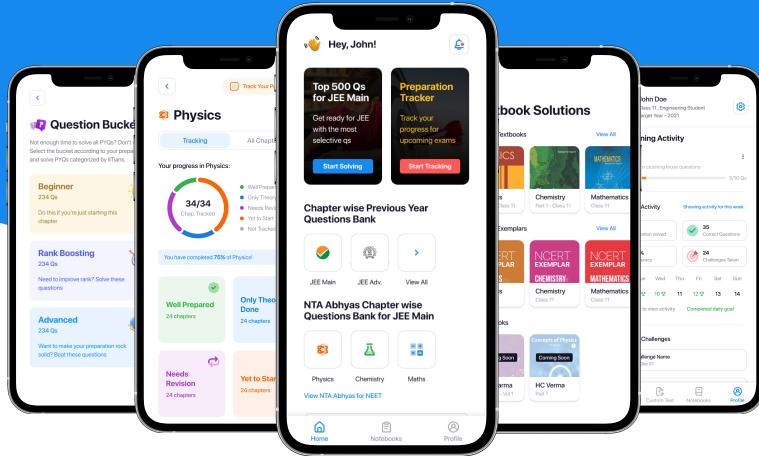




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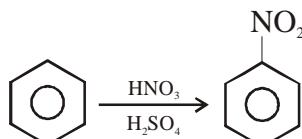
# AMINES

## NITRO COMPOUNDS

### PREPARATIONS

#### (1) By direct nitration of Benzene:

Benzene undergoes electrophilic substitution reaction with  $\text{HNO}_3/\text{H}_2\text{SO}_4$



The electrophile is  $\text{NO}_2^+$  (nitronium ion) produced by the given reaction,

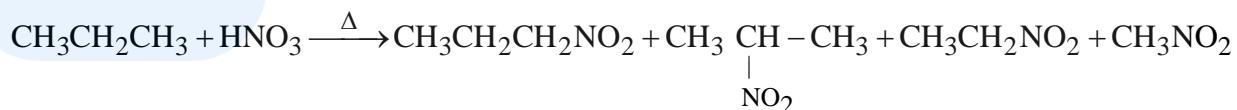


In this reaction,  $\text{HNO}_3$  acts as a base and  $\text{H}_2\text{SO}_4$  acts as an acid.

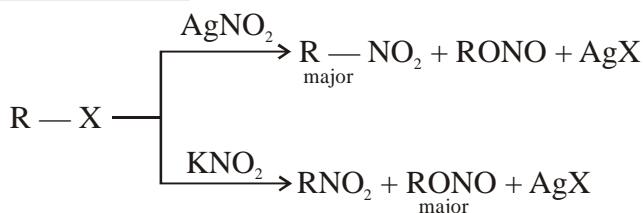
During nitration, the number of solute particles increases (the Van't Hoff factor is greater than one), therefore, freezing point decreases.

#### (2) Vapour phase nitration of alkane:

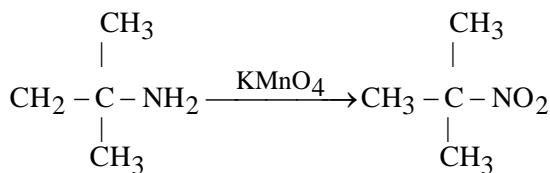
Alkane undergoes nitration at 475 K to 675 K in the presence of conc.  $\text{HNO}_3$  and follows free radical mechanism. This is called vapour phase nitration and may results in the carbon-carbon cleavage.



