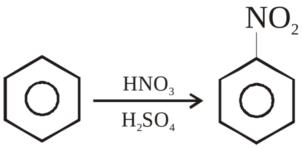
AMINES

NITRO COMPOUNDS

PREPARATIONS

(1) By direct nitration of Benzene:

Benzene undergoes electrophilic substitution reaction with HNO_3/H_2SO_4



The electrophile is NO_2^+ (nitronium ion) produced by the given reaction,

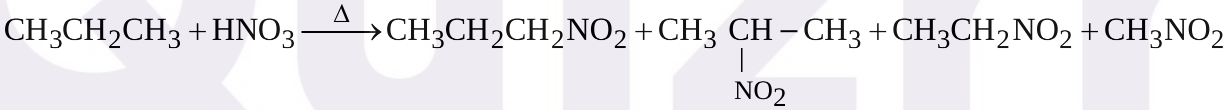
$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

In this reaction, HNO_3 acts as a base and H_2SO_4 acts as an acid.

During nitration, the number of solute particles increases (the Van't Hoff factor is greater than one), therefore, freezing point decreases.

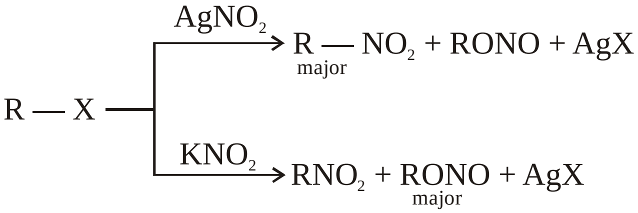
(2) Vapour phase nitration of alkane:

Alkane undergoes nitration at 475 K to 675 K in the presence of conc. HNO_3 and follows free radical mechanism. This is called vapour phase nitration and may results in the carbon-carbon cleavage.

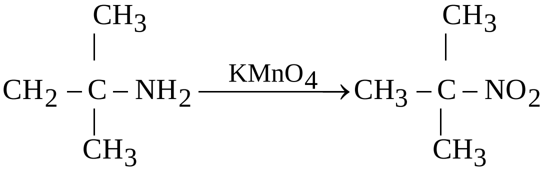


$$CH_3CH_2CH_3 + HNO_3 \xrightarrow{\Delta} CH_3CH_2CH_2NO_2 + CH_3\underset{\underset{NO_2}{|}}{CH} - CH_3 + CH_3CH_2NO_2 + CH_3NO_2$$

(3) From Halo compounds:



(4) From amines:



$$CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - NH_2 \xrightarrow{KMnO_4} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - NO_2$$

PHYSICAL PROPERTIES :

(1) Nitroalkanes are colourless pleasant smelling liquids.

(2) Nitrobenzene is a yellow oily liquid, heavier than H_2O, smell of bitter almonds, steam volatile.

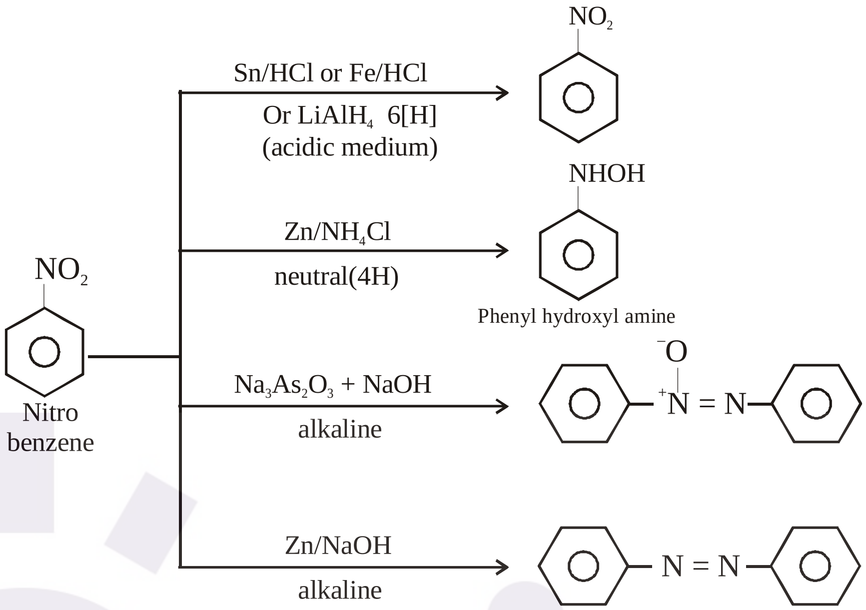
(3) Nitroalkanes are less soluble in water, b.p. are much higher than alkyl nitrites.

