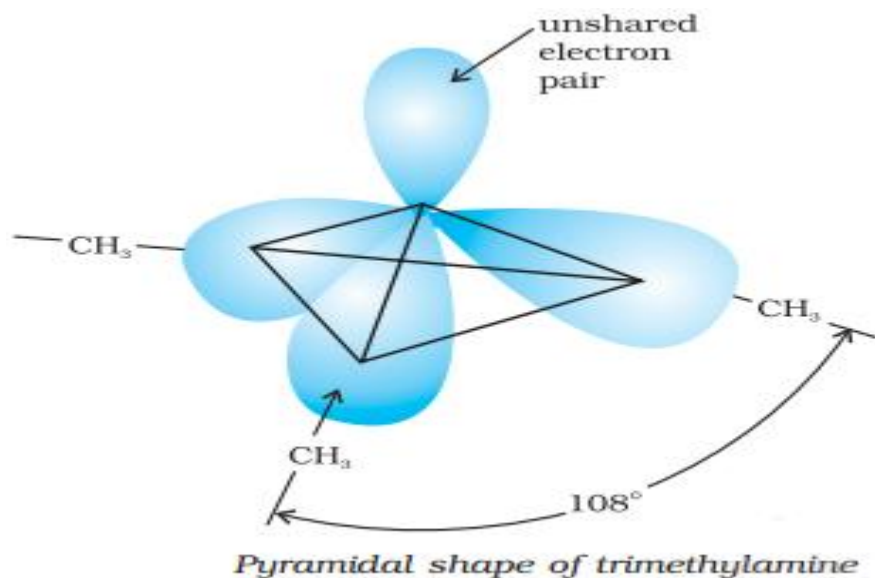


Organic Compounds Containing Nitrogen

Amine



Structure of amines: Trigonal Pyramidal

Basicity of Amines

a) Aliphatic Amine:

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

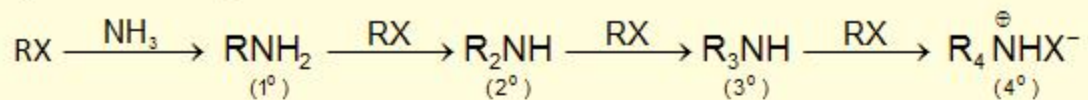
b) Aromatic Amine:

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

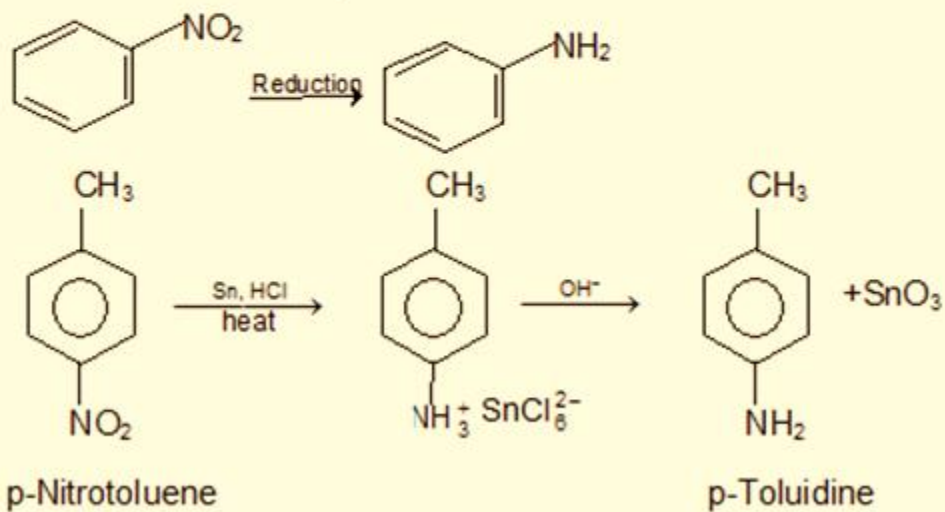
Benzene ring decreases the electron density over N atom due to resonance effect.