#### (3) From Halo compounds:



#### (4) From amines:



### PHYSICAL PROPERTIES :

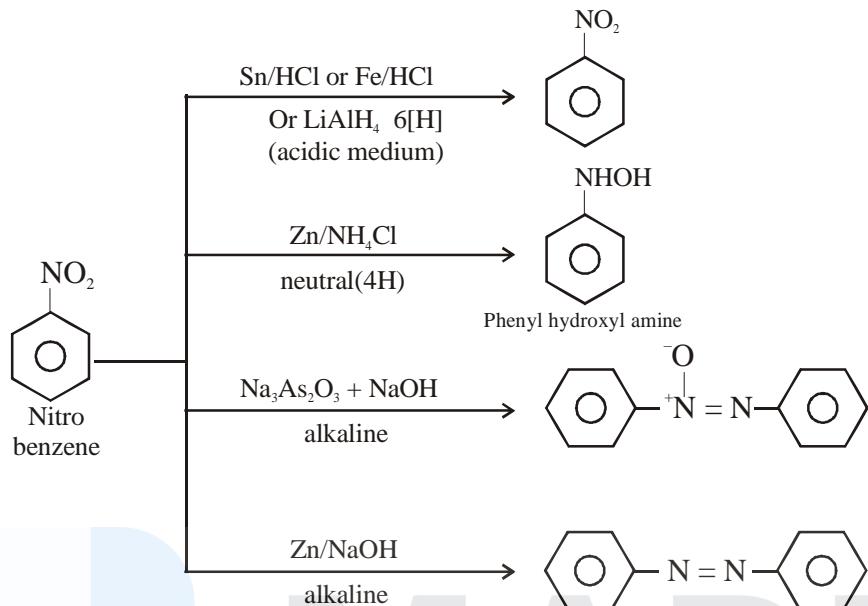
- (1) Nitroalkanes are colourless pleasant smelling liquids.
- (2) Nitrobenzene is a yellow oily liquid, heavier than  $\text{H}_2\text{O}$ , smell of bitter almonds, steam volatile.
- (3) Nitroalkanes are less soluble in water, b.p. are much higher than alkyl nitrites.

## CHEMICAL PROPERTIES :

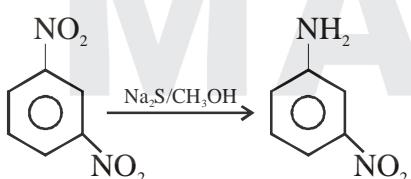
### (1) Reduction :

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

Nitrobenzene

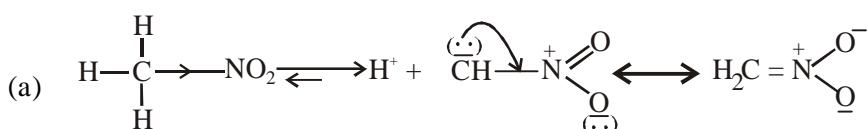


Note :- The reduction of selectively one nitro group in dinitrobenzene, can also be performed.

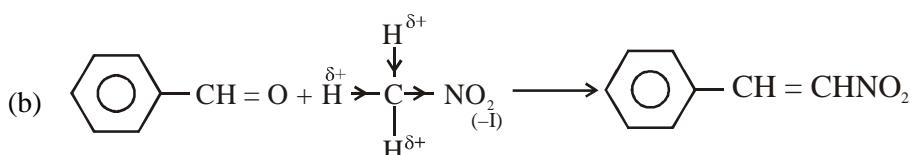
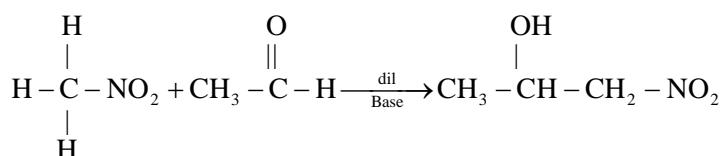


### (2) Acidic $\alpha\text{H}$ of nitro alkanes :

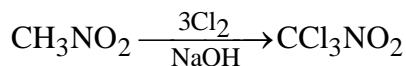
Nitromethane contains acidic  $\alpha$ -hydrogen and can undergo condensation reaction with carbonyl compounds.



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

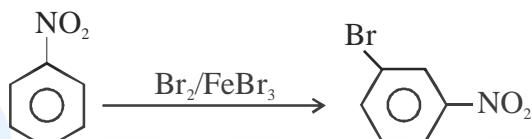
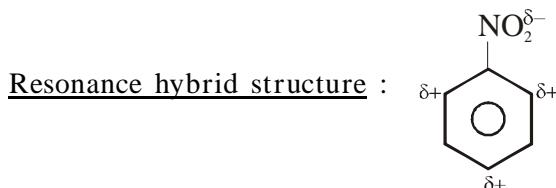
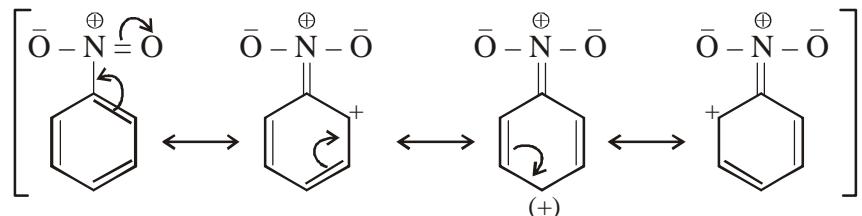


