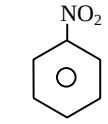
ORGANIC CHEMISTRY –II

5. NITROGEN CONTAINING COMPOUNDS

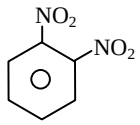
- NO_2 and – ONO are isomeric forms

$R – NO_2$	R – ONO
Nitro alkane	Alkyl nitrite
$CH_3 – NO_2$	$CH_3 – ONO$
Nitro methane	Methyl nitrite
$CH_3 – CH_2 – CH_2 – NO_2$	$CH_3–CH_2–CH_2–ONO$
1 – Nitro propane	Propyl – 1- nitrite
$CH_3 – \underset{\displaystyle NO_2}{\underset{\vert}{CH}} – CH_3$	$CH_3 – \underset{\displaystyle ONO}{\underset{\vert}{CH}} – CH_3$
2- Nitro propane	Propyl – 2-nitrite

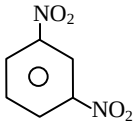
- Nitroalkane and alkyl nitrites are functional isomers.
- Naming of Nitro arenes :



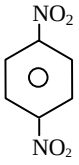
Nitrobenzene



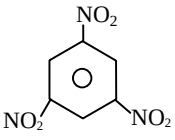
O-dinitro benzene



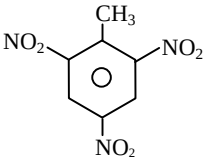
m-dinitro benzene



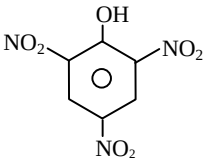
P – dinitrobenzene



1,3,5-trinitro benzene(TNB)



2,4, 6 – trinitrotoluene (TNT)

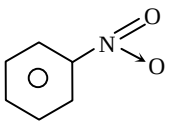


2,4, 6 – trinitrophenol (TNP)

NITRO BENZENE :

Formula : $C_6H_5 – NO_2$

Structure :



- Common name : Oil of mirbane
- **Preparation :** Benzene is heated with the mixture of conc. HNO_3 and conc. H_4SO_4 at about 60°C to give nitro benzene.
- In the nitration mixture con.HNO_3 acts as base
- Con.HNO_3 will produce NO_2^+ on reaction with con. H_2SO_4.
- If temperature is more than 60°C, dinitro or trinitro benzene may be formed.



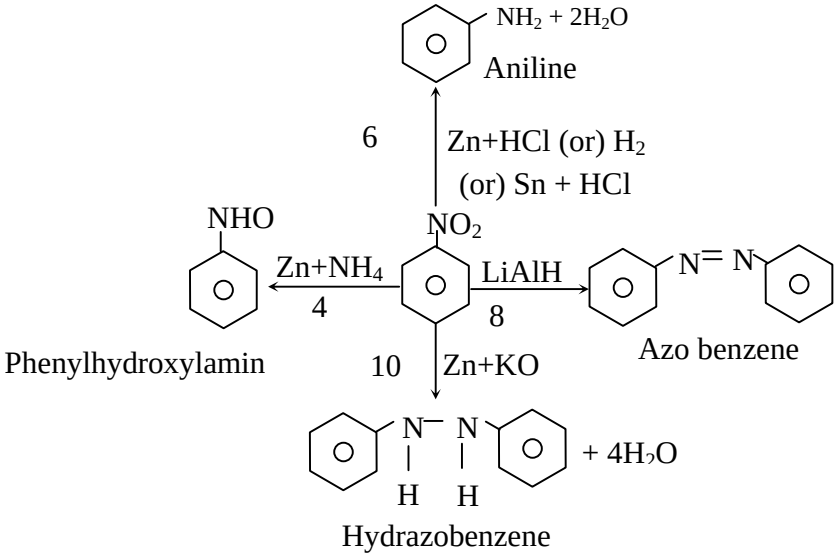
$$+ HO - NO_2 \xrightarrow[< 60^\circ C]{con.H_2SO_4} + H_2O$$

Physical properties :

- It is pale yellow oily liquid
- It has smell of bitter almonds
- It is insoluble in H_2O and soluble in organic solvent
- It is high boiling organic solvent
- It is steam volatile

CHEMICAL PROPERTIES :

