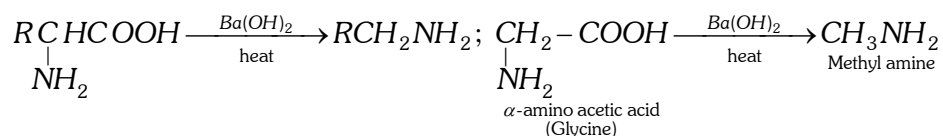


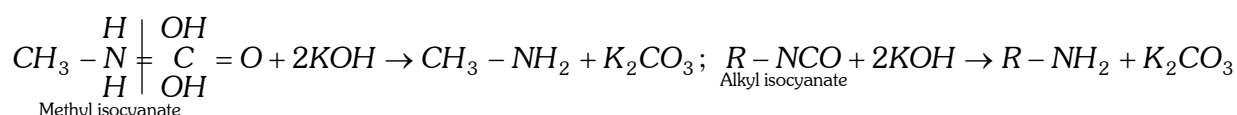
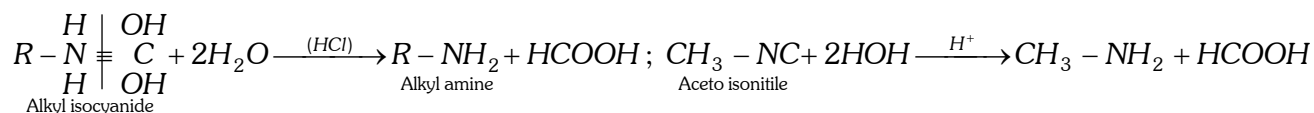
Nitrogen containing compounds Part 1

(g) By decarboxylation of α -amino acids



(h) By means of a Grignard reagent and chloramine : $\text{RMgX} + \text{ClNH}_2 \rightarrow \text{RNH}_2 + \text{MgXCl}$

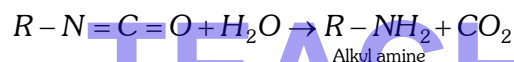
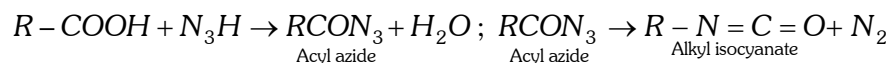
(i) By hydrolysis of Isocyanides or Isocyanates



(j) By Schmidt reaction : $R-\text{COOH} + \text{N}_3\text{H} \xrightarrow{\text{Conc. H}_2\text{SO}_4} R-\text{NH}_2 + \text{N}_2 + \text{CO}_2$

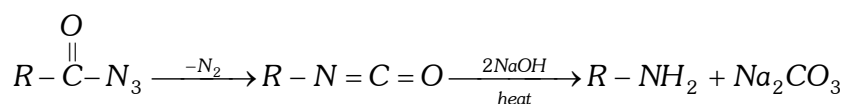
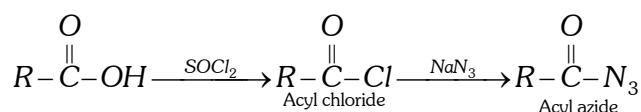
Acid Hydrazoic acid Alkyl amine

In this reaction the acyl azide ($R-\text{CON}_3$) and alkyl isocyanate ($R-\text{NCO}$) are formed as an intermediate.

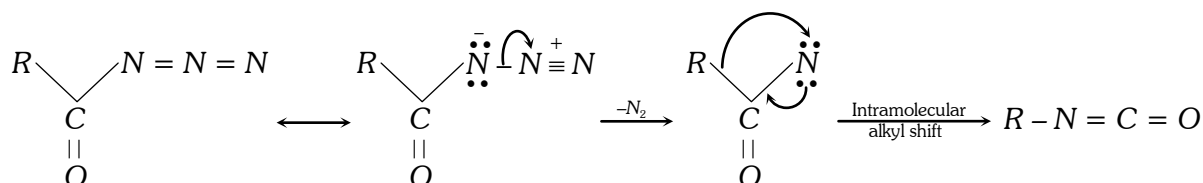


The overall reaction which proceeds by the elimination of nitrogen from acyl azide followed by acidic or alkaline hydrolysis to yield primary amine containing one carbon less, is called **Curtius Degradation**.

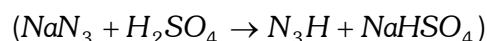
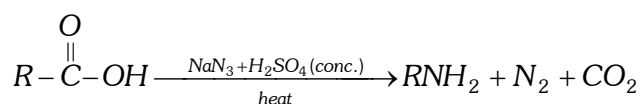
The method uses acid chloride to prepare primary amine through acyl azide.



The mechanism of **curtius rearrangement** is very similar to Hofmann degradation.

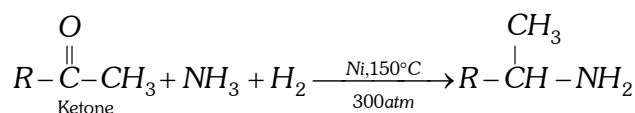
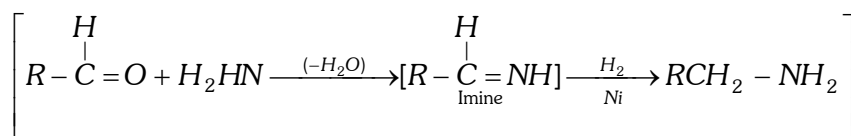
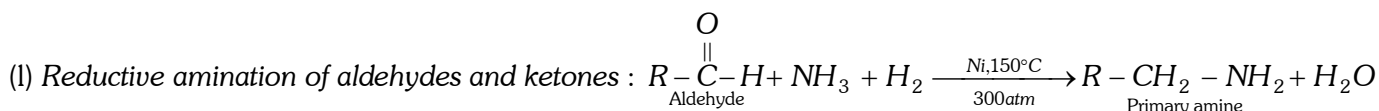
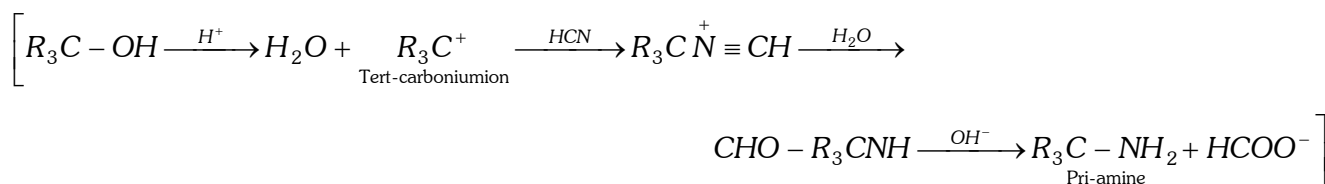
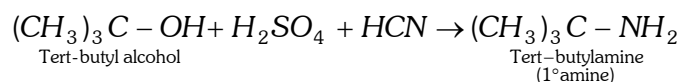


Schmidt reaction converts $R-\text{COOH}$ to $R-\text{NH}_2$, which is a modification of curtius degradation. In this reaction a carboxylic acid is warmed with sodium azide (Na^+N_3^-) and conc. H_2SO_4 . The carboxylic acid is directly converted to the primary amine without the necessity of isolating alkyl azide.



