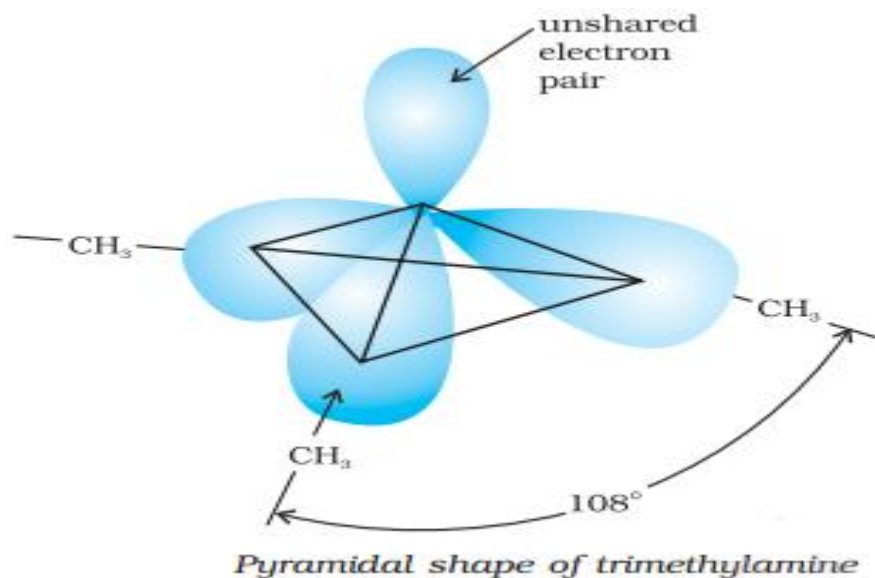


## Organic Compounds Containing Nitrogen

### Amine



**Structure of amines:** Trigonal Pyramidal

### Basicity of Amines

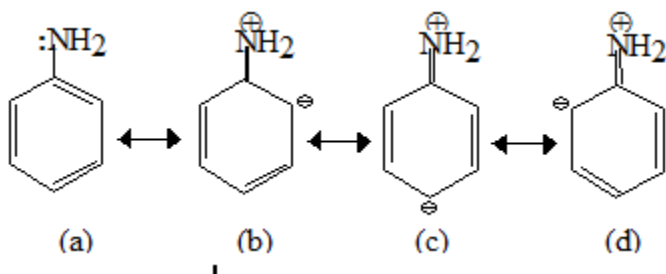
#### a) Aliphatic Amine:

Basic Strength:  $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N}$ ,

#### b) Aromatic Amine:

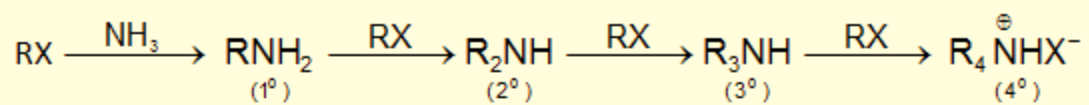
Basic Strength:  $\text{NH}_3 > \text{Ar-NH}_2 > \text{Ar}_2\text{-NH}_2$

Benzene ring decreases the electron density over N atom due to resonance effect.

