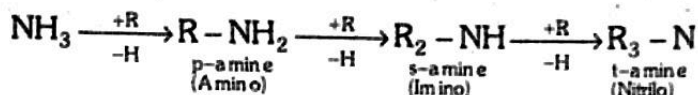


Subjective Matter : For Self Study

● Introduction

Derivatives of ammonia obtained by replacing one or more hydrogen atoms by same number of alkyl or aryl groups are called amines.

Mono, di and tri alkyl derivatives of ammonia are respectively primary, secondary and tertiary amines.



● Classification :

➤ On the basis of number of alkyl groups attached to nitrogen atom, amines are classified into :

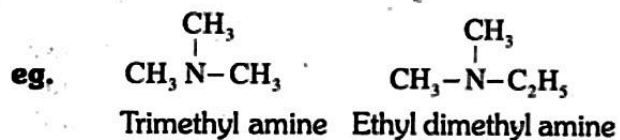
a) **Primary amines** : These are monoalkyl derivatives of ammonia. These contain -NH₂ Amino group

e.g. C₂H₅-NH₂ -Ethyl amine

b) **Secondary amines** : These are dialkyl derivatives of ammonia. These contain -NH- Amino group

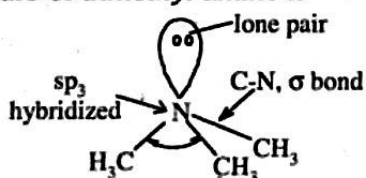
e.g. CH₃-NH-CH₃ CH₃-NH-C₂H₅
 Dimethyl amine Ethyl methyl amine

c) **Tertiary amines** : These are trialkyl derivatives of ammonia. These contain -N= Amino group .



● Structure of amines:

- N atoms in amine is sp³-hybridized.
- Three sp³-orbitals contain one electron each, form sigma bonds either with H-atoms or the alkyl or aryl groups while the fourth one contains a lone pair of electrons is not involved in bond formation.
- The structure of trimethyl amine is



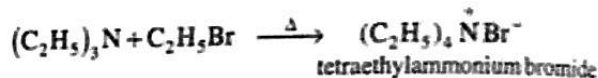
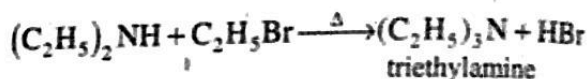
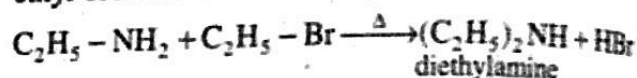
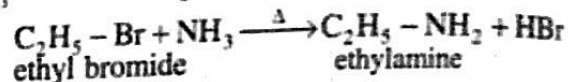
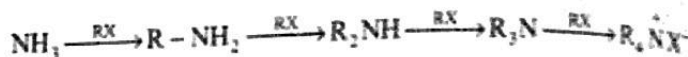
➤ As lone-pair-bond pair repulsions are much greater than bond pair-bond pair repulsion, therefore the bond angle between any two adjacent H-atoms or alkyl groups decreases from the tetrahedral angle of 109°28' to 107° in 1° and 2° amines.

● ISOMERISM IN AMINES :

➤ They show chain, position, functional, isomerism.

● Preparation of amines :

(1) **By Ammonolysis of alkyl halides [Hofmann's ammonolysis] :**

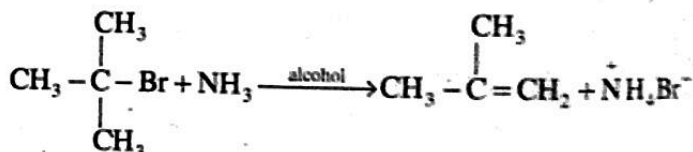


● Limitations :

(a) This method is not useful for preparation of primary amines because a mixture of primary, secondary and tertiary amines along with quaternary ammonium salt is obtained which is difficult to separate.

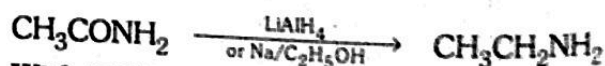
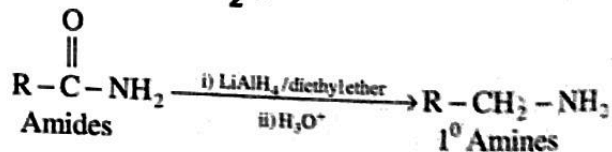
➤ But we can prepare primary amine as a major product if we heated alkyl halide with excess of alcoholic ammonia.

(b) tert-Butylamine is not prepared by this reaction because tert alkyl halides gives alkene with alcoholic ammonia.

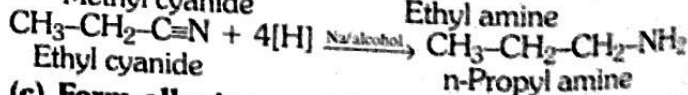
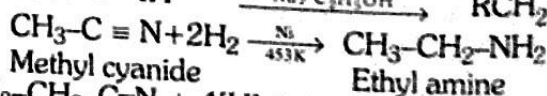
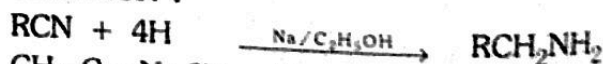


(2) **By reduction of amides, oximes, cyanides, alkylisocyanides and nitroalkanes :**