CHEMICAL PROPERTIES :

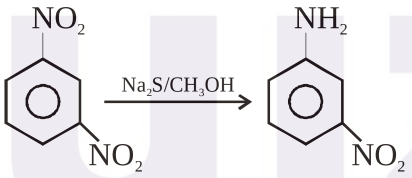
(1) Reduction :

Reduction of nitro alkane (or nitro benzene) gives variety of products depending upon the reducing agent used.

Nitrobenzene



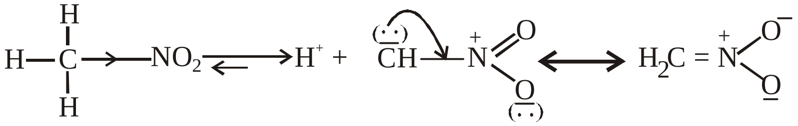
Note :- The reduction of selectively one nitro group in dinitrobenzene,can also be performed.



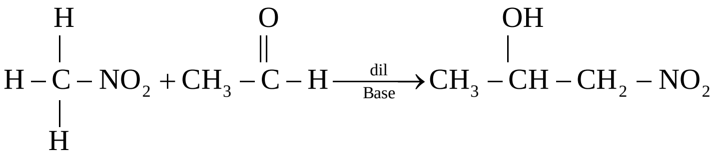
(2) Acidic αH of nitro alkanes :

Nitromethane contains acidic $\alpha-$hydrogen and can undergo condensation reaction with carbonyl compounds.

(a)

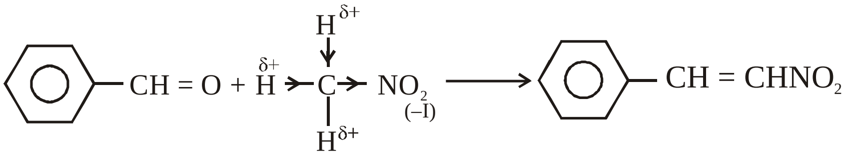


When Nitromethane is reacted with carbonyl molecules like acetaldehyde, than condensation product is formed. In given reaction, nitro methane releases proton and acetaldehyde



$$H-\underset{H}{\overset{H}{C}}-NO_2 + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{Base}]{\text{dil}} CH_3-\overset{OH}{CH}-CH_2-NO_2$$

(b)

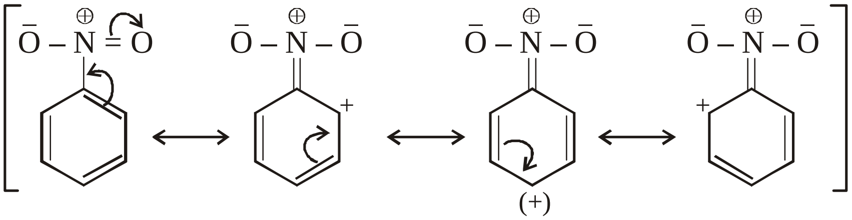


(3) With chlorine : nitromethane forms chloropicrin. (used as an insecticide)

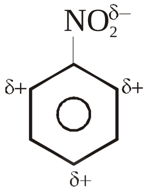
$$CH_3NO_2 \xrightarrow[NaOH]{3Cl_2} CCl_3NO_2$$

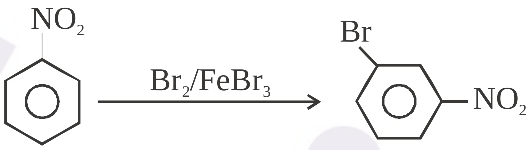
(4) Ring substitution in nitrobenzene : NO_2 group is m-directing and deactivating group, for incoming electrophiles.

Due to –M– effect, the ring gets partial +ve charge at ortho and para position.



Resonance hybrid structure :





CYANIDES AND ISOCYANIDES

Alkyl cyanides RCN and alkyl iso-cyanides (RNC) are isomers. CN^- and NC^- are ambident nucleophiles.