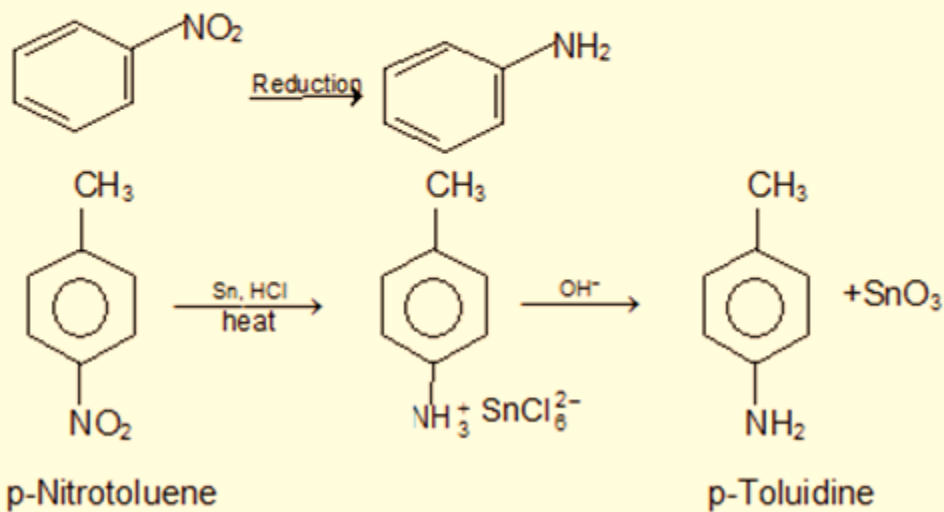


## Preparation of Amines

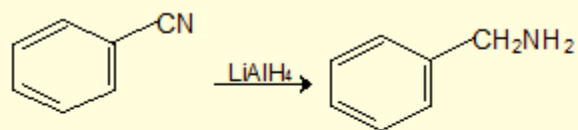
### a) From Alkyl halides:



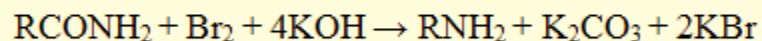
### b) From Nitro Compounds:



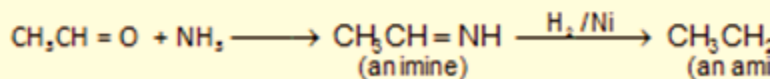
**c) From Nitriles :**



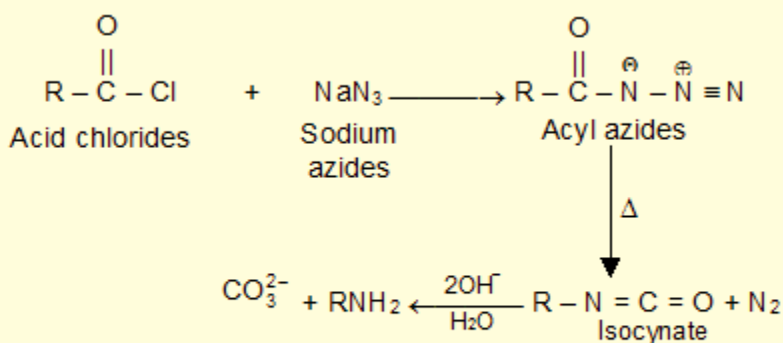
**d) Hofmann Bromamide or Hofmann degradation:**



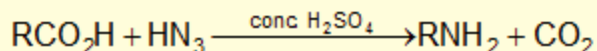
**e) From carbonyl compounds (Reductive Amination)**



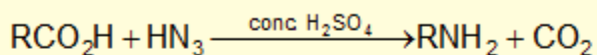
**f) Curtius reaction:**



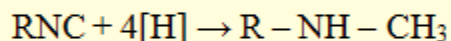
**g) Schmidt reaction :**



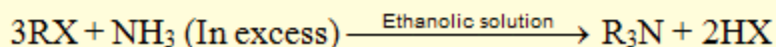
**g) Schmidt reaction :**



**h) Reduction of Alkyl isocyanide:**



**i) Preparation of tertiary amine:**



## Chemical Reactions

### a) Acylation:

$\text{RNH}_2 + \text{R}'\text{COCl} \rightarrow \text{R}'\text{CO NHR}$  an N-substituted amide

$\text{R}_2\text{NH} + \text{R}'\text{COCl} \rightarrow \text{R}'\text{CO.NR}_2$  an N,N disubstituted amide

### b) Benzoylation (Schotten Baumann Reaction)

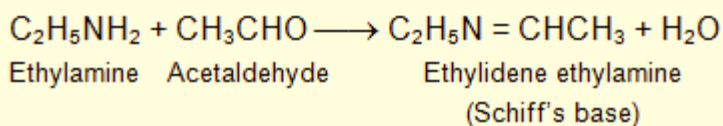
Primary amine reacts with benzoyl chloride to give the acylated product

