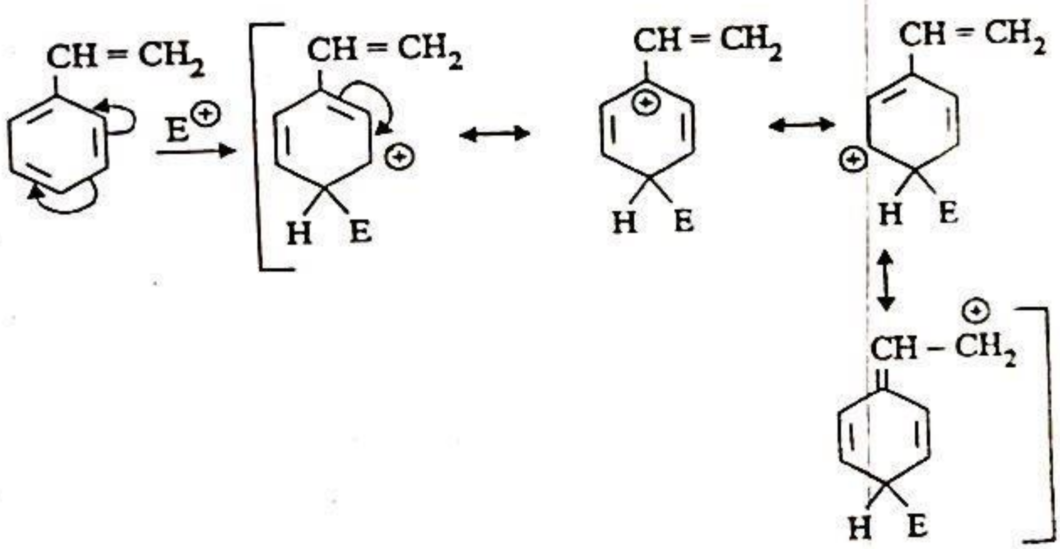
### (i) Attack at o-position



### (ii) Attack at m-position

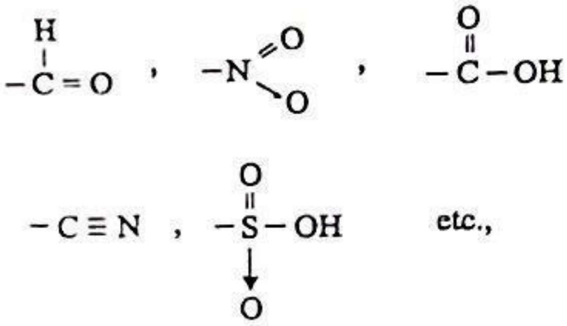


### (iii) Attack at p-position



### 3.3.3 Effect of meta - directing groups in aromatic compounds

m- Directing groups either possess a positive charge (or) the key atom of the group has a more electronegative atom linked by a multiple bond.



$-\overset{\overset{\displaystyle H}{|}}{C}=O$ , $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

$-C\equiv N$ , $-\underset{\underset{\displaystyle O}{\downarrow}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH$ etc.,

All the three effects are in such a manner that the displacement of electrons takes place away from the nucleus and towards the group. In other words $-M$, $-I$ and $-E$ effects operate in the molecule.

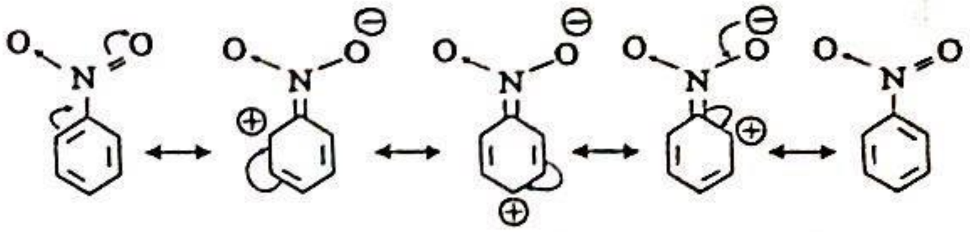
All the three effects reinforce each other in the case of m-directing groups and hence withdraw electrons from the o- and p- positions. The overall result is that the m-position becomes the point of relatively high electron density and thus the new entrant will go to m-position.

The meta substitution is also explained on the basis of the stability of intermediate carbonium ion formed.

**1. Effect of $-NO_2$ group**

The $-M$ and $-I$ effects of the nitro group in the molecule decrease the electron density of the ring. That means the ring gets deactivated. Hence further electrophilic substitution becomes much more difficult.

The meta position is richer in electron density when compared with o- and p- positions. Hence meta substitution takes place.