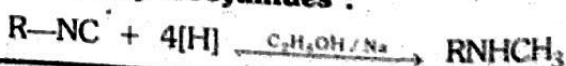
(a) **From RCONH₂ :**

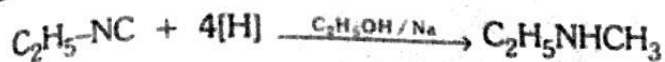


(b) **With RCN :**

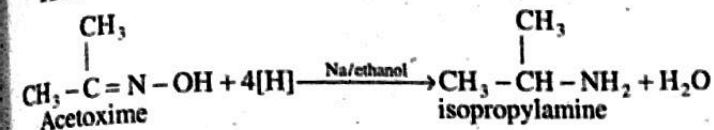
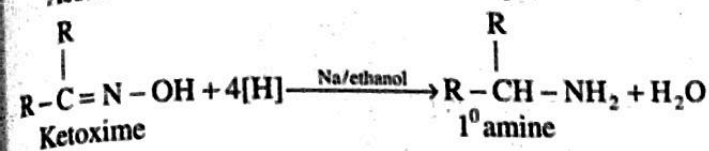
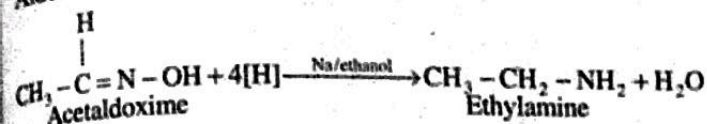
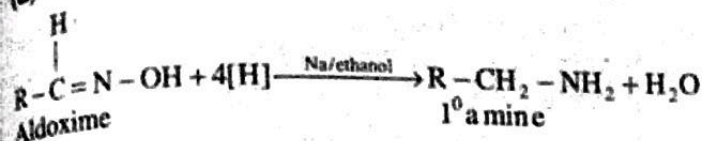
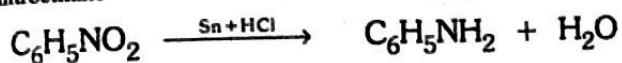
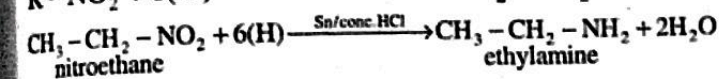
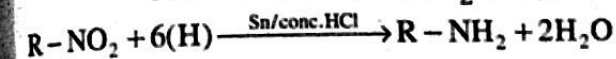
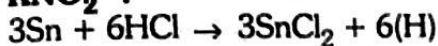


(c) **Form alky isocyanides :**



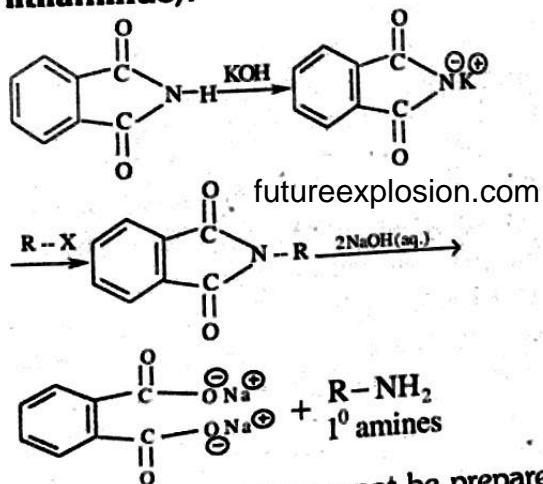


(d) Form Oximes :

(e) Form RNO_2 :

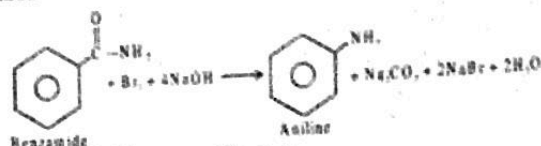
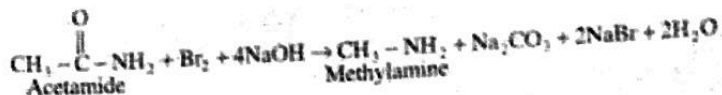
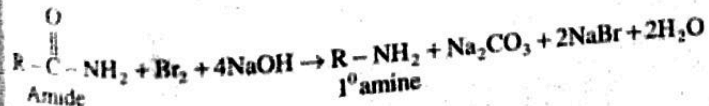
> In lab method we use Sn/HCl while in industrial method we use Fe / HCl.

(3) Gabriel Phthalimide Synthesis (Alkylation of Phthalimide):



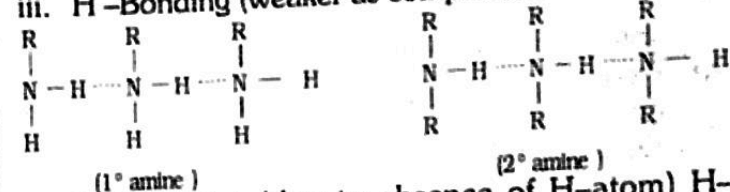
> Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

(4) By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction) :



● Physical Properties :

- i. The lower aliphatic amines are colourless gases having characteristic fishy odour. Aryl amines are colourless liquids and toxic in nature.
- ii. The 1° amine having three or more carbon atoms are liquids and the higher ones are solids.
- iii. H-Bonding (weaker as compared to H-O-H).



> In 3° amine (due to absence of H-atom) H-bonding is not possible.

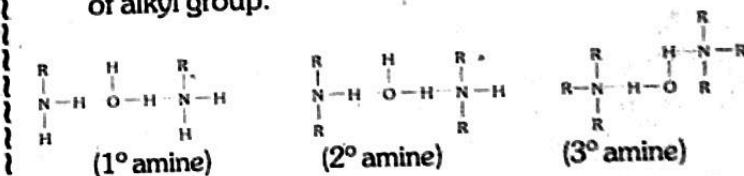
(iv) **Boiling point** : Due to polar nature of amines, they can form hydrogen bonding and hence they have higher boiling point than corresponding molecular weight of alkanes.

