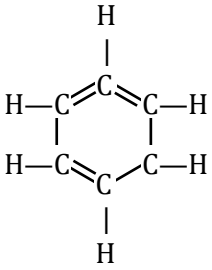
04 Aromatic Compounds

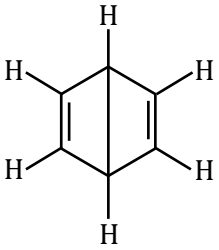
Introduction:

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behavior.

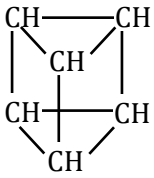
Proposed structure of benzene:



Kekule benzene



Dewar's benzene



[Prism like structure proposed by Albert Ladenburg]

* Benzene mostly represents by Kekule structure.

Huckel's (4n + 2) rule for aromaticity:

An aromatic compound must have cyclic clouds of delocalised $(4n + 2)\pi$ electrons above and below the plane of the molecule or in other words a compound which is cyclic, planar and have complete cyclic delocalisation of 2,6,10.....π electrons is an aromatic compound, according to Huckel's rule.

The following three rules are useful in predicting whether a particular compound is aromatic or non-aromatic.

(i) Aromatic compounds are cyclic and planar.

(ii) Each atom in an aromatic ring is sp^2 or sp hybridised.

(iii) The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2)\pi$ electrons, i.e., 2, 6, 10, 14 ..... π electrons. Where n = an whole number 0, 1, 2, 3, ...

Characteristic reaction of aromatic compounds:

* Aromatic compounds prefer **electrophilic substitution** rather than electrophilic addition reaction.

* In aromatic electrophilic substitution reaction benzene ring serve as source of electrons that is as a base or nucleophile.

* Electrophilic aromatic substitution includes a wide variety of reactions :
e.g. Halogenation, Nitration, Sulphonation, Friedel Crafts alkylation & acylation but reactions like Nitrosation and Diazocoupling undergoes only by rings of high reactivity.

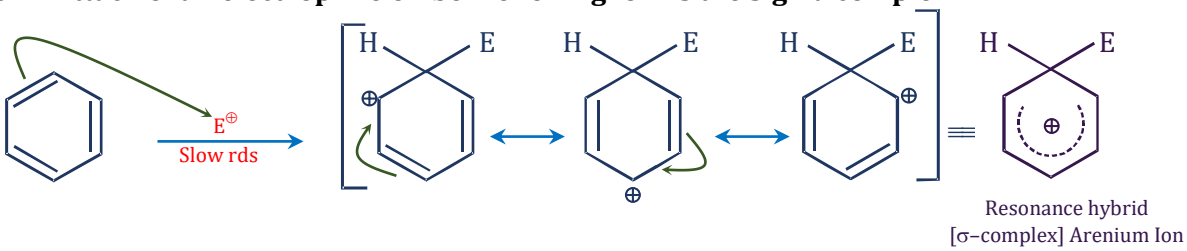
Electrophilic substitution reaction of aromatic compounds:

Like an alkene, benzene has cloud of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system still they are available to attack with a strong electrophile to give a carbocation. This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond.

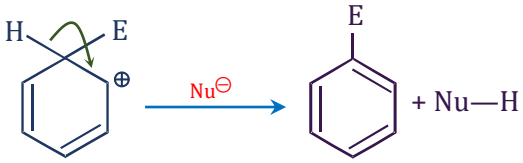
The sigma complex (also called an arenium ion) is not aromatic because the sp^3 hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of thus first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

The overall reaction is the substitution of an electrophile $(\overset{\oplus}{E})$ for a proton $(\overset{\oplus}{H})$ on the aromatic ring so it is called **electrophilic aromatic substitution**.

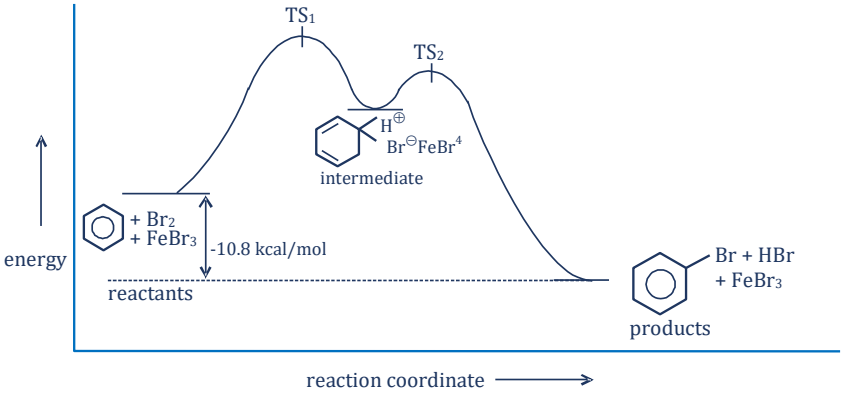
Step 1 : Attack of an electrophile on benzene ring forms the sigma complex



Step 2 : Loss of a proton gives the substitution product.



Energy diagram: For bromination reaction, electrophile is bromonium ion ($Br^{\oplus}$)



For an electrophilic aromatic substitution reaction to overcome the high activation energy that characterizes the first step, the electrophile must be a fairly reactive one. Many of the electrophilic reagents that react rapidly with alkenes do not react at all with benzene. For example peroxy acids and diborane, fall into this category, others such as bromine react with benzene only in presence of catalysts that increases their electrophilicity.

Effect of substituent groups in monosubstituted benzene:

(A) Ortho-para directing and activating groups:

All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.

(B) Ortho para directing but deactivating groups:

Halogens are deactivating but ortho-para directing groups.

Reactivity of benzene decreases by –I effect of halogens and ortho-para directing nature is decided by +m effect of halogens.

(C) Meta directing and deactivating groups :

Mostly electron withdrawing groups (–m, –I) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^- > -NH_2 > -NHR > -NR_2 > -OH$	Very strongly activating	Ortho–para directing
2.	$-O^- > -NH-\overset{\overset{O}{\|\|}}{C}-R > -O-\overset{\overset{O}{\|\|}}{C}-R$	Strongly activating	Ortho–para directing
3.	$-OR, -Ar, -CH=CH_2$	Activating	Ortho–para directing
4.	$-X(F,Cl,Br,I), -N=O, -CH_2X, -CHX_2$	Deactivating	Ortho–para directing
5.	$-CHO > -\overset{\overset{O}{\|\|}}{C}-R > -COOH,$ $-COOR, -COCl, -C\equiv N, -SO_3H$	Strongly deactivating	Meta directing
6.	$-NO_2, -\overset{\oplus}{N}R_3, -\overset{\oplus}{S}R_2, -CF_3$	Very strongly deactivating	Meta directing

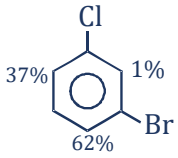
Effect of substituent groups in disubstituted benzene:

(1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.

(2) If both groups present in a system are deactivator then position of electrophile will be determined by stronger deactivator.

(3) If both the groups are activating group then position of electrophile will be determined by stronger activator.

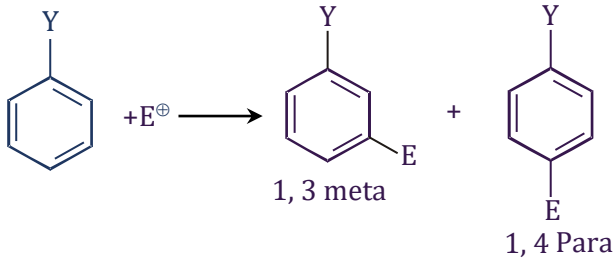
(4) There is often little substitution between two groups that are meta to each other.

Example : Nitration product of 

(% nitro product)

Orientation and reactivity in electrophilic aromatic substitution:

In the case of benzene we get just one monosubstituted product in electrophilic aromatic substitution as all the positions are equivalent. However, for substitution in a compound which already has a group attached to the ring, three disubstituted products, (1, 2), (1, 3) (1, 4) commonly called ortho, meta and para meaning next to, between and opposite respectively are possible. These are abbreviated as o, m and P.



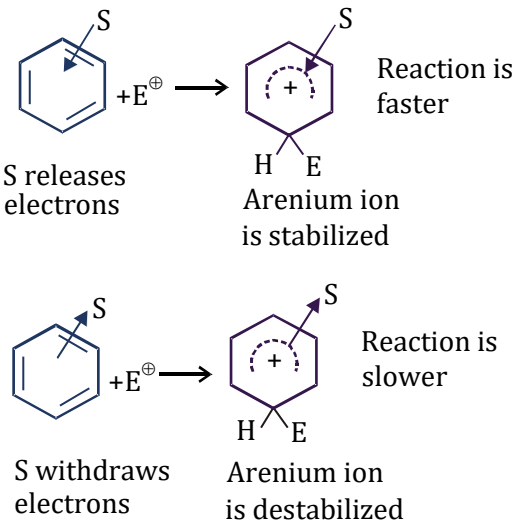
Reactivity :

We have now seen that certain groups activate the benzene ring toward electrophilic substitutions, while other groups deactivate the ring. We mean that an aromatic compound with an activating group reacts faster in electrophilic substitutions than benzene. When we say that a group deactivates the ring, we mean that an aromatic compound with a deactivating group reacts slower than benzene.

We have also seen that we can account for relative reaction rates by examining the transition state for the rate-determining steps. Any factor that increases the energy of the transition state relative to that of the reactants decreases the relative rate of the reaction. It does this because it increases the free energy of activation of the reaction. In the same way, any factor that decreases the energy of the transition state relative to that of activation and increases the relative rate of the reaction.

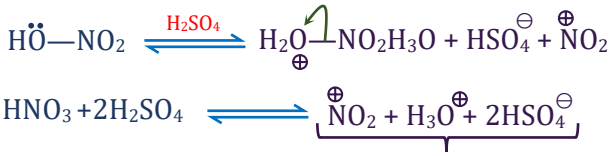
The rate-determining step in electrophilic substitutions of substituted benzene compounds is the step that results in the formation of arenium ion. We can write the formula for a substituted benzene in a generalized way if we use the letter S to represent any ring substituent including hydrogen, (if S is hydrogen, the compound is benzene). We can also write the structure for the arenium ion in the way shown here. By this formula we mean that S can be in any position -ortho, meta or para - relative to the electrophile, E. Using these conventions, we can write the rate-determining step for electrophilic aromatic substitution in the following way.

When we examine this step for a large number of reactions, we find that the relative rates of the reactions depend on whether S withdraws or release electrons. If S is an electron-releasing group (relative to hydrogen), the reaction occurs faster than the corresponding reaction of benzene. If S is an electron withdrawing group, the reaction occurs slower than that of beznene.

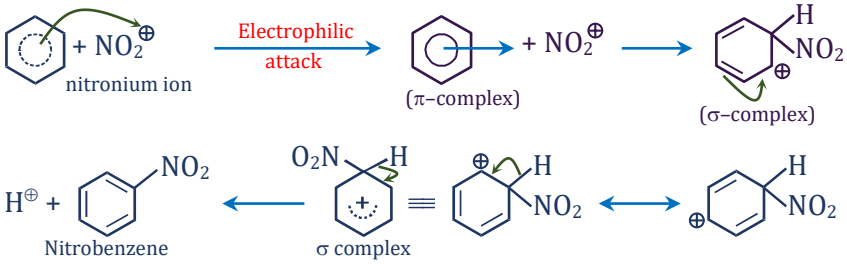


It appears, that the substituent (S) must affect stability of the transition state relative to that of the reactants. Electron-releasing groups apparently make the transition state more stable, while electron withdrawing groups make it less stable. that is entirely reasonable, because the transition state resembles the arenium ion, and the arenium ion is a delocalized carbocation.

Nitration :



HNO_3 act as a base in the above reaction.

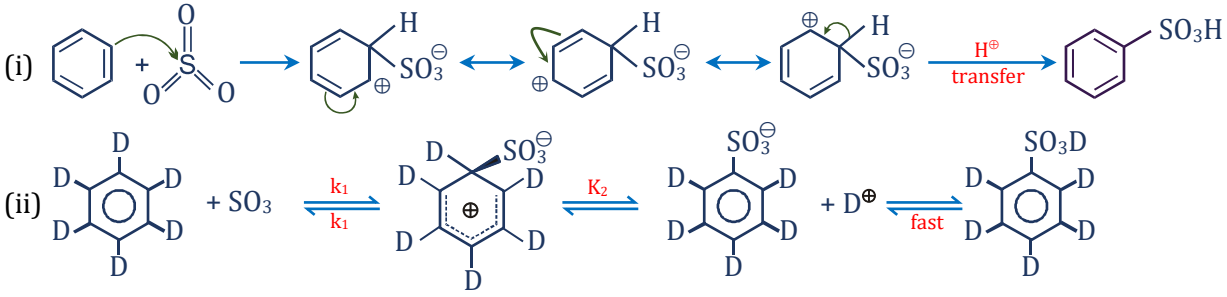


* Purpose of sulphonic acid in the reaction is to increase the concentration of nitronium ion ($NO_2^{\oplus}$)

Sulphonation :

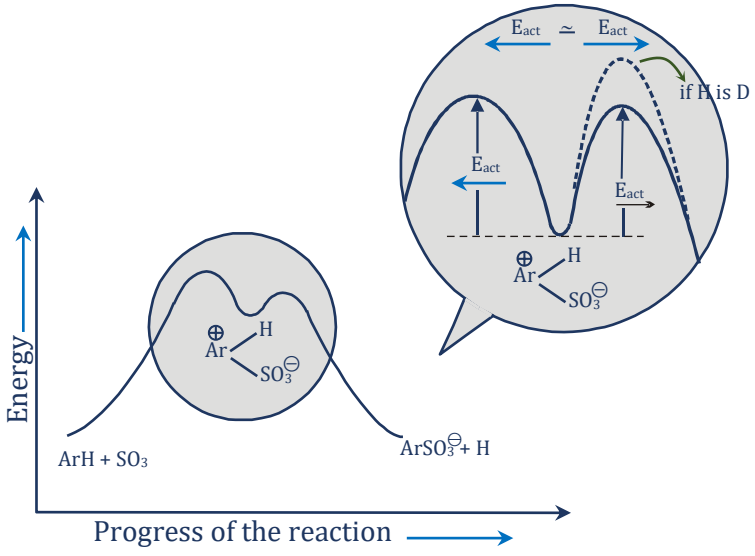
Sulphur trioxide in sulphuric acid is used as the sulphonation agent.

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



Sulphonation, is **reversible** and takes place in concentrated sulphuric acid. ($K_{-1} \simeq K_2$).

Energy Diagram :



Some $\overset{\oplus}{Ar}\!\!<\!\!\begin{matrix}H\\SO_3^{\ominus}\end{matrix}$ or $\overset{\oplus}{Ar}\!\!<\!\!\begin{matrix}D\\SO_3^{\ominus}\end{matrix}$ go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.

Isotope Effects :

The next question which comes up is how do we ascertain the presence of two discrete steps in the mechanism and also that the formation of σ - complex is the rate determining step. Answer to this question can be obtained from the study of kinetic isotope effect. If the rate of a reaction depends on a step which involves breaking of a C—H bond, then a kinetic isotope effect (K_H/K_D) of 6 to 7 is expected. Absence of any significant isotope effect in aromatic electrophilic substitution (except sulphonation) suggests that the proton is lost in the fast step, subsequent to rds. We see that the isotope effect study has provided two pieces of important information regarding the mechanism. Firstly, it has shown that the reaction takes place in two steps and secondly, that the first step is slower than the second step.

Halogenation:

Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on the reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may acts as electrophiles. In the case of nonpolar solvents, halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$, Reactivity of halogens has the following order,

$$I_2 < Br_2 < Cl_2$$

Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, Cl_2—$AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give $Cl^{\oplus}$.