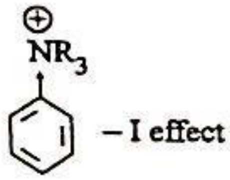


–M effect in Nitrobenzene

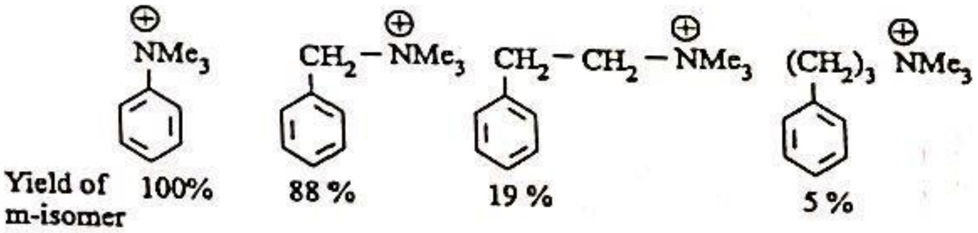
The meta substitution is also explained on the basis of stability of the intermediate carbonium ion formed as a result of attack by the electrophile.

## 2. Effect of $-\overset{\oplus}{N}R_3$ group

Due to the presence of positive charge on the nitrogen atom, the group will exert a strong –I effect and withdraw the electrons from o- and p- positions. Thus the meta position becomes the point of relatively high electron density where substitution takes place.

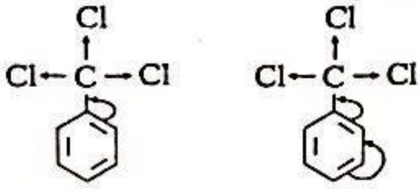


It can be easily demonstrated that the positive charge of the nitrogen atom is responsible for meta substitution. As the distance of the positive charge from the benzene nucleus increases by introduction of $-CH_2-$ group, the yield of meta product decreases accordingly.



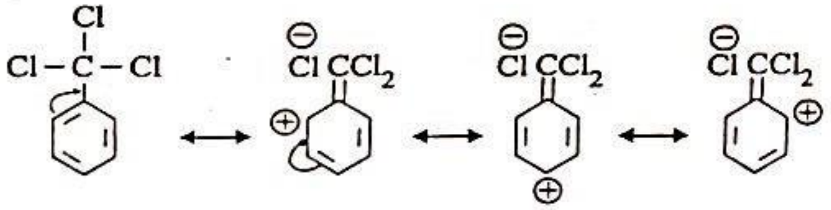
## 3. Effect of $-CCl_3$ group

The meta directing influence of $-CCl_3$ group is entirely due to $-I$ effect. Chlorine is more electronegative than carbon. Thus all the three chlorine atoms would attract electrons from the carbon atom. The carbon atom would become positively charged. In turn, this positively charged carbon atom would attract electrons from the benzene nucleus.



- I effect in benzotrichloride

The m-directing influence of $-CCl_3$ group may also be explained by hyperconjugation.



## 4. Effect of $-\overset{\overset{O}{\|}}{C}-OH$ group and carboxylate ion

The carboxyl group is meta directing. The line of argument is the same as for nitro group. But carboxylic acids form carboxylate ions in the presence of alkali. This carboxylate ion is o-, p- directing. It is again explained on the basis of inductive effect. The presence of negative charge on the oxygen atom pushes the electrons into the o- and p- positions of the nucleus which become the point of attack for the electrophile.

### 3.3.4 Ortho/para ratio

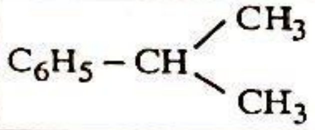
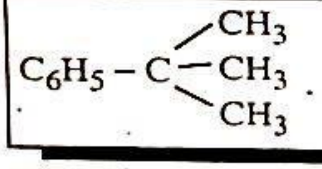
A monosubstituted benzene has two o- positions and one para positions. Hence it is expected that the ratio of the o- and p- isomers (of disubstituted derivatives) should be 67:33 (or) 2:1. But it is never found to be so due to the following factors:

(i) Steric factor

(ii) Inductive effect of the group already present

#### (i) Steric factor

It has been found that larger the size of the group, which is already present, the smaller will be the percentage of the o- isomer formed. This is due to the steric effect of o-position, which is already occupied. This is absent in p-isomer So p-position is ready for attack. If the attacking group is bigger o/p ratio is smaller. The following results were obtained on nitration.

| Name of the compound | % of ortho | % of para | o/p ratio |
|---|---|---|---|
| $C_6H_5-CH_3$ | 58.5 | 37.2 | 1.57 |
| $C_6H_5-CH_2-CH_3$ | 45 | 48.5 | 0.93 |
|  $C_6H_5-CH(CH_3)_2$ | 30 | 62.3 | 0.48 |
|  $C_6H_5-C(CH_3)_3$ | 15.8 | 72.7 | 0.22 |

#### (ii) Inductive effect

However, it is seen that the steric factor is not the only factor at work during substitution reactions.