### c) Carbylamine Reaction (Given Only by Primary Amines):

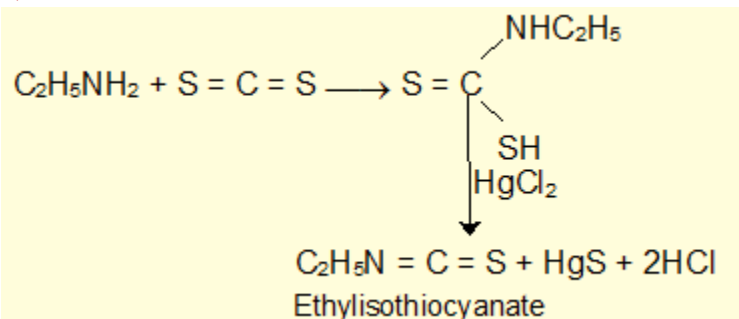
$\text{C}_2\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{C}_2\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$

$\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{C}_6\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$

### d) Action with Aldehyde and Ketone:

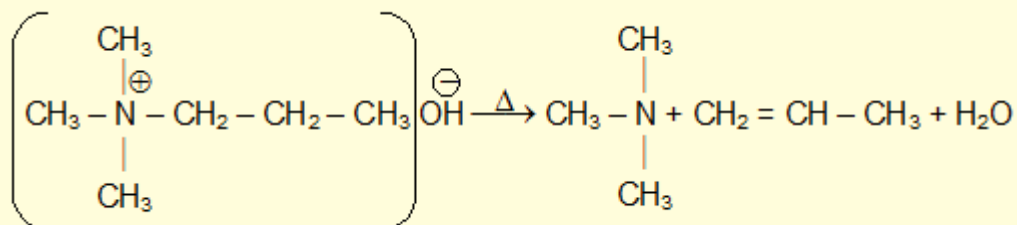


### e) Hofmann Mustard Oil Reaction:

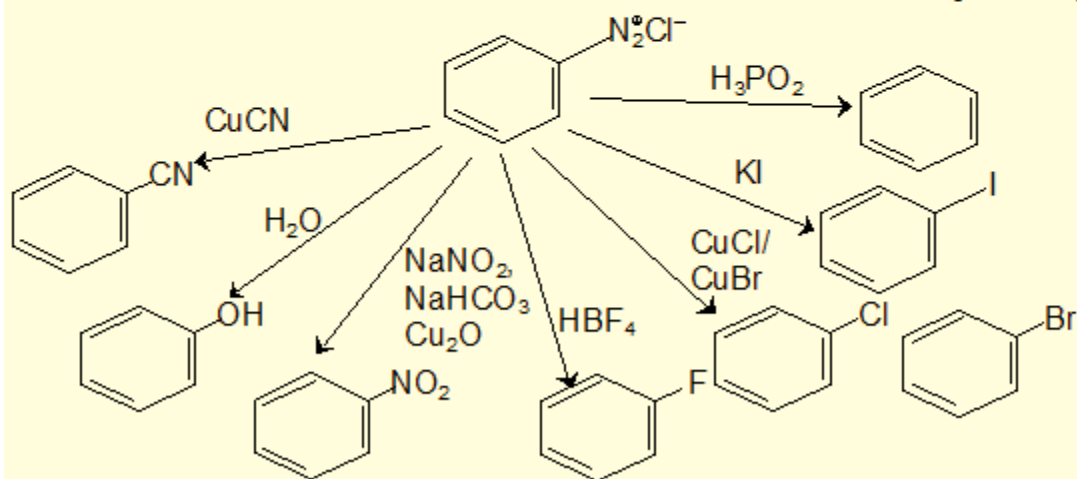
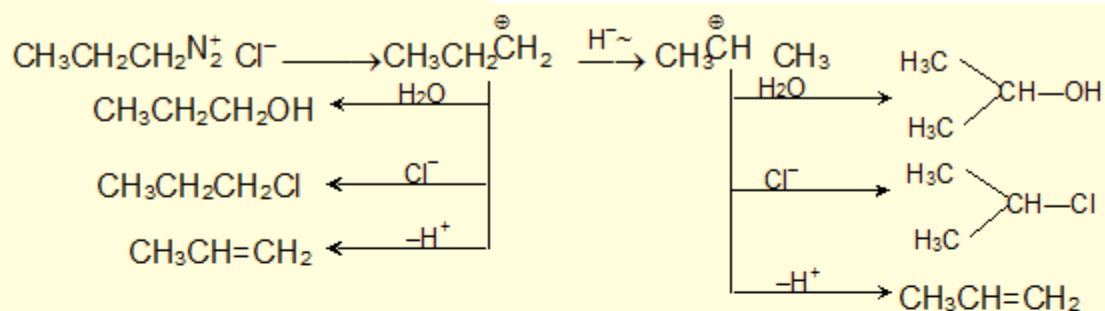
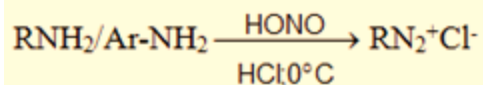