> Boiling point \propto molecular weight

> **Order of B.P.** : 1° amine > 2° amine > 3° amine

> **Order of volatile nature** : 3° amine > 2° amine > 1° amine

(v) **Solubility** : Low molecular weight amines (< six carbon) are very soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



Order of solubility : p-amine > s-amine > t-amine

● **Chemical Properties** : Amines are reactive organic compounds due to presence of lone pair of electron with nitrogen

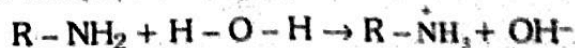
1. Basis nature of amines:

(a) Lewis theory:

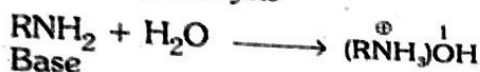
> They are basis in nature due to the presence of lone pair on nitrogen atom.

> Amines acts as a base, according to Lewis concept, the species which can donate the lone pair are called as Lewis base.

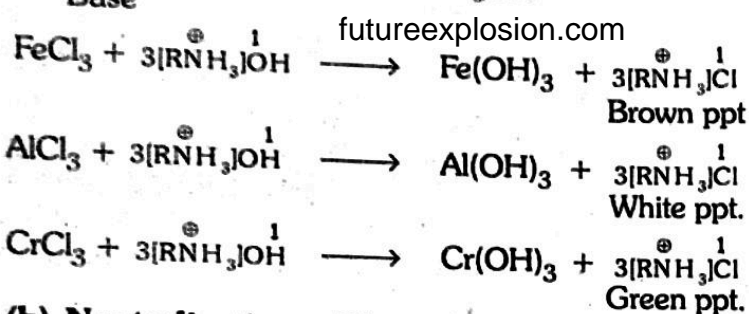
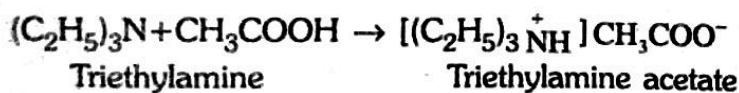
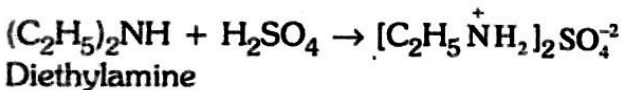
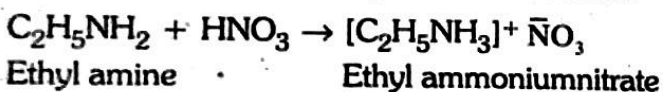
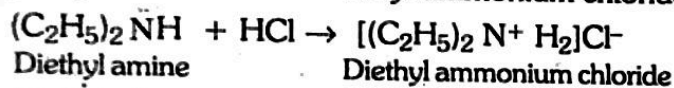
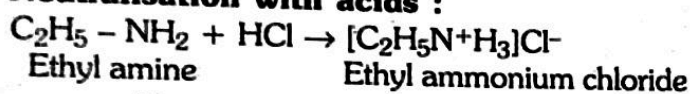
> **Amines are weak bases** : In aqueous solution of amines, following equilibrium exists.



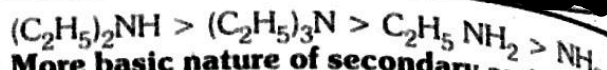
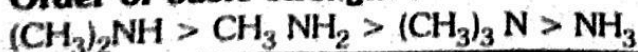
- > But hydroxyl ions have greater attraction for protons than amine. Therefore the aqueous solution of amine mainly contains undissociated amine molecules. Hence amines are weak bases.
- > Here, nitrogen atom donate the lone pair of electrons to H^+ ion to formed a co-ordinate bond.
- > Amine also acts as Bronsted-Lowry base as it accepts a proton from acid to form salt.
- > Aqueous solution of amines are basic and they turn red litmus paper blue.
- > Amines forms alkyl ammonium hydroxide with water ammonium hydroxides are used for precipitation of IInd and IIIrd group cations in qualitative analysis



Base

**(b) Neutralisation with acids :****● Relative basic strenght of amines:**

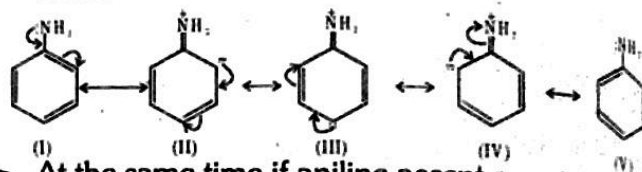
- > Due to +I effect of alkyl groups the electron density on nitrogen increases and the lone pair of electrons becomes readily available for protonation.
- > The alkyl ammonium ion gets stabilized due to the dispersal of positive charge by the +I effect of alkyl group. Thus aliphatic amines are stronger base than ammonia.
- > Basic strength of amines depends on electron donating tendency.

Order of basic strength :**(A) More basic nature of secondary amines than tertiary amine is due to**

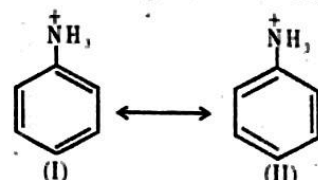
- (i) **Steric hindrance:** In case of tertiary amines due to more +I effect lone pair is easily available for donation, but due to more steric hindrance there path is blocked. At the same time tertiary amines show less solvation effect.

(B) Aromatic amines are less basic than aliphatic amines: The lone pair of electron present on N-atom in aromatic amines is involved in resonance hence it less available for donation and they bcomes less basic.

- > Resonance in aniline.