PREPARATION

(1) From alkyl halide:

$$R-X+alc.KCN \rightarrow \underset{(major)}{R-CN}+RNC$$

(2) From amides by dehydration:

$$R-CONH_2 \xrightarrow[Heat]{P_4O_{10}} R-CN+H_2O$$

(3) Using Grignard reagent:

$$R-MgX+\underset{\substack{cyanogen\\chloride}}{Cl-C\equiv N} \rightarrow R-CN+MgX\ Cl$$

(4) From oxime:

$$R-CH=NOH \xrightarrow[\Delta]{P_4O_{10}} R-CN+H_2O$$

PREPARATION OF RNC

(1) From RX:

$$RX+Ag\ CN(alc.) \rightarrow \underset{(major)}{R-NC}+RCN$$

(2) By carbylamine reaction:

$$R-NH_2+CHCl_3+3KOH\xrightarrow{\text{warm}}R-NC+3H_2O+3KCl$$

This reaction is given by only 1° amines. Hence is used as test for 1° amines. The reaction intermediate used in reaction is dichlorocarbene.

CHEMICAL PROPERTIES

(1) Hydrolysis:

(a) Cyanide:

$$R-CN\xrightarrow[H_2SO_4]{\text{dil.}}RCONH_2\xrightarrow[\substack{H_2SO_4\\ \text{acid}}]{\text{dil.}}RCOOH$$

(b) Hydrolysis of Isocyanide:

$$\underset{\substack{\text{Alkyl}\\ \text{isocyanides}}}{R-NC}\xrightarrow[H^+]{H_2O}RNH_2+HCOOH$$

Note : HCOOH gives silver mirror with tollen’s reagent. Partial hydrolysis of RCN gives acid amides.

(2) Reduction

(a) Complete reduction:

(i) $$R-C\equiv N\xrightarrow[\text{reduction}]{\text{complete}}\underset{(1^\circ\text{amine})}{R-CH_2-NH_2}$$

⇒ using $LiAlH_4$, H_2/Ni or Pt, the same result as above can be obtained.

(ii) $R-C\equiv N\xrightarrow{Na/C_2H_5OH}R-CH_2NH_2$, the reaction is known as Mendius reaction.

(b) Partial reduction:

$R-C\equiv N$ on partial reduction with $SnCl_2$/HCl followed by hydrolysis gives aldehyde (Stephen’s reduction)

$$R-C\equiv N\xrightarrow{SnCl_2/HCl}RCH=NH\xrightarrow[H^+]{H_2O}RCHO$$

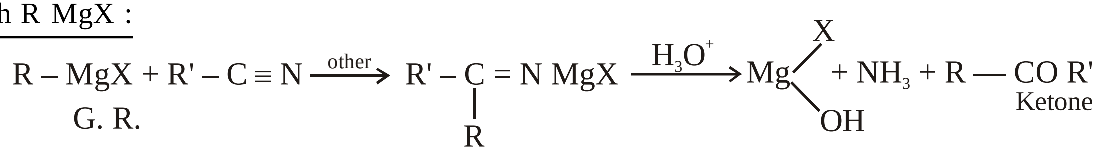
Note : RNC on reduction with H_2/Pt gives N-alkyl alkanamine.

$$R-NC\xrightarrow{H_2/Pt}R-NH\ CH_3$$

(3) Effect of heat at 250°C converts RNC into RCN :

$$R-CN\ f\ R-NC$$

(4) With R MgX :

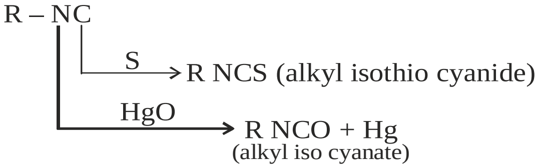


$$\underset{\text{G. R.}}{R-MgX}+R'-C\equiv N\xrightarrow{\text{other}}R'-\underset{\substack{|\\ R}}{C}=N\,MgX\xrightarrow{H_3O^+}Mg\begin{matrix}X\\ OH\end{matrix}+NH_3+\underset{\text{Ketone}}{R-CO\,R'}$$

(5) Addition reaction of RNC

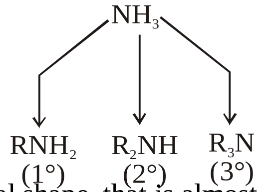
RNC gives addition reaction due to the presence of lone pair of electron on carbon atom.