f) Reaction with Carbonyl Chloride:  $\text{C}_x\text{H}_y - \text{NH}_2 + \text{COCl}_2 \rightarrow \text{C}_x\text{H}_y\text{NCO} + 2\text{HCl}$

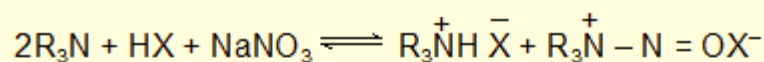
g) Hofmann Elimination: When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene



**h) The diazonium salts of amines:**



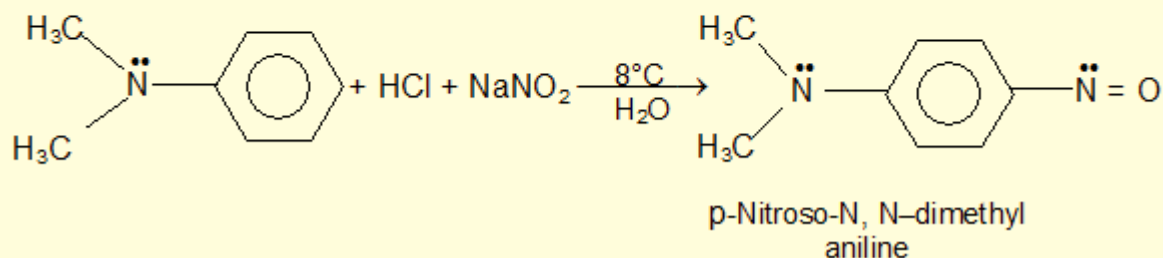
**i) Reaction of Tertiary amines with Nitrous acid:** When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.