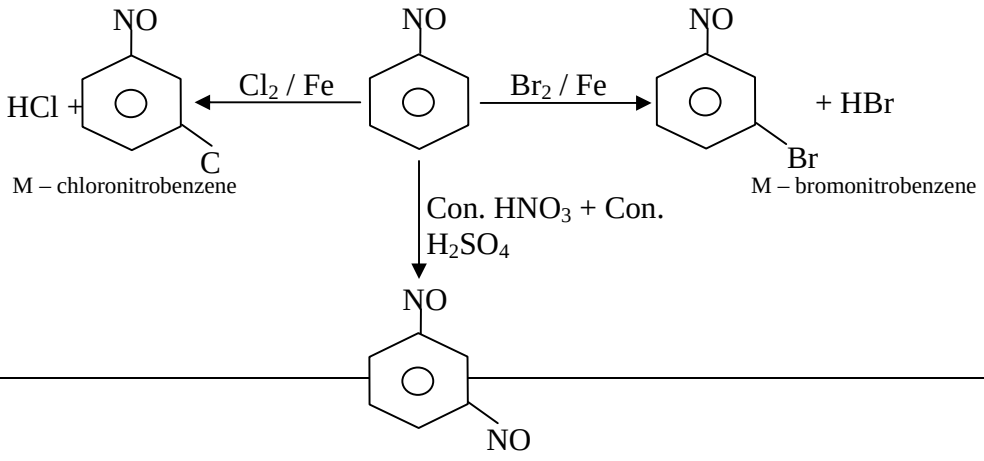
1) Reduction of nitro group of Nitro benzene :



- Nitro group on complete reduction converts to $– NH_2$ group.
- In the reduction process all others are intermediates.
- NO_2 group is highly polar and $C – NO_2$ bond is very strong and it cannot be replaced by groups like
  $– OH, – NH_2$ etc.

2) Reactions of benzene ring of nitro benzene :

- $–NO_2$ group is meta director and ring deactivator. NO_2 group withdraws electron density from benzene and deactivates the benzene of nitrobenzene. It is less reactive than pure benzene towards electrophilic substitutions
- It undergoes halogenation and nitration only



Uses of nitrobenzene :

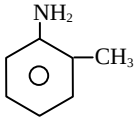
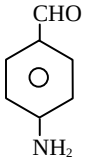
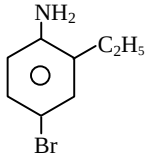
- In the preparation of floor polishes
- As solvent
- As oxidising agent
- In perfumes under the name of oil of mirbane
- In dyes and explosives

AMINES :

- Amines are organic derivatives of NH_3.
- In nitrogen fixation, atmospheric nitrogen is reduced to NH_3.
- Based on the nature of hydrocarbon part, attached to nitrogen, amines are of two types.
  a) Alkyl amines : $R - NH_2$ or $R - N <$
  Nitrogen is attached to sp^3 carbon
  Ex. CH_3 - NH_2 , $C_2H_5 - NH_2$, $CH_3 - NH - CH_3$. $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}} - C_2H_5$,
  b) Aryl amines or Arenamines : Benzene ring is attached to nitrogen through sp^2 carbon.
  Ex. $Ar - N <$, $C_6H_5 - NH_2$, $C_6H_5 - NH - C_6H_5$, $C_6H_5 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}} - C_6H_5$
- Based on the degree of substitution at nitrogen, amines are of three types.
  a) Primary amines: one carbon is attached to nitrogen of amino group.
  Ex. $R - NH_2$,$CH_3 - NH_2$, $C_2H_5 - NH_2$, $C_6H_5 - NH_2$
  b) Secondary amines : Two carbons are attached to nitrogen of amino group.
  Ex. $R - NH - R^1$, $CH_3 - NH - CH_3$,
  $CH_3 - NH - C_2H_5$, $CH_3 - NH - C_6H_5$
  C) Tetriary amines : Three carbons are attached to nitrogen of amino group.
  Ex. $R - \underset{\displaystyle R^{11}}{\overset{\displaystyle |}{N}} - R^1$, $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}} - CH_3$, $CH_3 - \underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{N}} - C_2H_5$

NAMING OF AMINES :