$R-\overset{+}{N}\equiv C:\Leftarrow$ structure of alkyl isocyanide.

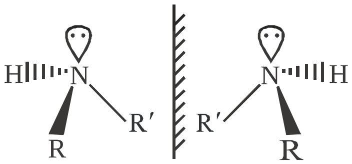


AMINES

Amines are derivatives of ammonia and are formed by the replacement of one or more hydrogen atom by R or aryl group.



Aliphatic amines have pyramidal shape, that is almost tetrahedral. Amines which have three different group attached to nitrogen, has chiral nitrogen. But, such optically active amines can't be resolved into its enantiomers because of rapid inter convertion of enantiomers to its mirror image.

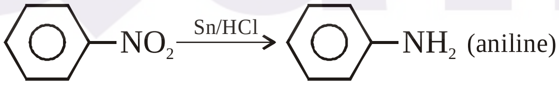


But on the other hand quaternary ammonium salt having four different groups attached to nitrogen show optically activity and its enantiomers can be resolved.

PREPARATION OF AMINES

(1) Reduction:

(i) $$R-NO_2 \xrightarrow[\text{Sn / HCl}]{\text{Fe / HCl} \atop \text{or}} \underset{(1^\circ\ \text{amine})}{R-NH_2}$$



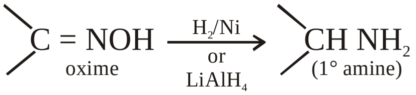
(ii) From Amides:

$$\underset{(\text{amides})}{R-CONH_2} \xrightarrow{LiAlH_4} \underset{(1^\circ\ \text{amine})}{RCH_2NH_2}$$

(iii) From Nitrites:

$$\underset{\text{nitriles}}{R-CN} \xrightarrow{LiAlH_4} \underset{(1^\circ\ \text{amine})}{R\,CH_2NH_2}$$

(iv) From oximes:



$$\underset{\text{oxime}}{>C=NOH} \xrightarrow[\text{LiAlH}_4]{H_2/Ni \atop \text{or}} \underset{(1^\circ\ \text{amine})}{>CH\,NH_2}$$

(2) From Hydroxy compound:

$$R-OH+NH_3 \xrightarrow[\text{or } ThO_2]{Al_2O_3,\Delta} RNH_2+H_2O$$

(3) Preparation of amines with step down:

(i) By Hofmann bromamide reaction:

$$R-CONH_2 \xrightarrow{Br_2/KOH} R\ NH_2 + KBr + K_2CO_3 + H_2O$$

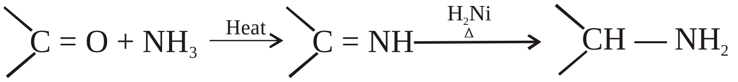
(ii) By Curtius rearrangement:

$$R-COCl \xrightarrow[Heat]{NH_3} R\ NH_2 + HCl + N_2$$

(iii) (Schmidt reaction)

$$R\ COOH + HN_3 \rightarrow R\ NH_2 + N_2 + CO_2$$

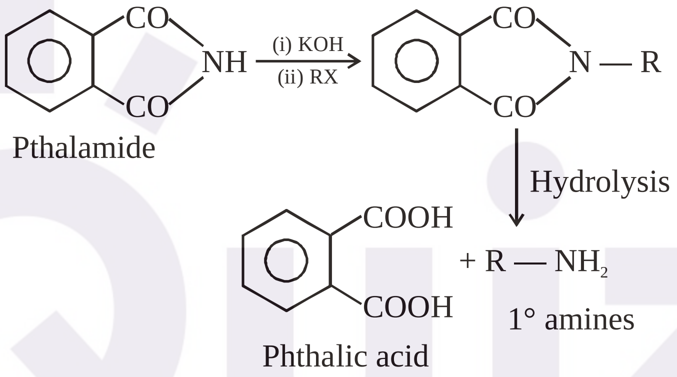
(4) Reductive aminationof aldehydes and ketones:



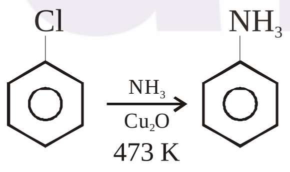
The reaction can also be used to prepare secondary and tertiary amines.

(5) Gabriel phthalimide synthesis:

Exclusively for the preparation of primary amines.