### (3) With chlorine : nitromethane forms chloropicrin. (used as an insecticide)



- (4) Ring substitution in nitrobenzene :  $\text{NO}_2$  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.

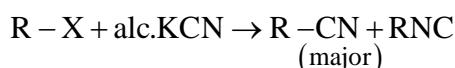


## CYANIDES AND ISOCYANIDES

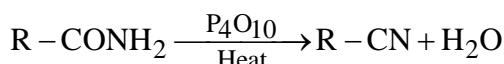
Alkyl cyanides  $\text{RCN}$  and alkyl iso-cyanides ( $\text{RNC}$ ) are isomers.  $\text{CN}^-$  and  $\text{NC}^-$  are ambident nucleophiles.

## PREPARATION

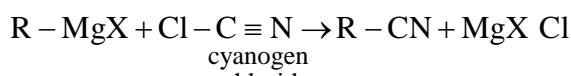
- (1) From alkyl halide:



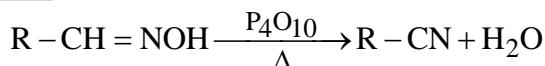
- (2) From amides by dehydration:



- (3) Using Grignard reagent:

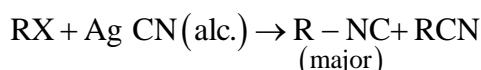


- (4) From oxime:

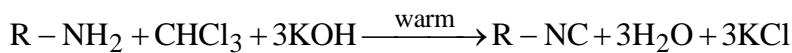


## PREPARATION OF RNC

- (1) From RX:



- (2) By carbylamine reaction:



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

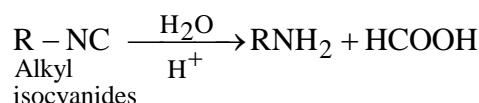
## CHEMICAL PROPERTIES

### (1) Hydrolysis:

#### (a) Cyanide:



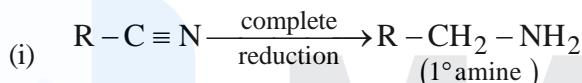
#### (b) Hydrolysis of Isocyanide:



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

### (2) Reduction

#### (a) Complete reduction:

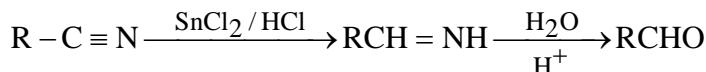


⇒ using LiAlH<sub>4</sub>, H<sub>2</sub>/Ni or Pt, the same result as above can be obtained.

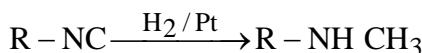


#### (b) Partial reduction:

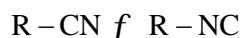
R - C ≡ N on partial reduction with SnCl<sub>2</sub>/HCl followed by hydrolysis gives aldehyde (Stephen's reduction)



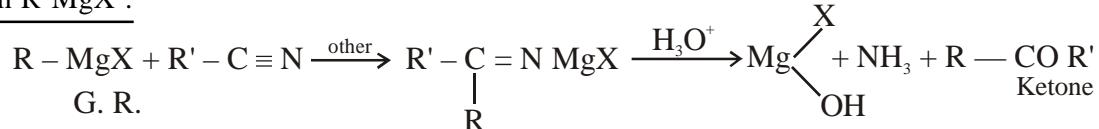
Note : RNC on reduction with H<sub>2</sub>/Pt gives N-alkyl alkanamine.