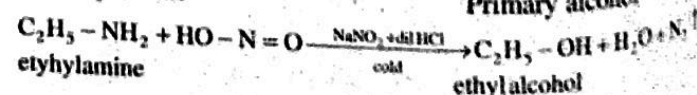
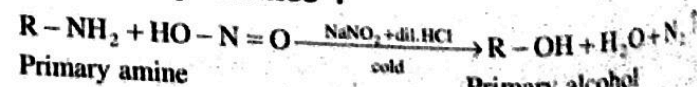


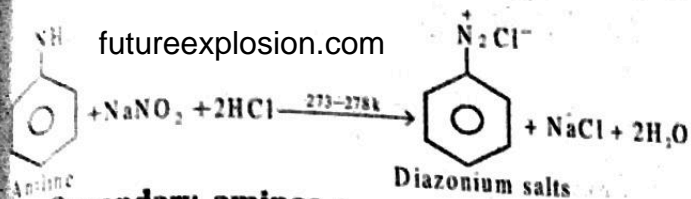
- > At the same time if aniline accept a proton it gives anilinium ion has only two resonance structure.



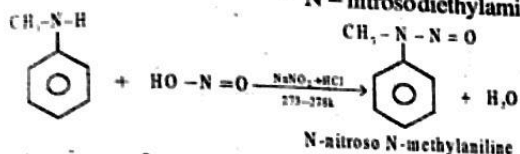
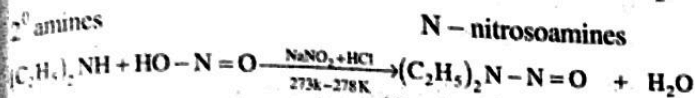
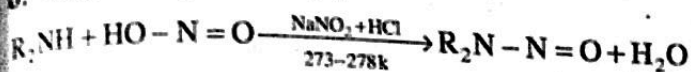
- > As, we know that more the resonating structure more is the stability. Thus aniline is more stable than anilinium ion.
- > Hence, aniline or any aryl amine accept proton less readily i.e. they are less basic in nature than ammonium.
- > In case of substituted aniline, electron releasing group like $-OCH_3$, $-CH_3$, $-NH_2$ increase the basic strength whereas electron withdrawing groups like $-NO_2$, $-C_6H_5$, $-SO_3$, $-COOH$, $-CN$, $-X$ decreases the basic strength.

- > **The basic order :** Pyridine > Aniline > Pyrrole > N-methylethanamine > propan-1-amine > aniline > Ammonia > benzene-1, 4-diamine > 4-aminobenzoic acid > phenylmethylaniline > N-Methylaniline > N-phenylaniline

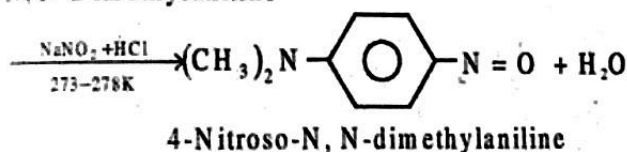
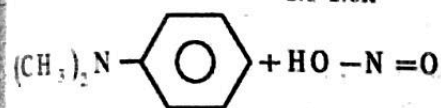
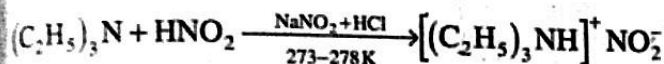
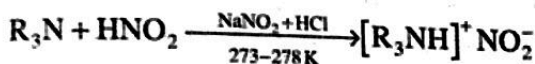
(2) Reaction with HNO_2 : Primary, secondary and tertiary amines react differently with nitrous acid and form different visible products hence it is used to distinguish between them.**a. Primary amines :**



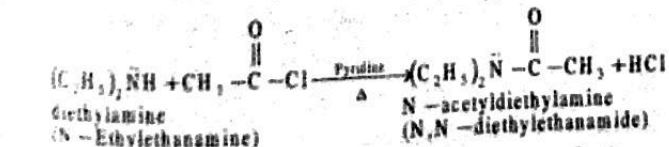
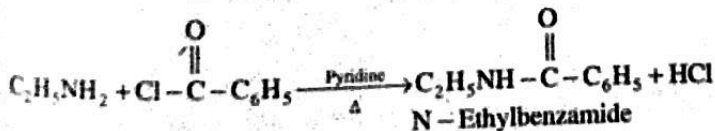
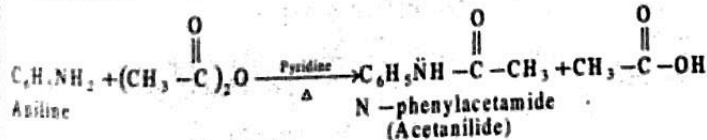
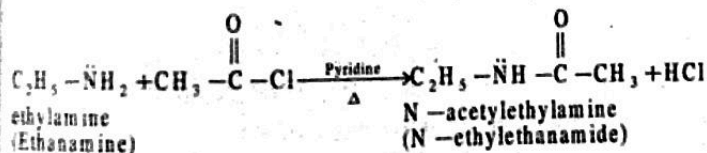
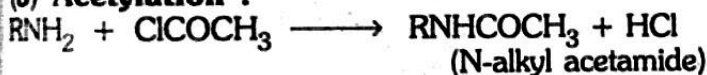
b. Secondary amines :



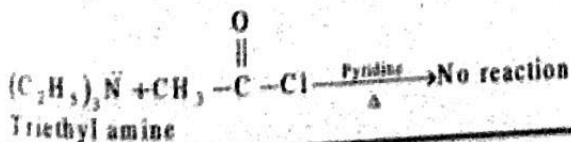
c. Tertiary amines :



(3) Acetylation :

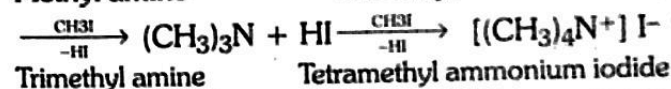
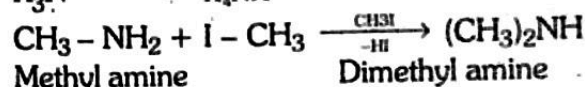
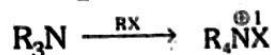
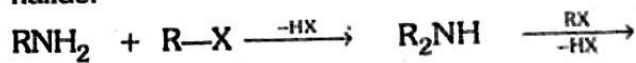


> Tertiary amine does not undergo acetylation.