(6) From Chlorobenzene by S_N reaction :



(7) Preparation of aniline from benzene sulphonic acid:

PROPERTIES OF AMINES

(1) Boiling Point : Out of isomeric amines, the b.p. order is 3° < 2° < 1°

(2) Solubility : Lower amines are soluble in water due to H-bonding and solubility decreases down the homologous series. Out of the three isomeric amines, the solubility order is

3° < 2° < 1°

BASICITY OF AMINES:

(i) Amines are basic in nature due to the presence of lone pair of electron on N-atom. Amines are weak bases as they give OH^- ion in aq. solution

$$R\ NH_2 + H_2O \rightleftharpoons R\ NH_3^+ + OH^-$$

where, $$\boxed{K_b = \frac{\left[RNH_3^+\right]\left[OH^-\right]}{\left[RNH_2\right]}}$$

K_b = base dissociation constant.

- Basicity increases as K_b value increases.
- Basicity $\propto K_b \propto pK_a \propto \frac{1}{pk_b}$

(ii) Except for amines containing $(CH_3)_3$ C group, all lower aliphatic amines are stronger bases than NH_3 because of the +I effect of alkyl group.

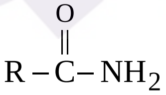
As the number of R group at N-atom increases, basicity should also increase, but the observed basicity order in case of lower member is

$$2° > 1° > 3°$$

This anamalous behaviour is due to steric factor. In 3° amines, the alkyl groups are so larger in size that amine comes under strain and becomes energetically unfavourable to accept any extra H^+ ion.

(iii) The order of basic nature is

R group	Basic strength order
CH_3—	$2° > 1° > 3° > NH_3$
C_2H_5—	$2° > 3° > 1° > NH_3$
$(CH_3)_2CH$	$2° > 1° > NH_3 > 3°$
$(CH_3)_3C$	$NH_3 > 1° > 2° > 3°$

(iv) Amides  $R-\overset{\overset{O}{\|}}{C}-NH_2$ are weaker bases than amines due to the delocalization of lone pair on N with carbonyl group.

(v) As the % character in N-atom increases, basicity decreases.

$$CH_3CH_2NH_2 \rightarrow N\left(sp^3\right) \rightarrow \text{ 25\% s-character}$$

$$CH_3CH = NH_2 \rightarrow N\left(sp^2\right) \rightarrow \text{ 33\% s-character}$$

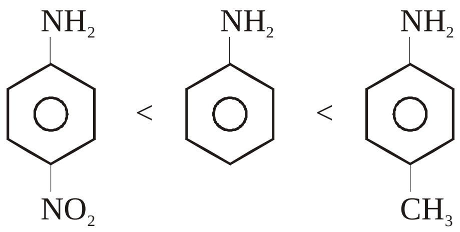
$$CH_3C \equiv N \rightarrow N\left(sp\right) \rightarrow \text{ 50\% s-character}$$

The basicity order is

$$CH_3C \equiv N < CH_3CH = NH < CH_3CH_2 - NH_2$$

(vi) Aniline is a weaker base than ethylamine because the lone pair on N is involved into resonance with the benzene ring. The electron density on N-atom decreases, basicity decreases.

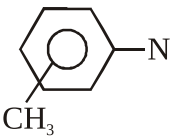
⇒ The presemce pf EDG increases the basicity and EWG decreases the basicity of aniline.



increasing basicity order

(vii) N-alkylated anilines are stronger bases than aniline because of steric hindrance. The basic character order is $C_6H_5N(C_2H_5)_2 > C_6H_5NHC_2H_5 > C_6H_5N(CH_3)_2 > C_6H_5NHCH_3 > C_6H_5NH_2$

(viii) In toluidines



$-NH_3$, the basicity order is

⇒

p > m > o

←

(ix) In nitro anilines : The order is, p > m > o

←

REACTION OF AMINES:

(1) Amines are basic in nature, dissolves in HCl to form salt:

$$RNH_2 + HCl \rightarrow RNH_3^+Cl^-$$

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

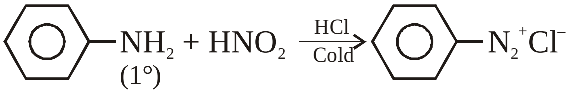
(2) In H_2O, amines gives OH^- which reacts with $FeCl_3$ to give reddish brown ppt. of $Fe(OH)_3$:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$FeCl_3 + 3OH^- \rightarrow Fe(OH)_3 + 3Cl^-$$