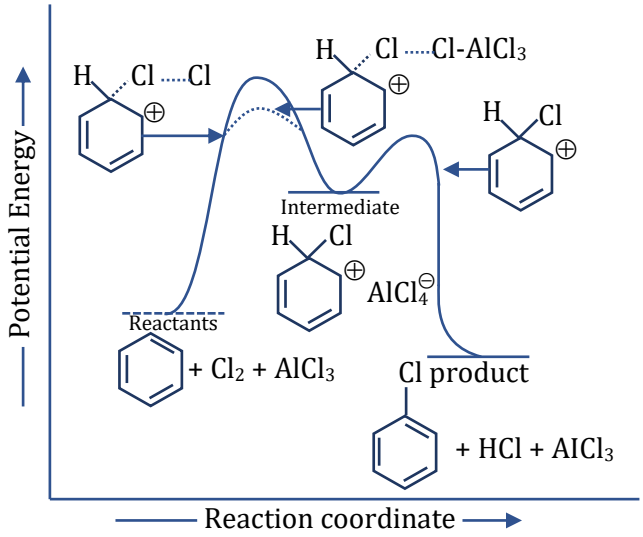
Step-I : $Cl—\ddot{Cl}: + AlCl_3 \rightleftharpoons AlCl_3 \rightleftharpoons Cl—\overset{\oplus}{Cl}—\overset{\ominus}{AlCl_3}$

(anhydrous)

Step-II :  $+ Cl—\overset{\oplus}{Cl}—\overset{\ominus}{AlCl_3} \xrightarrow{\text{slow}}$  $+ \overset{\ominus}{AlCl_4}$

Step-III :  $+ \overset{\ominus}{AlCl_4} \xrightarrow{\text{Fast}}$  $+ AlCl_4 + HCl$

However, there is no significant evidence for the involvement of $Cl^{\oplus}$ as an electrophile and it is likely that the complex itself attacks the substrate. In the Cl_2—$AlCl_3$ complex, role of the Lewis acid is to polarize the halogen molecule and weaken the Cl—Cl bond. This lowers the activation energy for the formation of σ-complex.



Bromination follows a similar mechanism. As said above, Iodine is weakest of the three halogens and even in the presence of a Lewis acid, it can halogenate reactive aromatics only. Therefore, in most other cases iodine-monochloride is used in the presence of Lewis acid, $ZnCl_2$.

Halogenation may be effected by hypohalous acids, $\overset{\delta-}{HO}—\overset{\delta+}{X}$, also. This is markedly slower than with molecular halogens as $HO^{\ominus}$ is a poorer leaving group from $\overset{\delta-}{HO}—\overset{\delta+}{X}$, than, $X^{\ominus}$ is from $\overset{\delta+}{X}—\overset{\delta-}{X}$. The reaction is speeded in the presence of $X^{\ominus}$, however, as HO—X is then converted into the more reactive X_2,

e.g. : $^{\ominus}OCl + Cl^{\ominus} + 2H^{\oplus} \longrightarrow Cl_2 + H_2O$

In the presence of strong acid, however, HO—X becomes a very powerful halogenating agent due to the formation of a highly polarized complex :

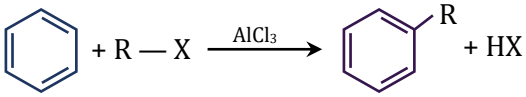
$$H\ddot{O}—X + H^{\oplus} \longrightarrow H_2\overset{\oplus}{O}—X \longrightarrow H_2O + X^{\oplus}$$

The evidence is that this species is the effective electrophile under these conditions and does not support the further conversion of complex into $X^{\oplus}$, i.e. unlike the case with $H_2O^{\oplus}$ —NO_2. F_2 reacts vigorously with benzene, but C—C bond breaking occurs and the reaction is of no preparative significance.

Fridel-Crafts Alkylation:

Alkyl halides react with benzene in presence of aluminium chloride to yield alkyl benzenes. Alkylation of benzene with alkyl halides in the presence of aluminium chloride was discovered by Charles Friedel and James. M. Crafts in 1877.

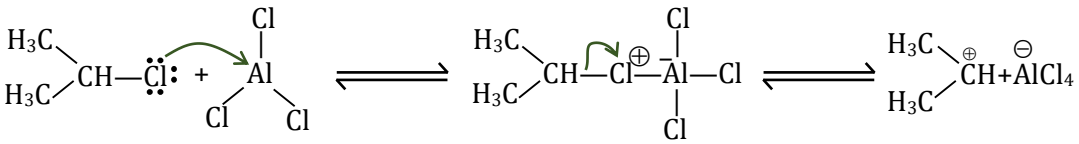
A general equation for a friedel-Crafts alkylation reaction is the following



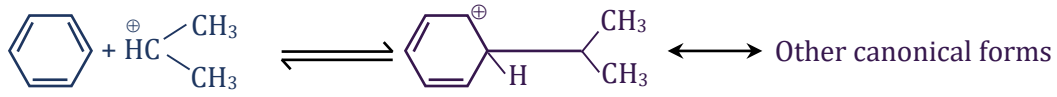
Alkyl halides by themselves are insufficiently electrophilic to react with benzene. $AlCl_3$ serves as a Lewis acid catalyst to enhance the electrophilicity of the alkylating agent. The mechanism for the reaction (shown in the following steps, with isopropyl chloride as R—X) starts with the formation of carbocation (step I). The carbocation then acts as an electrophile (step II) and attacks the benzene ring to form an arenium ion. The arenium ion (Step III) then loses a proton to generate isopropyl benzene. Sometimes carbocation rearranges to a more stable carbocation.

Mechanism for the Reaction :

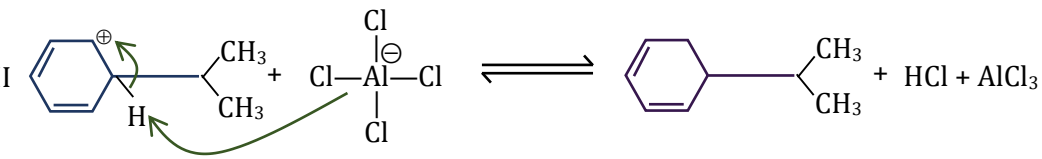
Step -I



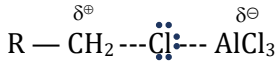
Step -II



Step-III

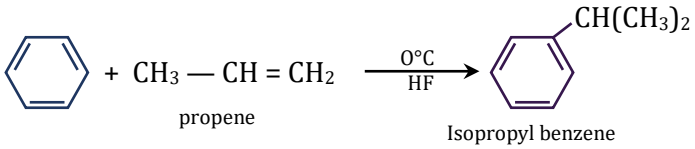


With R–X is a primary halide, a simple carbocation probably does not form. Instead, the $AlCl_3$ forms a complex with the alkyl halide and this complex acts as the electrophile. In the complex the carbon halogen bond is nearly broken and one in which the carbon atom has a considerable +ve charge.

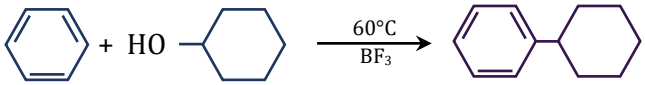


These complexes are so carbocation like that they also undergo typical carbocation rearrangements.

Friedel-Crafts alkylations are not restricted to the use of alkyl halides and $AlCl_3$. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well. These possibilities include the use of a mixture of an alkene and an acid.



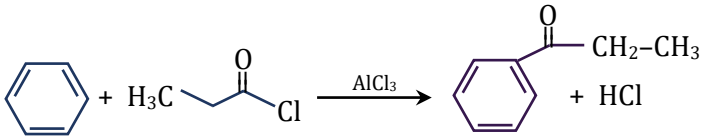
A mixture of an alcohol and an acid may also be used.



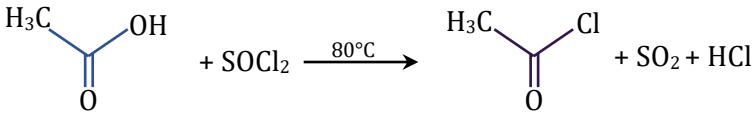
Friedel-crafts Acylation:

The group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called an acylation reaction.

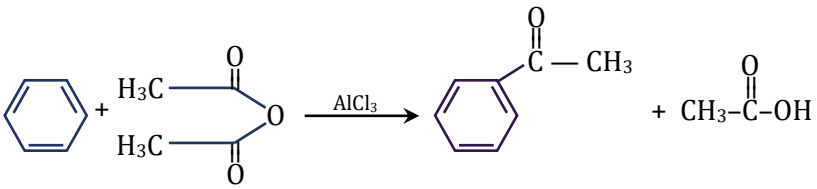
The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



Acyl chlorides (also called acid chlorides) are early prepared by treating carboxylic acids with thionyl chloride ($SOCl_2$) or phosphorous pentachloride (PCl_5).

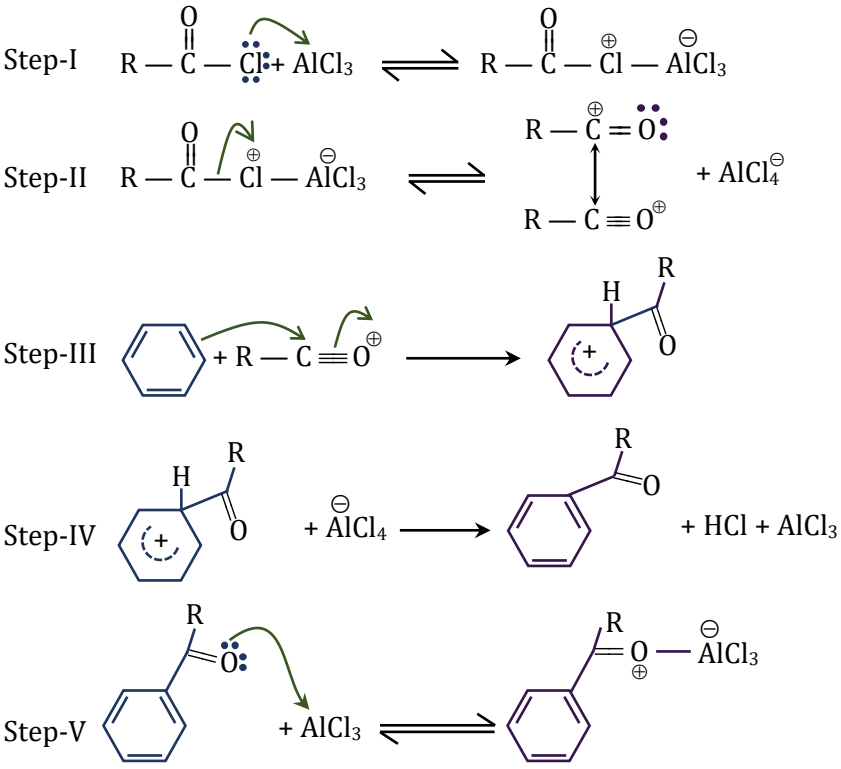


Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides. eg.

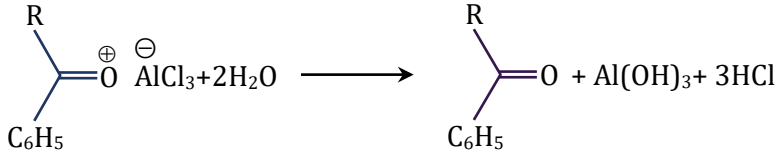


Mechanism of the Reaction:

In most Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.



In the last step, $AlCl_3$ (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.

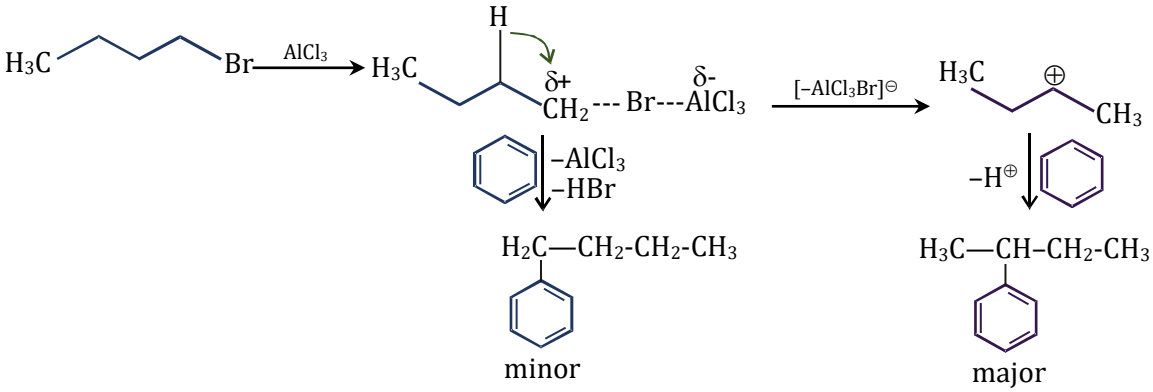


Limitations of Friedel - Crafts Reactions:

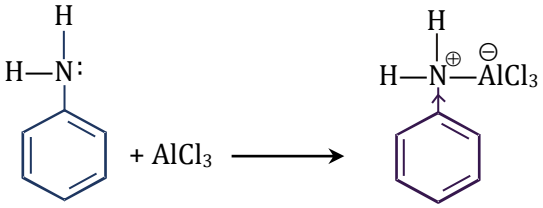
Several restrictions limit the usefulness of Friedel - Crafts reactions.

(a) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift-some developing 1° carbocations (see following reactions) become more stable 2° carbocations. The benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butylbenzene.

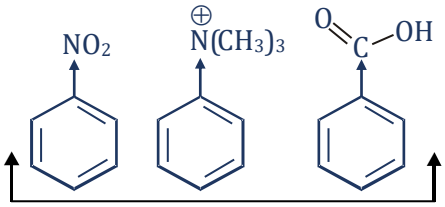


(b) An aromatic ring less reactive than that of halobenzene don't undergo Friedel Craft's reaction. Aromatic ring containing - NH_2, –NHR, $–NR_2$, groups does not undergo Friedel craft's alkylation due to formation of anilinium complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.



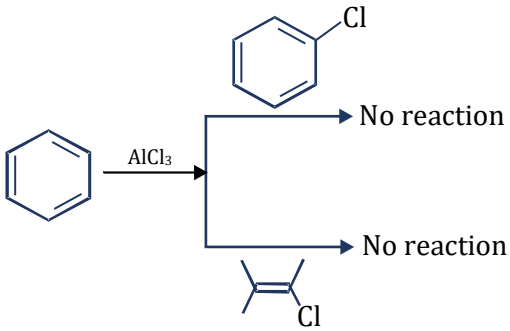
Meta directing group
and does not go
Friedal Craft's reaction

(c) Friedel-Crafts reactions do not occur when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an $–NH_2$, –NHR or $–NR_2$ group. This applies to both alkylation and acylation.

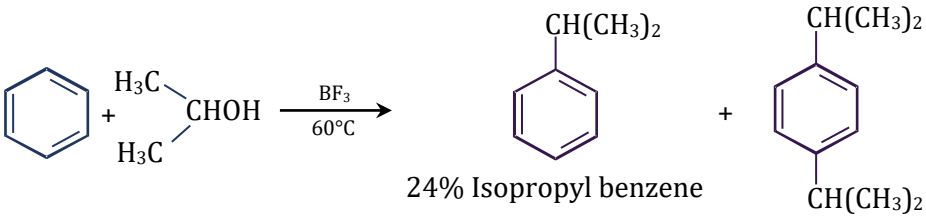


These do not undergo Friedel -Crafts reactions

(d) Aryl and vinylic halides cannot be used as the halide component because they do not form carbocations readily.



(e) Polyalkylations often occur - Alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.



24% Isopropyl benzene

14% Di–isopropylbenzene

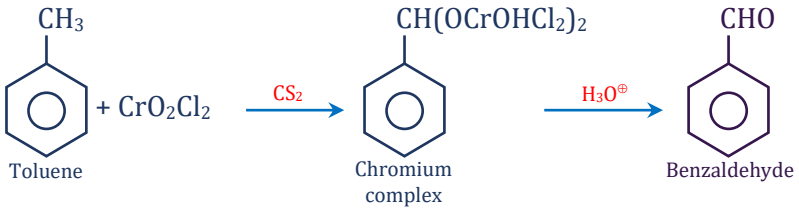
Polyacylation are not a problem in Friedel-Crafts acylation however. The acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with $AlCl_3$ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.