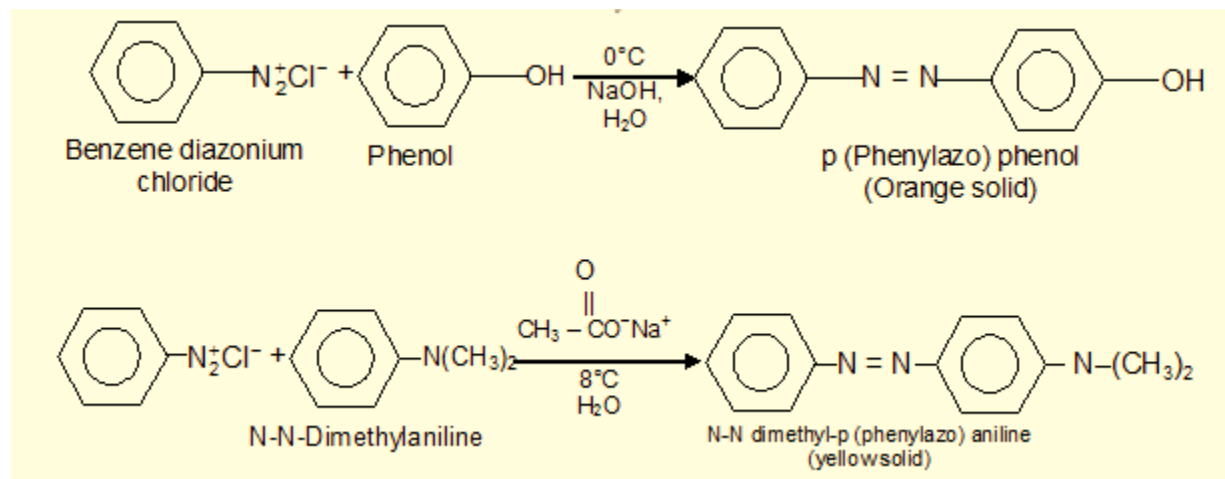
Tertiary aliphatic amine

Amine salt

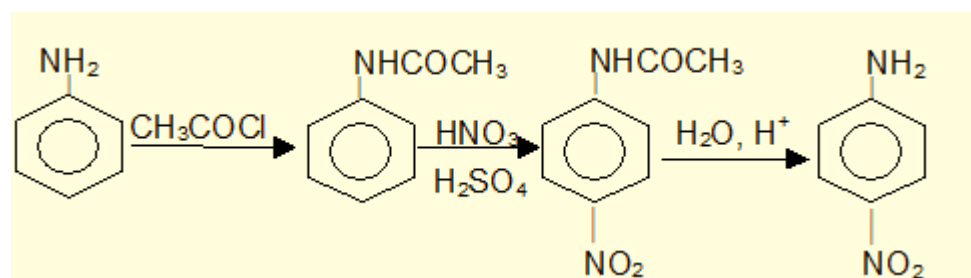
N-Nitrosoammonium compound



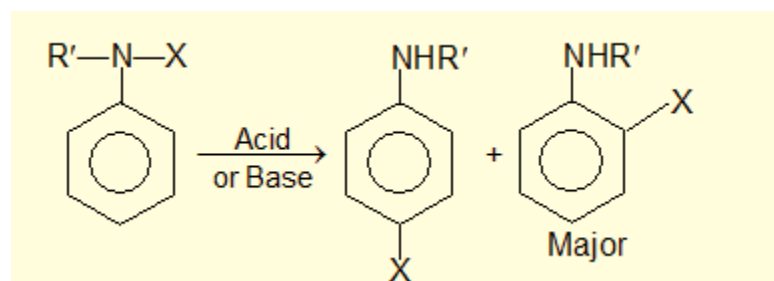
### j) Coupling Reactions of Arene Diazonium Salts:



### k) Ring Substitution in Aromatic Amines:

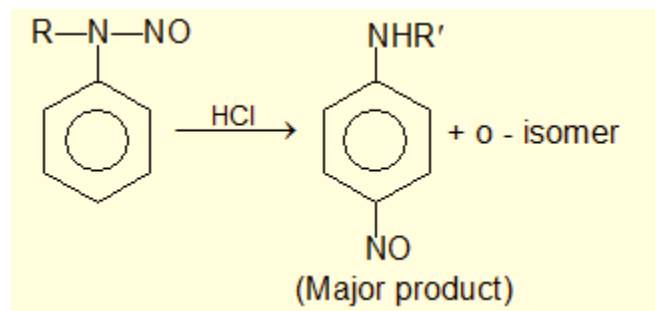


### l) Aniline -X rearrangement:



Such compounds are not much stable so the group X migrates mainly at p-position.

#### 1. Fisher-Hepp rearrangement

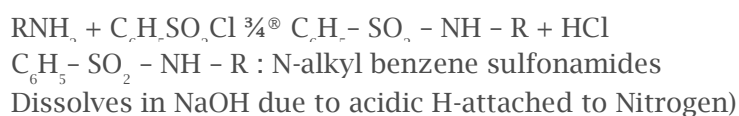


## 2. Phenylhydroxylamine - *p*-aminophenol rearrangement.

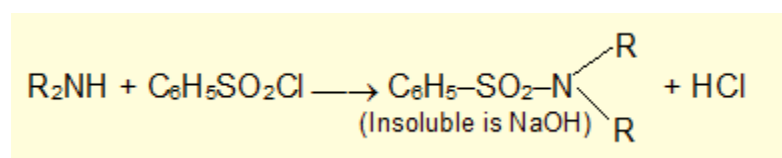
Separation of a Mixture of Amines:

### a) Hinsberg's Method

**Primary amine:**



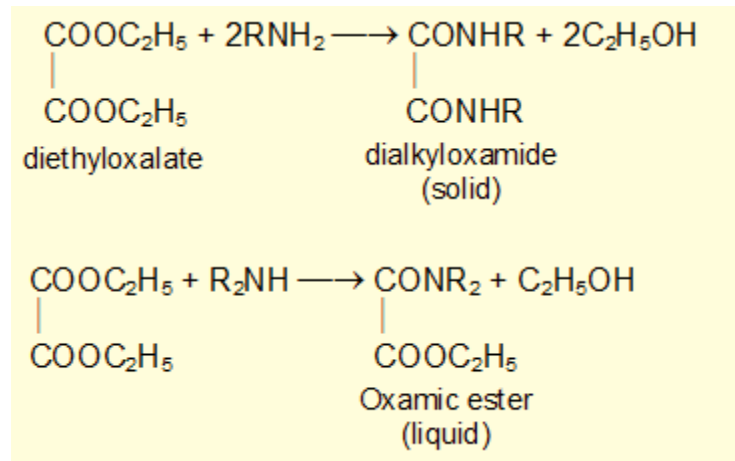
**Secondary amine**



**Tertiary amine** : Tertiary amines do not react with Hinsberg's reagent.

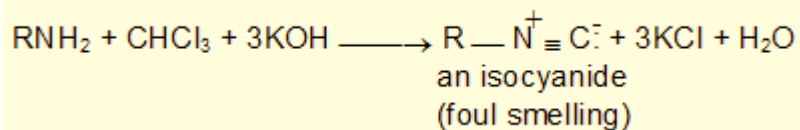
### a) Hofmann's Method:

The mixture of amines is treated with diethyloxalate, which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react.



## Test for Amines

**Primary amine** is treated with a strong base in presence in chloroform, an isocyanide is formed and this isocyanide thus formed has a very foul smell.



**Secondary amine** is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solutions warmed with phenol and concentrated  $\text{H}_2\text{SO}_4$ , a brown or red colour is formed at first soon it changes to blue and then to green. The colour changes to red on dilution and further changes to greenish blue on treating with alkali.

**Tertiary arylamines** react with nitrous acid to form o-nitroso aromatic compound

### polymers formed from single monomeric species

#### Copolymers

Addition polymers formed from two different monomeric species

#### Condensation polymers

Formed by repeated condensation of different bi or tri-functional monomer units.

#### Fibres

Long thin, threadlike bits of material that are characterized by great tensile (pulling) strength in the direction of the fiber. The natural fibres - cotton, wool, silk - are typical. The lining-up is brought about by drawing - stretching - the return to random looping and coiling is overcome by strong intermolecular attractions.

#### Elastomers

Possesses the high degree of elasticity that is characteristic of rubber: it can be greatly deformed - stretched to eight times its original length e.g., buna N and buna S, When the stretching force is removed, the molecular chains of an elastomer do not remain extended and aligned but return to their original random