STRUCTURE	IUPAC NAME	IUPAC NAME	COMMON NAME
$CH_3 - NH_2$	Amino methane	Methanamine	Methyl amine
$C_2H_5 - NH_2$	Amino ethane	Ethanamine	Ethyl amine
$CH_3 - CH_2 - CH_2 - NH_2$	1-Amino Propane	1 – Propanamine	n – propylamine
$CH_3 - \underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}} - CH_3$	2-Amino Propane	2-Propanamine	Isopropyl amine
$CH_3 - \underset{\displaystyle OH}{\overset{\displaystyle |}{CH}} - \underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}} - CH_3$	3-Amino Butan - 2- ol	--	--
$H_2N - CH_2 - CH_2 - NH_2$	1, 2-diamino ethane	1,2 –ethane diamine	Ethylenediamine
$H_2N - CH_2 - \underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}} - CH_3$	1, 2 – diamino propane	1,2 – propane diamine	--
$CH_3 - NH - CH_3$	N-methyl Amino methane	N- methyl methanamine	Dimethyl amine

STRUCTURE	IUPAC NAME	IUPAC NAME	COMMON NAME
$CH_3 - NH - CH(CH_3)_2$	N- methyl-2- Amino propane	N –methyl 2-propanamine	N – methyl N – isopropyl amine
$CH_3 - N(CH_3) - CH_3$	N, N –dimethyl Amino methane	N, N – dimethyl methanamine	Trimethylamine
$CH_3 - N(C_2H_5) - CH_2 - CH_2 - CH_3$	N – ethyl – N – methyl 1–Amino propane	N-ethyl , N – methyl 1-propanamine	Ethyl, Methyl , n –propyl amine
$C_6H_5 - NH_2$	Amino benzene	Benzenamine	Phenyl amine or Aniline
$C_6H_5 - CH_2 - CH_2 - NH_2$	2-Phenyl – Amino ethane	2 – phenyl ethanamine	--
	2 – methyl amino benzene	--	O – toludiene
	4 – Amino Benzene carbaldehyde	--	P – amino benzal dehyde
	4 – Bromo – 2-ethyl Amino benzene	--	P – bromo –O – ethyl aniline

ISOMERISM IN AMINES :

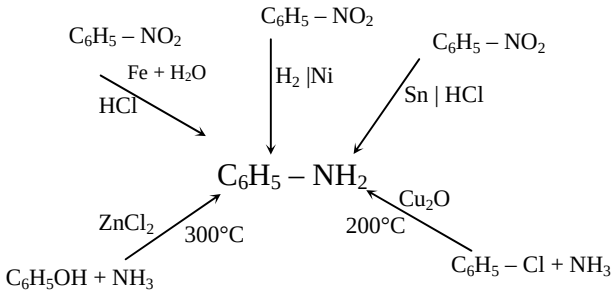
- Primary, secondary and tertiary amines having same molecular formula are functional isomers.
- Primary amines also exhibit chain and position isomerism.
- Secondary and tertiary amines also exhibit metamerism.

Aniline (Phenyl amine)

- Aniline was first prepared by unverborden.
- Destructive distillation of indigo gives aniline (Anil = Indigo)

Preparation of aniline :

- In laboratory aniline is prepared by the catalytic hydrogenation or chemical reduction of nitrobenzene.
- On large scale aniline is prepared by the reduction of nitrobenzene with Fe / H_2O and small amounts of HCl
- Phenol on heating with NH_3 in presence of $ZnCl_2$ gives aniline at 300°C.
- Chloro benzene on heating with NH_3 in presence of Cu_2O gives aniline at 200°C.



Physical properties :

- Freshly prepared aniline is colourless oily liquid with unpleasant smell.
- It is toxic in nature.
- It turns to brown when exposed to air due to oxidation.
- It is denser than H_2O, slightly soluble in H_2O but readily soluble in organic solvents.
- It is steam volatile and high boiling organic liquid.
- It forms weak hydrogen bonds.
- Extent of hydrogen bonding : $NH_3 > R – NH_2 > R_2NH > R_3N$

CHEMICAL PROPERTIES :

I) Reactions of $– NH_2$ group :

1 Basic nature of amines :

- Alkyl groups are electron releasing in nature by means of +ve inductive effect alkyl groups attached to nitrogen increases electron density on nitrogen and increases basic nature of amines.
- Thus electron releasing groups like alkyl groups increases the basic nature due to +ve inductive effect and electron with drawing groups like – Cl, –F, $– NO_2$, $– C_6H_5$ decreases the basic nature due to – ve inductive effect.