Preparations of Benzaldehydep:

(1) Oxidation of methyl benzene :

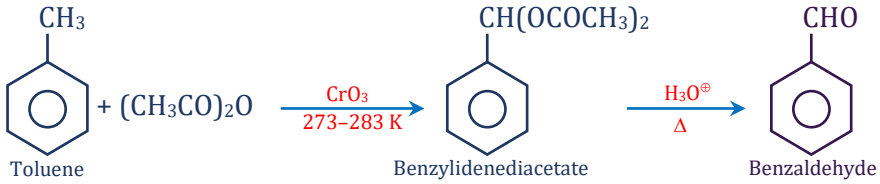
Strong oxidising agents oxidise toluene and its derivatives to benzoic acid. So, to stop the oxidation at aldehyde stage suitable reagents used.

a) Etard reactions : with chromyl chloride followed by hydrolysis

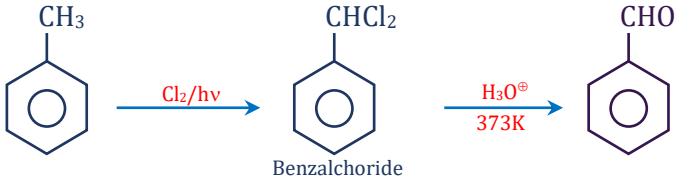


NOTE : Chromyl chloride (CrO_2Cl_2) oxidises methyl group in methylbenzene to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

b) With chromic oxide CrO_3 in acetic anhydride

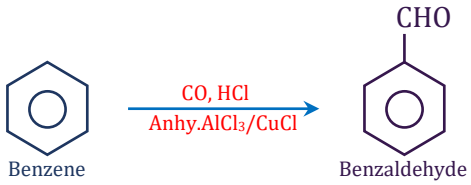


(2) By side chain chlorination followed by hydrolysis (Commercial Method):



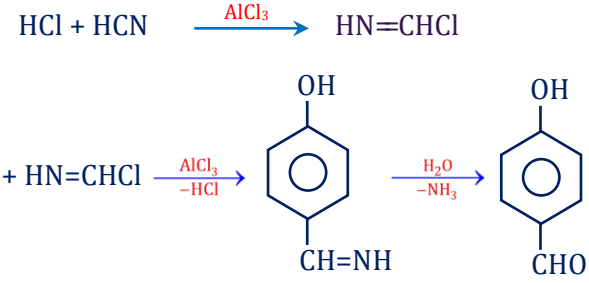
By Gattermann-Koch reaction:

Benzene or its derivative $\xrightarrow[\text{Anhy.}AlCl_3/CuCl]{CO,HCl}$ Benzaldehyde or substituted benzaldehyde



Gattermann aldehyde synthesis :

When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ it yields mainly p-hydroxybenzaldehyde (formylation)

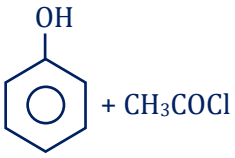
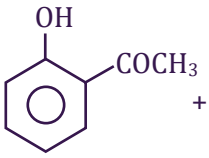


Friedel-Craft Acylation Reaction:

(i) $C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COCH_3 + HCl$
Acetophenone

(ii) $C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCl$
Benzophenone

(iii) $\underset{excess}{C_6H_6} + COCl_2 \xrightarrow[AlCl_3]{Dry} C_6H_5COC_6H_5 + HCl$
Benzophenone

(iv)  $+ CH_3COCl \xrightarrow{Anhydrous\ AlCl_3}$  $+$ 
o–hydroxy acetophenone p–hydroxy acetophenone

Nucleophilic Aromatic Substitution by the addition Elimination Mechanism:

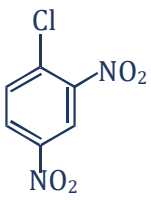
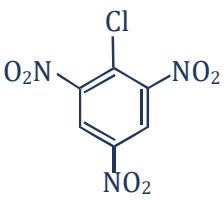
(i) The generally accepted mechanism for nucleophilic aromatic substitution in nitro-substituted aryl halides.

 $+ NaOCH_3 \xrightarrow[85°C]{CH_3OH}$  $+ NaCl$
p-Chloronitrobenzene p-Nitroanisole

(ii) An ortho - nitro group exert a comparable rate–enhancing effect, m-chloronitrobenzyne while much more reactive than chlorobenzyne itself, is thousands of times less reactive than either o-or p-chloronitrobenzene.

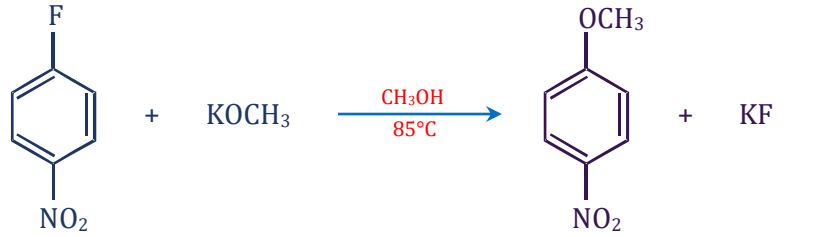
(iii) The effect of o- & p-nitro substituents is cumulative, as the rate data for substitution with methoxide ion in a series of nitro-substituted chlorobenzene derivative demonstrate increasing rate of reaction as:



	Chlorobenzene	1–Chloro–4–nitrobenzene	1–Chloro–2, 4–dinitrobenzene	2–Chloro–1, 3, 5–trinitrobenzene
Relative rate :	1.0	7×10^{10}	2.4×10^{15}	(too fast to measure)

(iv) In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an o-or a p-nitro group.



p-Fluoro nitrobenzene | Potassium methoxide | p-Nitroanisole (93%) | Potassium fluoride

(v) Indeed, the order of leaving group reactivity in nucleophilic aromatic substitution is the opposite of that seen in aliphatic substitution.

(vi) Fluoride is the best reactive leaving group in nucleophilic aromatic substitution, iodide the least reactive.

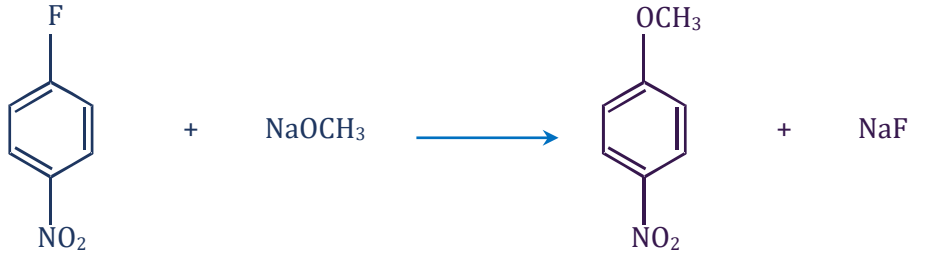
Relative reactivity towards sodium methoxide in methanol (50°C)

X =	F	Cl	Br	I
	312	1.0	0.8	0.4

(vii) Kinetic studies of many of the reactions described in the section have demonstrated that they follow a second-order rate law.

Rate = k[aryl halide] [nucleophile]

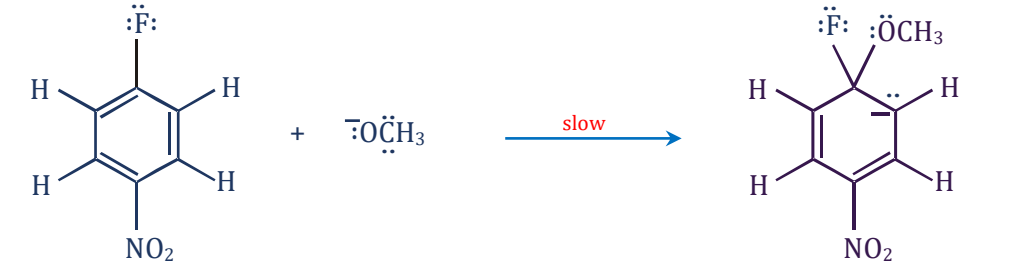
(viii) Second order kinetics is usually interpreted in terms of a bimolecular rate determining step.



p-Fluoronitrobenzene | Sodium methoxide | p-Nitroanisole | Sodium Fluoride

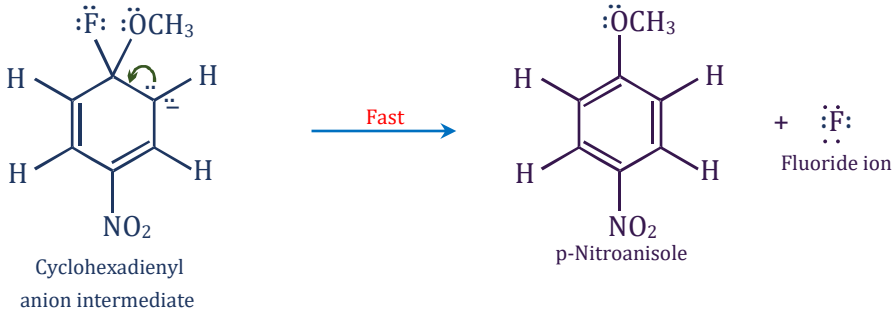
Mechanism :

Step–1 Addition stage. The nucleophile, in this case methoxide ion, adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



p-Fluoronitrobenzene | Methoxide ion | Cyclohexadienyl anion intermediate

Step -2 - Elimination stage. Loss of halide form the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.



Cyclohexadienyl anion intermediate

p-Nitroanisole

Illustration 1:

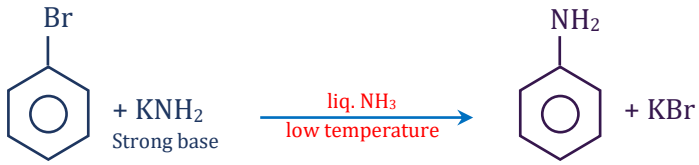
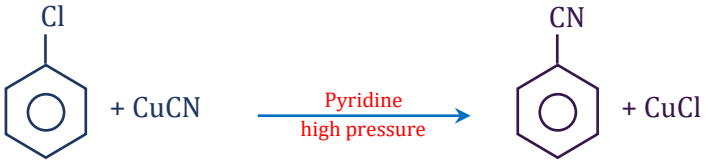


Illustration 2:

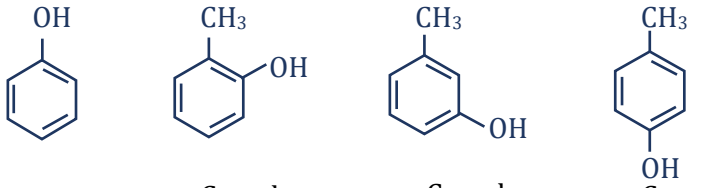


Phenol:

Phenol, also known as **carbolic acid**, was first isolated in the early nineteenth century from coaltar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives.

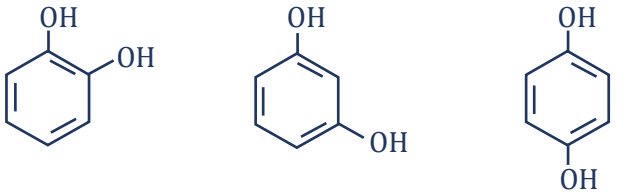
Some common examples are :

(i)



Common name :	Phenol	o-Cresol	m-Cresol	p-Cresol
IUPAC name :	phenol	2-methylphenol	3-methylphenol	4-methylphenol

(ii)



Common name :	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name :	Benzene-1,2- diol	Benzene-1,3- diol	Benzene-1,4- diol

Dihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.

Properties of phenol:

Phenol is a colourless crystalline solid, m.p. 43°C, b.p. 182°C, which turns pink on exposure to air and light.

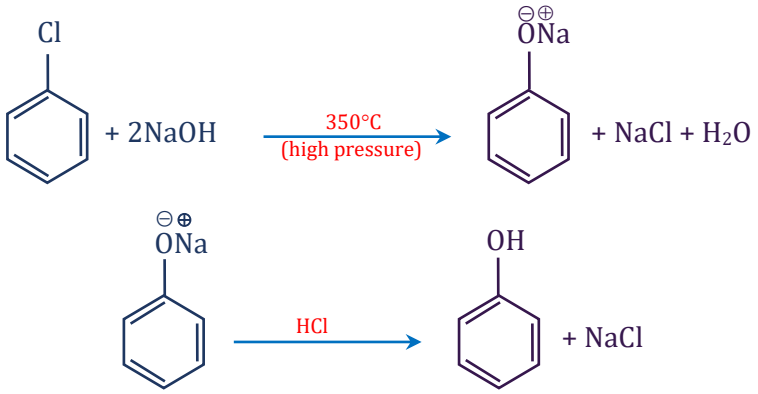
Phenol is used as an antiseptic and disinfectant and in the preparation of dyes, drugs, bakelite, etc.

Preparation of phenol:

(a) From Haloarenes:

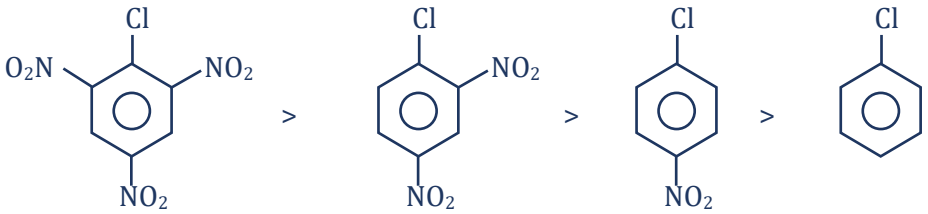
Dow Process – Hydrolysis of chlorobenzene:

Chlorobenzene is heated at 350°C under high pressure with aq. sodium hydroxide. This reaction produce sodium phenoxide which on acidification yields phenol.

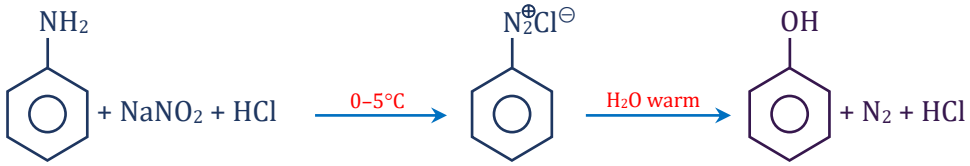


Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

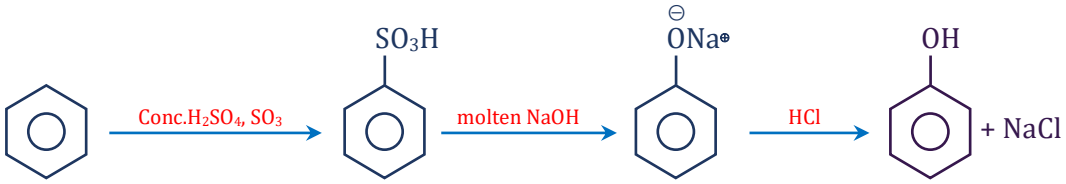
Reactivity Order : (Towards nucleophilic substitution)



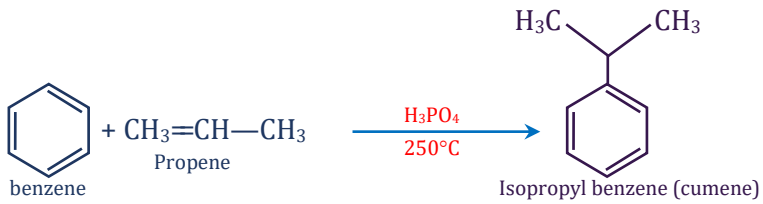
(b) From Diazonium salt :

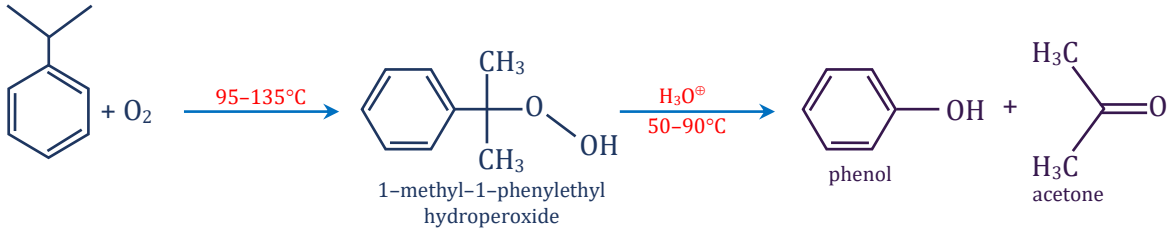


(c) From Benzene Sulphonic acid :



(d) From cumene hydroperoxide :





Mechanism for CHP (Cumene Hydro peroxide) rearrangement :