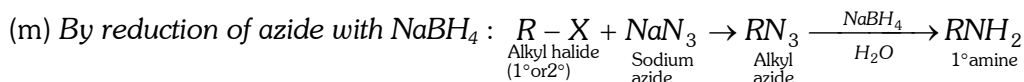
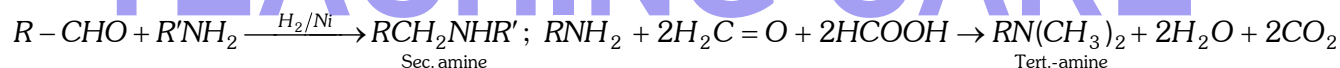
Nitrogen containing compounds Part 1

(k) *By Ritter reaction* : It is a good method for preparing primary amines having α -tertiary alkyl group.

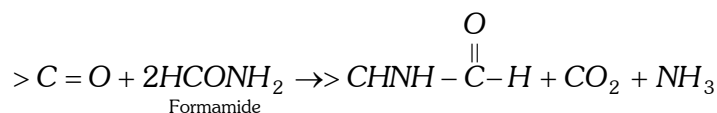
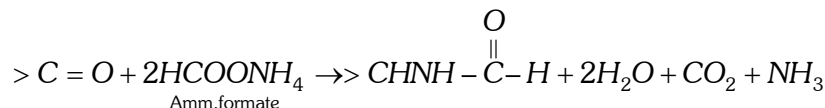


This reaction probably takes place through the formation of an imine (Schiff's base).

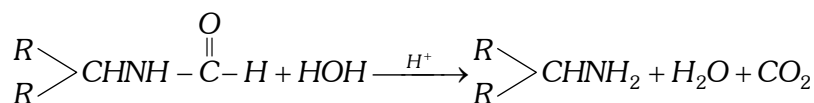
The primary amine can also be converted into sec. or tert. amines by the following steps



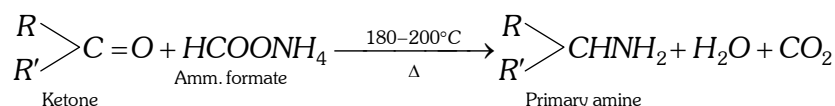
(n) *By Leuckart reaction* : Aldehydes or ketones react with ammonium formate or with formamide to give formyl derivative of primary amine.



These formyl derivatives are readily hydrolysed by acid to yield primary amine.

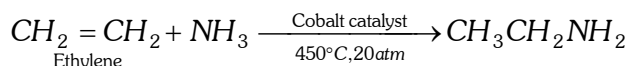


This is called Leuckart reaction, i.e.,



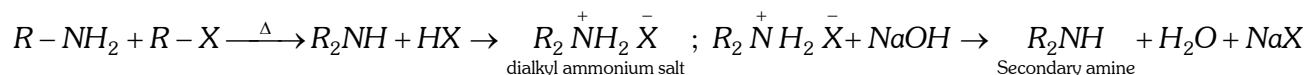
Nitrogen containing compounds Part 1

Note : ✱ On commercial scale, ethylamine is obtained by heating a mixture of ethylene and ammonia at 450°C under 20 atmospheric pressure in presence of cobalt catalyst.



(iii) Methods yielding secondary amines

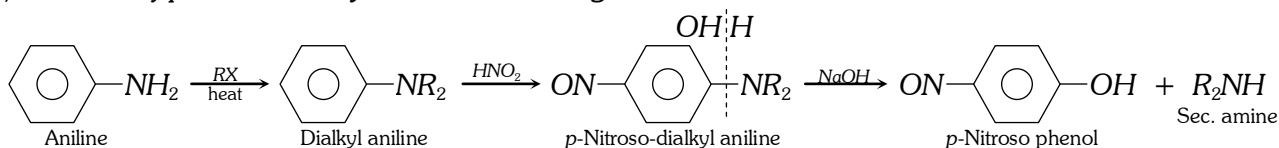
(a) Reaction of primary amines with alkyl halides



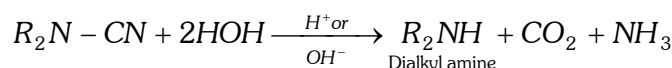
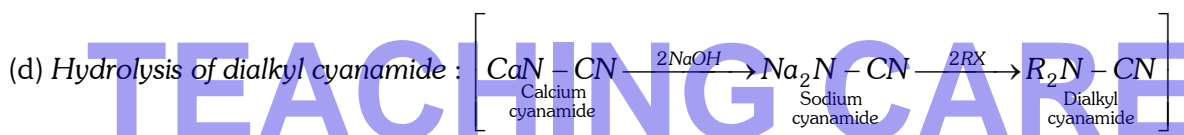
(b) Reduction of isonitriles : $\text{R}-\text{NC} + 4[\text{H}] \xrightarrow{\text{Pt}} \text{RNHCH}_3$
Alkyl isonitrile Sec. amine

Secondary amine formed by this method always possesses one $-\text{CH}_3$ group linked directly to nitrogen.

(c) Reaction of *p*-nitroso-dialkyl aniline with strong alkali solution :



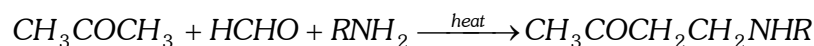
This is one of the best method for preparing pure secondary amines.



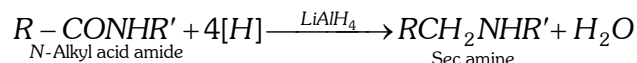
(e) Reduction of *N*-substituted amides : Reduction of *N*-substituted amides with LiAlH_4 yields secondary amines.

Alkyl β -amino ketones are formed by the action of ketone with formaldehyde and NH_3 (or primary or secondary amines).

The product is referred to as Mannich base and the reaction is called **Mannich Reaction**.

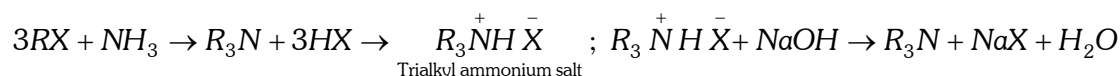


Which can be reduced to alkyl amines.

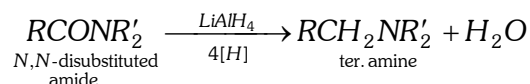


(iv) Methods yielding tertiary amines

(a) Reaction of alkylhalides with ammonia

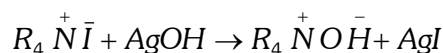


(b) Reduction of *N,N*-disubstituted amides : The carbonyl group is converted into $-\text{CH}_2$ group.

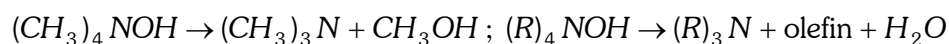


Nitrogen containing compounds Part 1

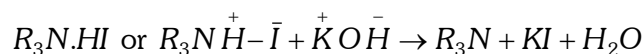
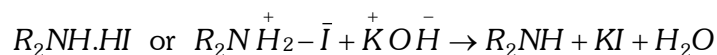
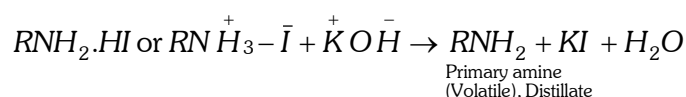
(c) *Decomposition of tetra-ammonium hydroxides* : The tetra-alkyl ammonium hydroxides are formed when corresponding halides are treated with moist silver oxide.



The hydroxides thus formed on heating decompose into tertiary amines. Tetramethyl ammonium hydroxide gives methyl alcohol as one of the products while all other tetra-alkyl ammonium hydroxides give an olefin and water besides tertiary amines.