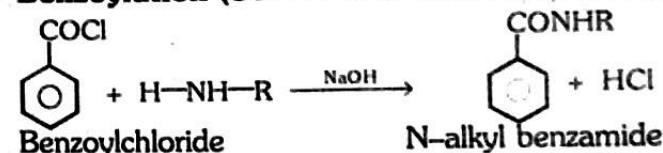


(4) Reaction with alkyl halides (Hoffmann's exhaustive alkylation): The replacement of hydrogen from nitrogen atom of amines by alkyl group to form quaternary ammonium salts is called **exhaustive alkylation of amines.**

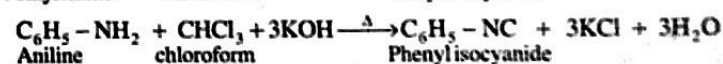
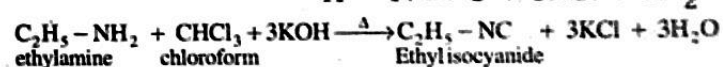
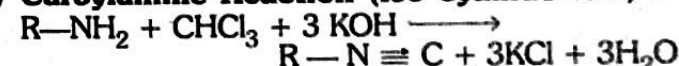
> When primary amine on heating with primary alkyl halide, it gives a mixture of secondary amine, tertiary amine along with tetraalkylammonium halide.



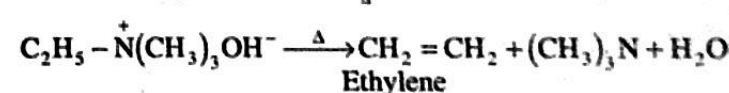
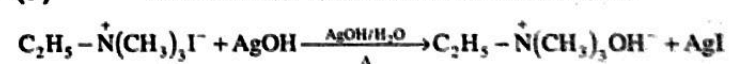
(5) Benzoylation (Schotten baumann reaction):



(6) Carbylamine Reaction (Iso cyanide test) :



(7) Hoffmann elimination reaction:

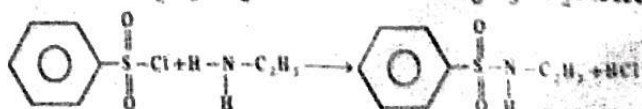
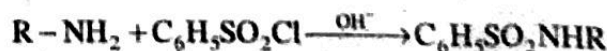


In this reaction the major product is least substituted alkene.

(8) Reaction With Aryl Sulphonyl Chloride :

Hinsberg's test : It is used to distinguish primary, secondary and tertiary amines by using benzene sulphonyl chloride i.e. $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (Hinsberg's reagent).

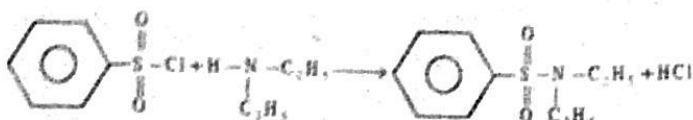
a. Primary amine :



Benzene sulphonyl chloride N-ethylbenzenesulphonyl amide

b. Secondary amines :





N, N-diethylbenzenesulphonyl amide

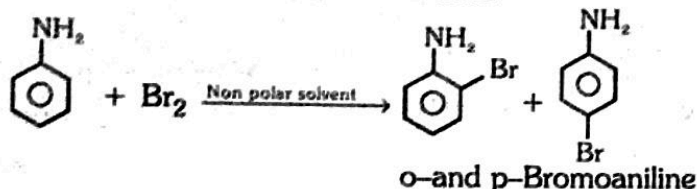
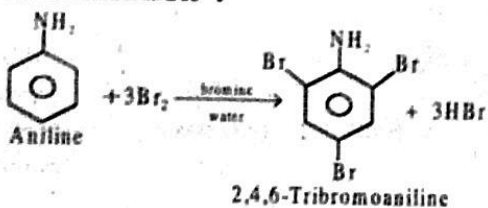
c. Tertiary amines :



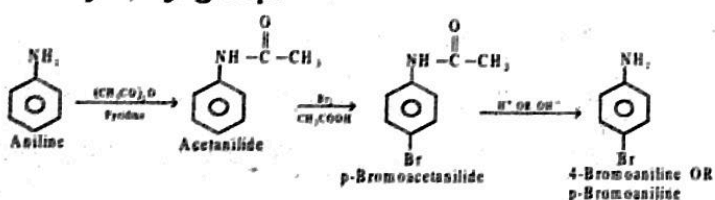
(9) Aromatic Electrophilic Substitution :-

NH₂ group in aniline is activating ortho-para directing group hence it undergoes electrophilic substitution reactions.