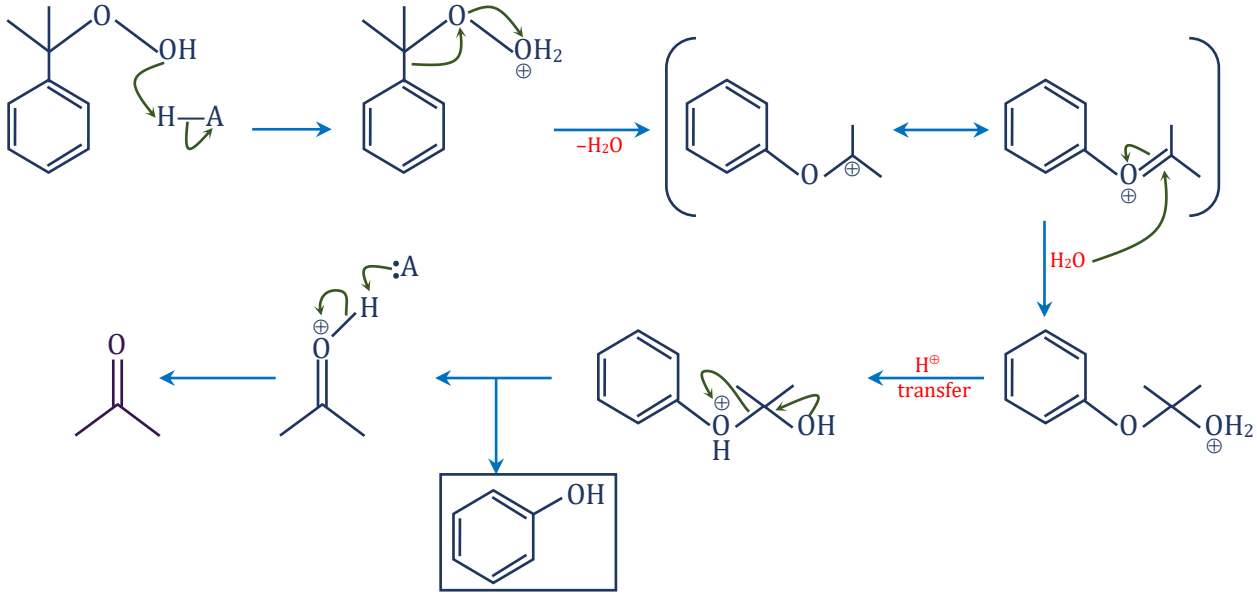


Illustration 3:

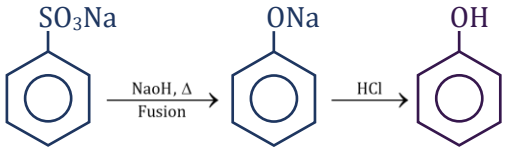


Illustration 4:

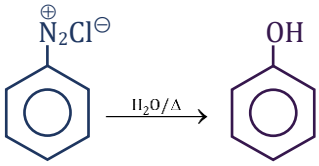


Illustration 5:

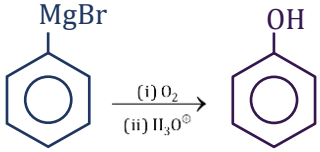


Illustration 6:

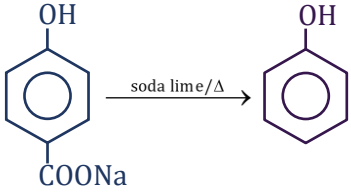


Illustration 7:

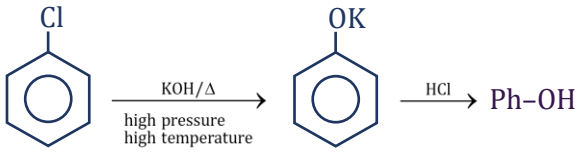


Illustration 8:

How many compounds of the following contain phenolic functional group.

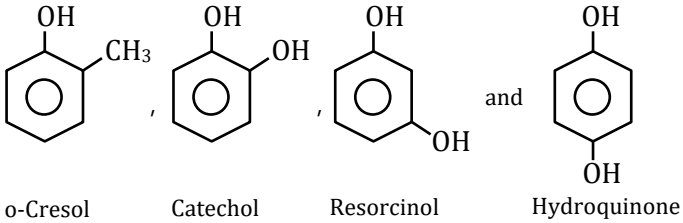
(A) Cresol (B) Catechol (C) Resorcinol (D) Hydroquinone (E) Quinol

(F) Anisole (G) Aniline (H) Glycerol (I) Phenetole

Ans. (4)

Solution:

Compounds containing phenolic functional group are :



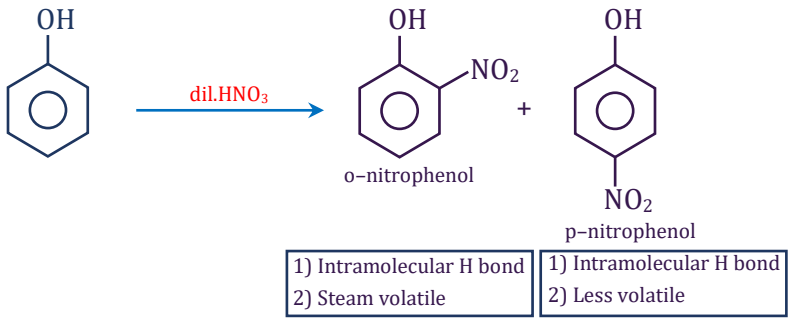
o-Cresol Catechol Resorcinol Hydroquinone

Total = 4

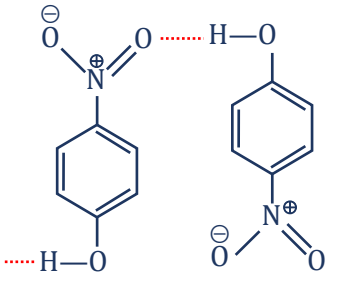
Electrophilic aromatic substitution reaction of phenol :

In phenol, —OH group is ring activating and ortho and para directing as these positions get more electron density through resonance.

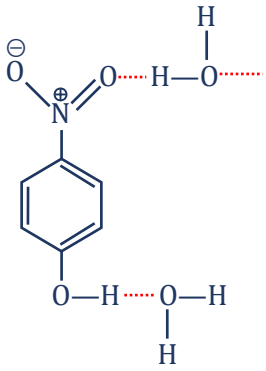
Nitration :



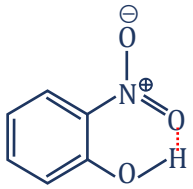
Phenol is colourless solid (m.p. 41°C) the colour if any associated with phenols is either due to the presence of some other functional group —NO_2 or due to presence of some oxidized product of phenol as impurity. Comparative solubility and boiling point is observed in the three isomers (o–m– and p) nitrophenols. p–nitrophenol is capable of forming intermolecular H bond between themselves and with water too, hence it has higher m.p. and more solubility in water m–nitrophenol also behaves the same way.



p–nitrophenol (intramolecular H–bond between two molecules



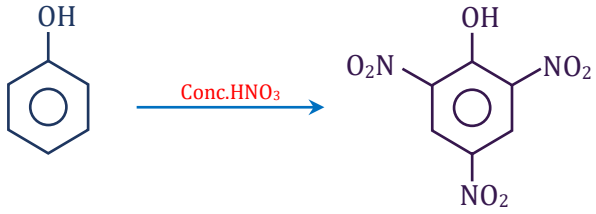
(Intramolecular H–bond with water)



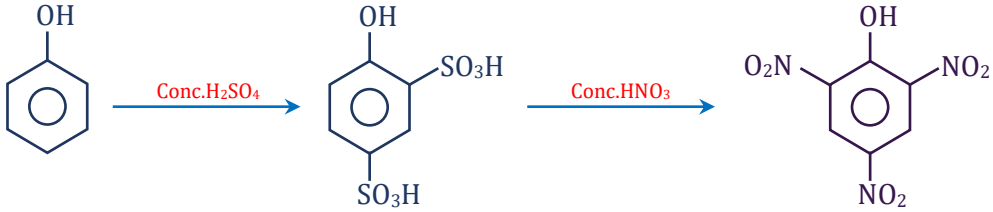
O-nitrophenol (intra molecular H-bonding restricts intermolecular H-bonding)

Nitration of phenol gives a poor yield because nitric acid also causes oxidation of phenol, to give unwanted product

Phenol when treated with conc. HNO_3 gives 2,4,6–trinitrophenol known as picric acid



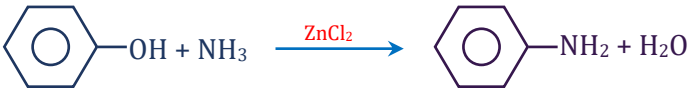
The yield in the reaction is poor. Now a days picric acid is prepared by treating phenol with conc. H_2SO_4 and then with conc. HNO_3.



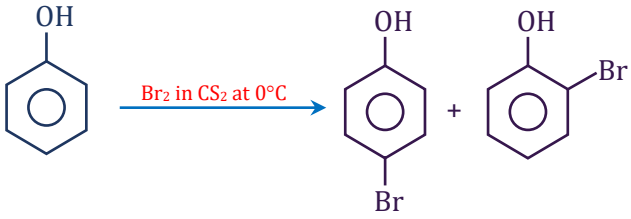
Picric acid

Reaction with Ammonia :

Phenol is converted to aniline when heated with ammonia under pressure or in presence of $ZnCl_2$.



Halogenation :

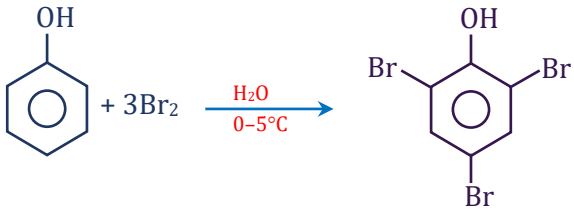


When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.

Here no lewis acids like $FeBr_3$ are required because highly activating effect of –OH group polarise bromine quickly.

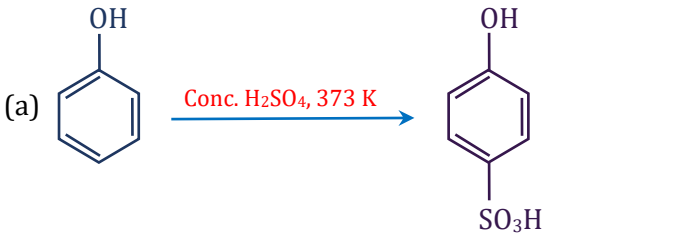
Phenol reacts with bromine water and give 2,4,6–tribromo phenol (white precipitate)

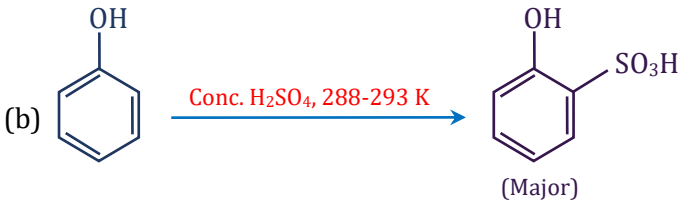
In water phenol forms phenoxide ion which activates the benzene ring.



Sulphonation:

Sulphonation of phenol is an electrophilic aromatic substitution reaction and is also reversible.



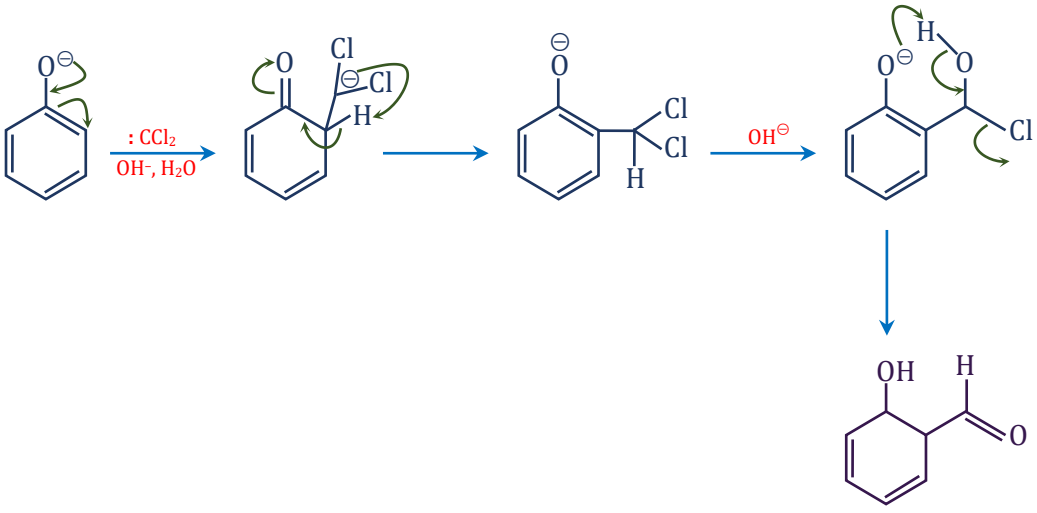


Reimer–Tiemann reaction:

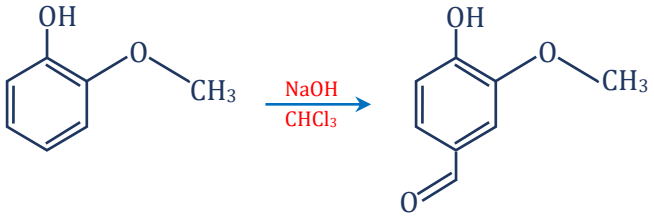
This reaction is carried out by refluxing an alkaline solution of phenol with chloroform at 60°C, distilling off the excess of chloroform, acidifying the residual liquid with sulphuric acid, and then stem–distilling it. Unchanged phenol and o–hydroxy–benzaldehyde distil over, leaving behind p–hydroxy–benzaldehyde. The mechanism of the Reimer–Tiemann reaction is believed to involve the formation of dichlormethylene.

$$CHCl_3 + OH^{\ominus} \rightarrow H_2O + \overset{\ominus}{C}Cl_3$$

$$CCl_3^{\ominus} \rightarrow :CCl_2 + Cl^{\ominus}$$

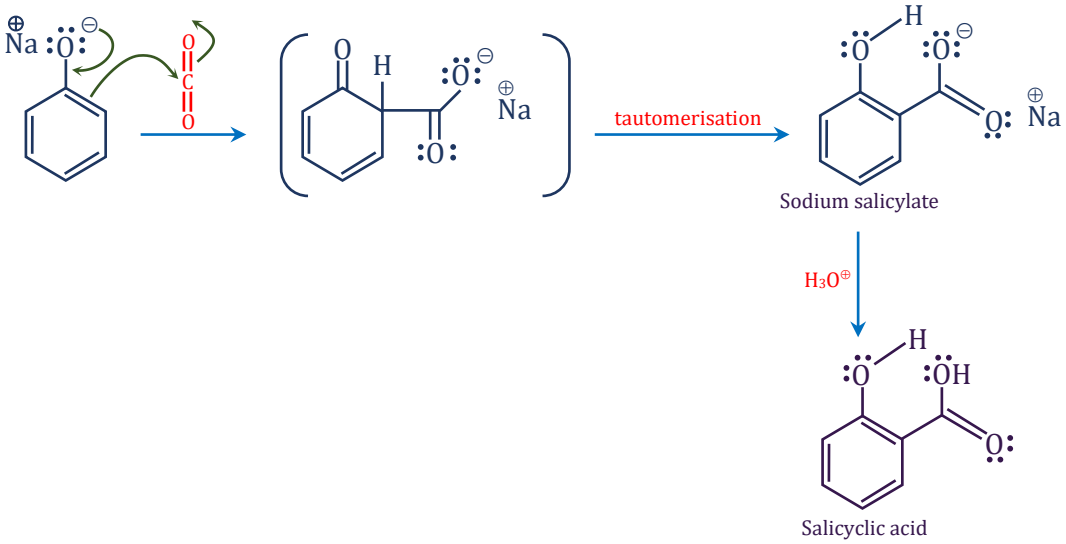


In the Reimer–Tiemann reaction, the o–isomer predominates, but if one of the o–position is occupied, the aldehyde group tends to go the p–position; e.g., guaiacol forms vanillin.



Kolbe Reaction:

Phenol in the presence of base NaOH, reacts with carbon dioxide at high temperature and pressure to yield sodium salicylate which on acidification yields salicylic acid. This reaction is electrophilic substitution reaction in where carbon dioxide behaves as an electrophile. The reaction is known as Kolbe reaction.



The Kolbe reaction is usually carried out by allowing sodium phenoxide to absorb carbon dioxide and then heating the product to 125° C under a pressure of several atmospheres of carbon dioxide. The unstable intermediate undergoes a proton shift. In this reaction substitution takes place only at ortho position. When potassium phenoxide is used, para isomer will be formed.