(5) **Separation of mixture of amines** : When the mixture consists of salts of primary, secondary and tertiary amines along with quaternary salt, **it is first distilled with KOH solution**. The mixture of three amines distils over leaving behind non-volatile quaternary salt.

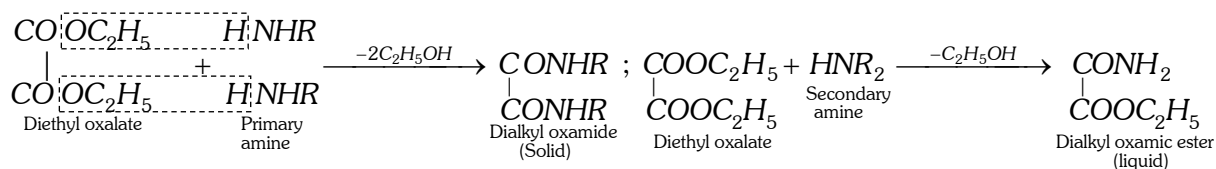


$R_4 \overset{+}{N} \bar{I}$ (non-volatile tetra-alkyl ammonium salt) has no reaction with KOH , however remains as residue.

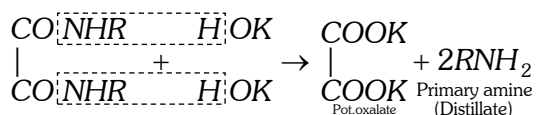
This mixture is separated into primary, secondary and tertiary amines by the application of following methods.

(i) **Fractional distillation** : The boiling points of primary, secondary and tertiary amines are quite different, i.e., the boiling point of $C_2H_5NH_2$ is $17^\circ C$, $(C_2H_5)_2NH$ is $56^\circ C$ and $(C_2H_5)_3N$ is $95^\circ C$ and thus, these can be separated by fractional distillation. This method is used satisfactorily in industry.

(ii) **Hofmann's method** : The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide, a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

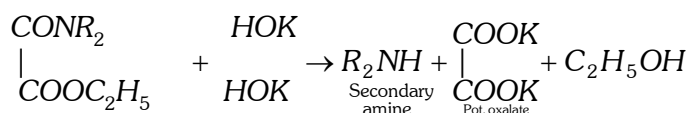


Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.



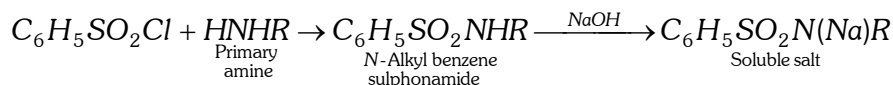
The liquid (mixture of oxamic ester+ tertiary amine) is subjected to fractional distillation when tertiary amine distils over.

The remaining liquid is distilled with KOH to recover secondary amine.

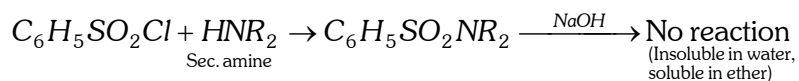


Nitrogen containing compounds Part 1

(iii) **Hinsberg's method** : It involves the treatment of the mixture with benzene sulphonyl chloride, i.e., **Hinsberg's reagent** ($C_6H_5SO_2Cl$). The solution is then made alkaline with aqueous alkali to form *sodium or potassium salt of monoalkyl benzene sulphonamide* (soluble in water).



The secondary amine forms *N,N*-dialkyl benzene sulphonamide which does not form any salt with $NaOH$ and remains as insoluble in alkali solution.

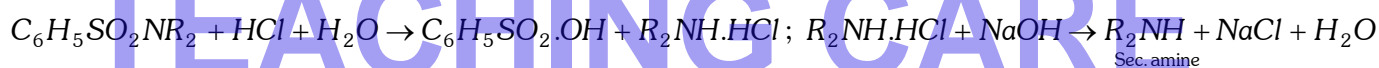


Tertiary amine does not react.

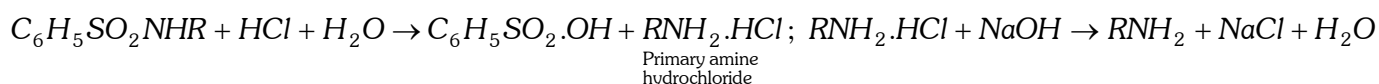
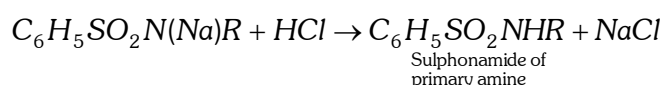
The above alkaline mixture of the amines is extracted with ether.

Two distinct layers are formed. Lower layer, the aqueous layer consists of sodium salt of *N*-alkyl benzene sulphonamide (primary amine) and upper layer, the ether layer consists of *N,N*-dialkyl benzene sulphonamide (secondary amine) and tertiary amine.

Two layers are separated. The upper layer is fractionally distilled. One fraction obtained is tertiary amine and the other fraction is treated with concentrated HCl to recover secondary amine hydrochloride which gives free secondary amine on distillation with $NaOH$.



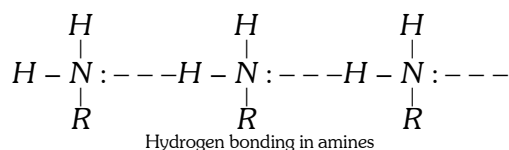
The aqueous layer is acidified and hydrolysed with dilute HCl . The hydrochloride formed is then distilled with $NaOH$ when primary amine distils over.



(6) Physical properties

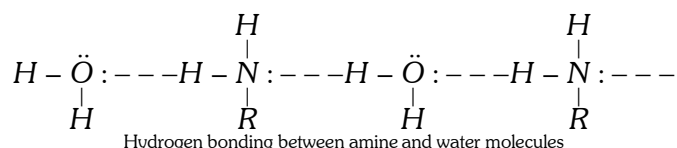
(i) Lower amines are gases or low boiling point liquids and possess a **characteristic ammonia like smell (fishy odour)**. Higher members are solids.

(ii) *The boiling points rise gradually with increase of molecular mass.* Amines are polar compounds like NH_3 and have comparatively higher boiling points than non-polar compounds of similar molecular masses. This due to the presence of **intermolecular hydrogen bonding**.



(iii) Amines are soluble in water. This is due to hydrogen bonding between amine and water molecules. Amines are also soluble in benzene and ether.

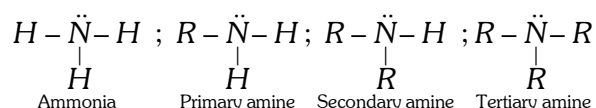
Nitrogen containing compounds Part 1



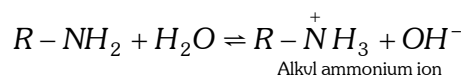
Solubility decreases with increase of molecular mass.

(7) Chemical properties : The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are **electrophilic reagents** as the lone pair of electrons can be donated to electron seeking reagents, (i.e., electrophiles).

(i) Basic nature of aliphatic amines : Amines like ammonia are basic in nature. The *basic nature is due to the presence of an unshared pair (lone pair) of electrons on nitrogen atom*. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acids.



Amines are weak bases as they combine partially with the water to form hydroxyl ions.

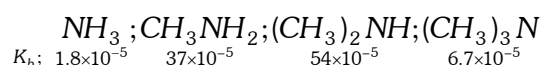


Applying law of mass action.

$$K_b = \frac{[\text{R} - \overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R} - \text{NH}_2]} \quad (\text{where } K_b \text{ is dissociation constant of the base})$$

[Concentration of water is considered constant as it is present in large amounts.]

The value of K_b describes the relative strength of the bases. *Strong bases have higher value of K_b while weak bases have low values.*



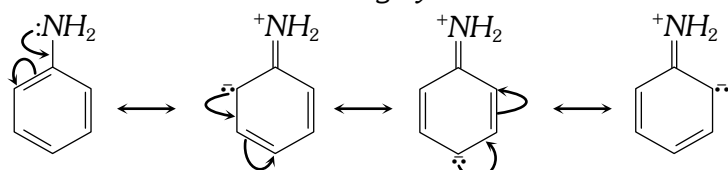
Except the amines containing tertiary butyl group, all *lower aliphatic amines are stronger bases than ammonia because of + I (inductive) effect*. The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic (larger K_b). Thus, it is expected that the basic nature of amines should be in the order tertiary > secondary > primary, but the *observed order in the case of lower members is found to be as secondary > primary > tertiary*. This anomalous behaviour of tertiary amines is **due to steric factors**, i.e., crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a proton relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked, resulting the reduced in its basicity.

The order of basic nature of various amines has been found **to vary with nature of alkyl groups**.

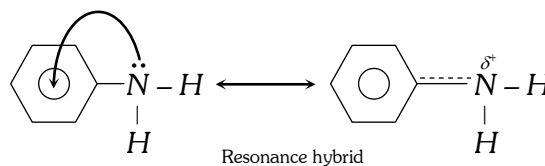
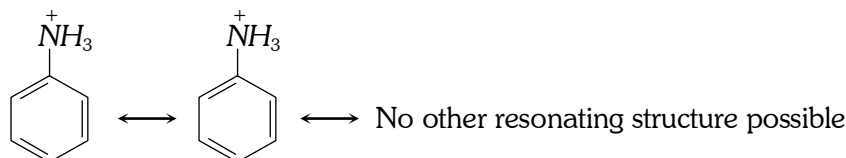
Alkyl group	Relative strength
$\text{CH}_3 -$	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$
$\text{C}_2\text{H}_5 -$	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3 > \text{R}_3\text{N}$
$(\text{CH}_3)_2\text{CH} -$	$\text{RNH}_2 > \text{NH}_3 > \text{R}_2\text{NH} > \text{R}_3\text{N}$
$(\text{CH}_3)_3\text{C} -$	$\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$

Nitrogen containing compounds Part 1

(ii) **Basic nature of aromatic amines** : In aniline or other aromatic amines, the **non-bonding electron pair** is delocalized into benzene ring by resonance.



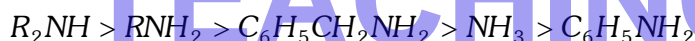
But anilinium ion is less resonance stabilized than aniline.



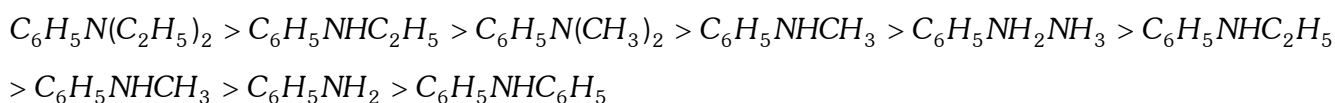
Thus, electron density is less on N atom due to which *aniline or other aromatic amines are less basic than aliphatic amines.*

However, any group which when present on benzene ring has electron withdrawing effect ($-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-Cl$, C_6H_5 , etc.) decreases basicity of aniline (Nitroaniline is less basic than aniline as nitro group is electron withdrawing group ($-I$ group) and aniline is more basic than diphenyl amine), while a group which has electron repelling effect ($-NH_2$, $-OR$, $R-$, etc.) increases basicity of aniline. Tolidine is more basic than aniline as $-CH_3$ group is electron repelling group ($+I$ group).

Further greater the value of K_b or lower the value of pK_b , stronger will be the base. The basic character of some amines have the following order,



N-alkylated anilines are stronger bases than aniline because of steric effect. Ethyl group being bigger than methyl has more steric effect, so *N*-ethyl aniline is stronger base than *N*-methyl aniline. Thus, basic character is,



In Toluidines $-p$ -isomer $> m$ - $> o$ -

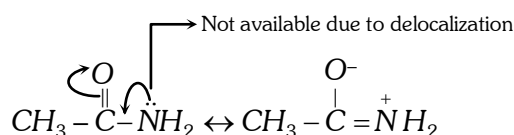
Chloroanilines $-p$ -isomer $> m$ - $> o$ -

Phenylene diamines $-p$ -isomer $> m$ - $> o$ -

Nitroanilines $-m$ -isomer $> p$ - $> o$ -

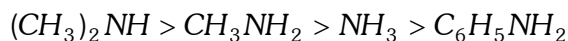
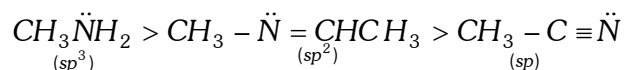
Note : * Aniline is less basic than ammonia. The phenyl group exerts $-I$ (inductive) effect, i.e., it withdraws electrons. This results to the lower availability of electrons on nitrogen for protonation.

* Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalised by resonance with the carbonyl group which makes it less available for protonation.

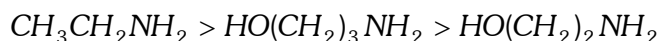
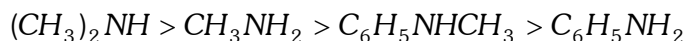


Nitrogen containing compounds Part 1

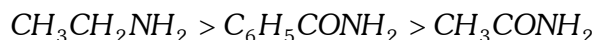
- The compounds with least 's' character (sp^3 -hybridized) is most basic and with more 's' character (sp -hybridized) is least basic. Examples in decreasing order of basicity are,



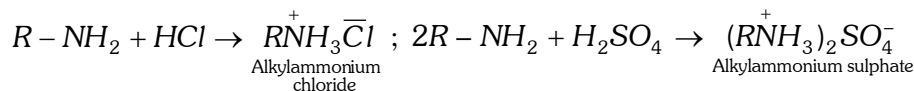
- Electron withdrawing ($C_6H_5 -$) groups decrease electron density on nitrogen atom and thereby decreasing basicity.



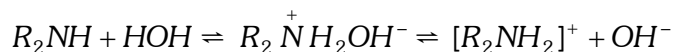
- Electron withdrawing inductive effect of the $-OH$ group decreases the electron density on nitrogen. This effect diminishes with distance from the amino group.



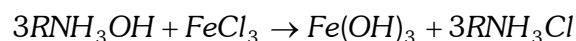
(iii) **Salt formation** : Amines being basic in nature, combine with mineral acids to form salts.



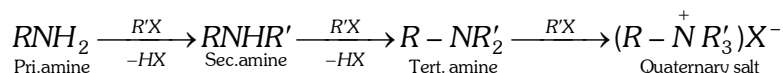
(iv) **Nature of aqueous solution** : Solutions of amines are alkaline in nature.



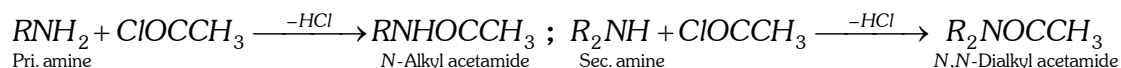
The aqueous solutions of amines behaves like NH_4OH and give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.