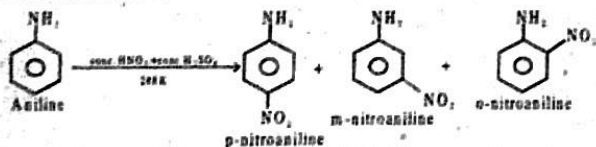
(a) Bromination :



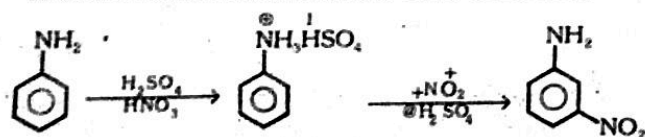
● **Formation of monobromo aniline:** To prepare monobromo derivatives -NH₂ group is deactivated by acetyl group.



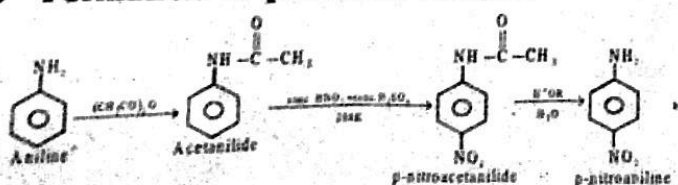
(b) Nitration :



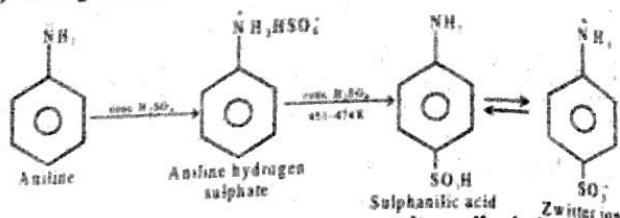
➤ In strong acidic medium -NH₂ group is converting to -NH₃⁺ group which acts as a meta directing and hence m-nitroaniline is also obtained.



● **Formation of paranitro aniline:**

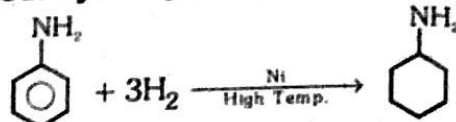


(c) Sulphonation:



➤ Sulphanilic acid exists as a salt, called dipolar ion or Zwitter ion. This is due to reaction between acidic.

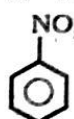
(17) Catalytic hydrogenation :

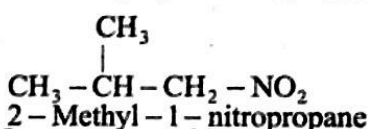
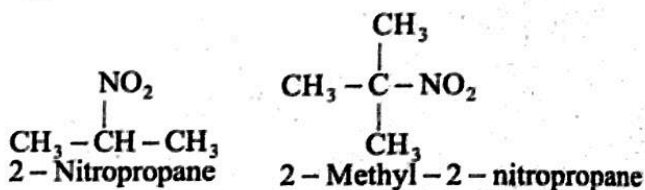


● **Uses of Aniline** Aniline is used in the manufacture of dyes, accelerators, antioxidants, acetanilide, indigo and sulph drugs.

Nitro Compounds:

R-NO₂ Aliphatic nitro compound

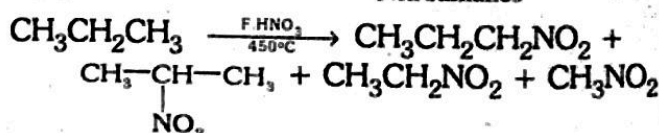
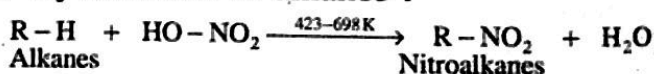
 Aromatic nitro compound



● **Isomerism :** Nitroalkanes shows chain, position, functional isomerism and Tautomerism.

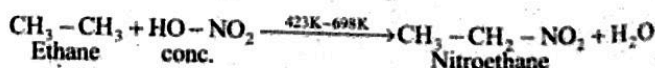
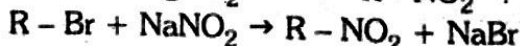
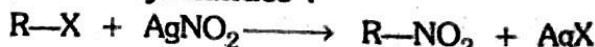
● **Preparation of nitroalkanes:**

1. By Nitration of alkanes :



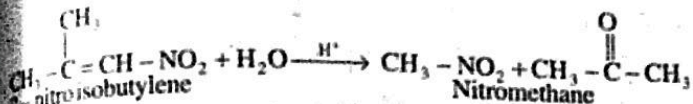
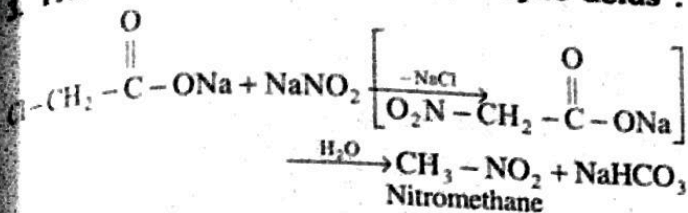
➤ The hydrocarbon is heated with conc. HNO₃ under pressure at 413 K. Nitration under these conditions is always slow and a large number of polynitro compounds are formed.