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

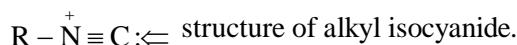


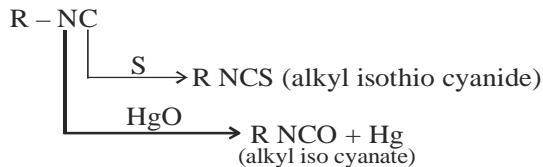
### (4) With R MgX :



### (5) Addition reaction of RNC

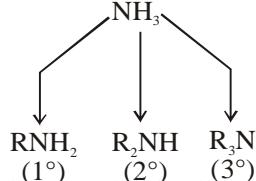
RNC gives addition reaction due to the presence of lone pair of electron on carbon atom.



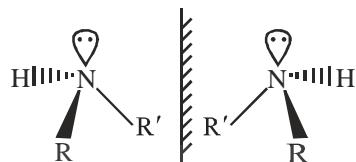


## AMINES

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



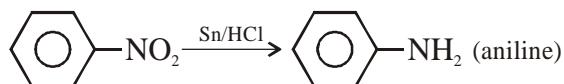
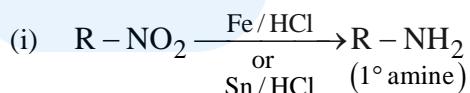
Aliphatic amines have pyramidal shape, that is almost tetrahedral. Amines which have three different group attached to nitrogen, has chiral nitrogen. But, such optically active amines can't be resolved into its enantiomers because of rapid inter conversion of enantiomers to its mirror image.



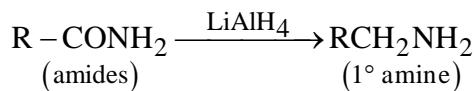
But on the other hand quaternary ammonium salt having four different groups attached to nitrogen show optically activity and its enantiomers can be resolved.

## PREPARATION OF AMINES

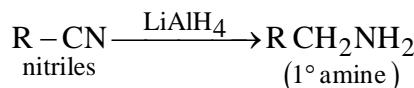
### (1) Reduction:



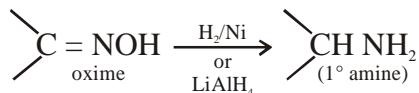
### (ii) From Amides:



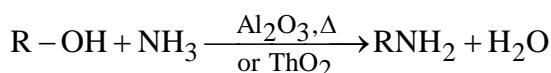
### (iii) From Nitrites:



### (iv) From oximes:



### (2) From Hydroxy compound:

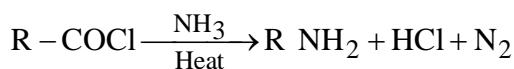


### (3) Preparation of amines with step down:

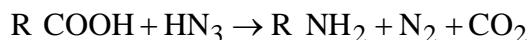
#### (i) By Hofmann bromamide reaction:



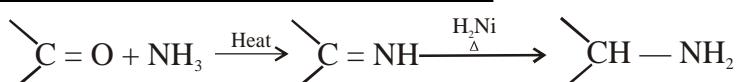
#### (ii) By Curtius rearrangement:



#### (iii) (Schmidt reaction)



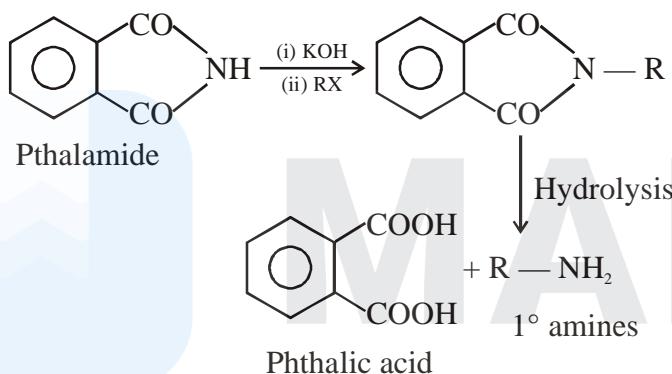
### (4) Reductive amination of aldehydes and ketones:



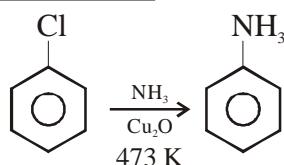
The reaction can also be used to prepare secondary and tertiary amines.

### (5) Gabriel phthalimide synthesis:

Exclusively for the preparation of primary amines.