(3) With HNO_2 ($NaNO_2$ + HCl):

(i) (a) $\underset{1^0}{RNH_2} + HNO_2 \rightarrow ROH + H_2O + N_2\uparrow\ (1°)$

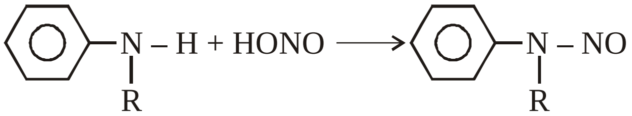


benzene diazonium chloride

This reaction is used to distinguish primary aliphatic amine and aniline.

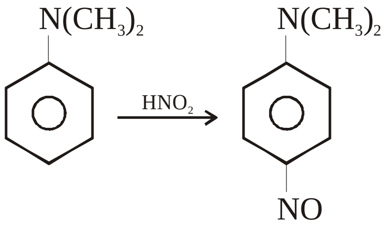
(ii) 2° amine (aliphatic and aromatic) both form nitroso compound.

(a) $R_2NH + HONO \rightarrow R_2N — NO$

(b) 

(iii) 3° aliphatic amines form salts with HNO_2 whereas 3° aromatic amine undergo electrophilic substitution reaction:

$$R_3N + HNO_2 \rightarrow R_3NH^+ONO^-$$



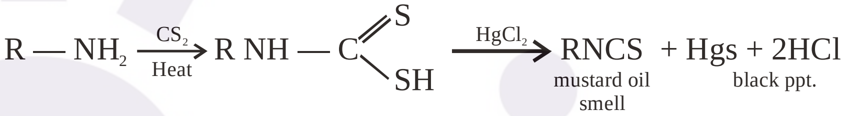
(4) <u>Carbylamine reaction (Isocyanide Test):</u>

This reaction is used to distinguish primary amines from secondary and tertiary. The reaction is given by both aliphatic and aromatic primary amines, only.

$$R-NH_2 + \underset{(alc.)}{3KOH} + CHCl_3 \xrightarrow{\text{warm}} \underset{\text{foul smell}}{R-NC} + 3KCl + 3H_2O$$

(Carbyl amine)

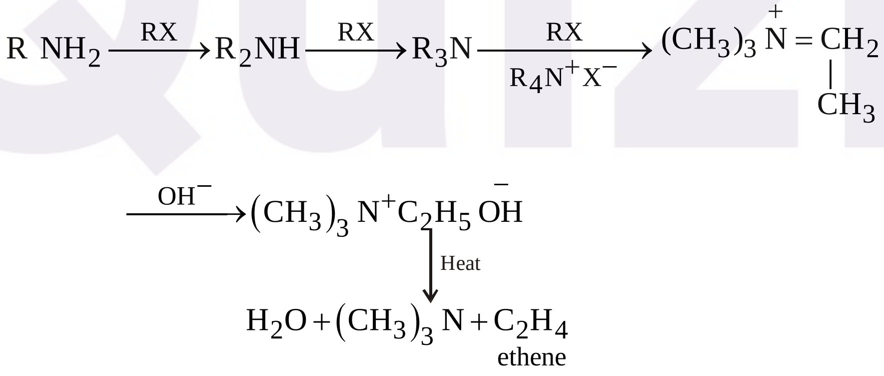
(5) <u>Hofmann's mustard oil reaction for primary amines:</u>



$$R-NH_2 \xrightarrow[\text{Heat}]{CS_2} R\,NH-C(=S)SH \xrightarrow{HgCl_2} \underset{\text{mustard oil smell}}{RNCS} + \underset{\text{black ppt.}}{Hgs} + 2HCl$$

Note: Secondary amines → no black ppt.

(6) <u>Alkylation of amine (Hofmann exhaustive alkylation):</u>

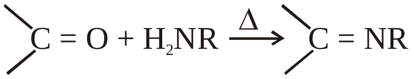


$$R\ NH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow[R_4N^+X^-]{RX} (CH_3)_3\overset{+}{N}(CH_3)=CH_2$$

$$\xrightarrow{OH^-} (CH_3)_3N^+C_2H_5\overset{-}{OH} \xrightarrow{\text{Heat}} H_2O + (CH_3)_3N + \underset{\text{ethene}}{C_2H_4}$$

⇒ This is called Hofmann elimination. In this method, the alkene is obtained with lesser number of alkyl group.

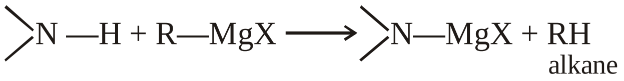
(7) <u>With aldehyde and ketones, amine form Schiff base:</u>



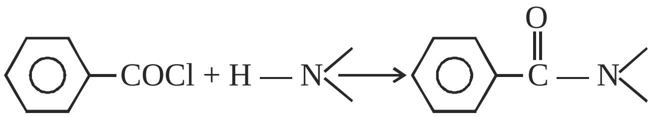
$$>C=O + H_2NR \xrightarrow{\Delta} >C=NR$$

Schiff base

(8) <u>With RMgX:</u>

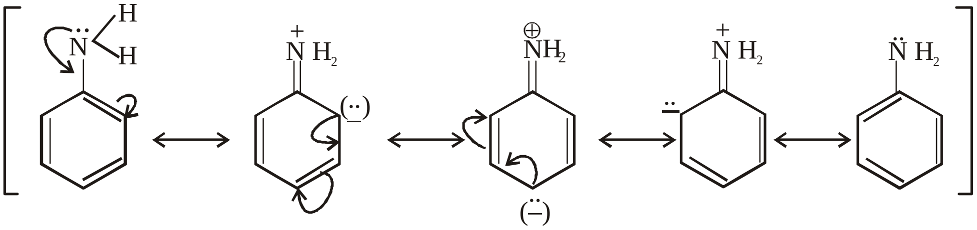


(9) Benzoylation of amines is known as Schotten-Bauman reaction :

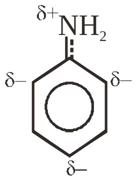


REACTION OF ANILINE :

Aniline is ortho-para directing group for incoming electrophiles because of + R or +M effect.



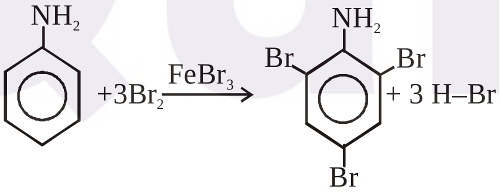
RESONANCE HYBRID STRUCUTRE



ELECTROPHILIC SUBSTITUTION REACTION

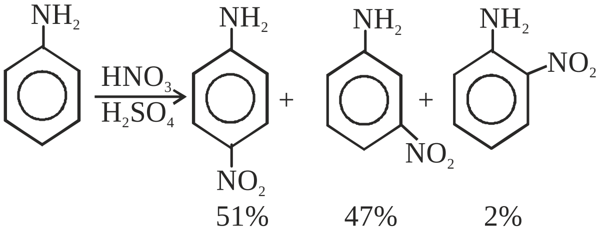
Anniline ring is largely activating for incoming electrophiles

1. Bromination:

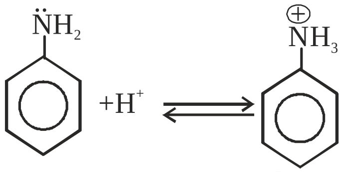


2,4, 6 Tribromo-aniline

2. Nirtration:



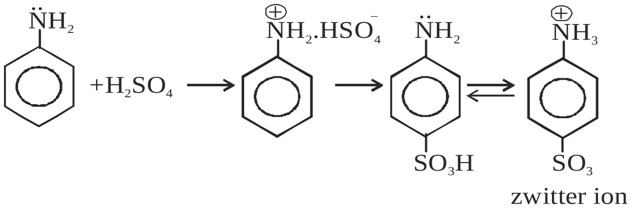
⇒ The meta proudct is formed, due to the formation of anilinium ion.