2. From alkyl halides :

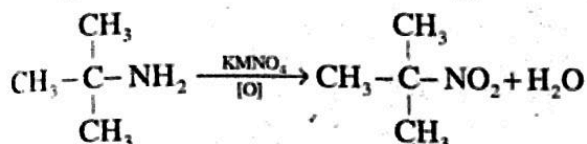
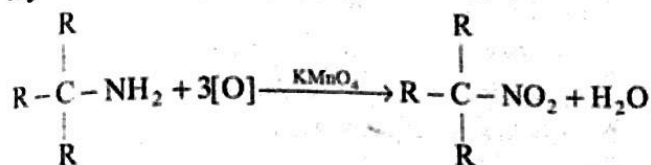




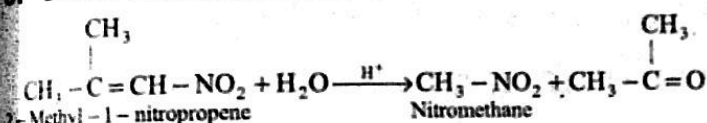
From salt of α-halogeno carboxylic acids :



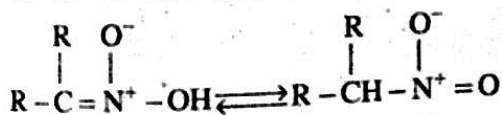
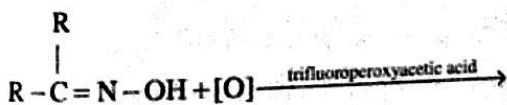
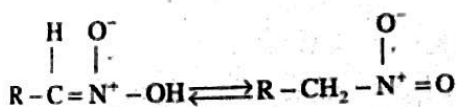
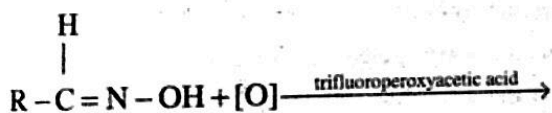
By oxidation of primary amines :



5. From α-nitroalkenes :



6. By oxidation of oximes :



Chemical properties :

1. Acidic Nature : Primary and secondary nitroalkanes undergo tautomerism and their aci-forms are weakly acidic in nature.

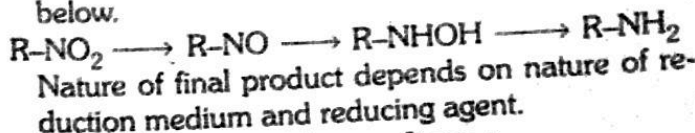


Nitroform

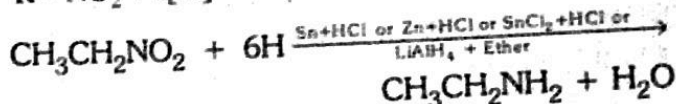
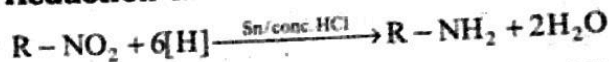
Aci-form

The primary and secondary nitroalkanes behave as acids in the presence of strong alkalis.

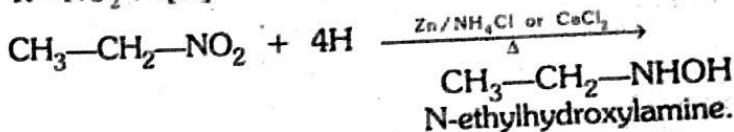
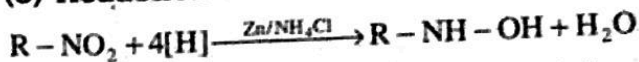
2 Reduction : Nitro alkanes can be reduced as below.



(a) Reduction in acidic medium :

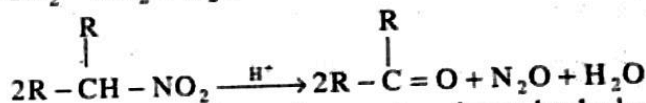
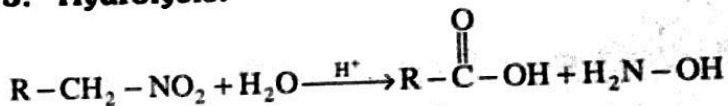


(b) Reduction in neutral medium :

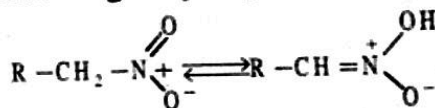


> With stannous chloride and hydrochloric acid are used as reducing agent, nitroalkanes are converted into N-alkylhydroxylamine and oxime.

3. Hydrolysis:



> Tertiary nitroalkanes does not undergo hydrolysis.
> Primary and secondary nitroalkanes i.e. those containing α-hydrogen atom, exhibit tautomerism.



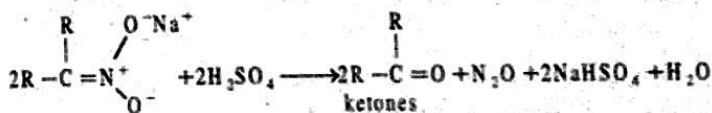
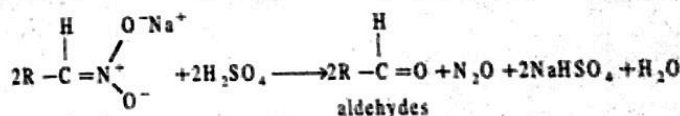
Nitro form

Isonitro form

(pseudo-acid form)

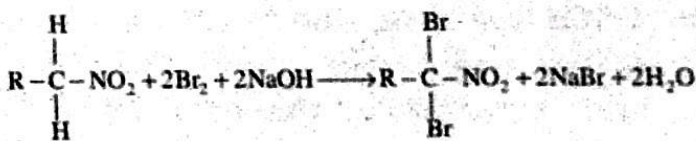
(acid-form or nitronic acid)

4. Nef carbonyl synthesis:



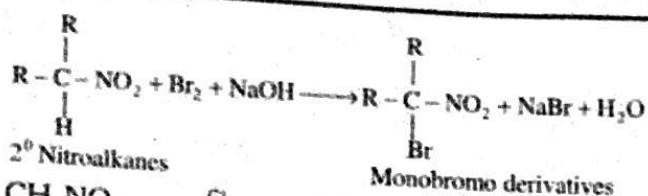
This reaction is known as **Nef carbonyl synthesis.**