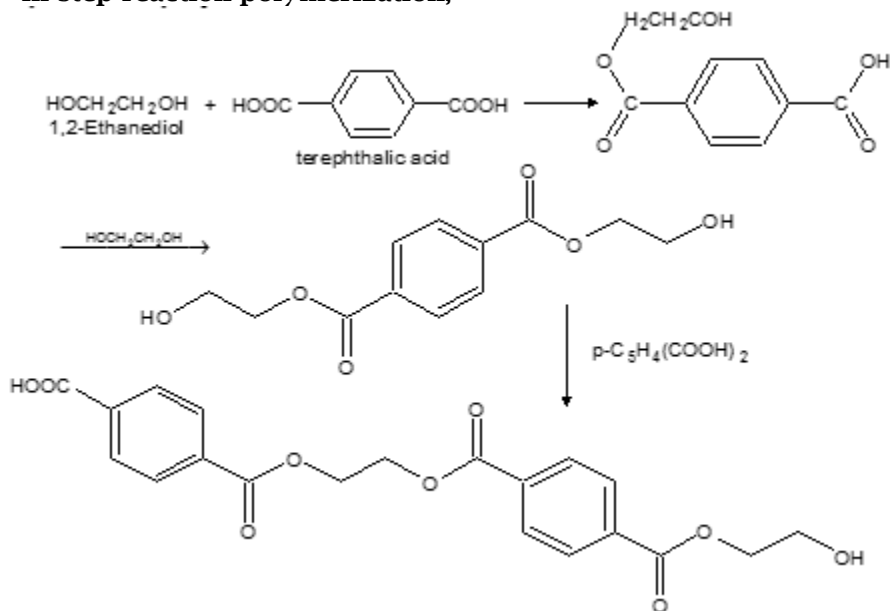
	conformations
<b>Thermoplastic polymers</b>	Soften on heating and stiffen on cooling. e.g polythene, polystyrene, PVC
<b>Thermosetting polymers</b>	Do not soften on heating and cannot be remoulded. Example, bakelite

**Polymers are formed in two general ways.**

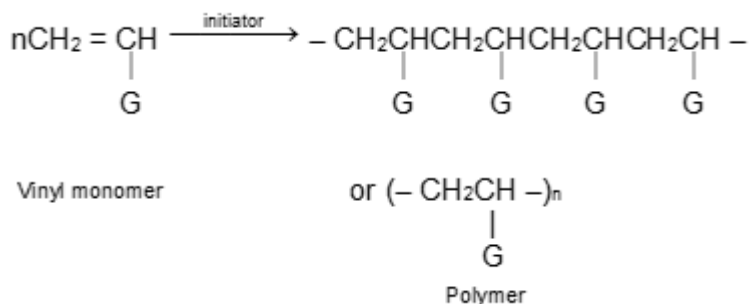
**a) In chain-reaction polymerization**



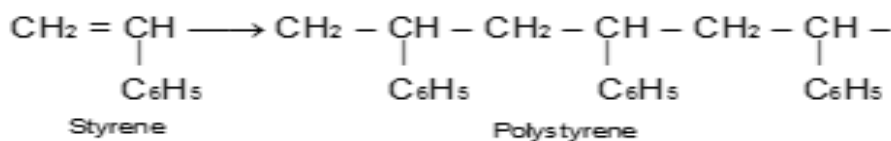
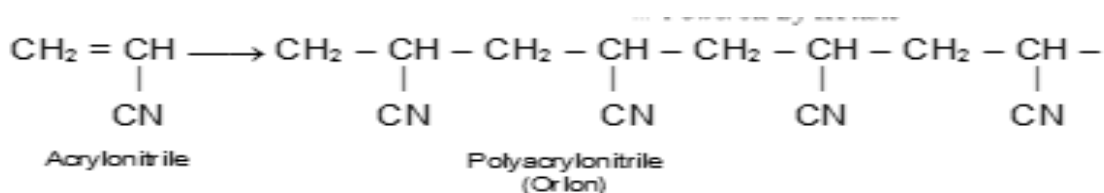
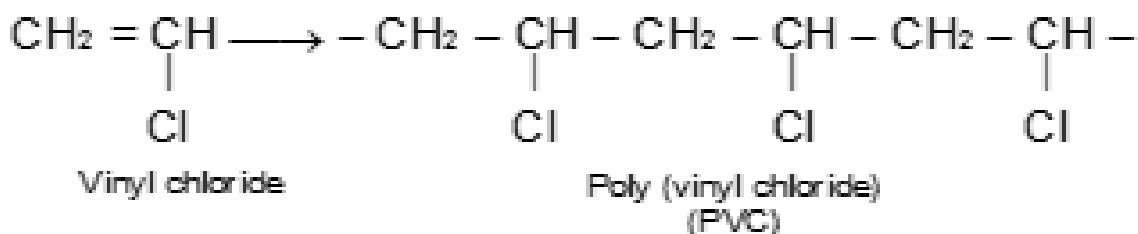
**b) In step reaction polymerization,**