  Ex. $R – NH_2 > Ar – NH_2$

  $H – NH_2 > Cl – NH_2$

  $R – NH_2 > H – NH_2$

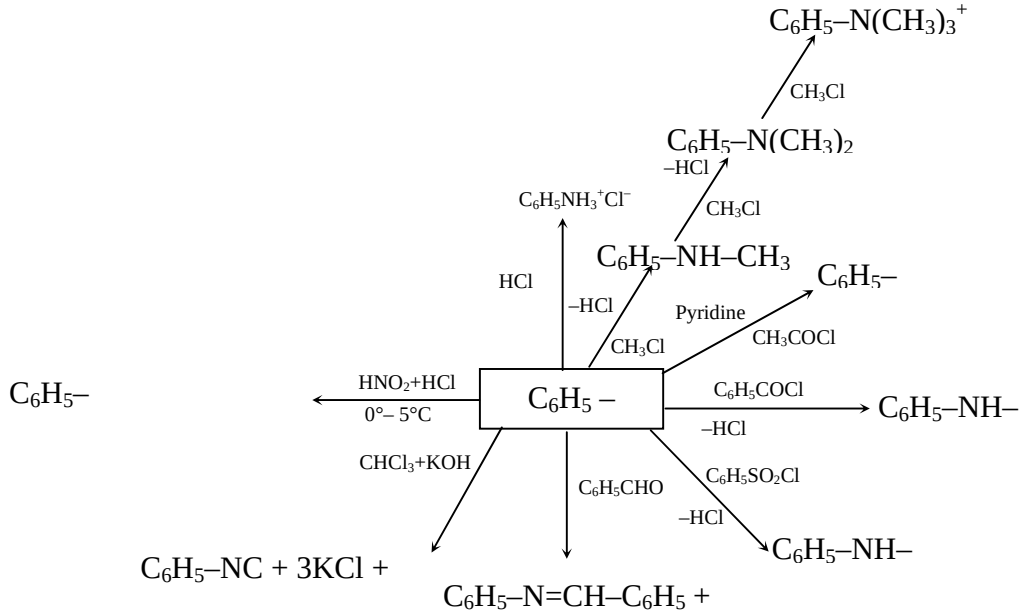
  $R – NH_2 > H – NH_2 > Ar – NH_2$
- Due to electron with drawing nature of C_6H_5 – group aniline is weak base and almost neutral to litmus paper. But aniline form salts with acids. These anilinium salts are acidic and then can be decomposed by basic substances like Na_2CO_3. $NaHCO_3$ and produces effervescence.
- If more hydrogens are present on nitrogen, it forms more number of hydrogen bonds and the basic nature is more.
- Due to stearic crowding of bulky alkyl groups, tertiary amine is less basic than those of secondary and primary amines.
- In view of all the three effects, the observed basic nature is

  $R_2 – NH > R–NH_2 > R_3N > NH_3 > C_6H_5 – NH_2$ (R = CH_3)

2. **Alkylation :** Aniline reacts with excess $CH_3 – Cl$ to give secondary amine, tertiary amine and quaternary salt.

To continue the alkylation , HCl produced is neutralised by basic casrsenate salt.