5. Halogenation :

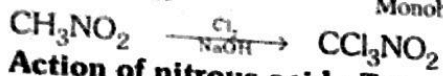


1^o Nitroalkanes

Dibromo derivatives

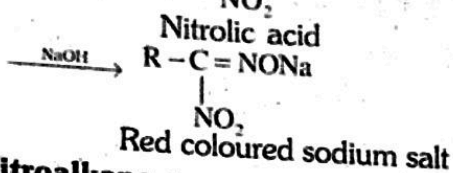
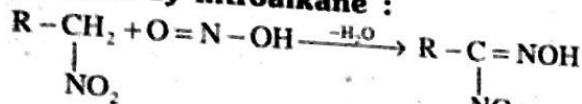


Monobromo derivatives

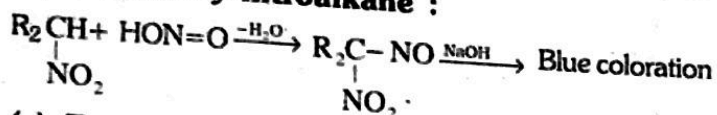


6. **Action of nitrous acid** : Test used to distinguish primary, secondary and tertiary nitroalkanes.

(a) **Primary nitroalkane** :

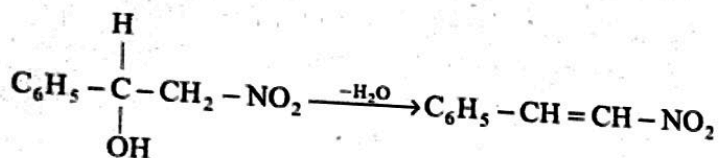
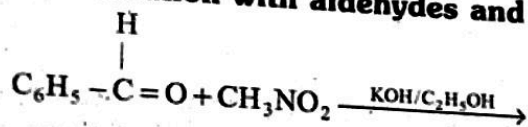


(b) **Secondary nitroalkane** :

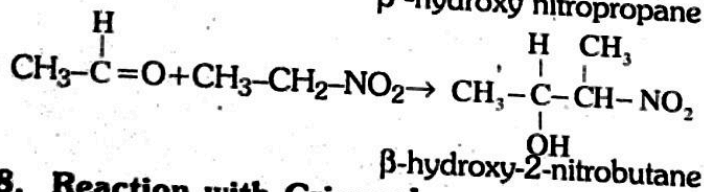
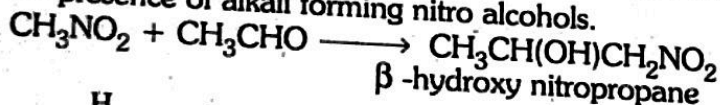


(c) **Tertiary nitroalkane** : These compounds do not react with nitrous acid.

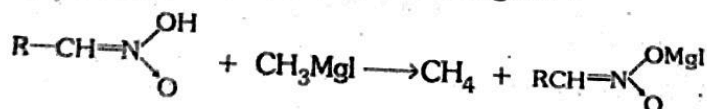
7. **Condensation with aldehydes and ketones**:



p and s nitroalkane condense with aldehyde in presence of alkali forming nitro alcohols.



8. **Reaction with Grignard reagent** :



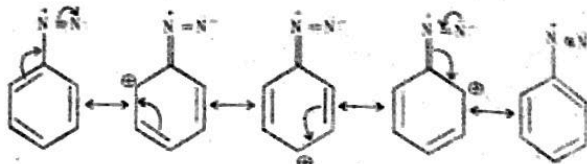
● **USES** : Used as solvents for oils, fats, resin dyes, rubbers, explosive and intermediates for the synthesis of many organic compounds.

futureexplosion.com

● **Diazonium salts**:



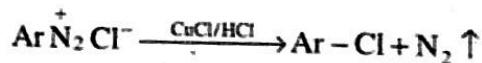
> Stability of arenediazonium ion can be explained on the basis of resonance.



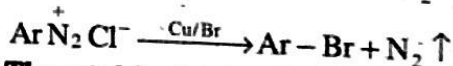
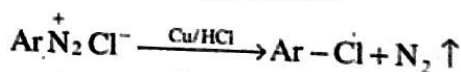
● **Chemical properties**:

A. **Reactions Involving Replacement of Diazonium Group**

1. **Replacement by -Cl, -Br and -CN**: Sandmeyer reaction:

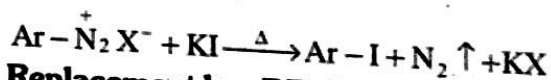


2. **Gattermann reaction**:

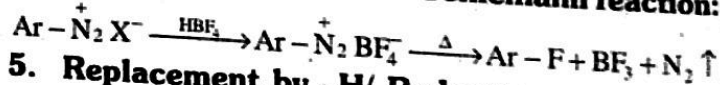


The yield obtained in Gattermann reaction is poor as compare to Sandmeyer's reaction.

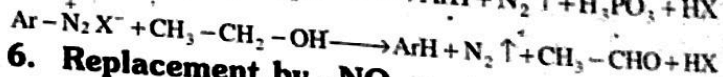
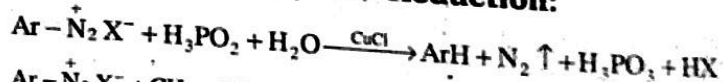
3. **Replacement by -I** :



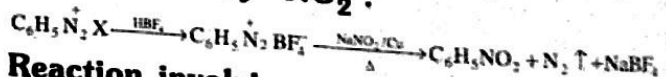
4. **Replacement by -F/Balz-Schiemann reaction**:



5. **Replacement by -H/ Reduction**:



6. **Replacement by -NO₂** :



B. **Reaction involving retention of diazonium group /Coupling reaction**:

