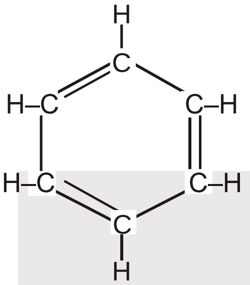
Aromatic Compounds

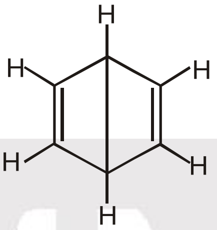
Introduction :

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

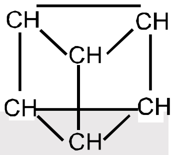
Proposed structure of benzene :



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)π 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)π electrons, i.e., 2, 6, 10, 14 .... π electrons. Where n = an whole number 0, 1, 2, 3,.............

Characteristic reaction of aromatic compounds :

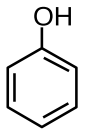
* Aromatic compounds prefer **electrophilic substitution** rather than electrophilic addition reaction.
* In aromatic electrophilic substitution reaction benzene ring serve as source of electrons that is as a base or nucleophile.
* Electrophilic aromatic substitution includes a wide variety of reactions :
e.g. Halogenation, Nitration, Sulphonation, Friedel Crafts alkylation & acylation but reactions like Nitrosation and Diazocoupling undergoes only by rings of high reactivity.

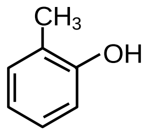
Section (A) : Phenol

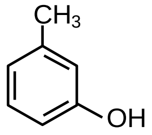
Phenol, also known as **carbolic acid**, was first isolated in the early nineteenth century from coaltar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives.

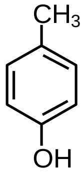
Some common examples are :

(i)



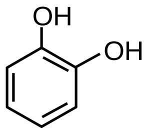


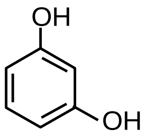


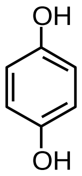


Common name :	Phenol	o-Cresol	m-Cresol	p-Cresol
IUPAC name :	phenol	2-methylphenol	3-methylphenol	4-methylphenol

(ii)





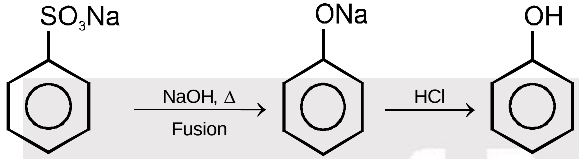


Common name :	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name :	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

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

(a) Preparation of phenol

(1)



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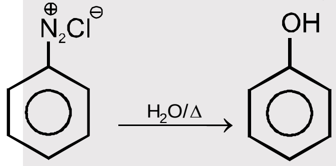

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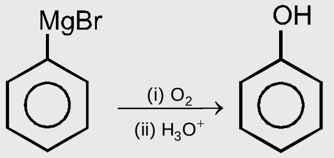

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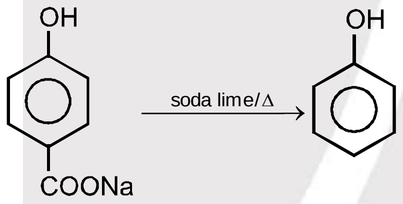

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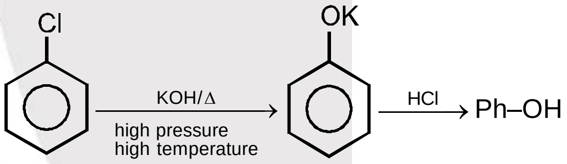
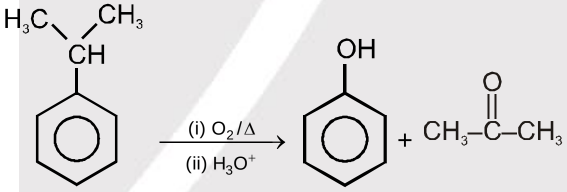
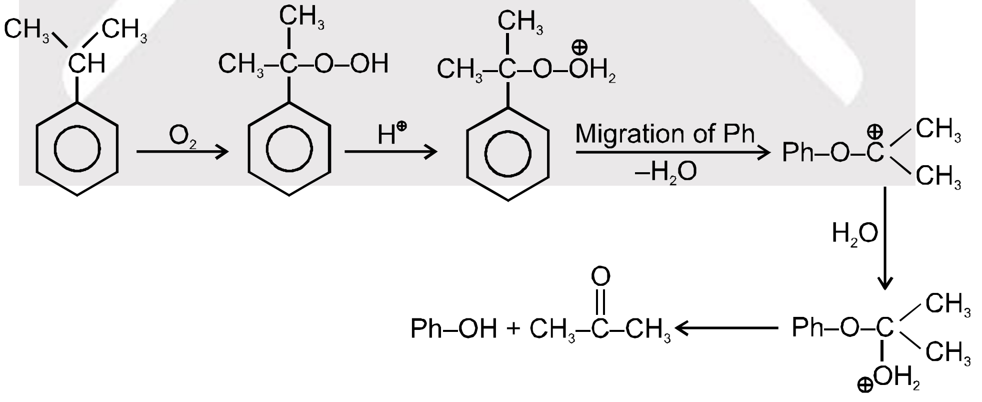


Mechanism (Cumene hydroperoxide method) :





(b) Properties of phenol :

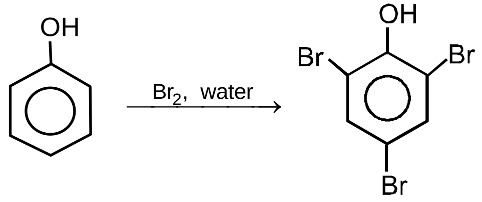
Phenol is a colourless crystalline solid, m.p. 43ºC, b.p. 182ºC, which turns pink on exposure to air and light.