(v) **Reaction with alkyl halides (Alkylation)**



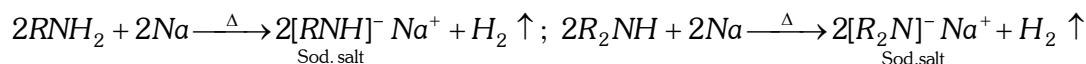
(vi) **Reaction with acetyl chloride (Acylation)**



Tertiary amines do not react since they do not have replaceable hydrogen on nitrogen.

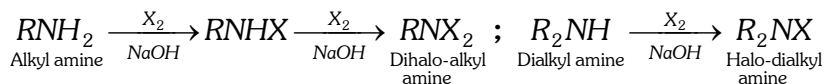
Therefore, all these above reactions are used to distinguish between P,S and T-amines.

(vii) **Action of sodium**

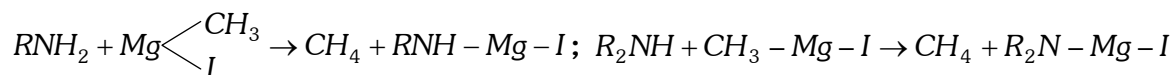


Nitrogen containing compounds Part 1

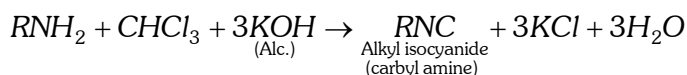
(viii) Action of halogens



(ix) Reaction with Grignard reagent



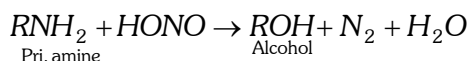
(x) **Carbylamine reaction** : This reaction is shown by only **primary amines**. This is a test of primary amines and is used to distinguish primary amines from secondary and tertiary amines.



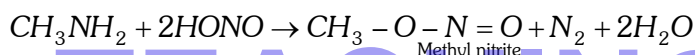
Isocyanides are bad smelling compounds and can be easily detected.

(xi) Reaction with nitrous acid

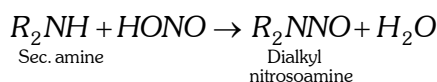
(a) Primary amines form alcohols with nitrous acid ($NaNO_2 + HCl$). Nitrogen is eliminated.



Methyl amine is an exception to this reaction, i.e.,

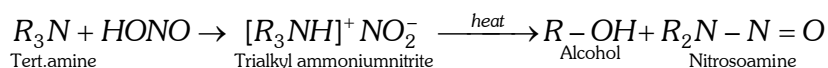


(b) Secondary amines form nitrosoamines which are water insoluble yellow oily liquids.



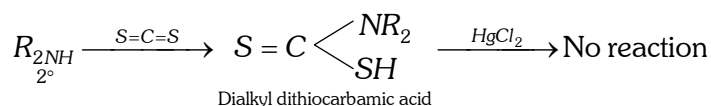
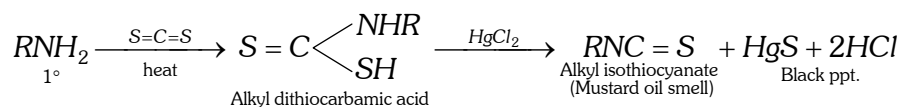
Nitrosoamine on warming with phenol and conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to **Liebermann's nitroso reaction** and is used for the test of secondary amines.

(c) Tertiary amines react nitrous acid to form nitrite salts which are soluble in water. These salts on heating give alcohols and nitrosoamines.



This reaction (nitrous acid test) is used to make distinction between primary, secondary and tertiary amines.

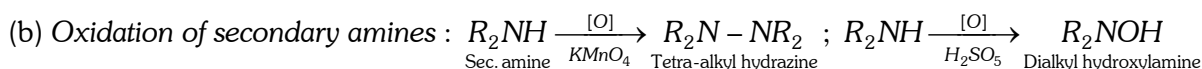
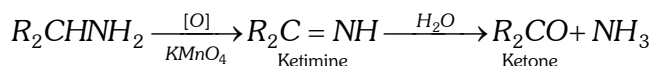
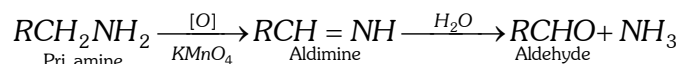
(xii) **Reaction with carbon di sulphide** : This **Hofmann's mustard oil reaction** and is used as a **test for primary amines**.



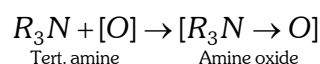
Nitrogen containing compounds Part 1

(xiii) **Oxidation** : All the three types of amines undergo oxidation. The product depends upon the nature of oxidising agent, class of amine and the nature of the alkyl group.

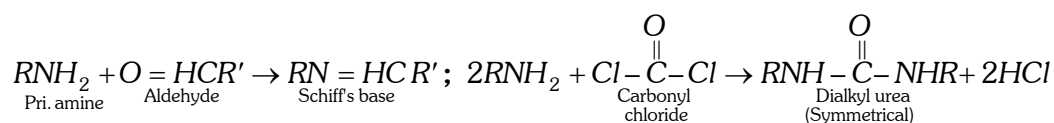
(a) Oxidation of primary amines



(c) Oxidation of tertiary amines : Tertiary amines are not oxidised by potassium permanganate but are oxidised by Caro's acid or Fenton's reagent to amine oxides.

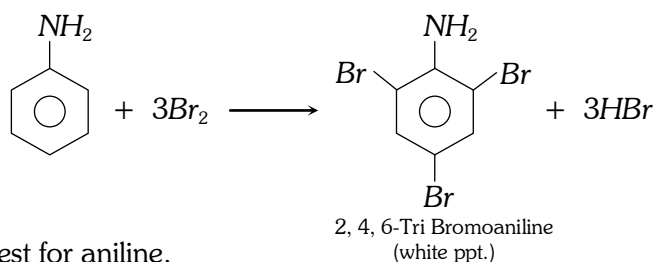


(xiv) **Reaction with other electrophilic reagents**



(xv) **Ring substitution in aromatic amines** : Aniline is more reactive than benzene. The presence of amino group activates the aromatic ring and directs the incoming group preferably to ortho and para positions.

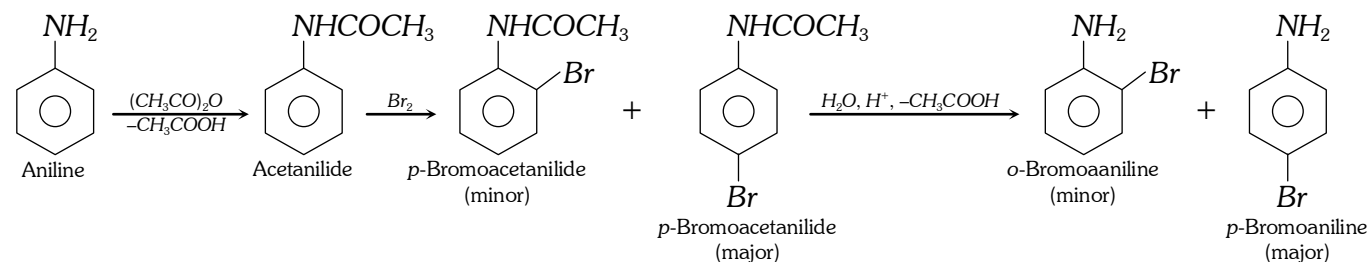
(a) Halogenation



This reaction is used as a test for aniline.