Annilinium ion

⇒ Anilinium ion is meta directing

Sulphonation:

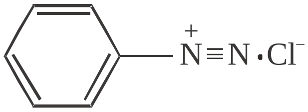


DIAZONIUM SALT

PREPARATION

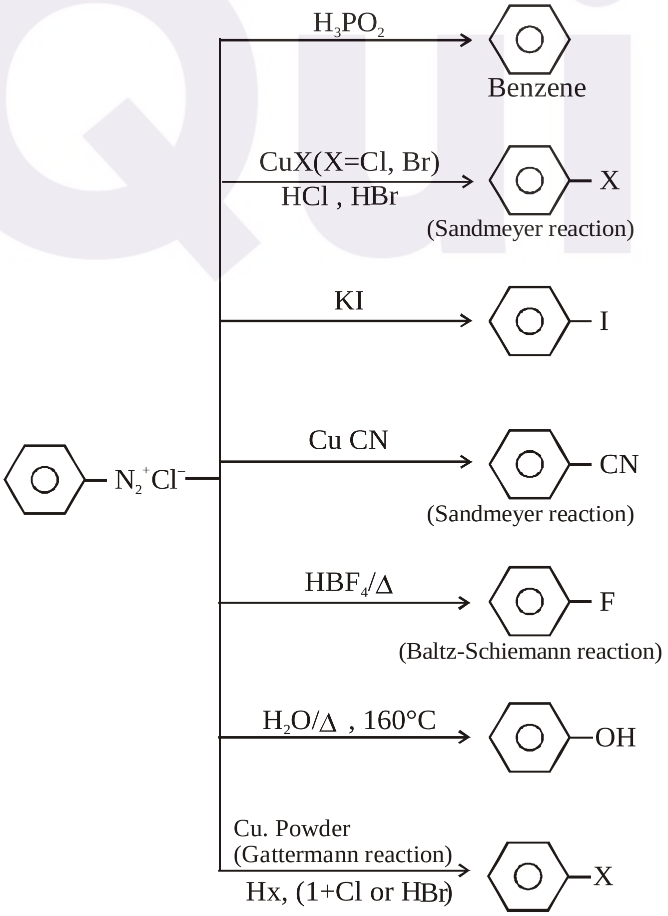
This reaction is given by compounds in which the —NH_2 group is directly bonded to the benzene ring. The aniline is treated with $NaNO_2$ and HCl at 0 to –4° C.

Structure of benzene diazonium chloride is



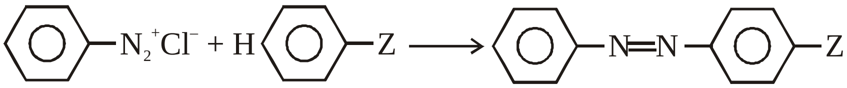
Benzene diazonium chloride gives various types of reaction

FEW CHEMICAL REACTIONS OF DIAZONIUM SALT:



(2) Coupling reaction

It involves the retention of diazonium group. No nitrogen gas is evolved. These is an examples of electrophilic substitution reaction.

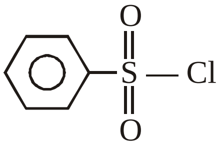


(Z=OH, OR,
NH_2, NHR, NR_2)

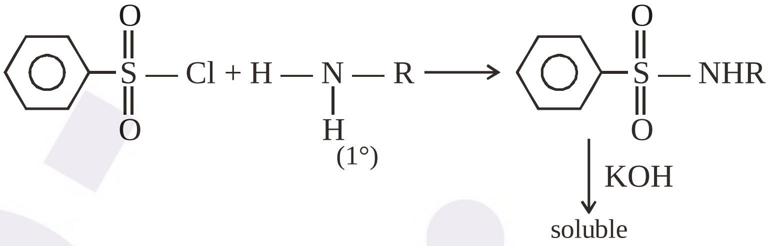
TEST FOR AMINES

(1) Hinsberg's test

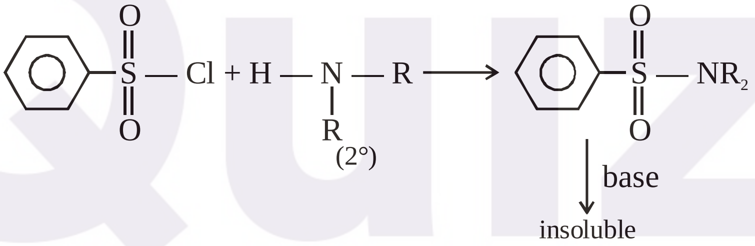
Hinsberg's reagent is benzene sulphonyl chloride.



1° amine gives a base soluble product with Hunsberg's reagent.



2° amine gives a base insoluble product with Hinsberg's reagent.



3° amines do not react with Hinsberg's reagent.