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

(c) Chemical reactions of phenol :

Phenol generally gives electrophilic substitution with electrophilic reagents.

(1)



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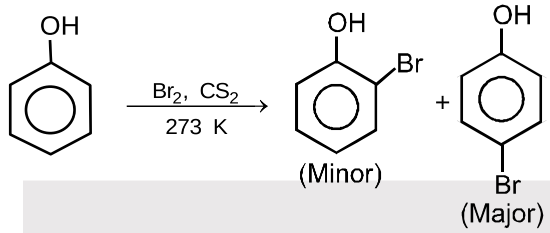

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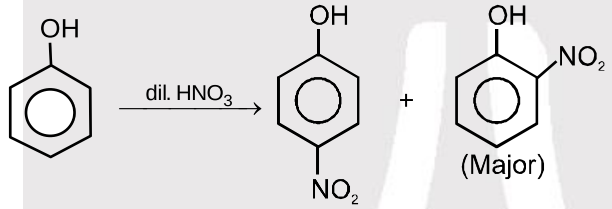

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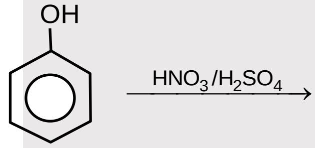
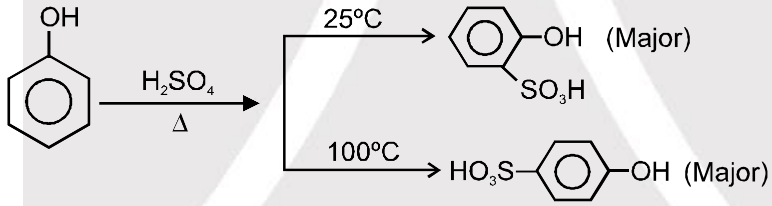
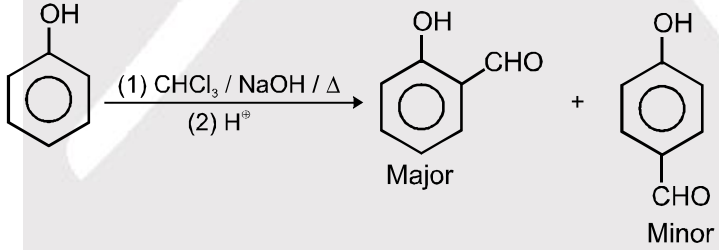


(Major is oxidative cleavage of ring) + Picric acid (small amount)

(5)



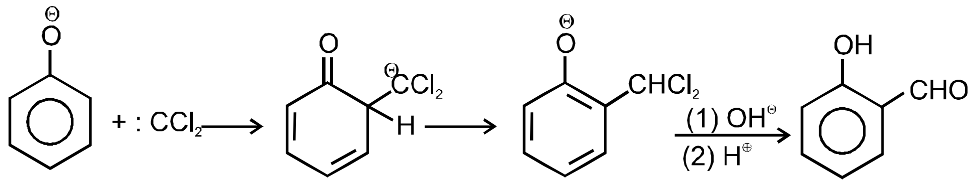
(6) **Reimer-Tiemann formylation reaction :**



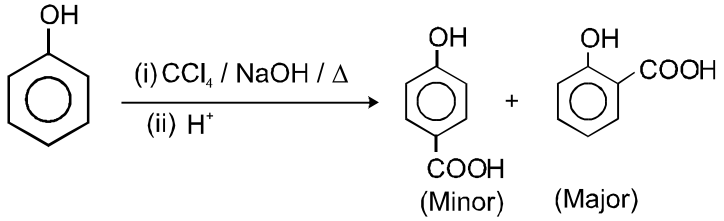
Mechanism :

Step (I) : $CHCl_3 + NaOH \longrightarrow \overset{\bullet\bullet}{\bar{C}}Cl_3 \longrightarrow :CCl_2$

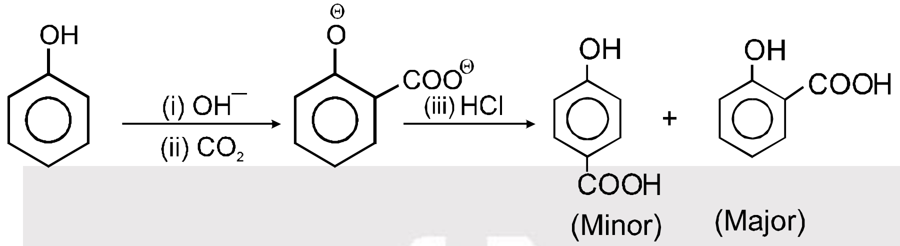
Step (II) :



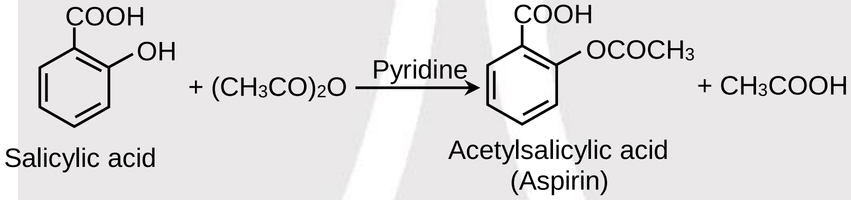
(7) Reimer-Tiemann carboxylation reaction :



(8) Kolbe carboxylation reaction :



Preparation of aspirin :