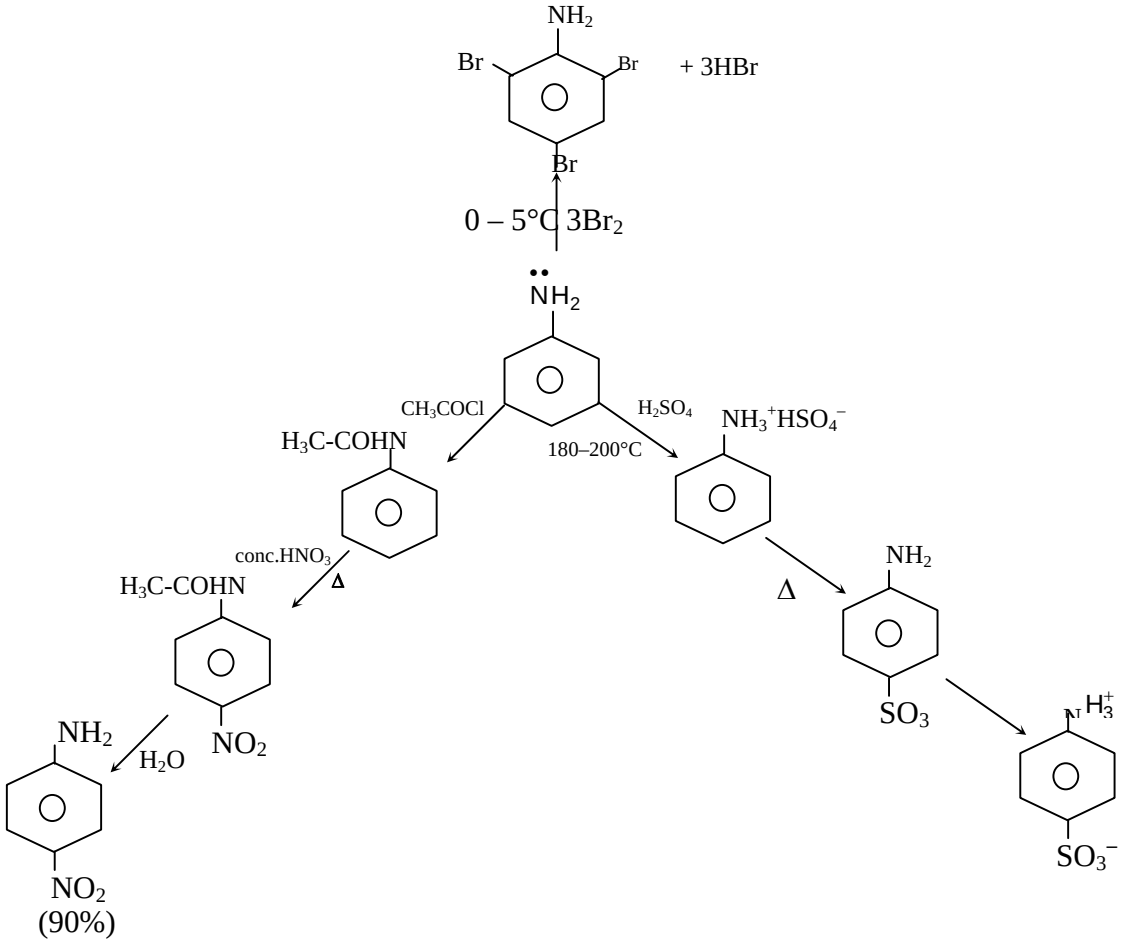
3. **Acylation :** Anilie on acylation with acetyl group, acetanilide is formed.
   Acetylating agents are CH_3COCl, $(CH_3CO)_2O$, $CH_3COOC_2H_5$
   Reactivity of acetylating agents : $CH_3COCl > (CH_3CO)_2O >> CH_3COOC_2H_5$
4. Benzoylation : (Schoten – Baumen Reaction) :
   Aniline reacts with benzoyl chloride to form benzanilide or N- phenyl benzamide.
5. Sulphonylation : Aniline reacts with benzene sulphonyl chloride to give N – phenyl benzene sulphonamide.
6. Condensation with benzaldehyde : Aniline condenses with benzaldehyde in presence of conc. H_2SO_4 to give benzilidene aniline or Schiff's base.
7. Carbyl amine reaction : Aliphatic or aromatic primary amines react with chloroform and alcoholic potash to give isocyanide having foul smell.
8. Diazotisation : HNO_2 is formed from $NaNO_2$ and HCl. Aniline reacts with HNO_2 / $NaNO_2$ + HCl at 0°C to form benzene diazonium chloride. These diazonium salts are useful in the synthesis of many important organic compounds.
   Only aromatic primary amines give these diazonium salts.



II. Reactions of benzene ring of aniline :

- $\ddot{N}H_2$ - group attached to benzene ring will activate the benzene ring towards electrophilic substitutions by it's electron releasing nature.
- $\ddot{N}H_2$ - group is O, P –director and substitution occurs at ortho and parapositions.
  1) **Bromination :** Aniline reacts with Br_2 instantaneously to give a white precipitate of 2, 4, 6 – tribromo aniline.
  2) **Sulphonation :** Aniline on heating with fuming sulphuric acid gives sulphanilic acid. The intermediate is anilinium hydrogen sulphate.

3) **Nitration :** Aniline is first acylated to protect – NH_2 group form getting oxidised. Then acetanilide is nitrated and subsequently hydrolysed to give 90% yield of para nitro aniline.