Preparation of Amines

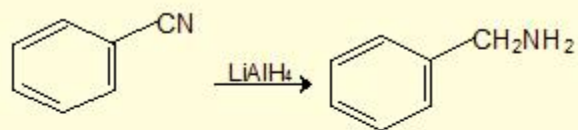
a) From Alkyl halides:



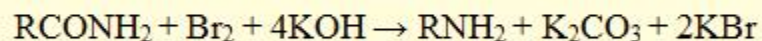
b) From Nitro Compounds:



c) From Nitriles :



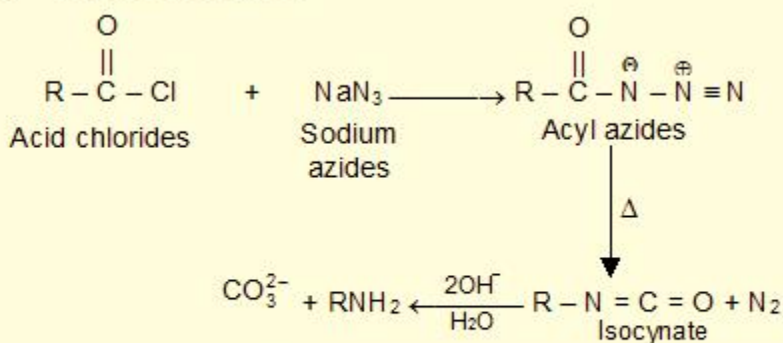
d) Hofmann Bromamide or Hofmann degradation:



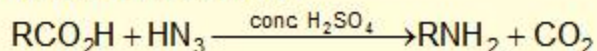
e) From carbonyl compounds (Reductive Amination)



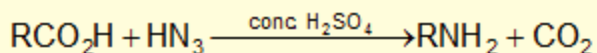
f) Curtius reaction:



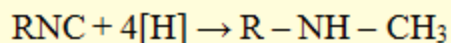
g) Schmidt reaction :



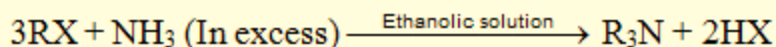
g) Schmidt reaction :



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)

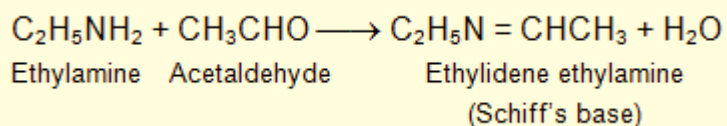
Primary amine reacts with benzoyl chloride to give the acylated product

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

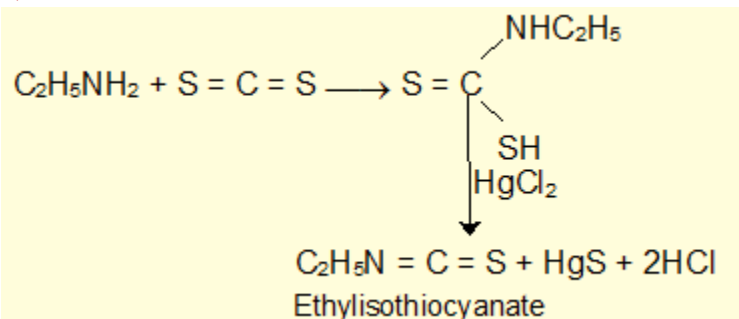
$\text{C}_2\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{C}_2\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$

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

d) Action with Aldehyde and Ketone:

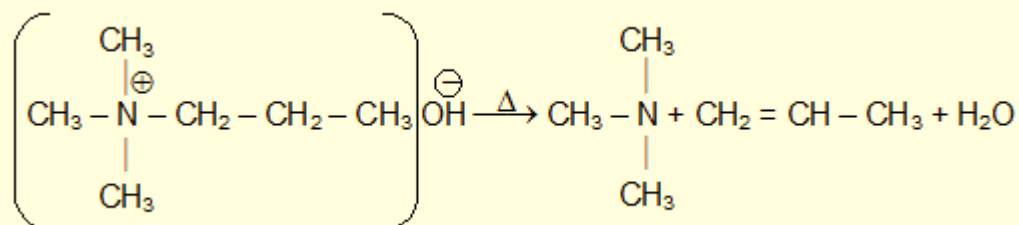


e) Hofmann Mustard Oil Reaction:

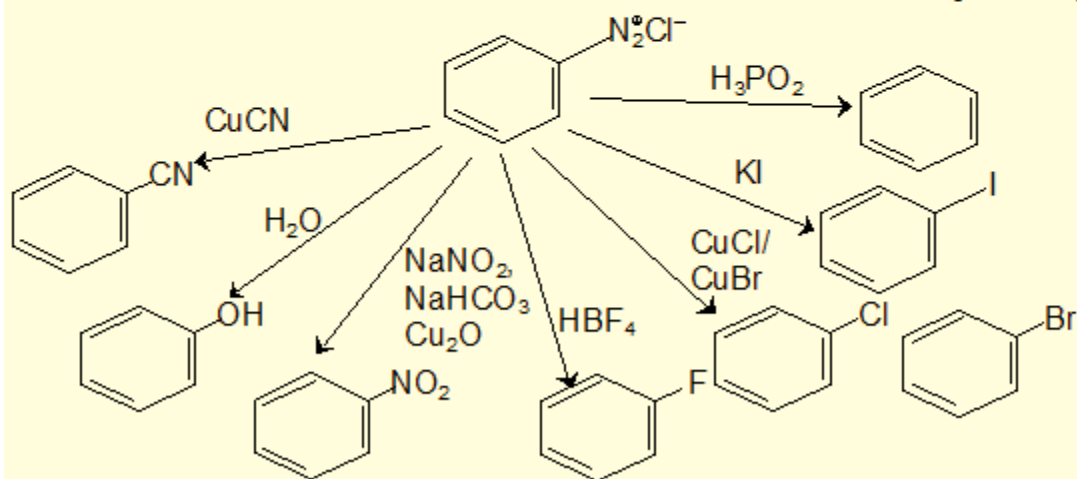
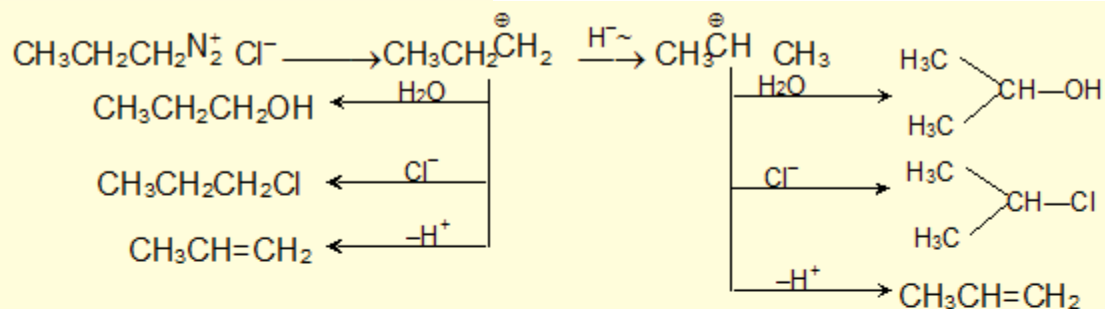
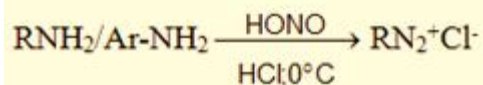


f) Reaction with Carbonyl Chloride: $\text{C}_x\text{H}_y - \text{NH}_2 + \text{COCl}_2 \rightarrow \text{C}_x\text{H}_y\text{NCO} + 2\text{HCl}$

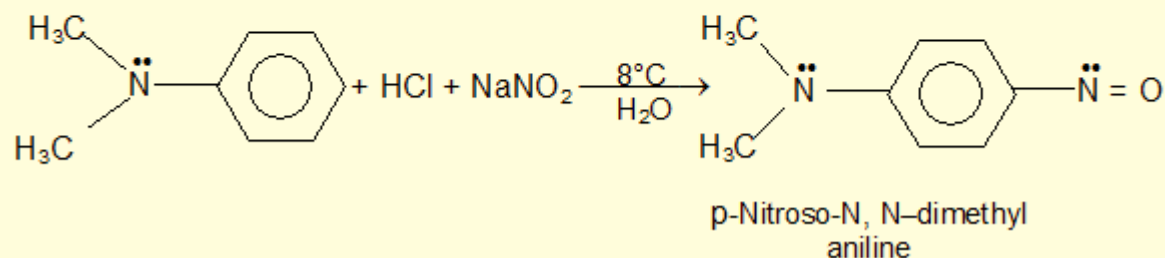
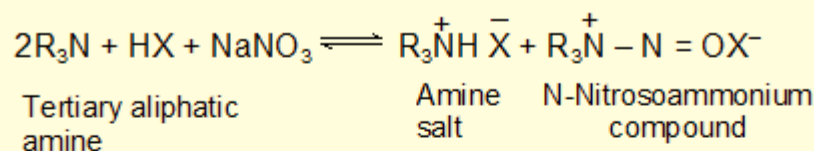
g) Hofmann Elimination: When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene



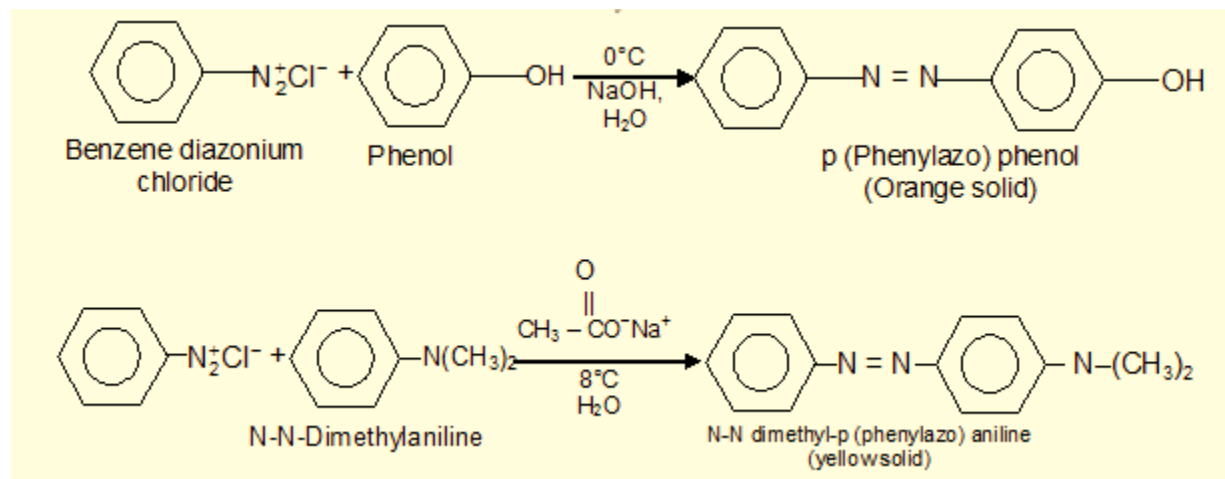
h) The diazonium salts of amines:



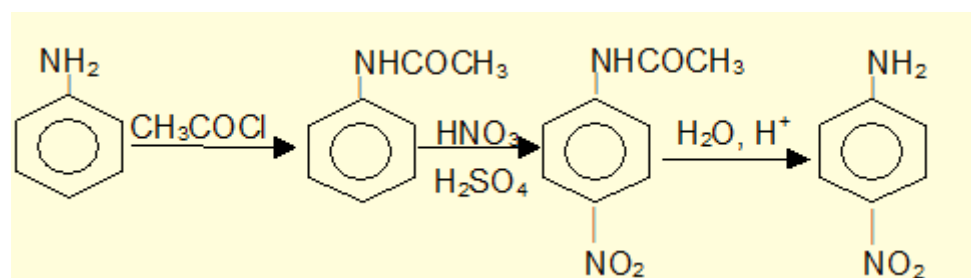
i) Reaction of Tertiary amines with Nitrous acid: When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.



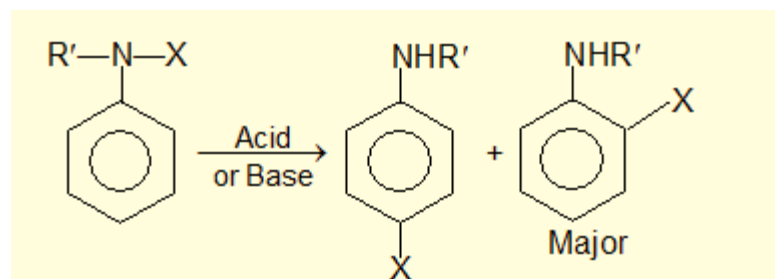
j) Coupling Reactions of Arene Diazonium Salts:



k) Ring Substitution in Aromatic Amines:

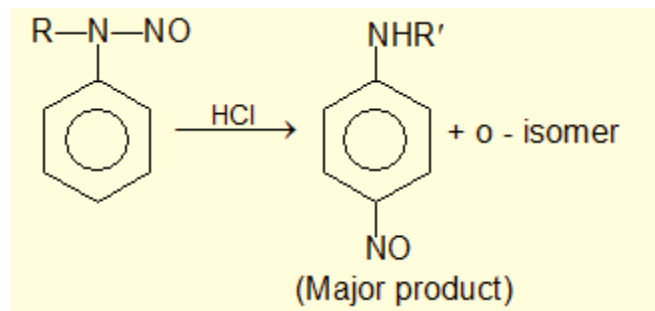


l) Aniline -X rearrangement:



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

1. Fisher-Hepp rearrangement



2. Phenylhydroxylamine - *p*-aminophenol rearrangement.

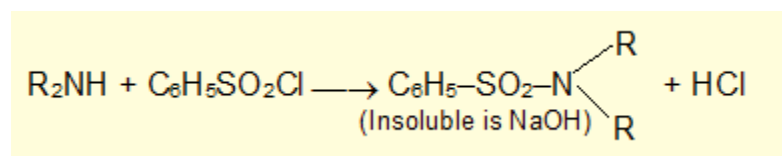
Separation of a Mixture of Amines:

a) Hinsberg's Method

Primary amine:

$\text{RNH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \xrightarrow{\frac{3}{4}} \text{C}_6\text{H}_5\text{-SO}_2\text{-NH-R} + \text{HCl}$
 $\text{C}_6\text{H}_5\text{-SO}_2\text{-NH-R}$: N-alkyl benzene sulfonamides
 Dissolves in NaOH due to acidic H-attached to Nitrogen)

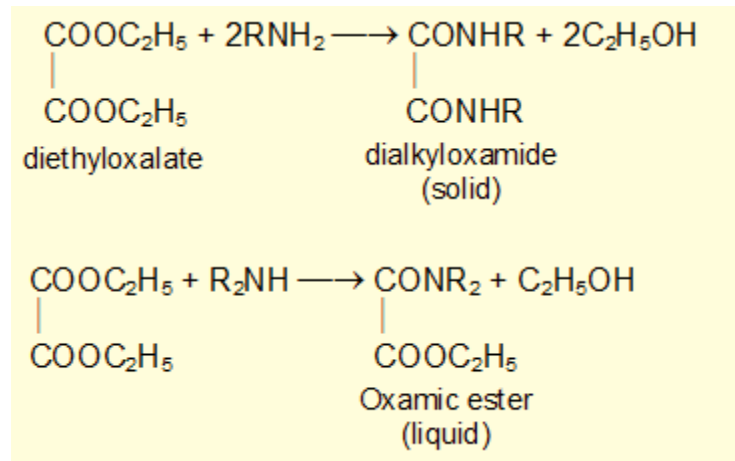
Secondary amine



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

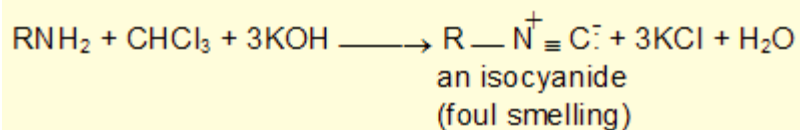
a) Hofmann's Method:

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 H_2SO_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.

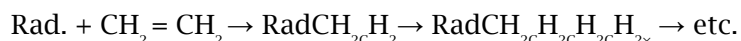
Elastomers

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
Thermoplastic polymers	Soften on heating and stiffen on Cooling. e.g polythene, polystyrene, PVC
Thermosetting polymers	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.

Some Important Polymers:

a) Natural Rubber:

Addition polymer of isoprene (2-methyl-1,3-butadiene)

An average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as **Gutta Percha** and this is the natural rubber obtained from bark of various trees.

Vulcanisation of rubber involves addition of sulphur to rubber and heating the mixture to increase the strength of natural rubber. sulphur forms short chains of sulphur atoms that link two hydrocarbon (isoprene) units together.

Vulcanised rubber is thus stronger and less sticky than the natural rubber.

b) Synthetic rubber:(Polychloroprene) or Neoprene)

It is obtained by free radical polymerisation of chloroprene in

A thermoplastic and need not to be vulcanised.

It is a good general purpose rubber and superior to natural rubber as it is resistant to the reaction of air, heat, light chemicals, alkalis and acids below 50% strength.

It is used for making transmission belts, printing rolls and flexible tubing employed for conveyance of oil and petrol.

c) Buna rubbers:

i) **Buna - N or GRA:** it is synthetic rubber obtained by copolymerisation of one part of acryl nitrile and two parts of butadiene.

It is more rigid responds less to heat and very resistant to swelling action of petrol, oils and other organic solvents.

ii) **Buna -S or GRS** (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.

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 ($F_2C=CF_2$) 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.

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