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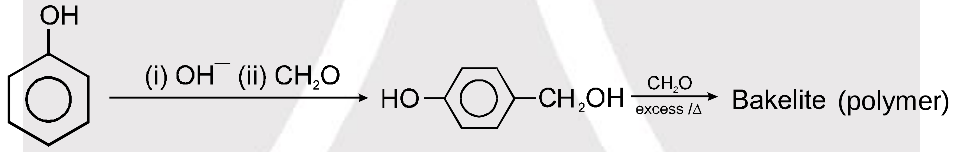

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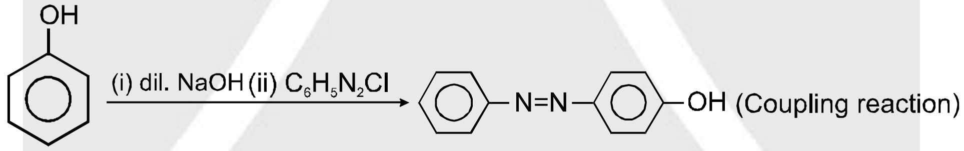

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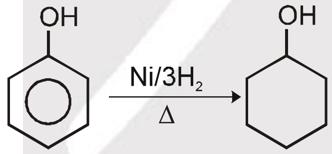

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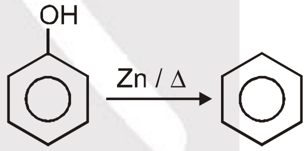
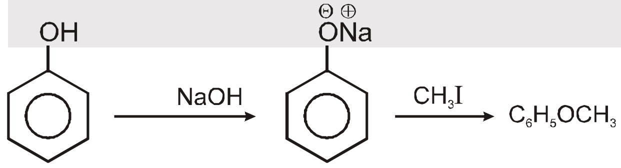
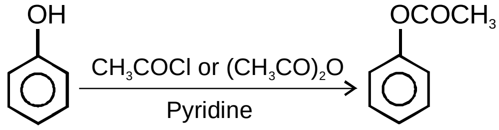
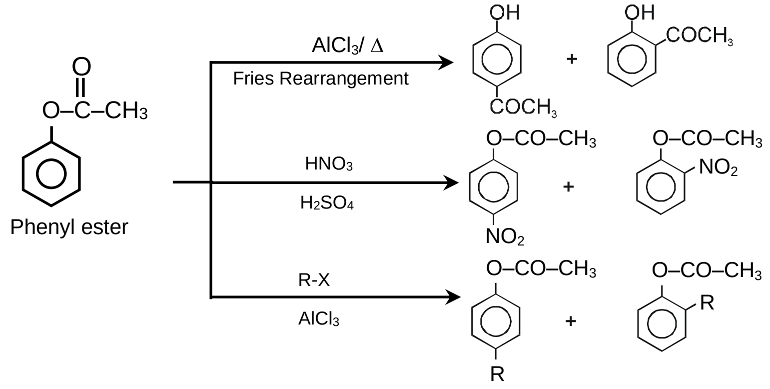


(13) Williamson ether synthesis

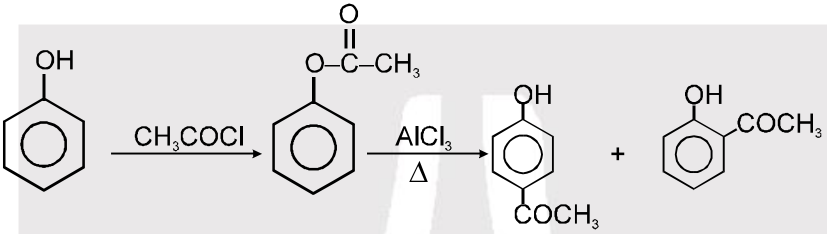


(14) Protection of –OH and –NH$_2$ group.

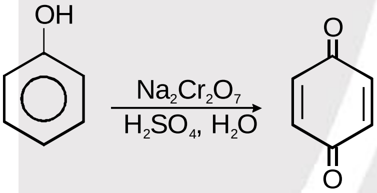




(15) Fries rearrangement :

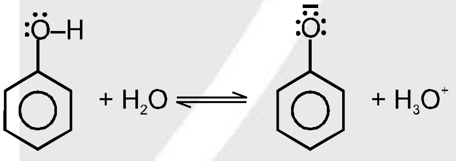


(16) Oxidation of phenol :



(d) Test of phenol :

(1) Phenols turn blue litmus red. Phenols behave as acid and ionise in aqueous solution to give H^+ ions.



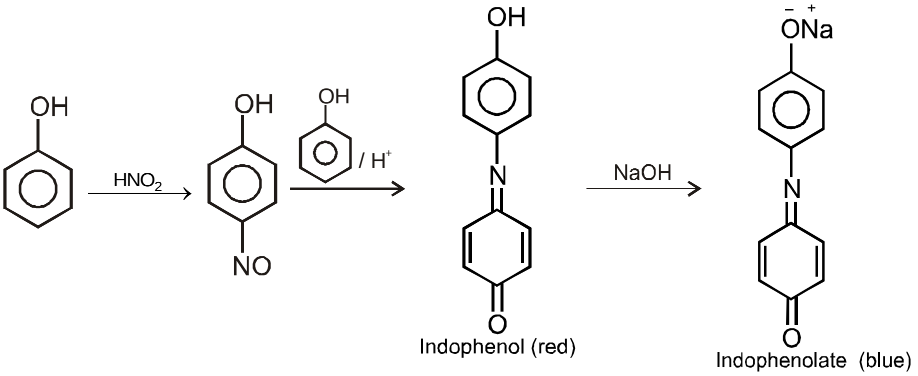
Phenol Phenoxide ion

(2) Reaction with ferric chloride : Phenol gives a violet-coloured water soluble complex with neutral ferric chloride.