- **Uses of Aniline :**
- In the preparation of acetanilide, Sulphanilic acid, sulpha drugs, azodyes etc.
- In the preparation of Schiff's bases which are used as antioxidants in rubber industry.
  In the preparation of diazonium chloride which is used as starting material in the synthesis of many important compounds

IDENTIFICATION OF $1^o, 2^o$ *and* 3^o AMINES

- **HINSBERG'S TEST :** (Action of benzene sulphonyl chloride)

  1^0 **amine:** N-alkylbenzene sulphonamide is formed, which is soluble in alkali

  $RNH_2 + ClSO_2.\ C_6H_5 \rightarrow RNH.SO_2C_6H_5 +$ HCl

  2^0 **amine:** N,N-dialkyl benzene sulphonamide is formed,which is insoluble in alkali

  $R_2NH + Cl.SO_2.C_6H_5 \rightarrow R_2N.SO_2.C_6H_5$

  3^0 **amine:** No characteristic change

- **HOFMANN MUSTARD OIL REACTION (REACTION WITH CS_2 FOLLOWED BY $HgCl_2$)**

  1^0 **AMINE:**Black precipitate is formed due to the formation of HgS

  $$RNH_2 + CS_2 \rightarrow RNH\diagdown C(=S)\diagup HS \xrightarrow{HgCl_2} HgS + RNCS + 2HCl$$

  2^0 **AMINE:**No precipitate is observed

  $$R_2NH + CS_2 \rightarrow R_2N - \underset{\displaystyle SH}{\underset{|}{C}} = S \xrightarrow{HgCl_2}$$

  no precipitate

  3^0 **AMINE:**No reaction

- **OXIDATION BY** $KMnO_4$

  1^0 **AMINE:**Aldehydes and ketones are formed

  $R.CH_2.NH_2 \xrightarrow{(O)}$ R.CHNH $\xrightarrow{H^+/H_2O} R - CHO + NH_3$

  $R_2CHNH_2 \xrightarrow{(O)} R_2C = NH \xrightarrow{H^+/H_2O} R_2CO + NH_3$

  2^0 **AMINE:**Tetraalkyl hydrazine is formed $R_2NH \xrightarrow{(O)} R_2N - NR_2$

  3^0 **amine:** No reaction

- **ACTION OF CARO'S ACID** (H_2SO_5)

  1^0 **amine:**Aldoxime and hydroxamic acid are produced

  $RCH_2NH_2 \xrightarrow{(O)}$ RCH=NOH aldoxime

  $$\xrightarrow{(O)} R - \underset{\displaystyle OH}{\underset{|}{C}} = N - OH \text{ hydroxamic acid}$$

  2^0 **AMINE:**Dialkyl hydroxyl amine is produced

  $R_2NH \xrightarrow{(O)} R_2NOH$

  3^0 **amine:**Tertiary amine oxide is formed

  $R_3N \xrightarrow{O} [R_3N \rightarrow O]$

- **CARBYLAMINE TEST :** **(Amine +** $CHCl_3$ **+ alc.KOH)**

  1^0 **AMINE:**Foul smell is observed due to the formation of RNC (isocyanide)

2^0 **AMINE:**No reaction

3^0 **AMINE:**No reaction

- **REACTION WITH NITROUS ACID)** ($NaNO_2 + HCl$

1^0 **AMINE:**Alcohols are formed with the liberation N_2 of gas . With CH_3NH_2 , it produces methyl nitrite with the liberation of N_2 gas

2^0 **AMINE:**Yellow coloured oily layered nitrosoamines are produced. This test is called Liberman's reaction

3^0 **AMINE:**Nitrite salts are produced, which are soluble in water

DIAZONIUM SALTS :

General formula of diazonium salts is $R\overset{+}{N}_2 X^-$. Here R is alkyl or aryl group and X^- may be Cl^- , Br^-, HSO_4^-, BF_4^- etc.

Primary aliphatic amines form highly unstable alkyl diazonium salts. Primary aromatic amines form arene diazonium salts which are stable for a short time in solution at low temperature (273-278K). The stability of arene diazonium ion is because of resonance.

N_2^+ group $(\overset{+}{N} \equiv N)$ is called diazonium group.

PREPARATION OF DIAZONIUM SALTS :

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^0 C}$$
$$C_6H_5N_2Cl + NaCl + 2H_2O$$

PROPERTIES OF BENZENE DIAZONIUM CHLORIDE :

- It is colourless crystalline solid
- It is highly soluble in water.
- It is stable at 0^oC, but on warming it reacts with water
- In dry state it easily decomposes, but in the form of benzene diazonium fluoroborate, it is water insoluble and stable at room temperature.