Action of Zinc dust on phenol:

Phenol on heating with zinc duct produces benzene.

Illustration 9:

Phenol generally gives electrophilic substitution with electrophilic reagents.

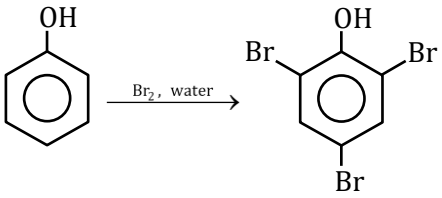


Illustration 10:

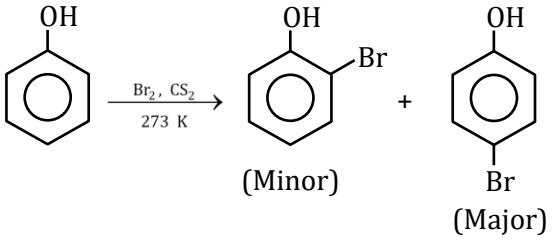


Illustration 11:

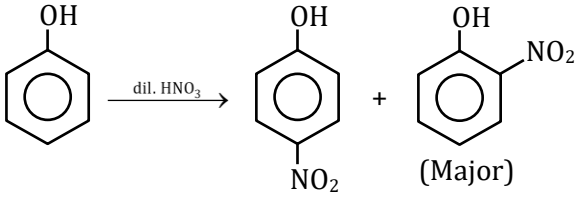


Illustration 12:

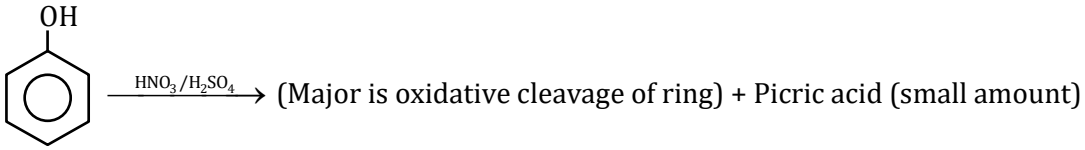
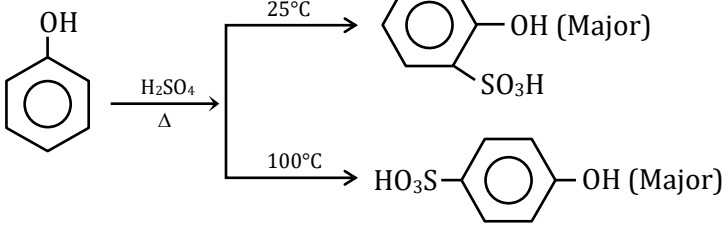
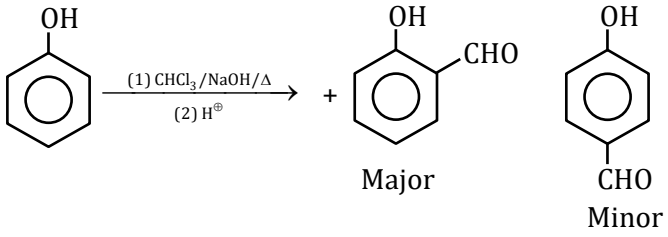


Illustration 13:



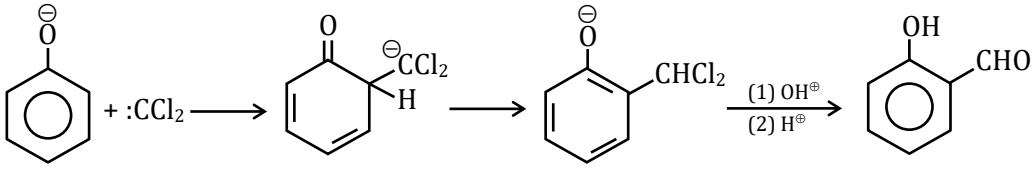
Reimer-Tiemann formylation reaction:



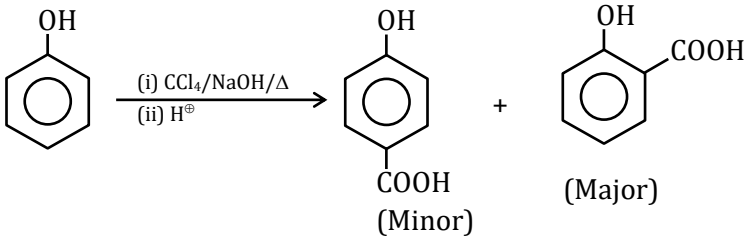
Mechanism :

Step (I) : $CHCl_3 + NaOH \longrightarrow \overline{\underset{\cdot\cdot}{C}}Cl_3 \longrightarrow :CCl_2$

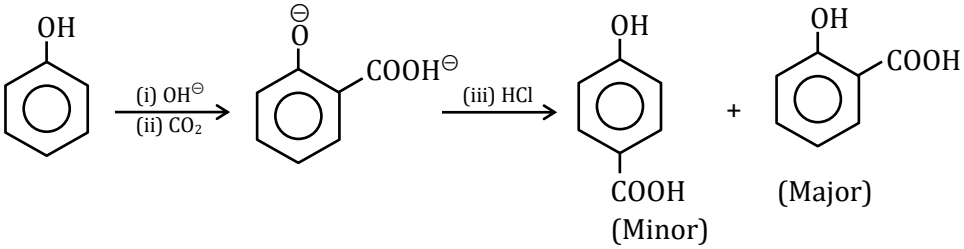
Step (II) :



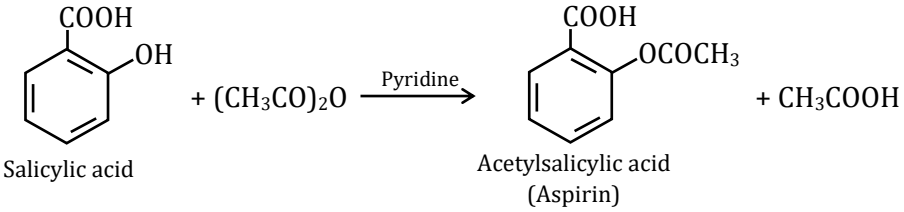
(7) Reimer-Tiemann carboxylation reaction:



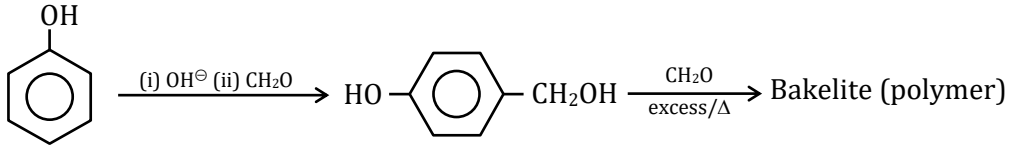
(8) Kolbe carboxylation reaction :



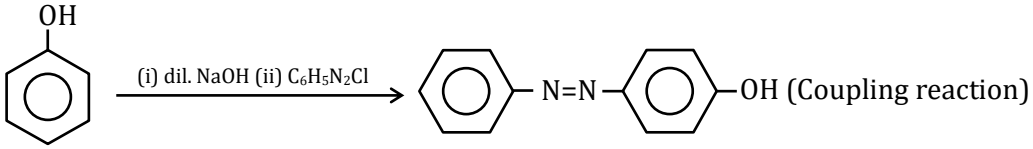
Preparation of aspirin:



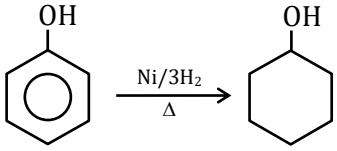
(9)



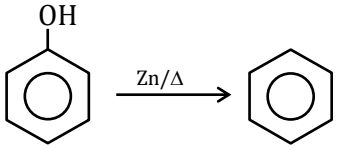
(10)



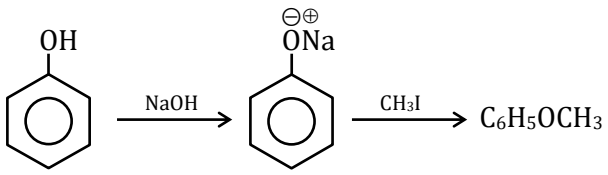
(11)



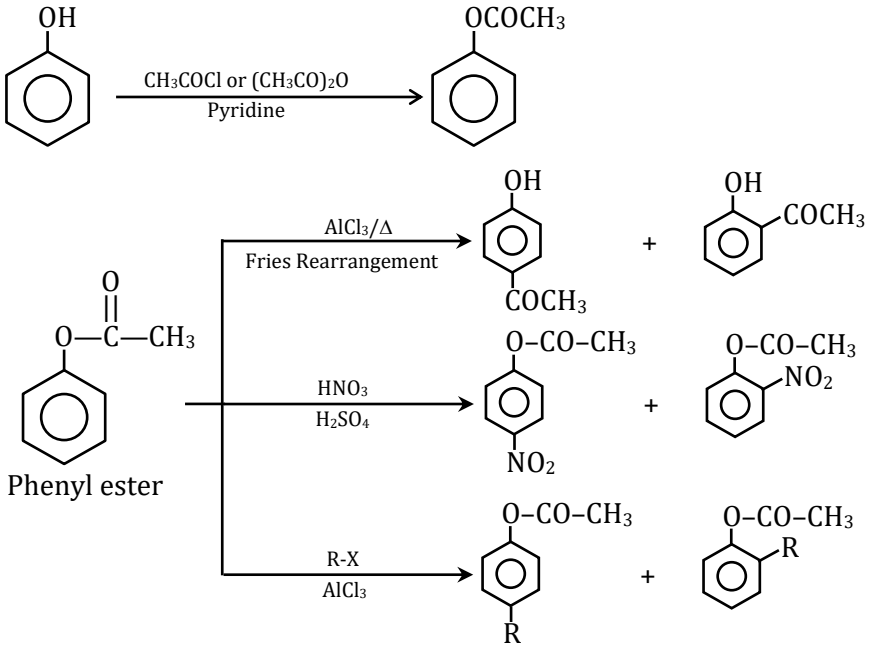
(12)



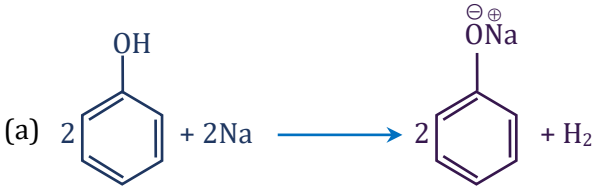
(13) Williamson ether synthesis



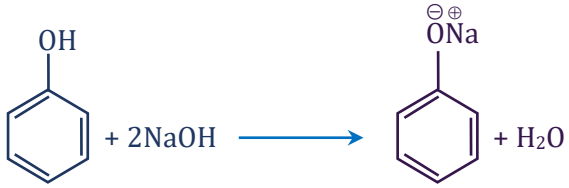
(14) Protection of –OH and –NH_2 group.



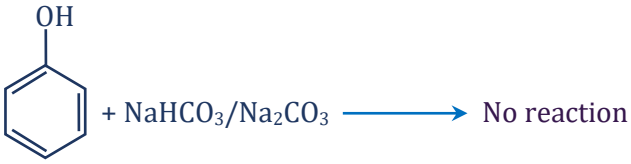
Chemical reaction of phenol as acid:



(b) Phenols also react with aqueous NaOH solution to produce the salt sodium phenoxide and water.

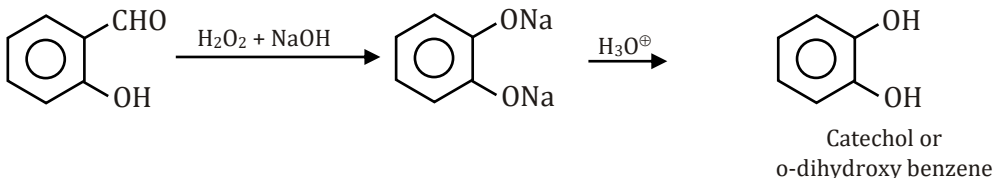


(c) Phenol does not liberate CO_2 with Na_2CO_3 or $NaHCO_3$ because phenol is weakly acidic than carbonic acid and carboxylic acids.



Dakin Reaction:

This reaction is characteristic of o- and p-hydroxy aldehyde or o-and-p amino aldehyde with alkaline H_2O_2, followed hydrolysis to give o-or p- dihydroxy benzene or o-or p aminophenol, e.g.,



Catechol or
o-dihydroxy benzene

MECHANISM

It involves 1,2 shift

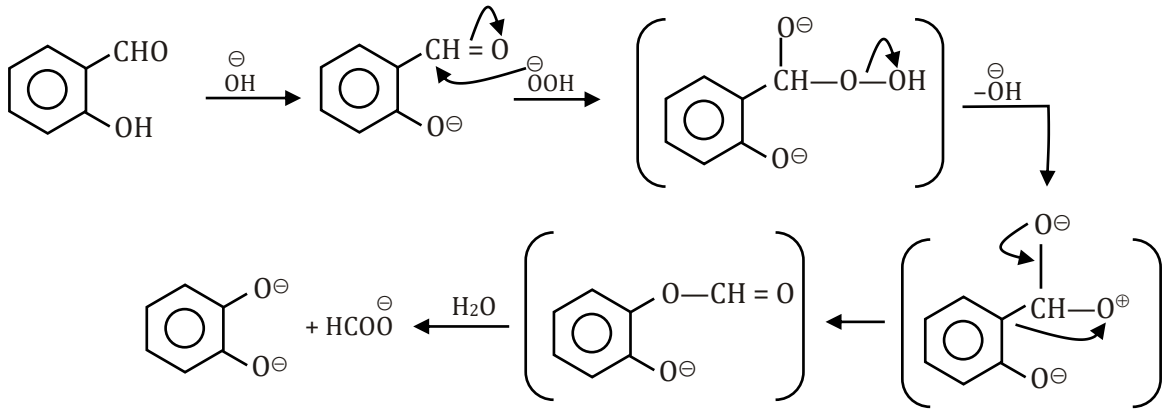
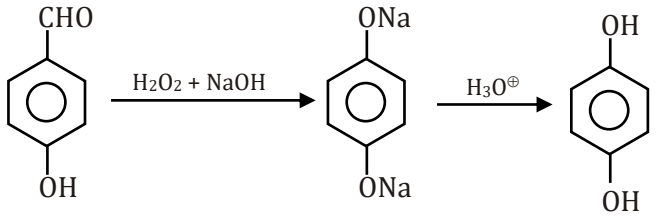
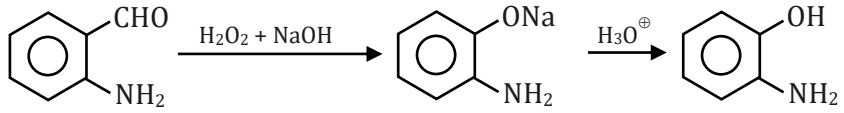


Illustration 14:



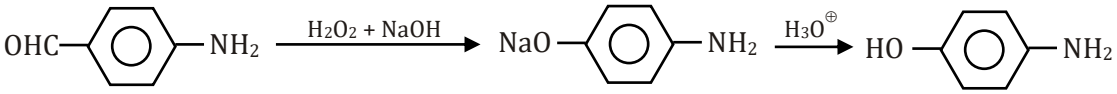
Quinol or
p-dihydroxy
benzene

Illustration 15:



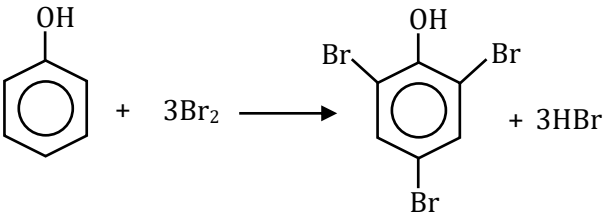
Catechol or
o-Amino phenol

Illustration 16:



p-Amino phenol

Illustration 17:



(A) Nucleophilic addition
(B) Nucleophilic substitution
(C) Electrophilic addition
(D) Electrophilic substitution

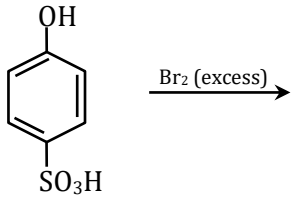
Ans. (D)

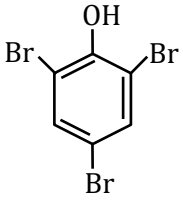
Solution:

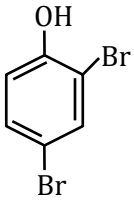
Given reaction is an example of electrophilic substitution reaction.