### (6) From Chlorobenzene by $\text{S}_\text{N}$ reaction :



### (7) Preparation of aniline from benzene sulphonic acid:

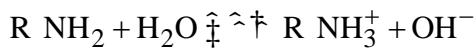


## PROPERTIES OF AMINES

- (1) Boiling Point : Out of isomeric amines, the b.p. order is  $3^\circ < 2^\circ < 1^\circ$
- (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  
 $3^\circ < 2^\circ < 1^\circ$

## 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  $\text{OH}^-$  ion in aq. solution



where,

$$K_b = \frac{[R\text{NH}_3^+][OH^-]}{[R\text{NH}_2]}$$

$K_b$  = 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  $(CH_3)_3C$  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

$$2^\circ > 1^\circ > 3^\circ$$

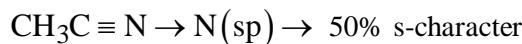
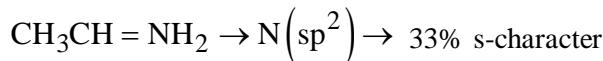
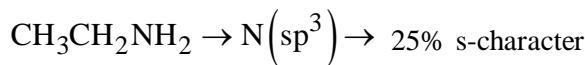
This anomalous behaviour is due to steric factor. In  $3^\circ$  amines, the alkyl groups are so larger in size that amine comes under strain and becomes energetically unfavourable to accept any extra  $H^+$  ion.

- (iii) The order of basic nature is

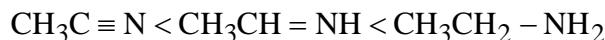
R group	Basic strength order
$CH_3-$	$2^\circ > 1^\circ > 3^\circ > NH_3$
$C_2H_5-$	$2^\circ > 3^\circ > 1^\circ > NH_3$
$(CH_3)_2CH$	$2^\circ > 1^\circ > NH_3 > 3^\circ$
$(CH_3)_3C$	$NH_3 > 1^\circ > 2^\circ > 3^\circ$

- (iv) Amides  $R-C(=O)-NH_2$  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.

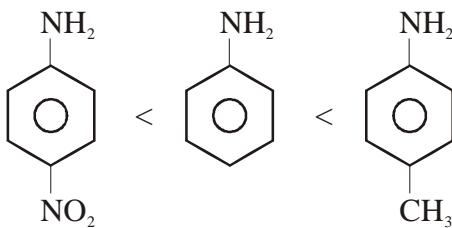


The basicity order is



- (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.

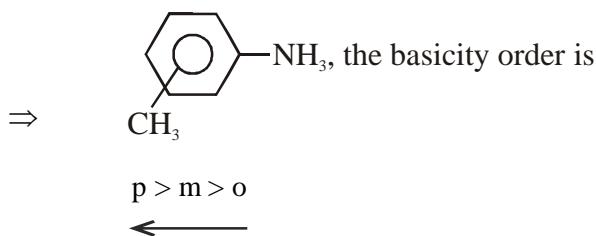
⇒ The presence of EDG increases the basicity and EWG decreases the basicity of aniline.



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

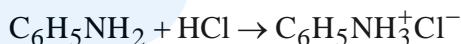
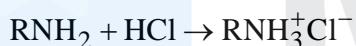


(ix) In nitro anilines : The order is,  $p > m > o$

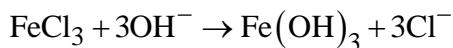
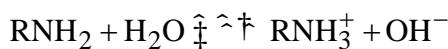
$\leftarrow$

### REACTION OF AMINES:

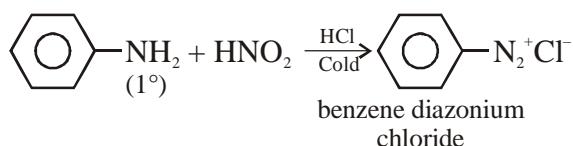
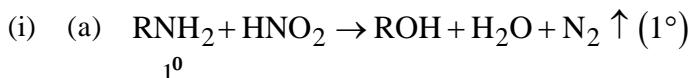
(1) Amines are basic in nature, dissolves in HCl to form salt:



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



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



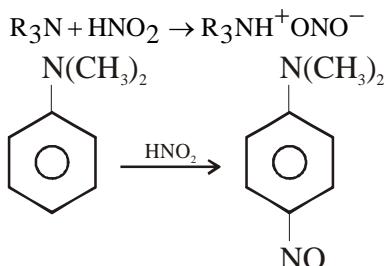
This reaction is used to distinguish primary aliphatic amine and aniline.