CHEMICAL PROPERTIES :

As diazonium group is a good leaving group, it may be substituted by $Cl^-, Br^-, I^-, CN^-, OH^-$ etc.

SANDMEYER'S REACTION :

$$C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2$$
$$C_6H_5N_2Cl \xrightarrow{Cu_2Br_2/HBr} C_6H_5Br + N_2$$
$$C_6H_5N_2Cl \xrightarrow{Cu_2(CN)_2/KCN} C_6H_5CN + N_2$$

GATTERMAN'S REACTION :

$$C_6H_5N_2Cl \xrightarrow{Cu/HCl} C_6H_5Cl + N_2 + CuCl$$
$$C_6H_5N_2Cl \xrightarrow{Cu/HBr} C_6H_5Br + N_2 + CuCl$$

More yield is observed in Sandmeyer's reaction than in Gatterman's reaction. In these reactions, nucleophile has been introduced into benzene ring.

REPLACEMENT BY I^- :

$$Ar\overset{+}{N}_2Cl^- + KI \rightarrow ArI + KCl + N_2$$

REPLACEMENT F^- :

$$Ar\overset{+}{N}_2Cl^- + HBF_4 \rightarrow Ar\ N_2^+BF_4^- \rightarrow ArF + BF_3 + N_2$$

fluoboric acid

REPLACEMENT BY 'H'

$$Ar\overset{+}{N}_2Cl^- + H_3PO_2 + H_2O \rightarrow ArH + N_2 + H_3PO_3 + HCl$$

hypophosphorous acid

$$Ar\overset{+}{N}_2Cl^- + C_2H_5OH \rightarrow ArH + N_2 + CH_3CHO + HCl$$

REPLACEMENT BY OH^- GROUP :

$$Ar\overset{+}{N}_2Cl^- + H_2O \xrightarrow{283\ K} ArOH + N_2 + HCl$$

REPLACEMENT BY NO_2^-

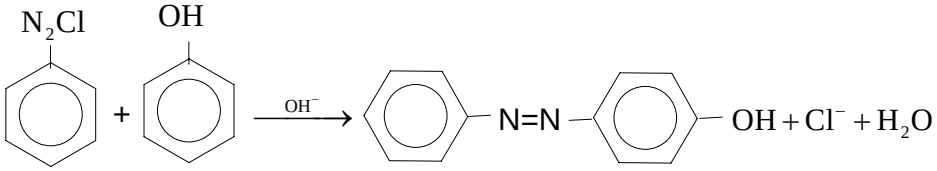
$$ArN_2^+Cl^- + HBF_4 \xrightarrow{NaNO_2/Cu,\ \Delta} Ar - NO_2 + N_2 + NaBF_4$$

IMPORTANCE OF DIAZONIUM SALTS IN SYNTHESIS OF AROMATIC COMPOUNDS

- Diazonium salts are intermediates in the preparation of variety of aromatic compounds including dyes.
- Substituted arenes are easily prepared through diazonium salts.
- Fluorides and iodides can not be prepared by direct reaction of halogen.
- Cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

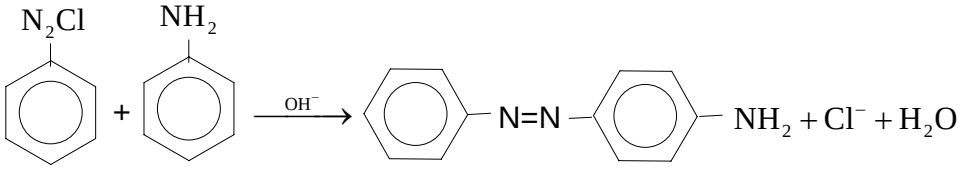
(AZODEYES) COUPLING REACTIONS :

Benzene diazonium chloride reacts with phenol, aniline etc in which these compounds attach to the diazonium ion through their para positions giving azo products. These reactions are electrophilic substitution reaction.



P-hydroxy azobenzene

(orange dye)



P-amino azobenzene

(yellow dye)

The azo products have extended conjugate system with aromatic ring and -N=N-. Therefore, these compounds are coloured and used as dyes.