However, if monosubstituted derivative is desired, aniline is first acetylated with acetic anhydride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis and only monosubstituted halogen derivative is obtained.

It may be noted that $-NH_2$ group directs the attacking group at *o*- and *p*-positions and therefore, both *o*- and *p*-derivatives are obtained.



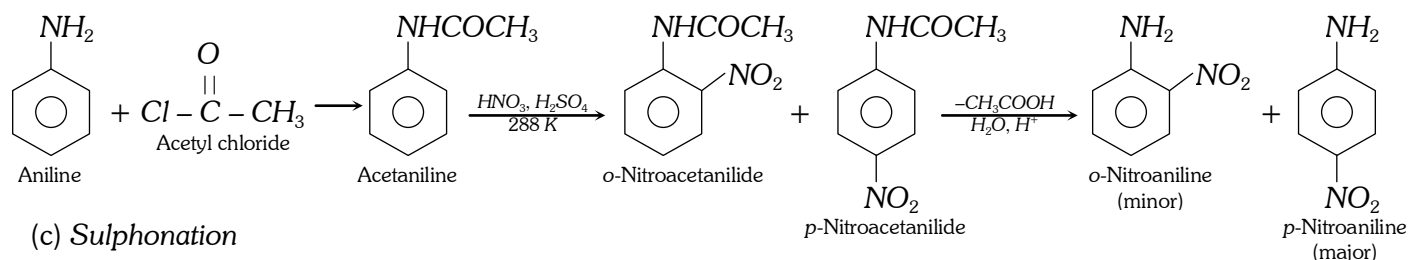
Nitrogen containing compounds Part 1

Acetylation deactivates the ring and controls the reaction to monosubstitution stage only because *acetyl group* is *electron withdrawing group* and therefore, the electron pair of N-atom is withdrawn towards the carbonyl group.

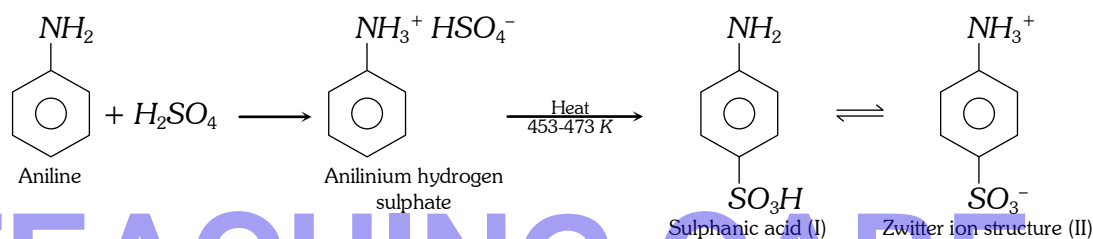
(b) *Nitration* : Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because, HNO_3 is a strong oxidising agent and results in partial oxidation of the ring to form a black mass.

Therefore, to solve this problem, nitration is carried out by *protecting the $-NH_2$ group by acetylation*. The acetylation deactivates the ring and therefore, controls the reaction.

The hydrolysis of nitroacetanilides removes the protecting acyl group and gives back amines.



(c) Sulphonation



The sulphanilic acid exists as a dipolar ion (structure II) which has acidic and basic groups in the same molecule. Such ions are called **Zwitter ions or inner salts**.

(8) Uses :

(i) Ethylamine is used in solvent extraction processes in **petroleum refining** and as a **stabiliser** for **rubber latex**.

(ii) The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.

(iii) Aliphatic amines of low molecular mass are used as solvents.

Distinction between primary, secondary and tertiary amines

Test	Primary amine	Secondary amine	Tertiary amine
Action of $CHCl_3$ and alcoholic KOH. (Carbylamine test)	Bad smelling carbylamine (Isocyanide) is formed.	No action.	No action.
Action of CS_2 and $HgCl_2$. (Mustard oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action
Action of nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test).	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.

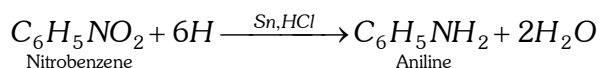
Nitrogen containing compounds Part 1

Action of acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No action.
Action of Hinsberg's reagent.	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
Action of methyl iodide.	3 molecules (moles) of CH₃I to form quaternary salt with one mole of primary amine.	2 moles of CH₃I to form quaternary salt with one mole of secondary amine.	One mole of CH₃I to form quaternary salt with one mole of tertiary amine.

Note : * Aniline does not form alcohol with nitrous acid but it forms benzene diazonium chloride which shows dye test.

Aniline

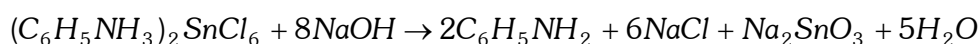
Aniline was first prepared by **Unverdorben (1826) by dry distillation of indigo**. In the laboratory, it can be prepared by the reduction of nitrobenzene with tin and hydrochloric acid.



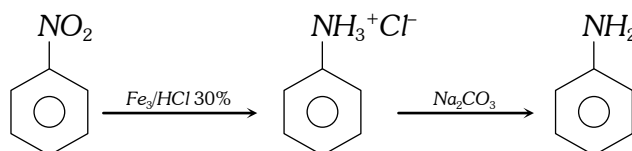
Aniline produced combines with H_2SnCl_6 ($SnCl_4 + 2HCl$) to form a double salt.



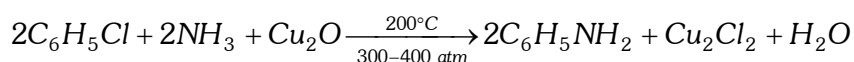
From double salt, aniline is obtained by treating with conc. caustic soda solution.



On a commercial scale, aniline is obtained by reducing nitrobenzene with iron filings and hydrochloric acid.



Aniline is also obtained on a large scale by the action of amine on chlorobenzene at 200°C under 300-400 atm pressure in presence of cuprous catalyst.



Properties Aniline when freshly prepared is a **colourless oily liquid (b.p. 184°C)**. It has a characteristic unpleasant odour and is not poisonous in nature. It is heavier than water and is only slightly soluble. It is soluble in alcohol, ether and benzene. Its colour changes to dark brown on standing.

It shows all the characteristic reactions discussed earlier.

Uses : (1) It is used in the preparation of diazonium compounds which are used in dye industry.

(2) Anils (Schiff's bases from aniline) are used as antioxidants in rubber industry.

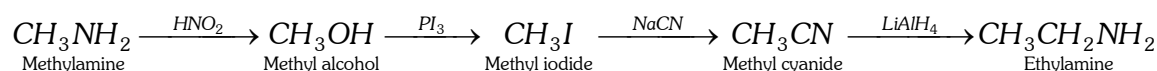
Nitrogen containing compounds Part 1

(3) It is used for the manufacture of its some derivatives such as acetamide, sulphanilic acid and sulpha drugs, etc.

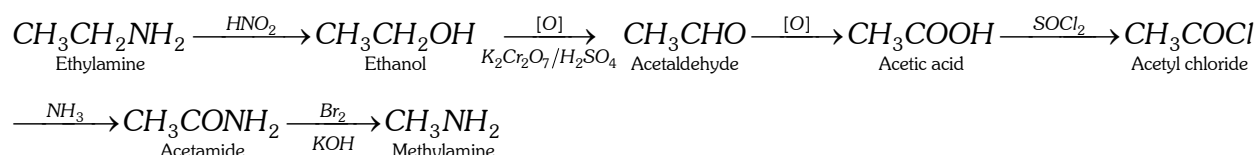
(4) It is used as an accelerator in vulcanizing rubber.