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



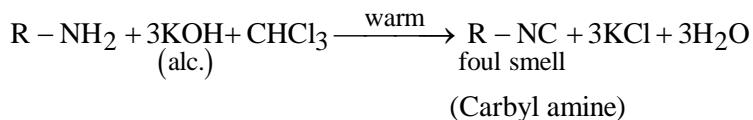


(iii)  $3^\circ$  aliphatic amines form salts with  $\text{HNO}_2$  whereas  $3^\circ$  aromatic amine undergo electrophilic substitution reaction:

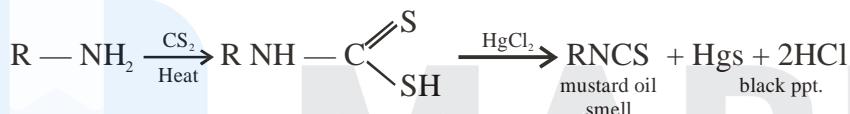


(4) Carbylamine reaction (Isocyanide Test):

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

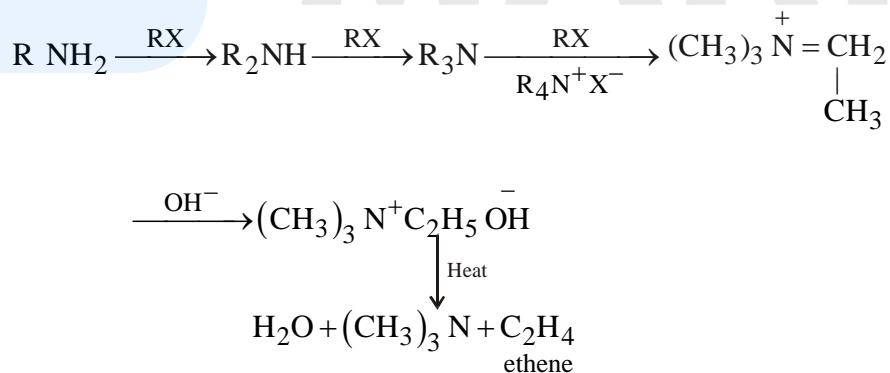


(5) Hofmann's mustard oil reaction for primary amines:



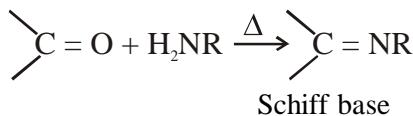
Note: Secondary amines  $\rightarrow$  no black ppt.

(6) Alkylation of amine (Hofmann exhaustive alkylation):

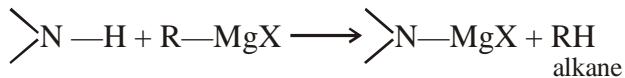


$\Rightarrow$  This is called Hofmann elimination. In this method, the alkene is obtained with lesser number of alkyl group.

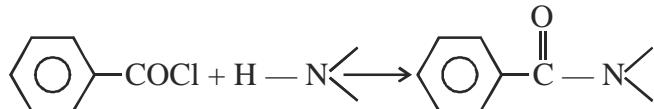
(7) With aldehyde and ketones, amine form Schiff base:



(8) With  $\text{RMgX}$ :

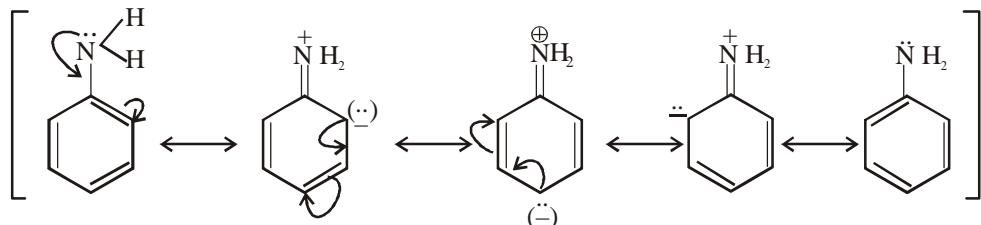


(9) Benzoylation of amines is known as Schotten-Bauman reaction :

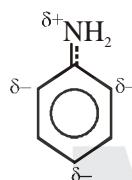


### REACTION OF ANILINE :

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



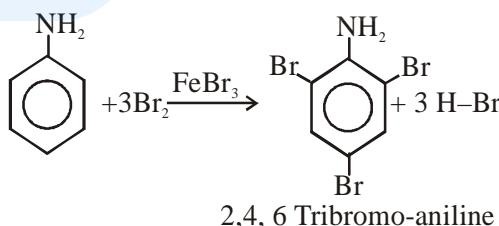
### RESONANCE HYBRID STRUCTURE



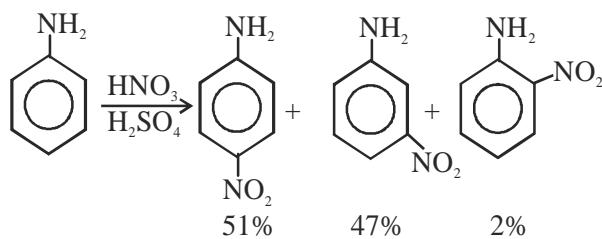
### ELECTROPHILIC SUBSTITUTION REACTION

Aniline ring is largely activating for incoming electrophiles

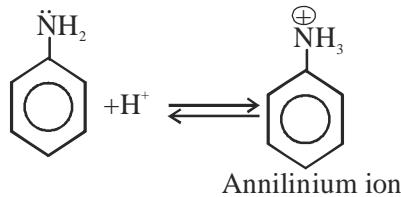
#### 1. Bromination:



#### 2. Nitration:

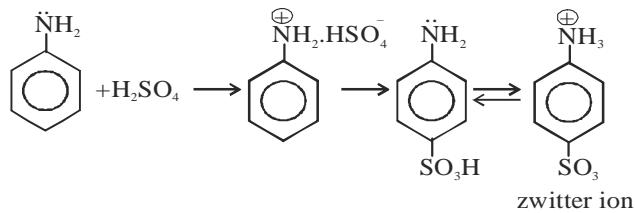


⇒ The meta product is formed, due to the formation of anilinium ion.



⇒ Anilinium ion is meta directing

### Sulphonation:



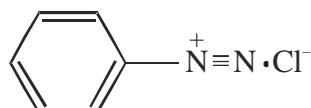
### DIAZONIUM SALT

#### PREPARATION

This reaction is given by compounds in which the  $\text{—NH}_2$  group is directly bonded to the benzene ring. The aniline is treated with  $\text{NaNO}_2$  and  $\text{HCl}$  at  $0$  to  $-4^\circ\text{C}$ .