$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{-3}} + 3H^+ + 3HCl$$

(3) Libermann's test : When a sodium nitrite ($NaNO_2$) is added to a phenol dissoved in conc. sulphuric acid, red or brown colour is produced and changes to blue by the addition of a strong alkali. This test can be used to distinguish between phenols from alcohols.

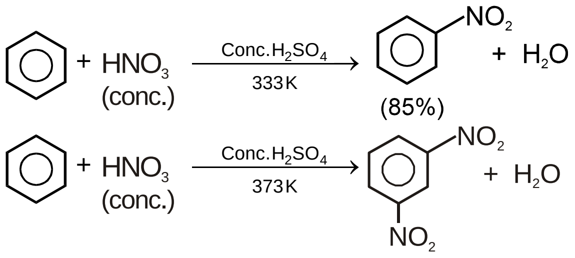
$$\underset{\text{Sodium nitrite}}{2NaNO_2} + H_2SO_4 \longrightarrow \underset{\text{Nitrous acid}}{2HNO_2} + Na_2SO_4$$



Indophenol (red) Indophenolate (blue)

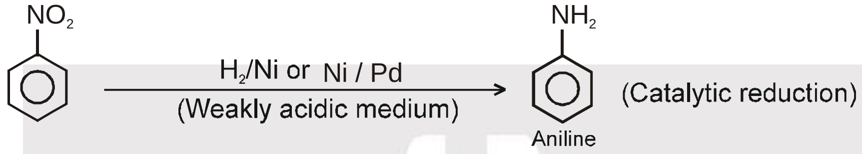
Section (B) : Nitrogen containing compounds (Nitrobenzene & Aniline)

(a) Preparation of nitrobenzene :



(b) Chemical reactions of nitrobenzene :

(1)



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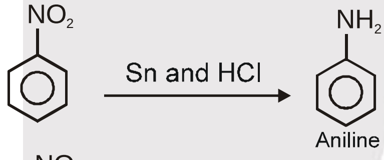

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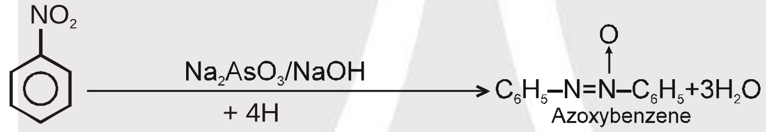

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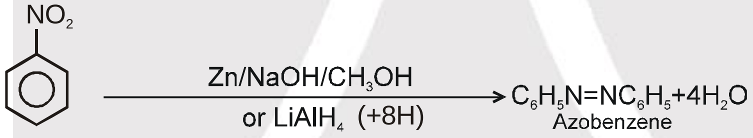

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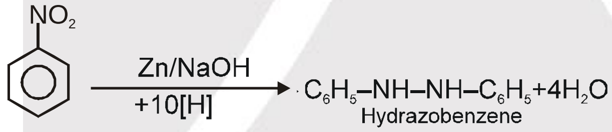

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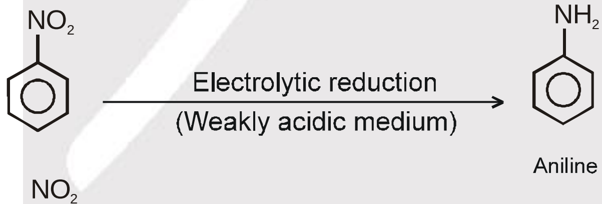

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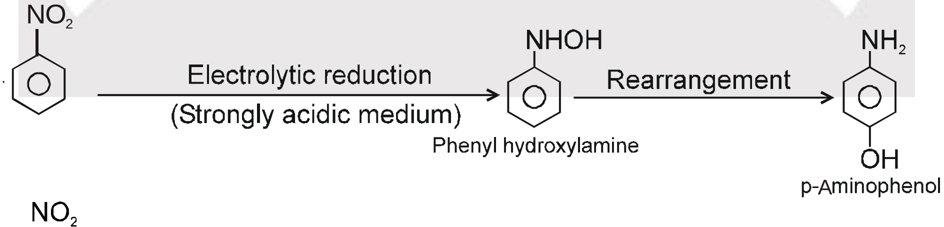

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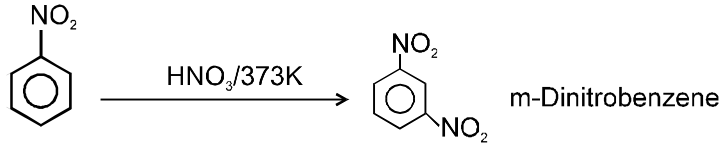

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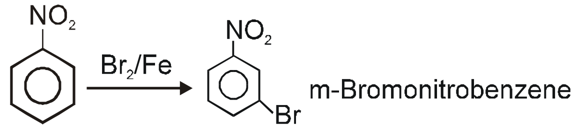
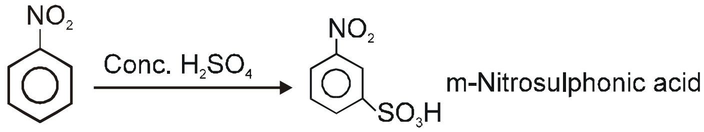
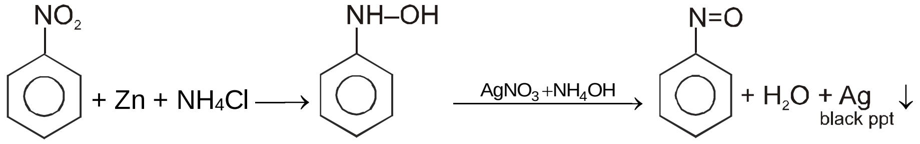
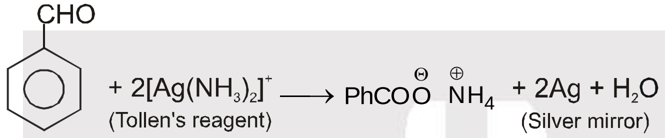


(10) 

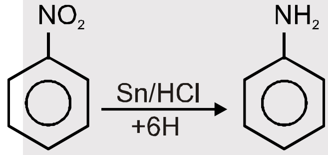
(c) Test of nitrobenzene : (Mulliken- Barker's test)

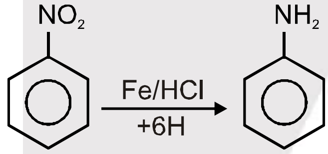


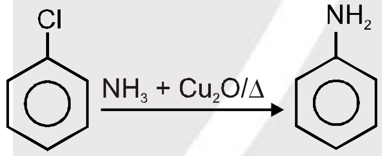
(d) Test of benzaldehyde (Aromatic aldehyde)



(e) Prepartion of aniline

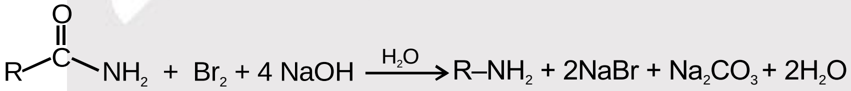
(1) 

(2) 

(3) 

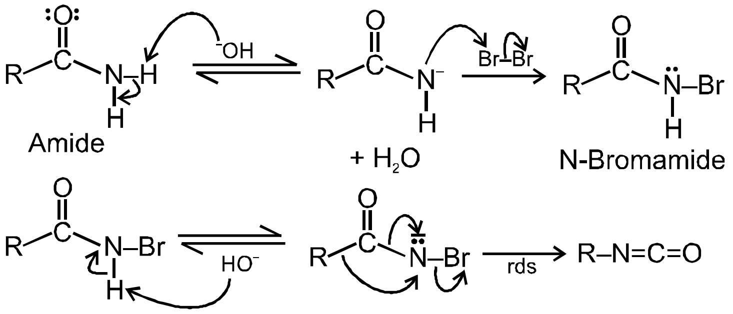
(4) Hofmann bromamide degradation reaction :

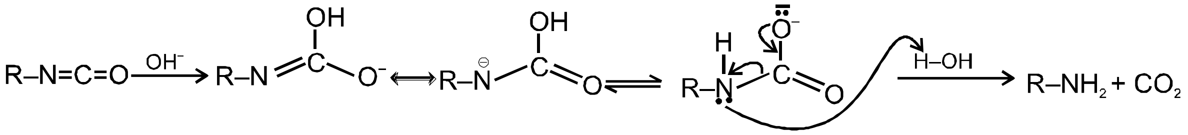
Hofmann developed a method for preparation of **primary amines** by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4\,NaOH \xrightarrow{H_2O} R-NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

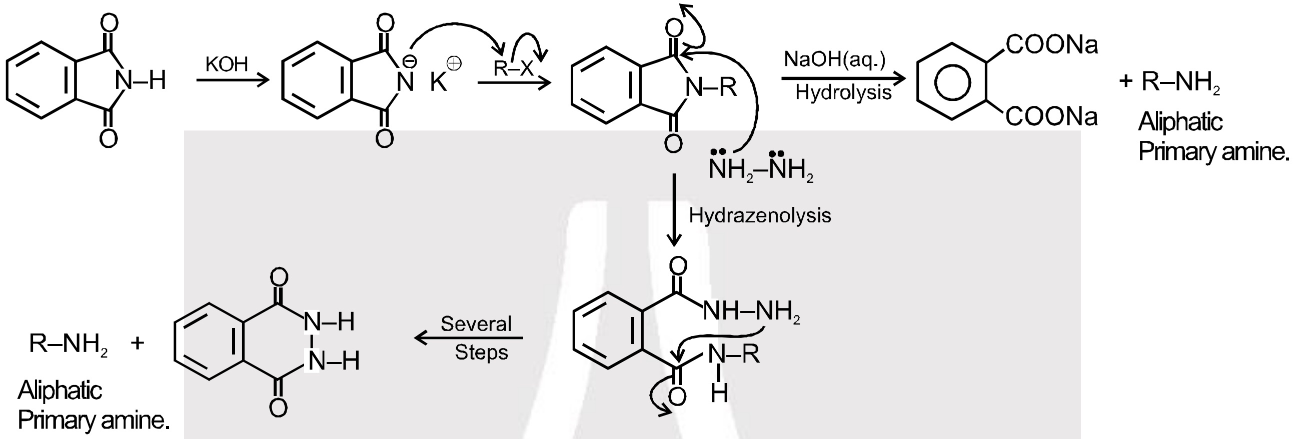
Mechanism :





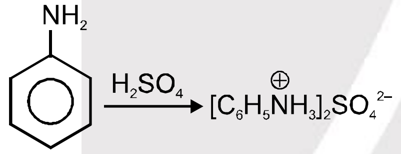
(5) Gabriel phthalimide synthesis :

Gabriel synthesis is used for the preparation of **aliphatic primary amines**. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. **Aromatic primary amines** cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



(f) Chemical reactions of aniline

(1)



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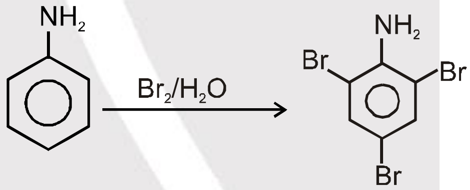