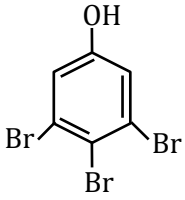
Illustration 18:

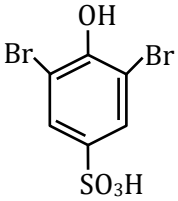
The major product of the following reaction is: **[JEE (Main) 2019]**



(1) 

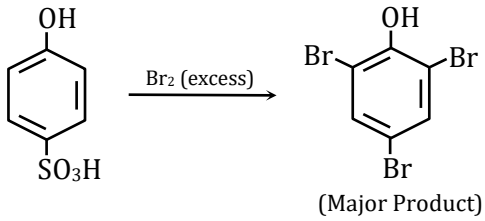
(2) 

(3) 

(4) 

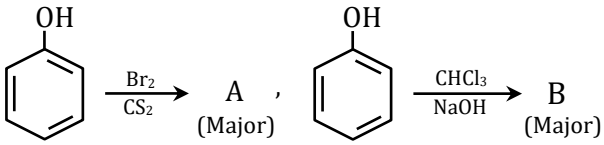
Ans. (1)

Solution:

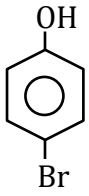


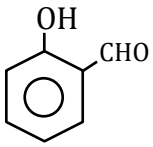
(Major Product)

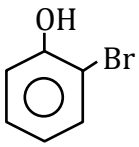
Illustration 19:

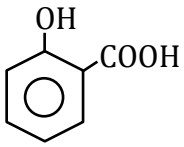


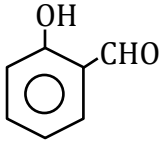
A and B are? **[JEE (Main) 2021]**

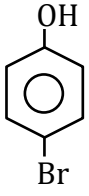
(1) A → 

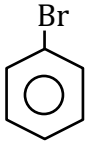
B → 

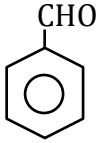
(2) A → 

B → 

(3) A → 

B → 

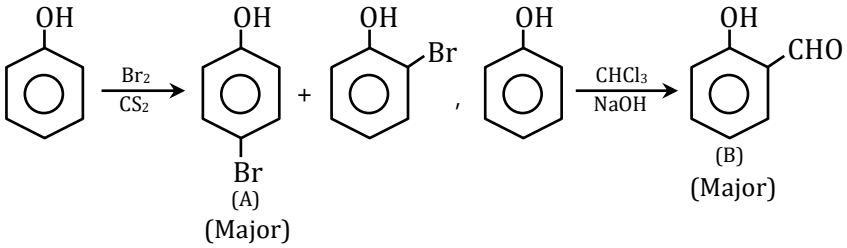
(4) A → 

B → 

Ans. (1)

Solution:

The product formed is :



Paragraph # 20 to 22

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.

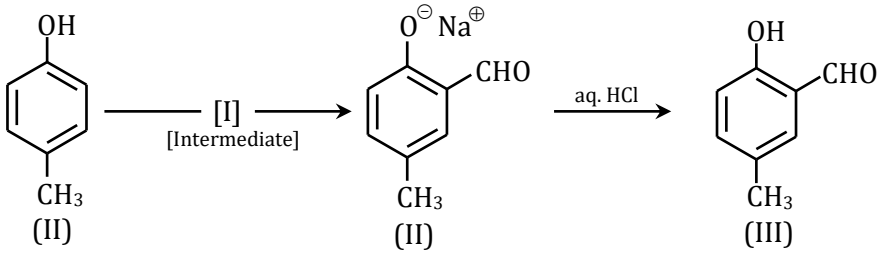


Illustration 20:

Which one of the following reagents is used in the above reaction ? **[JEE 2007]**

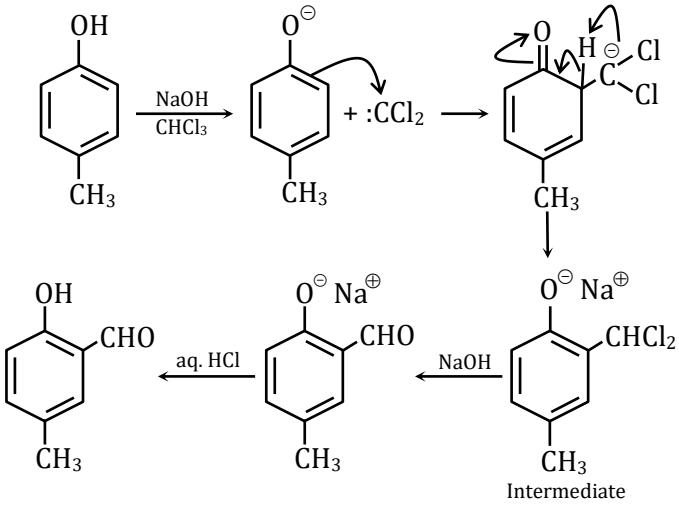
(A) aq. NaOH + CH_3Cl (B) aq. NaOH + CH_2Cl_2

(C) aq. NaOH + $CHCl_3$ (D) aq. NaOH + CCl_4

Ans. (C)

Solution:

The complete reaction sequence is :



$NaOH + CHCl_3$ is used as reagent.

Illustration 21:

The electrophile in this reaction is **[JEE 2007]**

(A) $:CHCl$ (B) $\overset{\oplus}{C}HCl_2$ (C) $:CCl_2$ (D) $\overset{\bullet}{C}Cl_3$

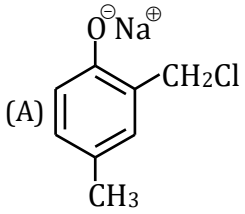
Ans. (C)

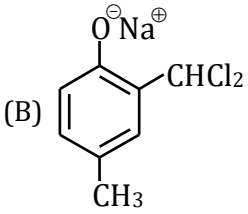
Solution:

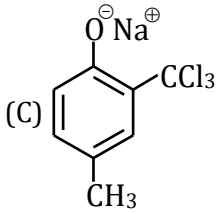
The electrophile involved in reaction is dichlorocarbene ($:CCl_2$).

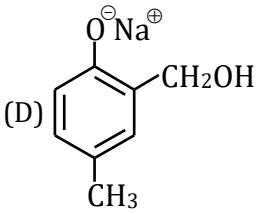
Illustration 22:

The structure of the intermediate I is: **[JEE-Main 2007]**

(A) 

(B) 

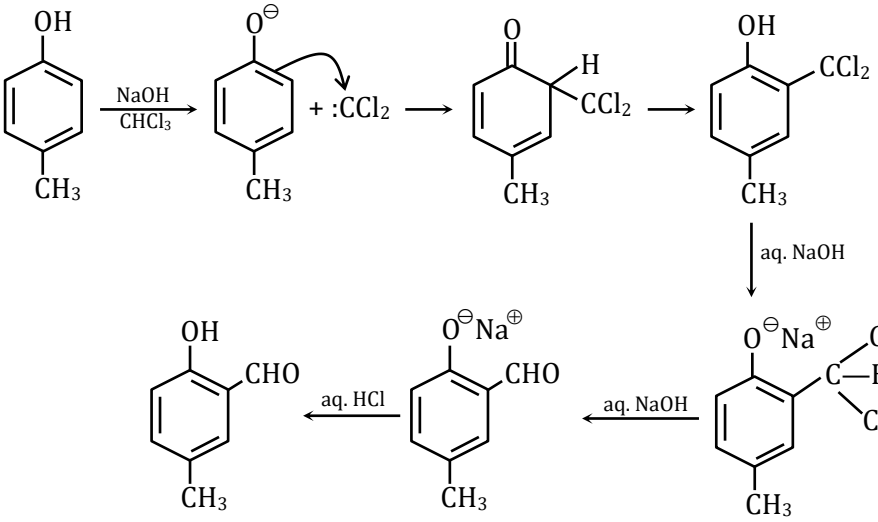
(C) 

(D) 

Ans. (B)

Solution:

The intermediate (I) is :



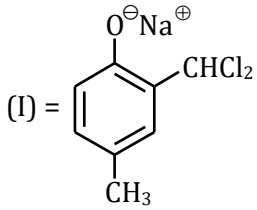
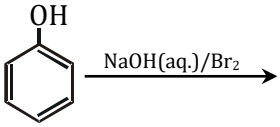
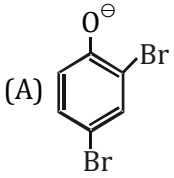
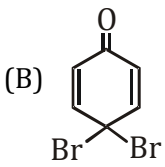
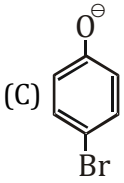
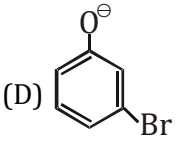
(I) = 

Illustration 23:

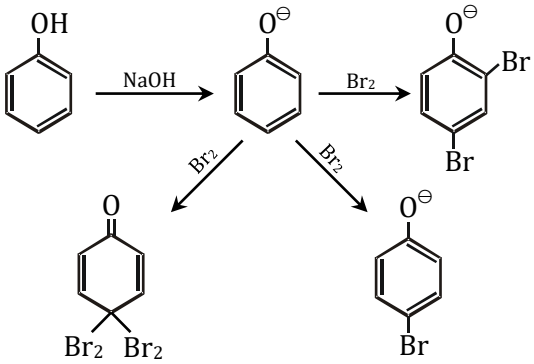
In the reaction  the intermediate(s) is(are) : **[JEE 2009]**

(A) 
(B) 
(C) 
(D) 

Ans. (A, B, C)

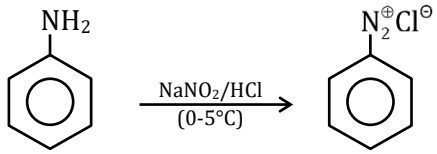
Solution:

The reaction involved is :



Diazotisation:

Preparation of benzenediazonium salt:

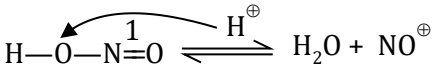


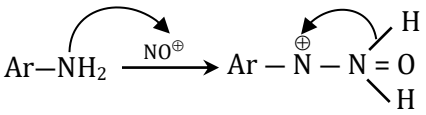
Benzene
Diazonium chloride

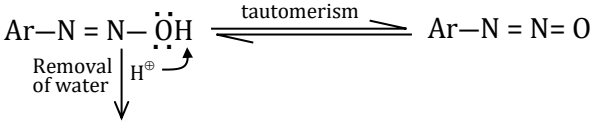
Diazonium salt are prepared by adding cold solution of $NaNO_2$ to aniline below 5°c this process is called diazotisation

Mechanism of diazotization :

Step-(1) Formation of $NO^{\oplus}$ (Nitrosonium ion):







$Ar—N \equiv N + H_2O$

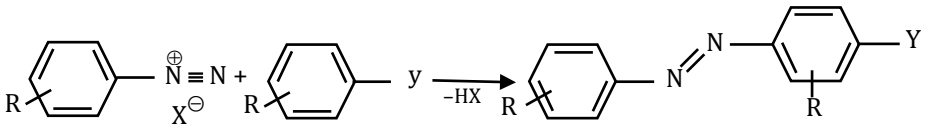
Compound containing —N= N— group are known as diazo compound.

General structure

Ar—N = N—Ar

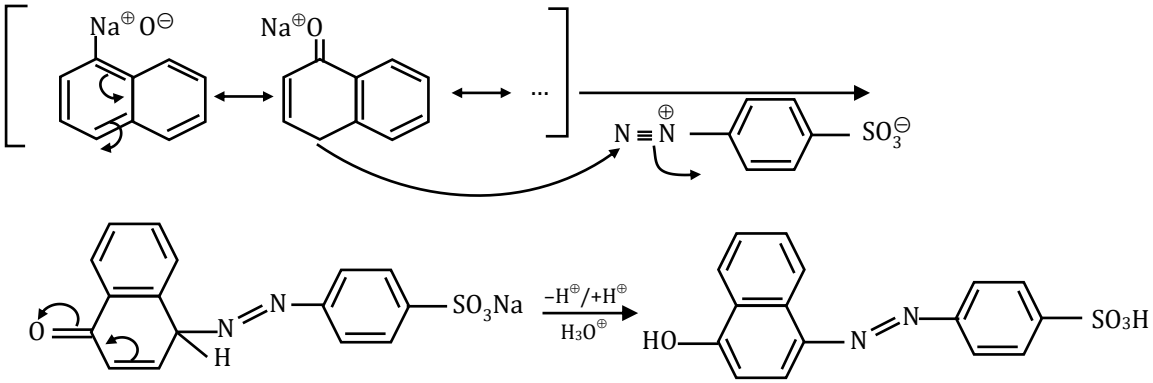
Use of diazo compound - Diazo compound are used as indicator & dye, methyl orange

Azo Coupling:

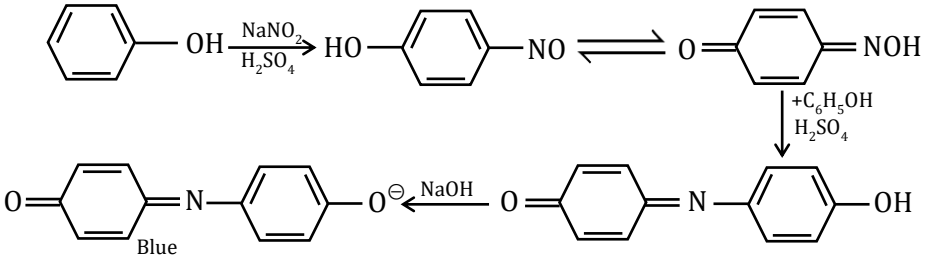


Azo coupling is the most widely used industrial reaction in the production of dyes, lakes and pigments. Aromatic diazonium ions acts as electrophiles in coupling reactions with activated aromatics such as anilines or phenols. The substitution normally occurs at the para position, except when this position is already occupied, in which case ortho position is favoured. The ph of solution is quite important; it must be mildly acidic or neutral, since no reaction takes place if the ph is too low.

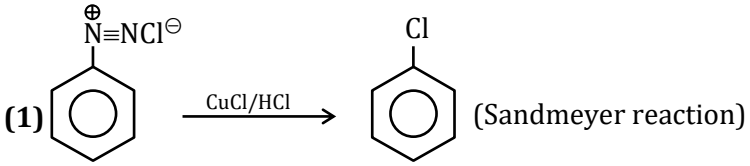
Mechanism of Azo Coupling



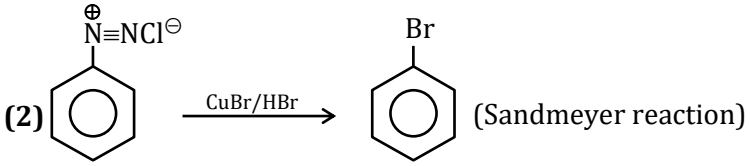
Phenol reacts with concentrated sulfuric acid and sodium nitrite forms a yellow colour quinone monoxime complex. With excess phenol and sulfuric acid, a deep blue indophenol complex is formed. On dilution, a red colour indophenol is formed which turns to deep blue colour sodium salt solution of indophenol on treatment with sodium hydroxide.



