Uses

- Aliphatic amines with low molecular mass are used as solvents.
- As intermediates in drug manufacture.
- Quaternary ammonium salts of long chain aliphatic amines are used as detergents.
- Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in rubber industry.

Identification of Primary, Secondary and Tertiary Amines

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitroso-amine test.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride (Hinsberg's reagent)	Gives N-alkylbenzene- sulphonamide soluble in alkali.	Gives N,N-dialkylbenzene sulphonamide insoluble in alkali.	No reaction
3.	Carbylamine test : Reactionwithchloroform and alcoholic KOH	Forms carbylamine or isocyanide (<i>R</i> NC) with characteristic unpleasant odour.	No reaction	No reaction
4.	Hofmann's mustard oil reaction : Reaction with CS_2 and $HgCl_2$.	Forms N-substituted isothiocyante with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

CYANIDES AND ISOCYANIDES

• Cyanides and isocyanides are isomeric compounds and also are derivatives of hydrogen cyanides which exist in two tautomeric forms.

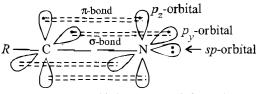
 $\mathbf{H} - \mathbf{C} \equiv \mathbf{N} = \mathbf{H} - \mathbf{N} \cong \mathbf{C}$

On replacing hydrogen atom of cyanide and isocyanide by an alkyl or aryl group we get corresponding cyanides and isocyanides.

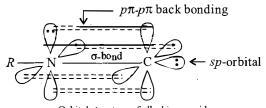
 $R - C \equiv N$ or $Ar - C \equiv N$ Alkyl cyanideAryl cyanide $R - N \equiv C$ orAlkyl isocyanideAryl isocyanide

Structure of -CN and -NC Group

• Both carbon and nitrogen of cyanide and isocyanide group are sp-hybridised. Orbital diagram of two can be shown as follows.



Orbital structure of alkyl cyanides



Orbital structure of alkyl isocyanides

Nomenclature of Cyanides and Isocyanides

• **Cyanides :** In common system these are named as alkyl cyanide or aryl cyanide.

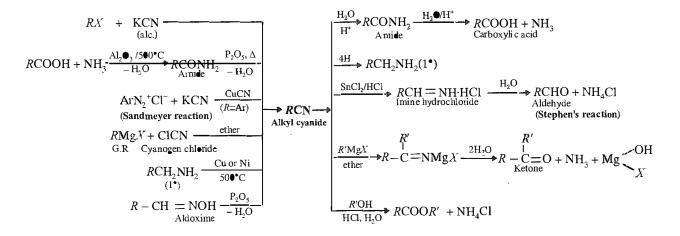
According to IUPAC system alkyl cyanide is named as alkane nitriles. Here we use suffix nitrile along with alkane. Here C-atom of — CN group is counted in chain and given as 1st position while counting the chain

$$\begin{array}{c} CH_3 - CN \\ Ethaneniwile \\ H_3 - CH_3 - CH_2 - CH_2 - CN \\ 0H \\ 3 - Hvdroxybutaneniwile \end{array}$$

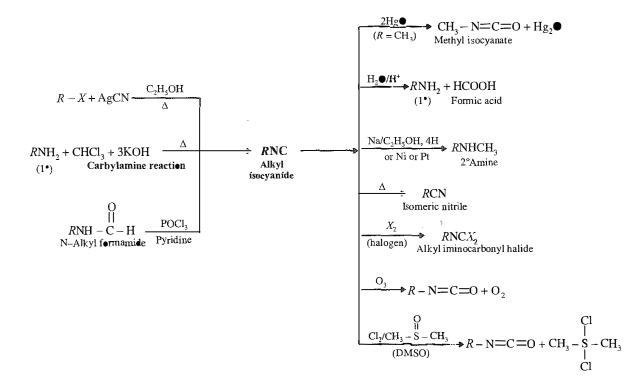
• **Isocyanides :** These are named by adding the word isocyanide after the alkyl or aryl. It is also named by adding suffix carbylamine to the name of alkyl or aryl. There is no IUPAC name for isocyanides.

 $CH_3 \cong NC$ Methylisocyanide or methylcarbylamine



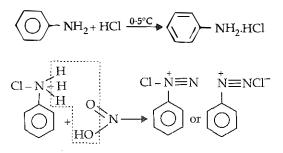


Methods of Preparation and Chemical Properties of Isocyanides

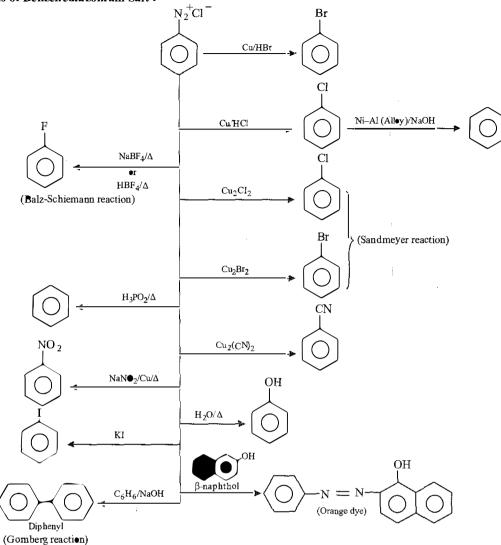


DIAZONIUM SALTS

• 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^+ is called diazonium ion group.



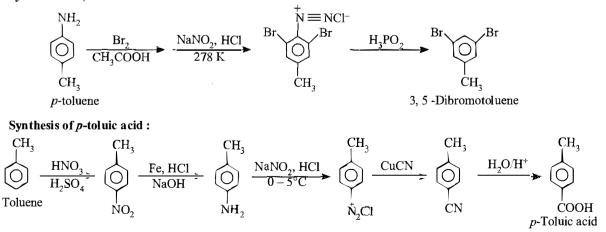
Reactions of Benzen edia zonium Salt :



Importance in Synthetic Organic Chemistry

- Diazonium salts are highly useful intermediates in the synthesis of large variety of aromatic compounds. These are used for the preparation of many organic compounds especially aryl halides.
 - > Synthesis of 3, 5-dibromotoluene :

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Similarly diazonium salts are used for the manufacture of azo dyes.