*Example*

The nitration of fluoro-, chloro- and bromobenzenes give the following result:

| Name | o- | p- | o/p ratio |
|---|---|---|---|
| $C_6H_5-F$ | 12.6 | 87.14 | 0.40 |
| $C_6H_5-Cl$ | 30.1 | 73.10 | 0.41 |
| $C_6H_5-Br$ | 37.1 | 62.5 | 0.59 |

If steric factor is the only governing factor then the o/p ratio must have fallen from fluorine to bromine as the size of the halogen increases from fluorine to bromine. But actually, the table result is the reverse. This is explained by the fact that the electron-withdrawing inductive effect.

(–I effect) influences the adjacent ortho positions such powerfully than the more distant p-position. And as the inductive falls from fluorine to bromine the ortho substitution must increase from fluorine to bromine and actually so in the table given above.

Other factors governing the o/p ratio are temperature and solvent.

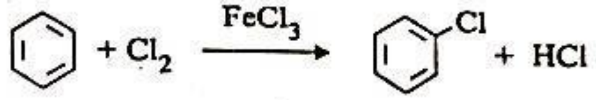
## 3.3.5 Nuclear and side-chain halogenation

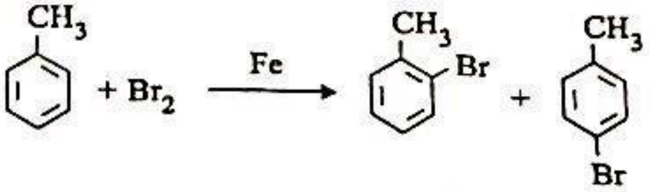
Displacement of hydrogen (or) a group by a halogen in an aromatic compound is called halogenation. Halogenation reactions in aromatic compounds is of two types. They are:

1. Nuclear halogenation
2. Side-chain halogenation

### 1. Nuclear halogenation

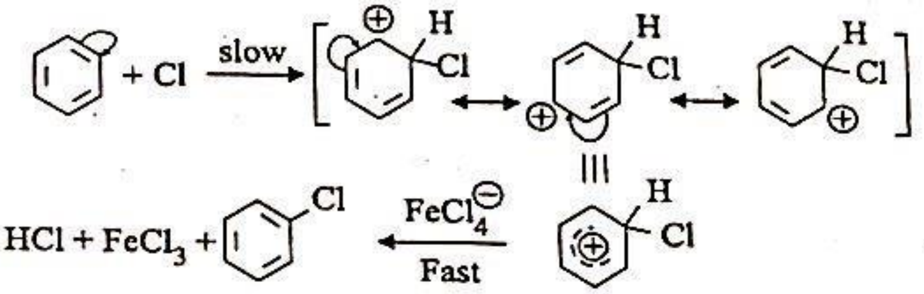
Displacement of hydrogen atom attached to the benzene ring by a halogen is called Nuclear halogenation. Nuclear halogenation is carried out at low temperatures and in the presence of halogen-carrier like Fe, $FeCl_3$ (or) $FeBr_3$.





## Mechanism

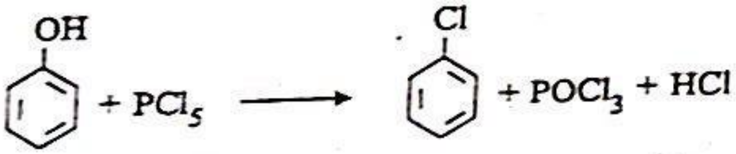
$$:\ddot{\underset{\cdot\cdot}{Cl}} - \ddot{\underset{\cdot\cdot}{Cl}}: + FeCl_3 \longrightarrow FeCl_4^{\ominus} + Cl^{\oplus}$$

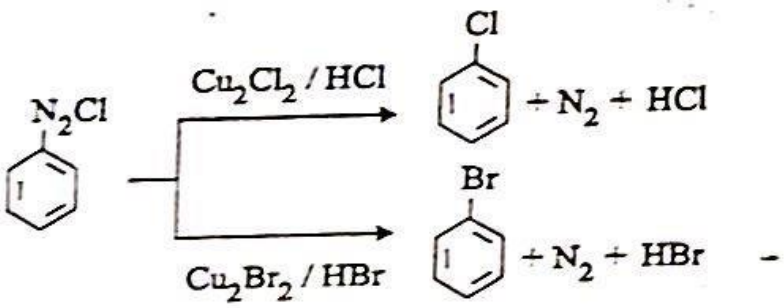


Nuclear halogenation is an aromatic electrophilic substitution. The common accepted mechanism is as follows:

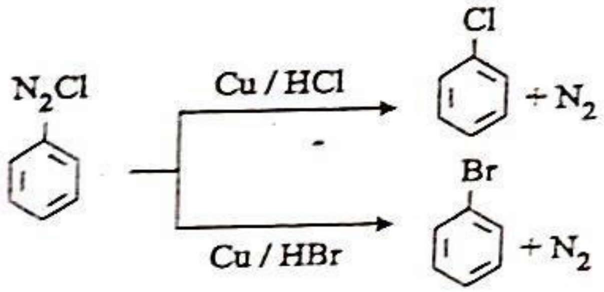
Iodo-derivatives cannot be prepared by direct iodination. This is because the reaction is reversible and HI produced is a strong reducing agent and it reduces iodo derivatives back to hydrocarbon.

Nuclear halogenation can also be effected from other compounds.

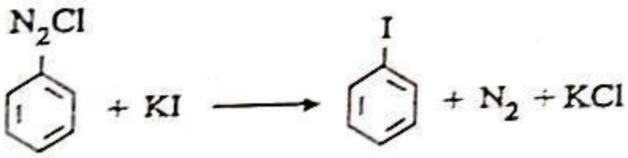




Sandmeyer's reaction



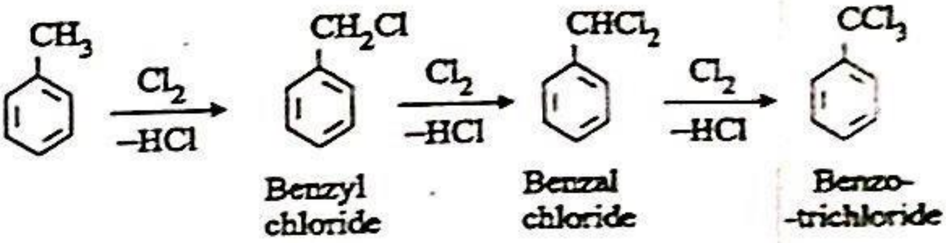
Gattermann reaction



## 2. Side-chain halogenation

Displacement of hydrogen atom of the side-chain by a halogen is called side-chain halogenation. High temperature, light and absence of halogen-carriers favour side-chain halogenation.

Chlorine reacts with toluene at its boiling point and in the presence of light to give the following products.

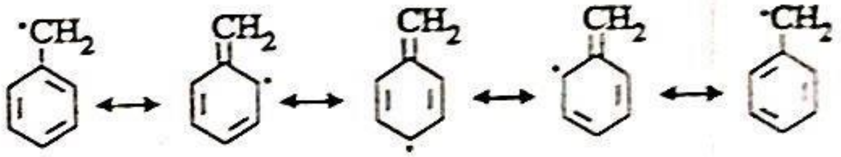


## Mechanism

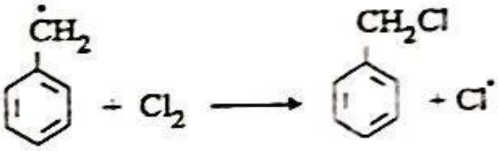
Side-chain halogenation proceeds via a free radical mechanism. This is because of the low bond dissociation energy of benzyl-hydrogen bond.

$\Delta H = -75\ \text{kJ mol}^{-1}$

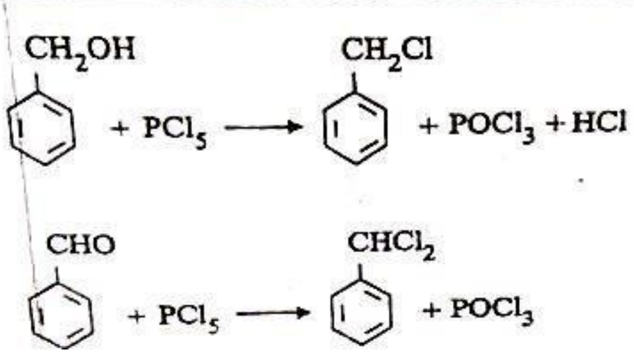
This benzyl radical is stabilised by delocalisation of the odd electron into the ring.



In the next step, benzyl radical reacts with $Cl_2$ to regenerate a chlorine radical which then continues the chain reaction.



Side-chain halogenation can also be carried out by the action of $PCl_5$ on aromatic alcohols and aldehydes.


CH$_2$OH
+ PCl$_5$
CH$_2$Cl
+ POCl$_3$ + HCl
CHO
+ PCl$_5$
CHCl$_2$
+ POCl$_3$