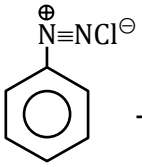
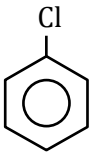
Chemical reactions of benzenediazonium chloride:

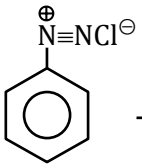
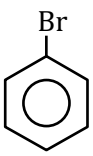


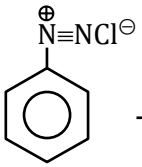
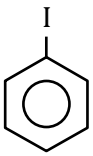
(Sandmeyer reaction)

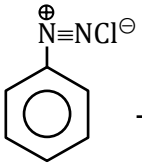


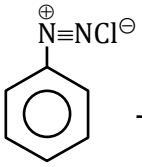
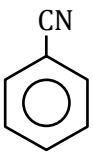
(Sandmeyer reaction)

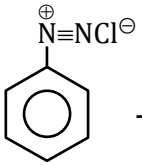
(3)  $\xrightarrow{Cu/HCl}$  (Gattermann reaction)

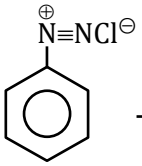
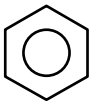
(4)  $\xrightarrow{Cu/HBr}$  (Gattermann reaction)

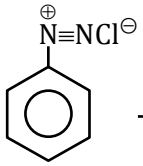
(5)  $\xrightarrow{KI,\ \Delta}$  $+N_2 + KCl$

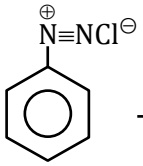
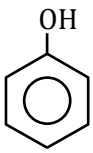
(6)  $\xrightarrow[-HCl]{HBF_4}$ $C_6H_5N_2^{\oplus}BF_4^{\ominus} \xrightarrow{\Delta} C_6H_5{-}F + BF_3 + N_2$ (Balz-Schiemann reaction)

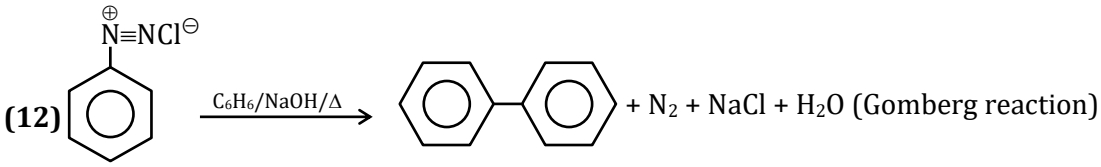
(7)  $\xrightarrow[\text{Or Cu powder}]{KCN/CuCN/\Delta}$ 

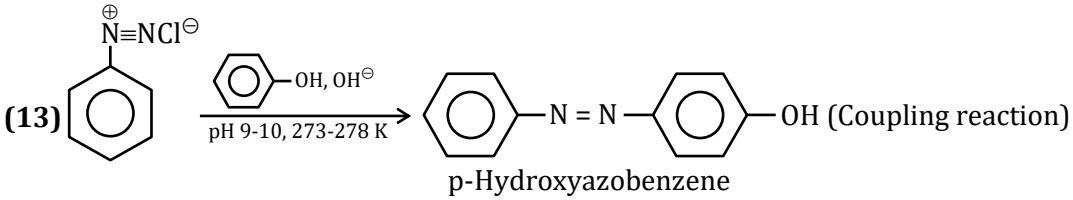
(8)  $\xrightarrow[-HCl]{HBF_4}$ $C_6H_5N_2^{\oplus}BF_4^{\ominus} \xrightarrow[Cu\ powder/\Delta]{NaNO_2} C_6H_5NO_2 + NaBF_4 + N_2$

(9)  $\xrightarrow{C_2H_5OH,\ \Delta}$  $+ N_2 + HCl + CH_3CHO$

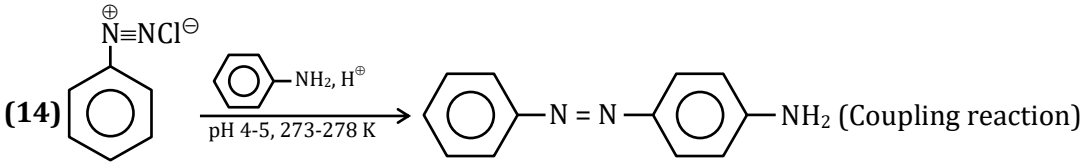
(10)  $\xrightarrow[(Hypophosphorus\ acid)]{H_3PO_2 + H_2O/Cu^{\oplus}}$  $+ N_2 + H_3PO_3 + HCl$ (Deamination)

(11)  $\xrightarrow{H_2O,\ \Delta}$  $+ N_2 + HCl$

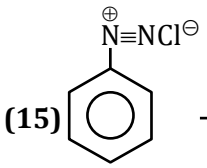


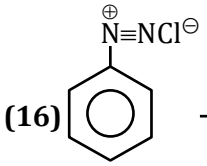


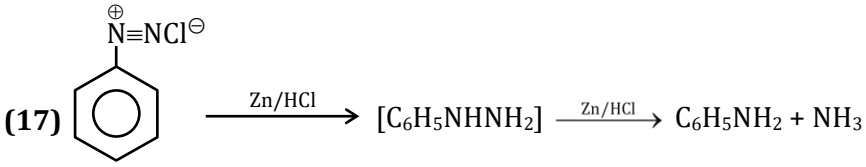
p-Hydroxyazobenzene



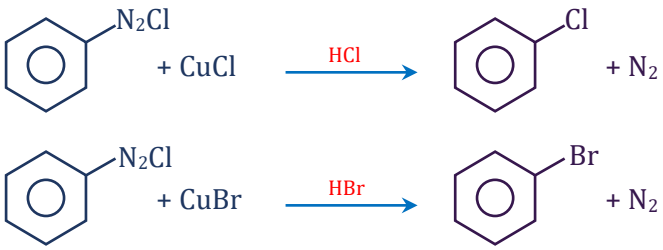
p-Aminoazobenzene
(yellow dye)





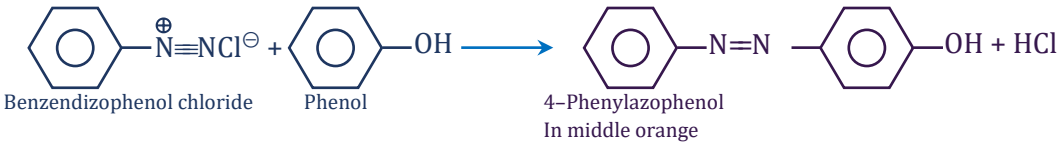


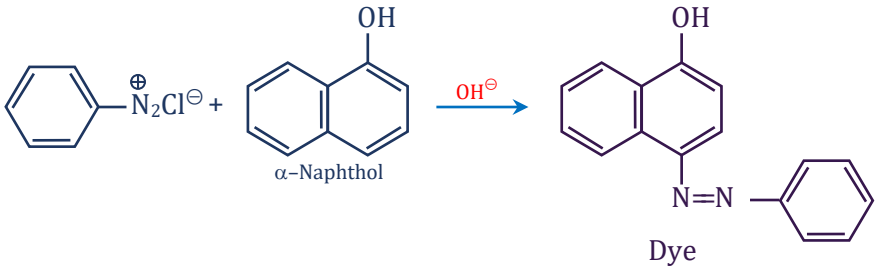
Sandmeyer's reaction:

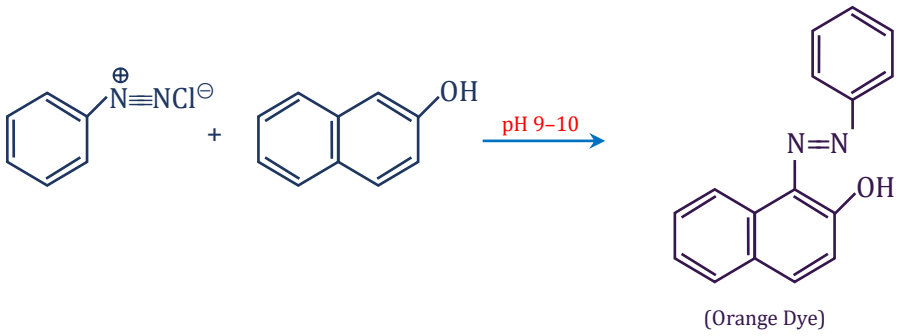


Diazo coupling Reaction :

Benzene diazonium salt react with electron rich compound like phenol, α–or 1–naphthol and β–naphthol to form bright (Orange Red) coloured azo compound in basic medium (pH 9–10)

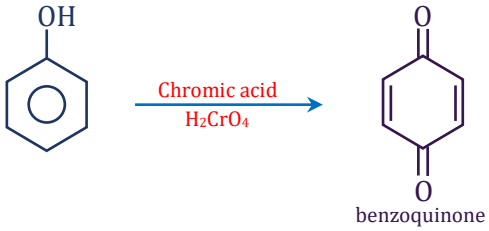




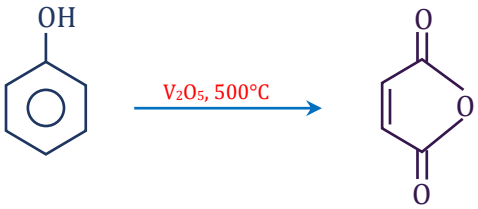


Oxidation of phenol:

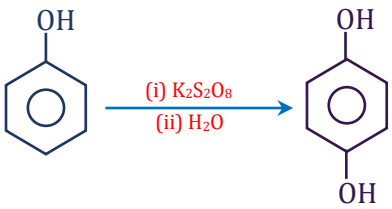
(A) Phenol on oxidation with chromic acid ($Na_2Cr_2O_7$ + H_2SO_4) produces benzoquinone, which is a conjugate diketone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



(B)



(C) Elbs Persulphate oxidation:



Fries rearrangement:

Phenyl acetate undergoes the Fries rearrangement with $AlCl_3$ to form ortho and para hydroxyl acetophenone. The ortho isomer is separated from the mixture by the steam–distillation.

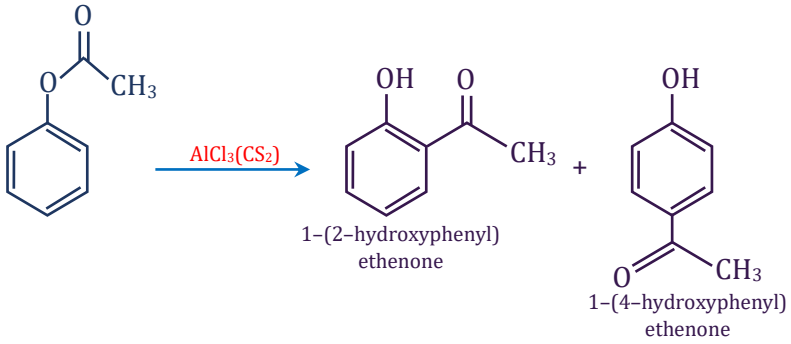
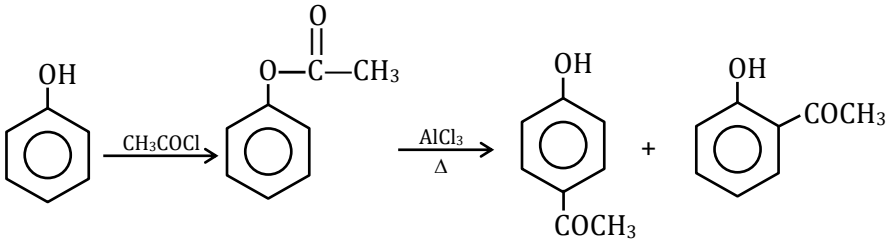


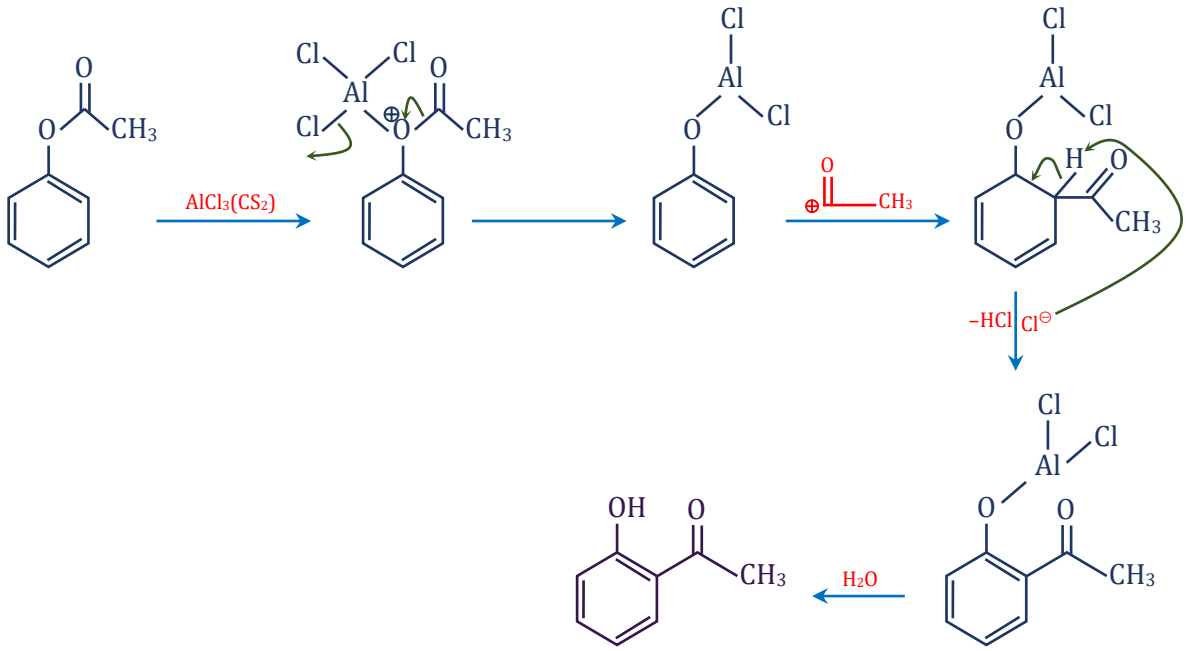
Illustration 24:



Intramolecular Mechanism :

If may be assumed to Friedel–Craft's acylation type in which the acylicum ion is supplied by the substrate, i.e. it self–acylation.

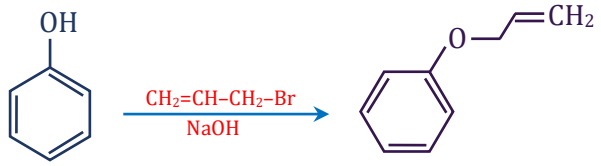
First of all, $AlCl_3$ complexes with the oxygen of the phenoxy group from which the acylium ion is generated, the acylium ion then attacks the benzene ring as in the case of Friedel–Craft acylation.



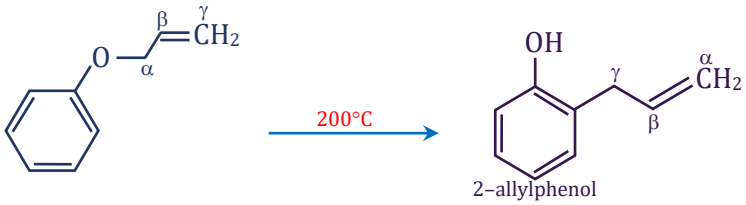
Similar attack at p–position gives the para isomer.

Alkylation:

When phenol is treated with allyl halide in the presence of NaOH formation of aryl ally ether takes place.



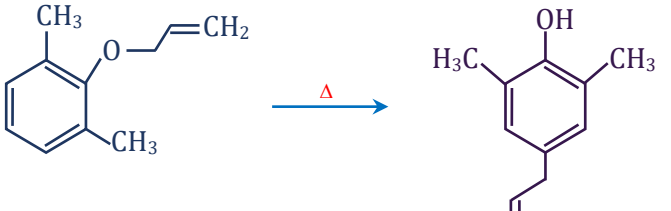
Allyl phenyl ethers rearrange to o–allyl phenol when heated at 200°C.



2–allylphenol

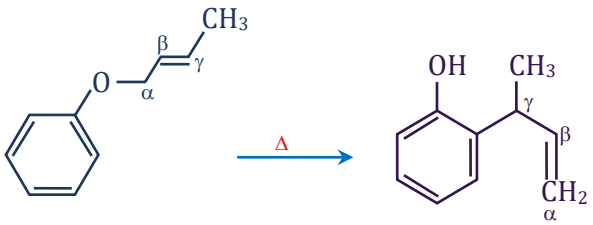
This rearrangement is known as **Claisen–rearrangement**

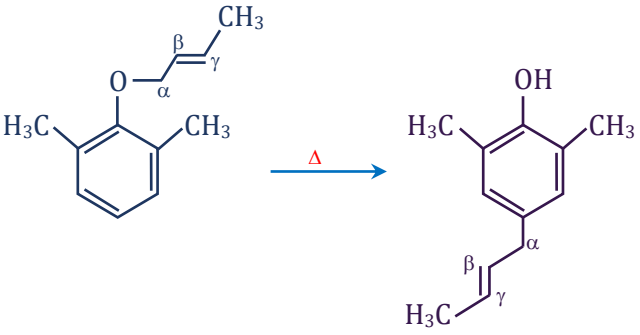
If ortho position is free, only positions are substituted then rearrangement takes place at para position.