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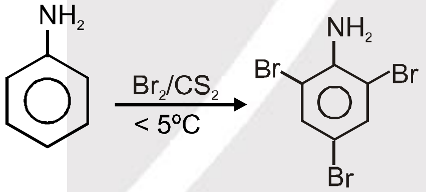

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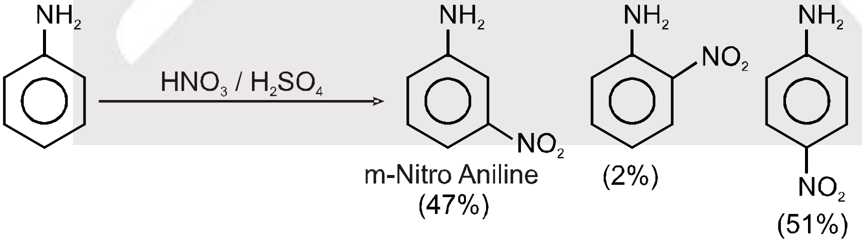

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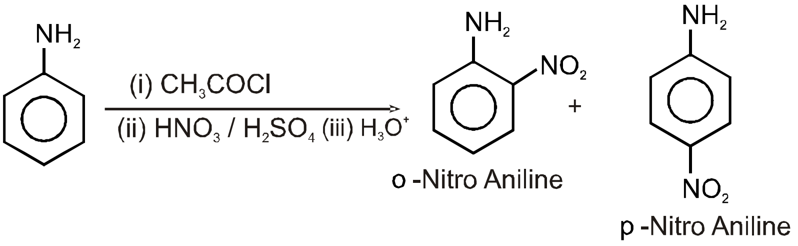

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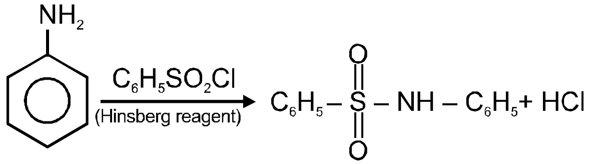

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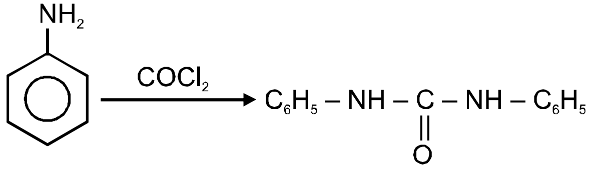

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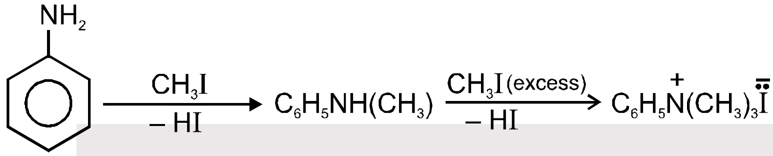

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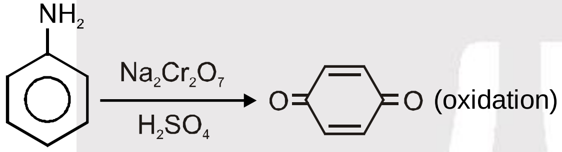

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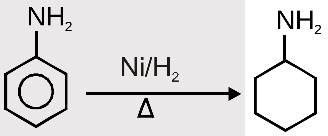
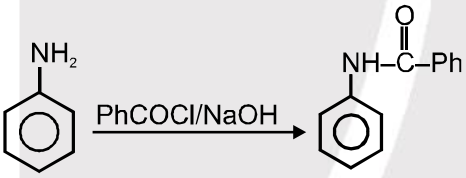


(11) Schotten Bauman reaction.



(g) Test of aniline :

(1) Carbylamine reaction

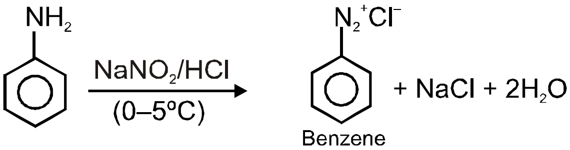
Primary amines (alphatic as well as aromatic) react with chloroform ($CHCl_3$) on heating in the presence of ethanolic solution of KOH to form isocyanides (also called carbylamines) which are foul smelling substances. Secondary and tertiary amines do not undergo this reaction, therefore this reaction is used as a test for Primary amines (alphatic as well as aromatic).

(Phenyl isocyanide)

(2) Reaction with nitrous acid

Amines of different classes react with nitrous acid (unstable acid). HNO_2 is prepared by the reaction of sodium nitrite ($NaNO_2$) and dilute hydrochloric acid.

Primary aromatic amines react with nitrous acid at low temperature (273-278 K) to give aromatic diazonium salts. This reaction is known as **diazotisation.**

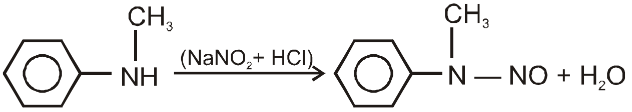


Benzene diazonium chloride

Primary aliphatic amines also react with nitrous acid to form diazonium salt, however, the aliphatic diazonium salts being unstable, decompose to yield mixture of alcohols, alkenes along with nitrogen gas.So this reaction is used to distinguish between aromatic and aliphatic 1° amines.

$$C_2H_5NH_2 \xrightarrow{NaNO_2\,/\,HCl} \underset{\text{(Unstable)}}{[C_2H_5\overset{+}{N}_2\overset{-}{Cl}]} \xrightarrow{H_2O} \underset{\text{(Major)}}{C_2H_5OH} + CH_2 = CH_2 + N_2 + H_2O$$

Secondary aliphatic and aromatic amines react with nitrous acid to produce nitroso-amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.



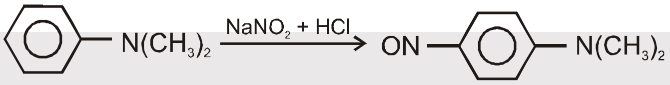
N-Methylaniline N–Nitroso–N–methylaniline

$(C_2H_5)_2NH + HNO_2 \longrightarrow (C_2H_5)_2NH—NO + H_2O$

Diethyl amine N-Nitrosodiethylamine

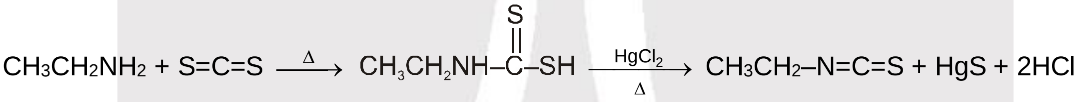
Tertiary aliphatic amines react with nitrous acid to form salts, which decompose on warming to nitrosoamine and alcohol while **tertiary aromatic amines** undergo electrophilic substitution at the ring.

$$R_3N + HNO_2 \longrightarrow \underset{\text{Nitrite salt}}{R_3N.HNO_2} \xrightarrow{\Delta} \underset{\text{Nitrosoamine}}{R_2N-N=O} + ROH$$



N,N-Dimethylaniline p-Nitroso-N, N dimethylaniline

(3) Hofmann mustard oil reaction



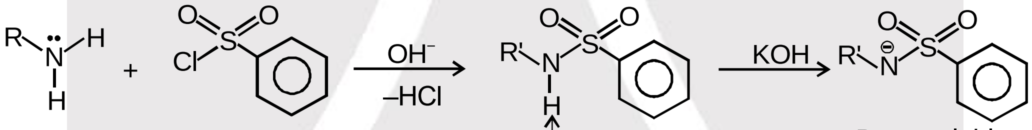
$$CH_3CH_2NH_2 + S=C=S \xrightarrow{\Delta} CH_3CH_2NH\text{–}\overset{\overset{\displaystyle S}{||}}{C}\text{–}SH \xrightarrow[\Delta]{HgCl_2} CH_3CH_2\text{–}N=C=S + HgS + 2HCl$$

(1° amine) Ethyl isothiocyanate

(4) The Hinsberg test :

The hinsberg test can be used to demonstrate whether an amine is primary, secondary or tertiary

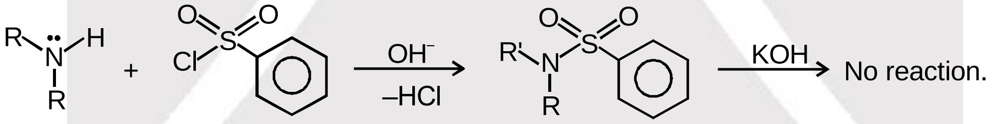
Primary amine :



Acidic hydrogen

Base soluble salt
(Clear solution)

Secondary amine :



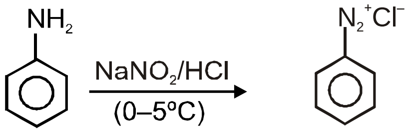
Insoluble in base
(Precipitate)

Tertiary amine :

If the amine is tertiary amine and it is water insoluble no apparent change will take place in the mixture as we shake it with benzene sufonyl chloride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

Section (C) : Benzenediazonium salt and its reaction

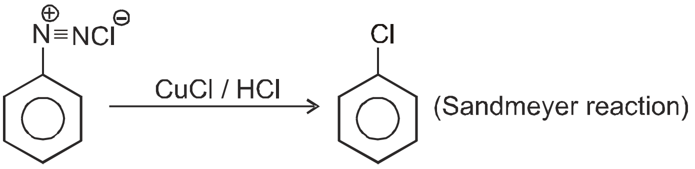
(a) Preparation of benzenediazonium salt



Benzene
diazonium chloride

(b) Chemical reactions of benzenediazonium chloride

(1)



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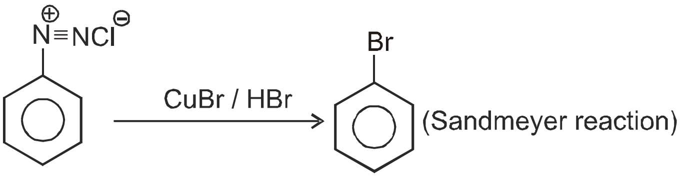

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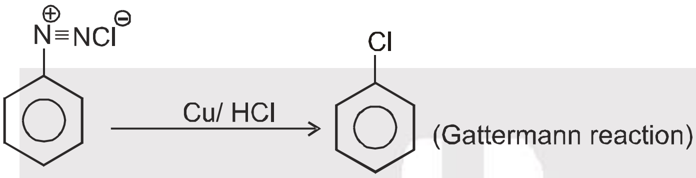

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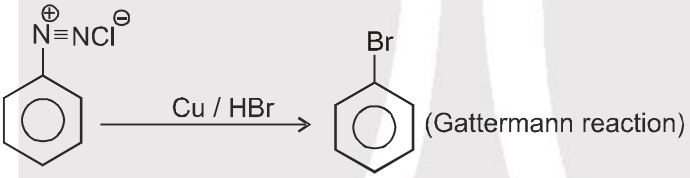

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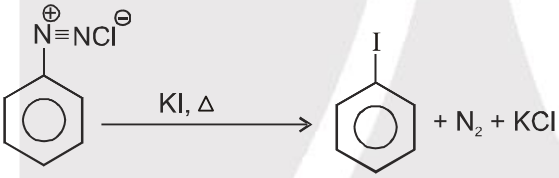