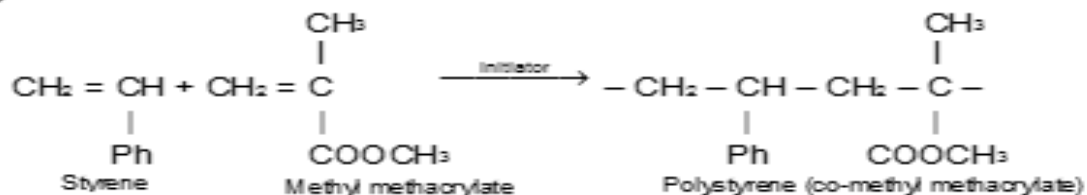
**c) Free-radical vinyl polymerization:**



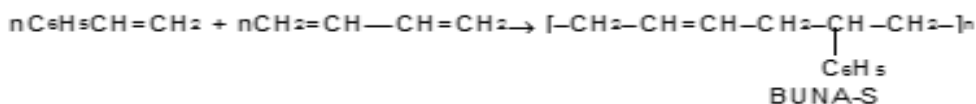
At the doubly bonded carbons — the vinyl groups — and is called vinyl polymerization. A wide variety of unsaturated monomers may be used, to yield polymers with different pendant groups (G) attached to the polymer backbone. For example.



#### d) Copolymerization:

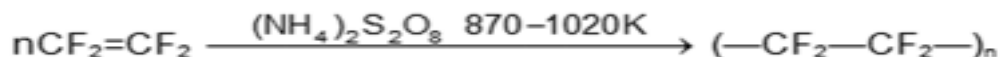






It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

**d) Teflon:** It is polymer of tetrafluorethylene ( $\text{F}_2\text{C}=\text{CF}_2$ ) which on polymerisation gives Teflon.



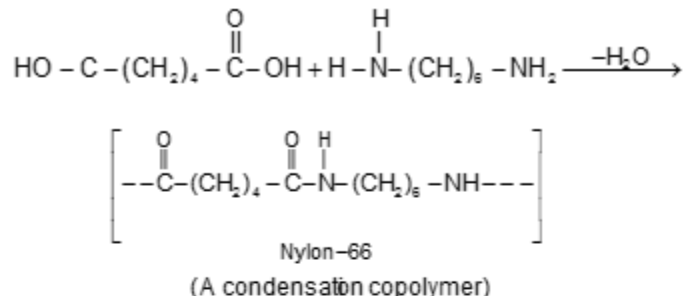
It is thermoplastic polymer with a high softening point (600K).

It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals.

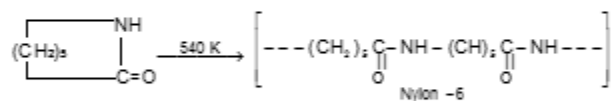
It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

**e) Nylon -66:**

A condensation polymer formed by reaction between adipic acid and hexamethylene diamine. It is a thermoplastic polymer.

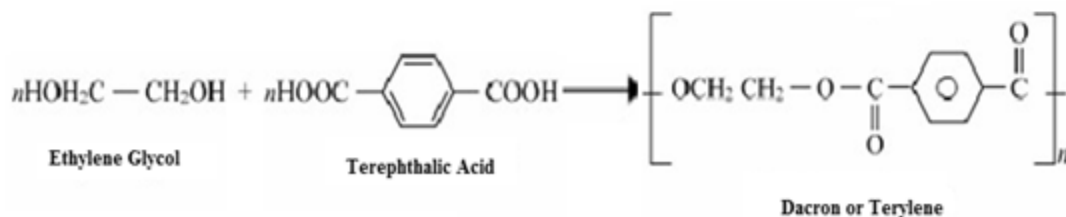


**f) Nylon 6 or Perlon - L:** A polyamide is prepared by prolonged heating of caprolactam at 530 - 540 K.



The fiber is practically identical to Nylon in properties

**g) Dacron:**



**h) Phenol-formaldehyde polymer: E.g., Bakelite Novolac**