4–allyl–2, 6–dimethylphenol

An interesting feature of the rearrangement is that when migration takes place to the ortho position, the γ–carbon of allyl group attaches itself to the benzene ring. In other words, there is an inversion of allylic chain. However, no such inversion of allylic chain takes place with p–migration.





Test for phenol:

(A) Ferric Chloride Test :

This test is based on the verity that phenols produce a colourful complex when mixed with a mental ferric chloride solution.

Phenol interacts with ferric ions of ferric chloride to generate a colourful complex.

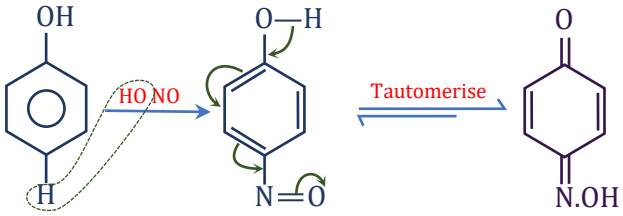
The reaction is as follows :

$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5O)_6]^{3\ominus} + 3HCl + 3H^{\oplus}$$

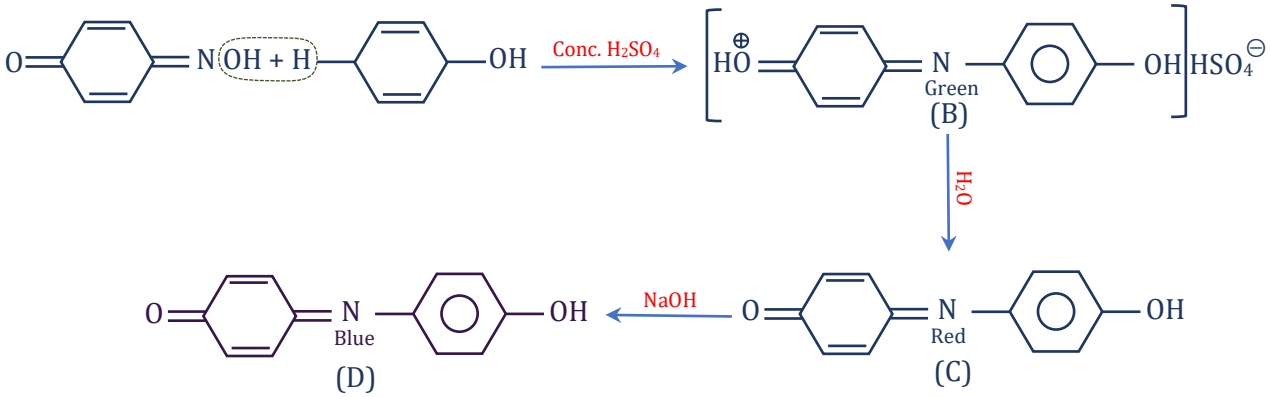
Phenol — Ferric chloride — Violet complex

(B) Libermann's nitroso reaction :

Phenol reacts with (HONO) to give p-nitrosophenol which is tautomeric with the monoxime of quinone.

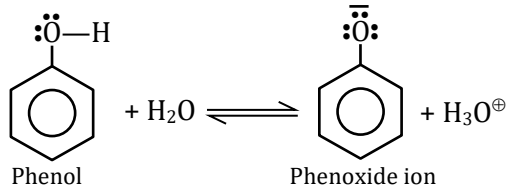


In the presence of conc. H_2SO_4 the monoxime condenses with phenol to give blue-green solution of indophenol monosulphate which on dilution gives indophenol (red). With NaOH, sodium salt of indophenol (deep blue) is produced. This is Libermann's nitroso reaction.



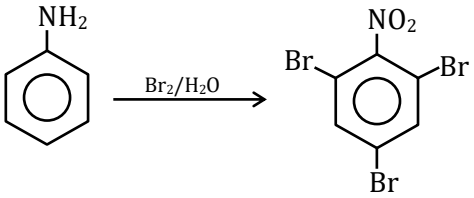
NOTE :

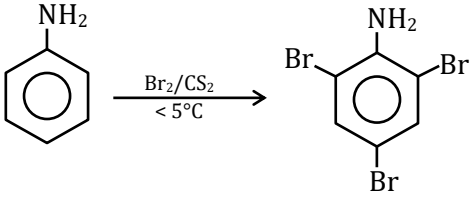
Phenols turn blue litmus red. Phenols behave as acid and ionise in aqueous solution to give $H^{\oplus}$ ions.

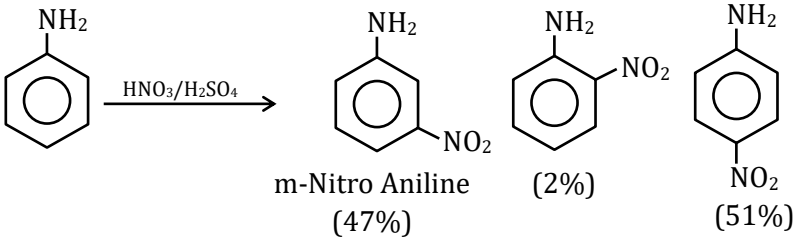


Chemical reactions of aniline :

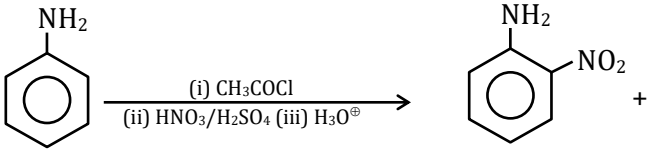
(1) $C_6H_5NH_2 \xrightarrow{H_2SO_4} [C_6H_5\overset{\oplus}{N}H_3]_2\,SO_4^{2\ominus}$

(2) 

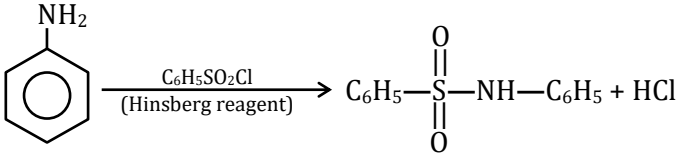
(3) 

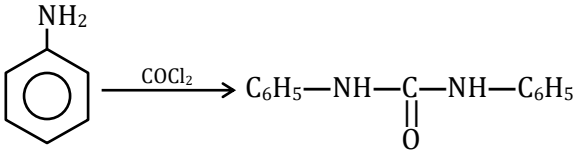
(4) 

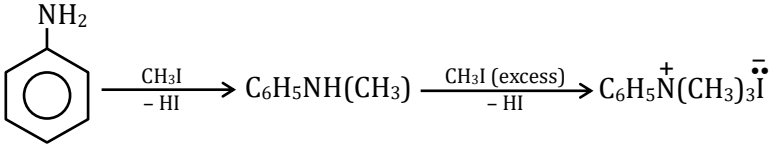
m-Nitro Aniline (47%) (2%) (51%)

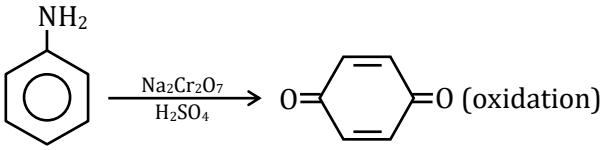
(5) 

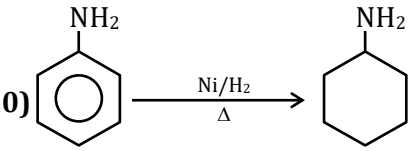
o-nitro aniline p-nitro aniline

(6) 

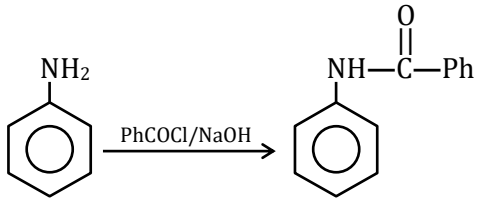
(7) 

(8) 

(9) 

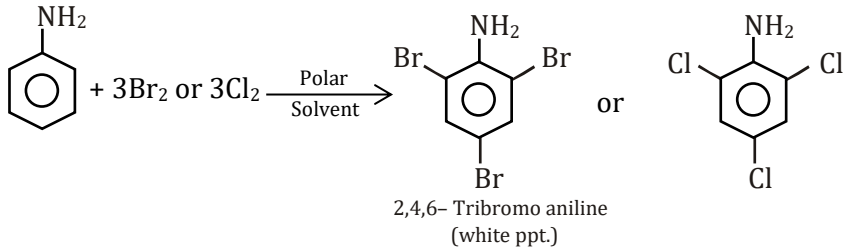
(10) 

(11) Scholten Bauman reaction.

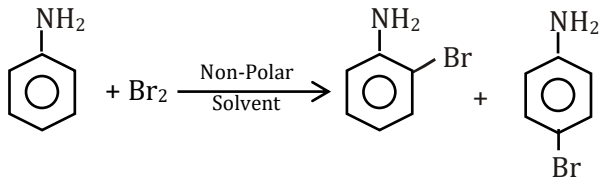


Halogenation:

In polar and nonpolar medium Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively.

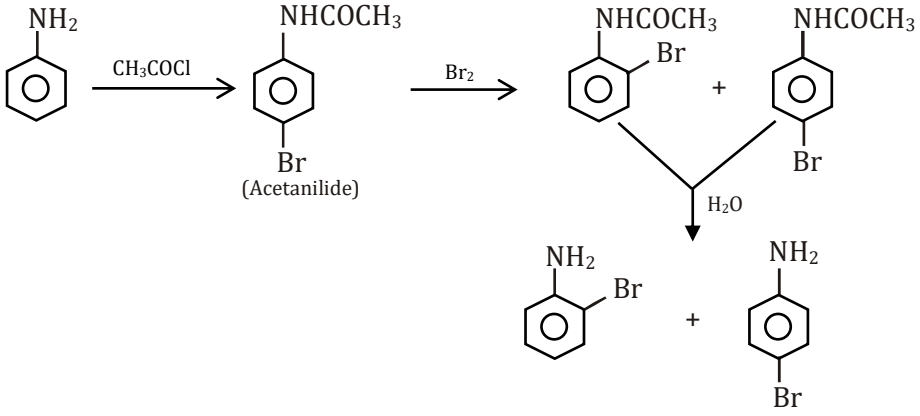


2,4,6– Tribromo aniline
(white ppt.)



Note :

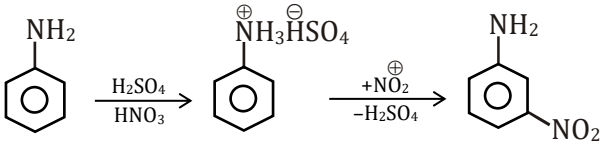
However, monobromo or chloro derivative of aniline can be prepared if -NH_2 group is first protected by acetyl group. Here the reactivity decreases due less –I effect on benzene ring.



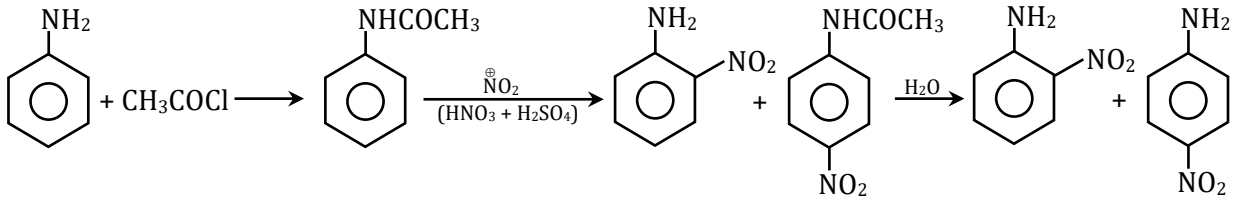
o– and p–Bromo aniline

Nitration :

(a) Direct nitration: The direct nitration of aniline by conc. HNH_3 and conc. H_2SO_4 give meta-nitroaniline. Due to positively charged N, m-position becomes electron rich as compared to o, p-position.

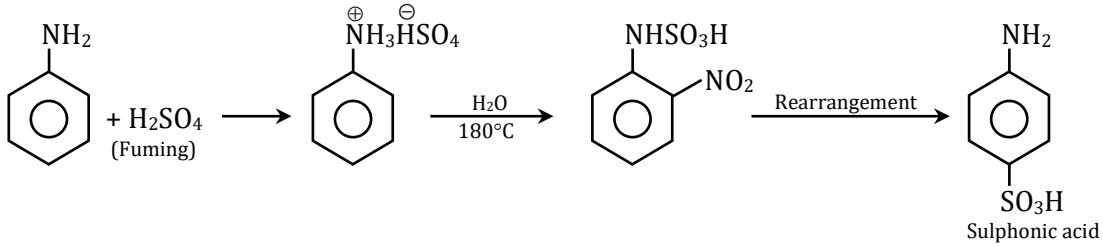


(b) Indirect nitration : In indirect nitration amino group is protected by acetylation to give acetanilide, which on nitration and subsequent hydrolysis give o-and p-nitro-aniline.



Sulphonation:

Aniline reacts with fuming H_2SO_4 to give sulphanilic acid.(p-Amino-benzene sulphonic acid)



Note :

This process is called baking.

Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.

The compounds in which both proton donating & proton accepting groups present are called ampholite (dipolar ion).

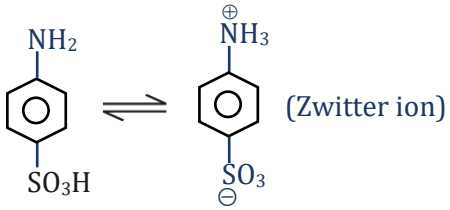
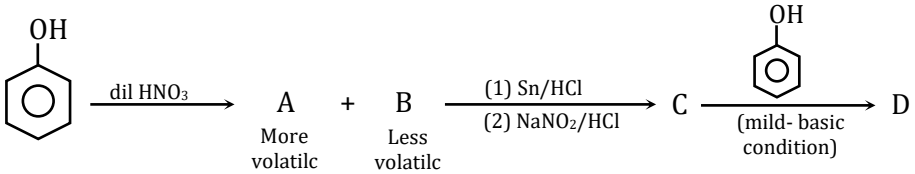


Illustration 25:

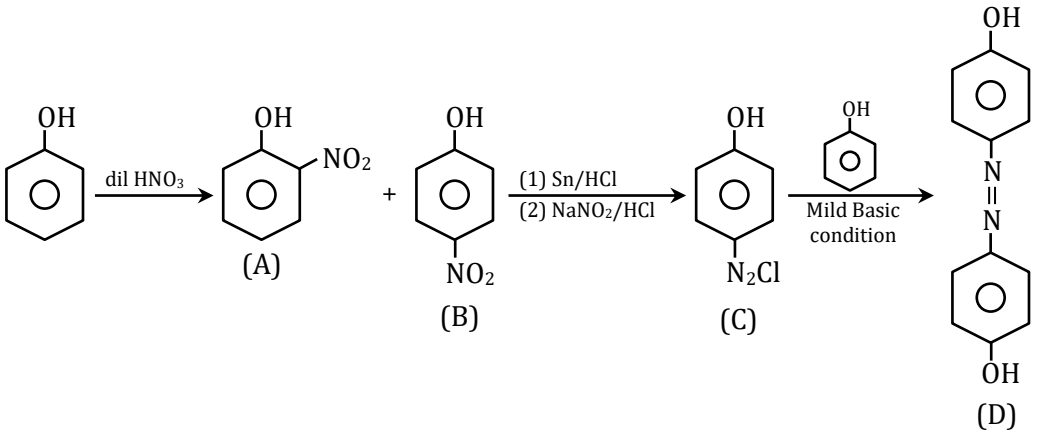


Double bond equivalent of D is:

Ans. (9)

Solution:

The complete reaction sequence is :



DU = 9

Illustration 26:

Benzenediazonium chloride on reaction with phenol in weakly basic medium gives: **[JEE 1998]**

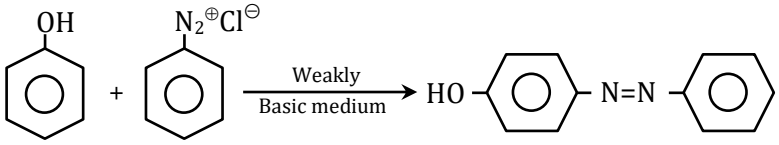
(A) Diphenyl ether (B) p-hydrooxyazobenzene

(C) Chlorobenzene (D) Benzene

Ans. (B)

Solution:

The azo coupling reaction will take place and product formed will be :



p-hydroxyazobenzene