Some important conversions

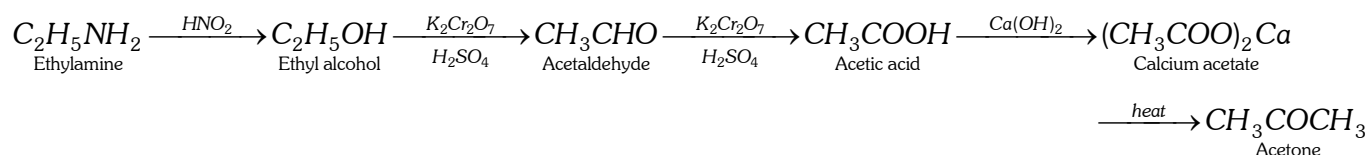
(1) Conversion of methylamine to ethylamine (Ascent)



(2) Conversion of ethylamine to methylamine. (Descent)

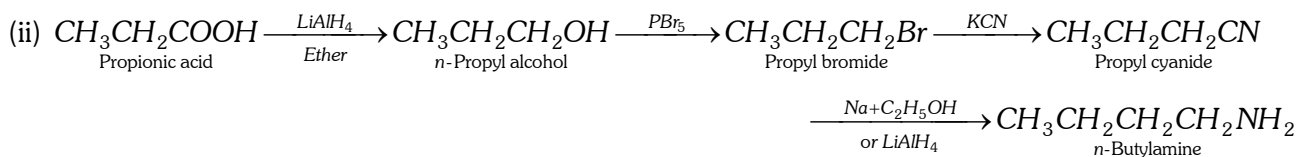
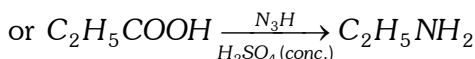
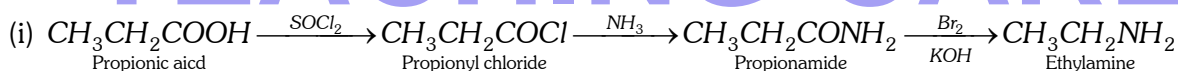


(3) Conversion of ethylamine to acetone



(4) Conversion of propionic acid to :

(i) Ethylamine, (ii) *n*-Butylamine.



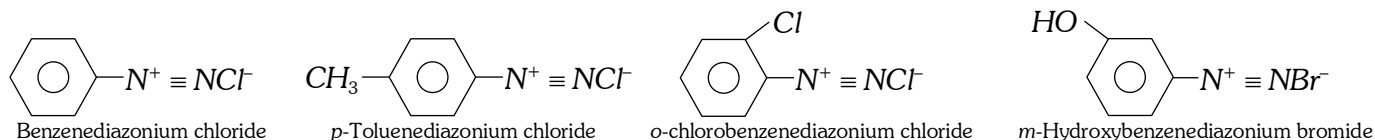
(5) Conversion of ethylene to 1,4-diaminobutane :



Diazonium salts

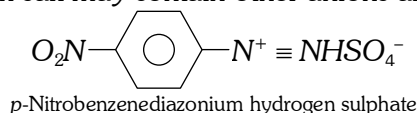
The diazonium salts have the general formula ArN_2^+X^- , where X^- may be an anion like Cl^- , Br^- etc. and the group N_2^+ ($-\text{N} \equiv \text{N}^+$) is called diazonium ion group.

(1) **Nomenclature** : The diazonium salts are named by adding the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,

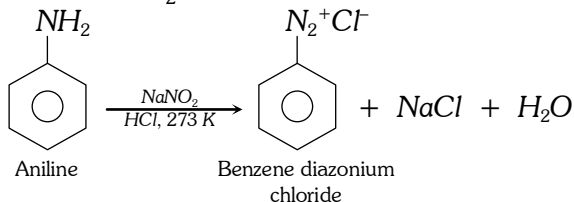


Nitrogen containing compounds Part 1

The diazonium salt may contain other anions also such as NO_3^- , HSO_4^- , BF_4^- etc.



(2) **Preparation of diazonium salts** : $\text{NaNO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HONO}$



The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation**.

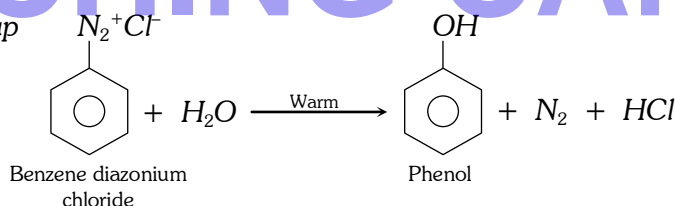
(3) **Physical properties of diazonium salts**

- (i) Diazonium salts are generally colourless, crystalline solids.
- (ii) These are readily soluble in water but less soluble in alcohol.
- (iii) They are unstable and explode in dry state. Therefore, they are generally used in solution state.
- (iv) Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.

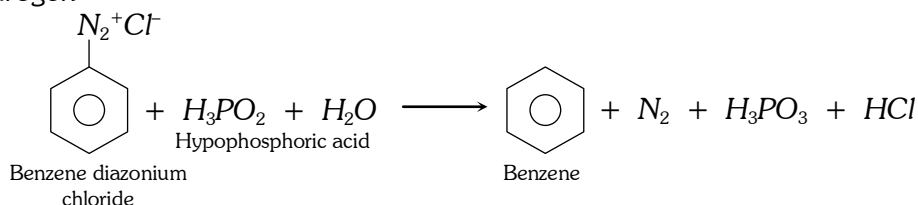
(4) **Chemical properties of diazonium salts**

(i) **Substitution reaction** : In substitution or replacement reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place.

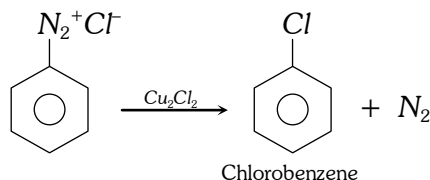
(a) Replacement by $-\text{OH}$ group



(b) Replacement by hydrogen

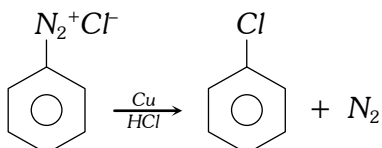


(c) Replacement by $-\text{Cl}$ group



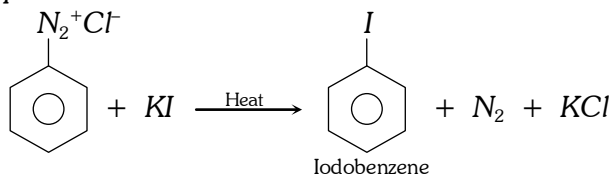
This reaction is called **Sandmeyer reaction**.

When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as **Gattermann reaction**.