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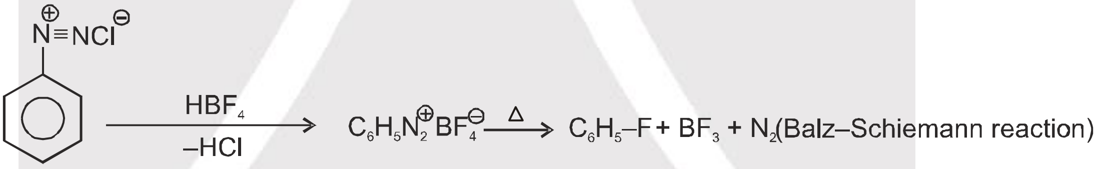

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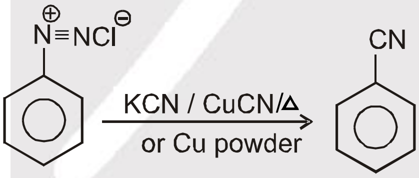

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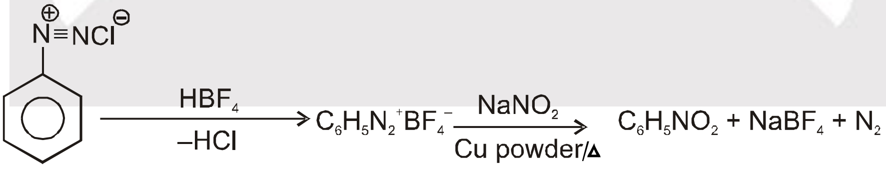

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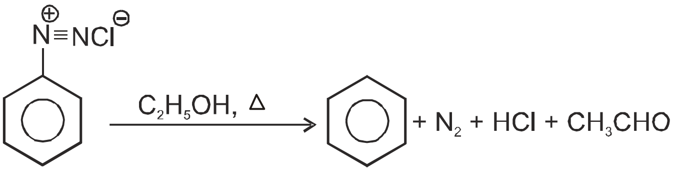

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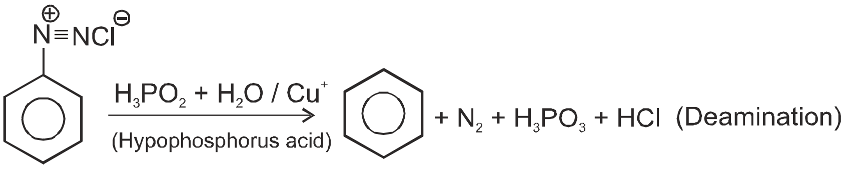

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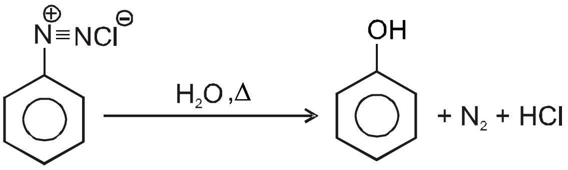

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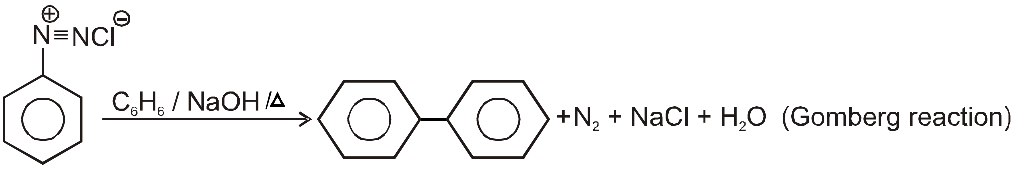

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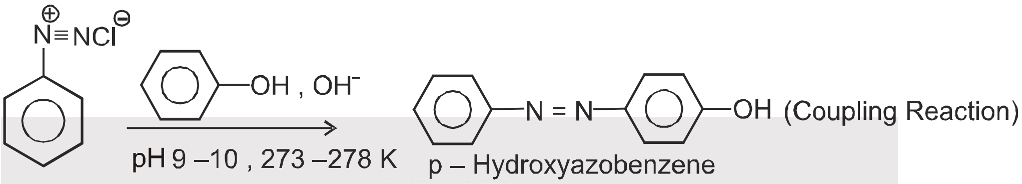

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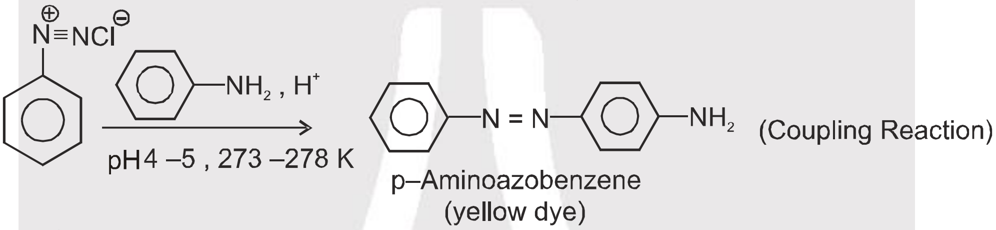

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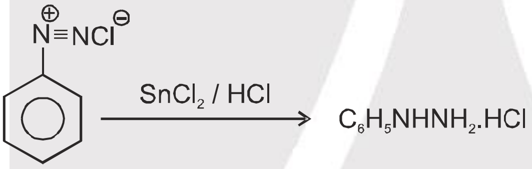

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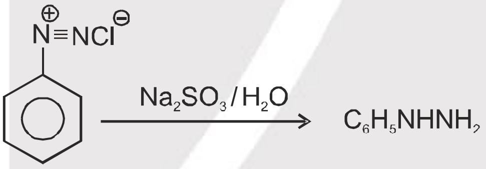

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