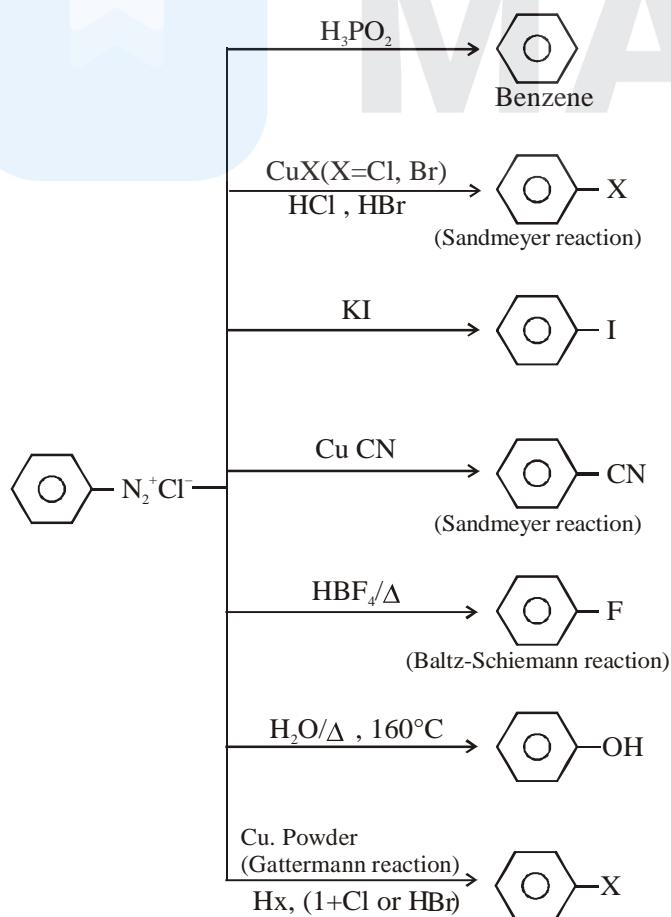


Structure of benzene diazonium chloride is

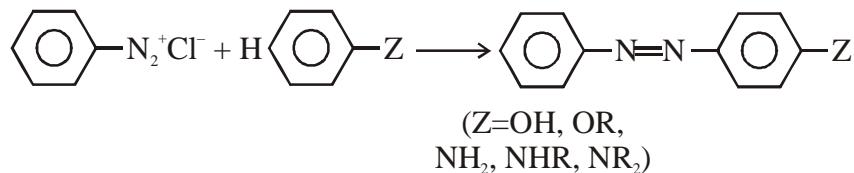


Benzene diazonium chloride gives various types of reaction

#### FEW CHEMICAL REACTIONS OF DIAZONIUM SALT:



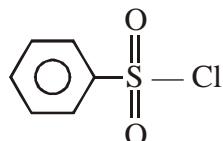
It involves the retention of diazonium group. No nitrogen gas is evolved. These is an examples of electrophilic substitution reaction.



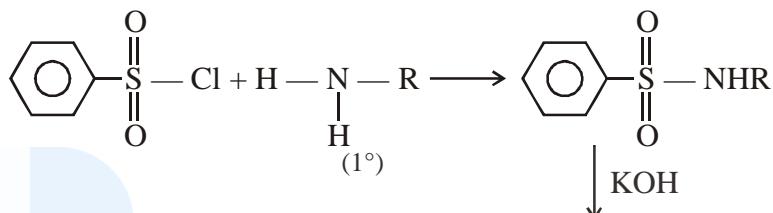
### TEST FOR AMINES

#### (1) Hinsberg's test

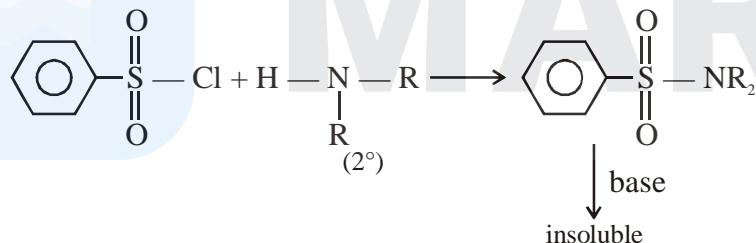
Hinsberg's reagent is benzene sulphonyl chloride.



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



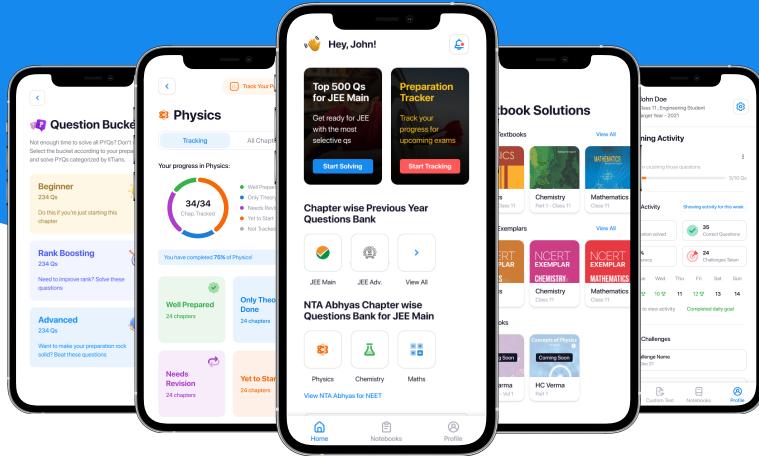
2° amine gives a base insoluble product with Hinsberg's reagent.



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



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