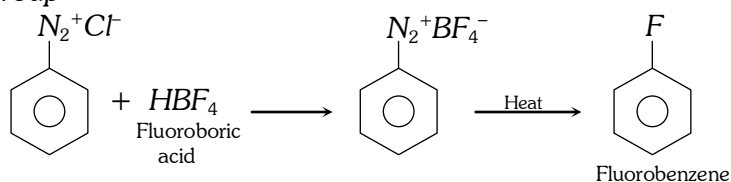


Nitrogen containing compounds Part 1

(d) Replacement by iodo (-I) group

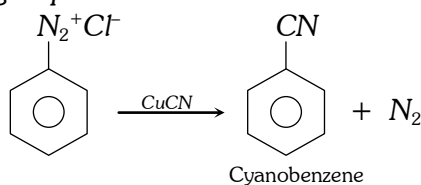


(e) Replacement by -F group

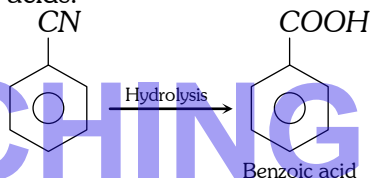


This reaction is called **Schiemann reaction**.

(f) Replacement by Cyano (-CN) group

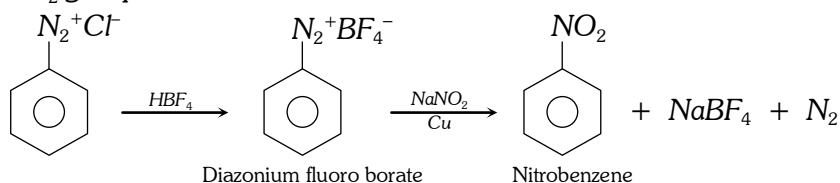


The nitrites can be hydrolysed to acids.

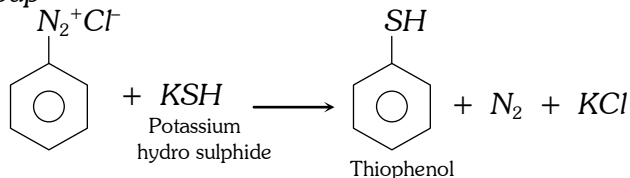


This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

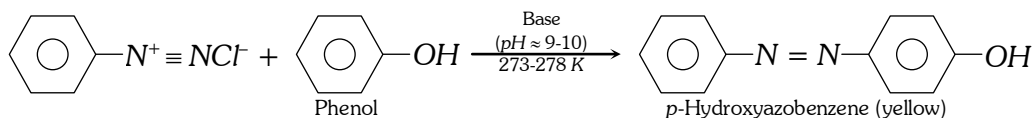
(g) Replacement by -NO₂ group



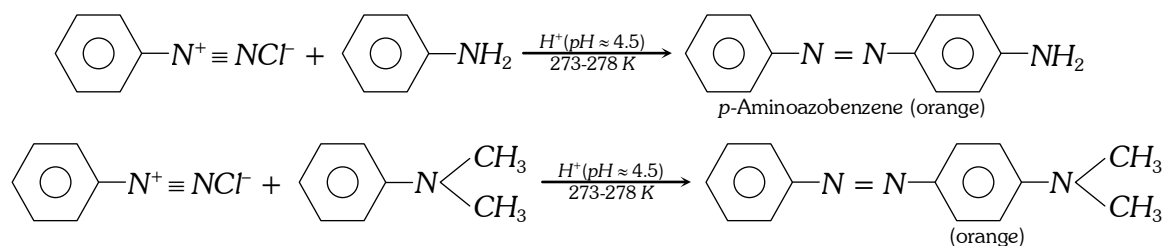
(h) Replacement by thio (-SH) group



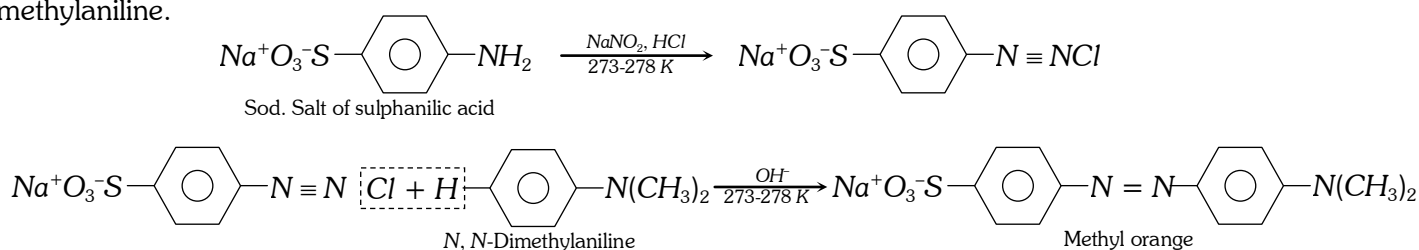
(ii) **Coupling reactions** : The diazonium ion acts as an electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds (Ar-H) activated by electron donating groups (-OH and -NH₂), which as strong nucleophiles react with aromatic diazonium salts. Therefore, benzene diazonium chloride couples with electron rich aromatic compounds like phenols and anilines to give azo compounds. The azo compounds contain -N=N- bond and the reaction is called **coupling reaction**.



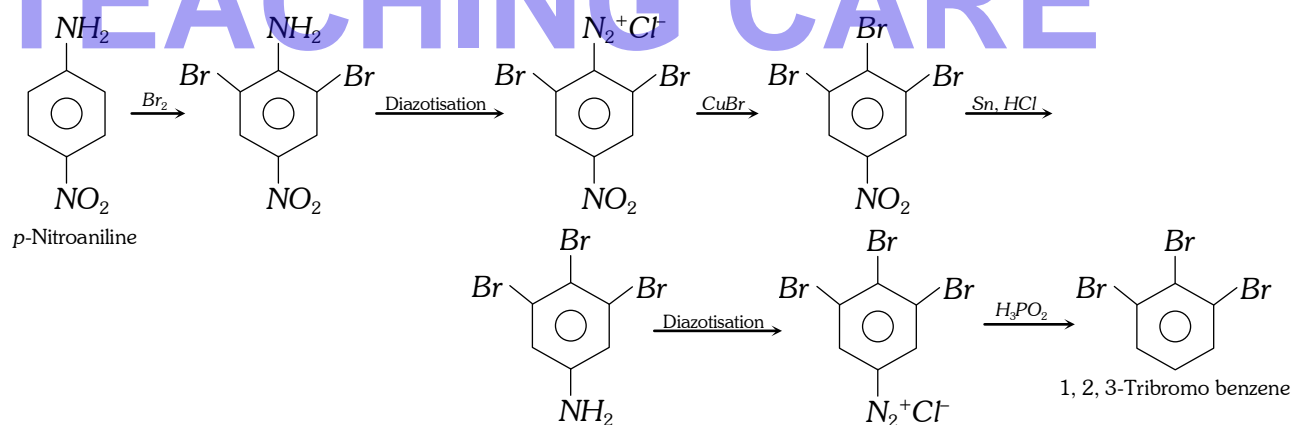
Nitrogen containing compounds Part 1



Coupling occurs para to hydroxy or amino group. All azo compounds are strongly coloured and are used as dyes. Methyl orange is an important dye obtained by coupling the diazonium salt of sulphanilic acid with *N,N*-dimethylaniline.



Note : * Diazonium salts are highly **useful intermediates** in the synthesis of large variety of aromatic compounds. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. For example, 1, 2, 3-tribromo benzene is not formed in the pure state by direct bromination of benzene. However, it can be prepared by the following sequence of reaction starting from *p*-nitroaniline through the formation of diazonium salts as :



(5) Uses of diazonium salts

- (i) For the manufacture of azo dyes.
- (ii) For the industrial preparation of important organic compounds like *m*-bromotoluene, *m*-bromophenol, etc.
- (iii) For the preparation of a variety of useful halogen substituted arenes.