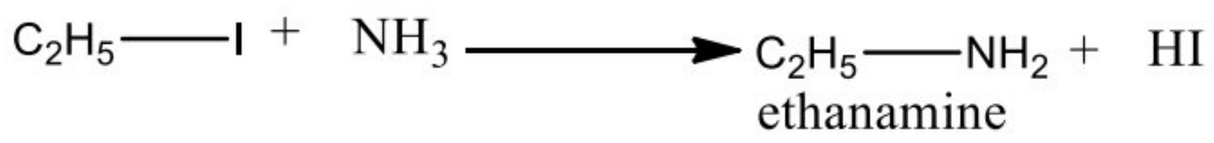
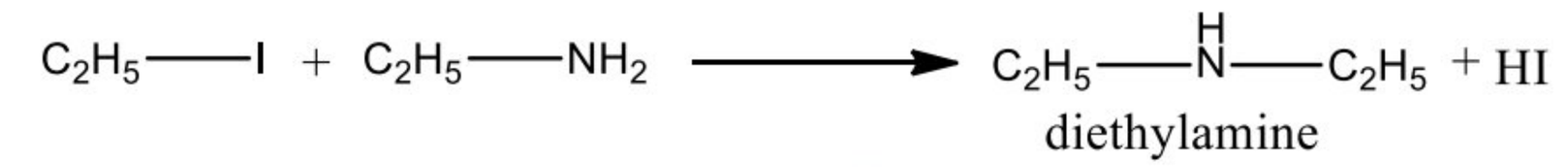
NITROGEN COMPOUNDS

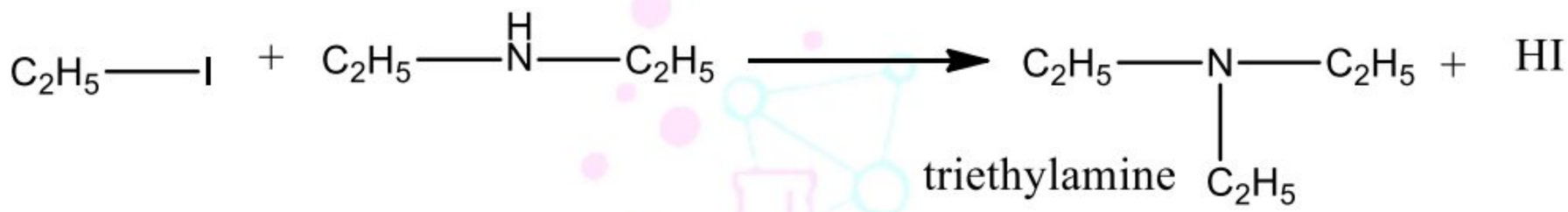
Preparation of Amines:

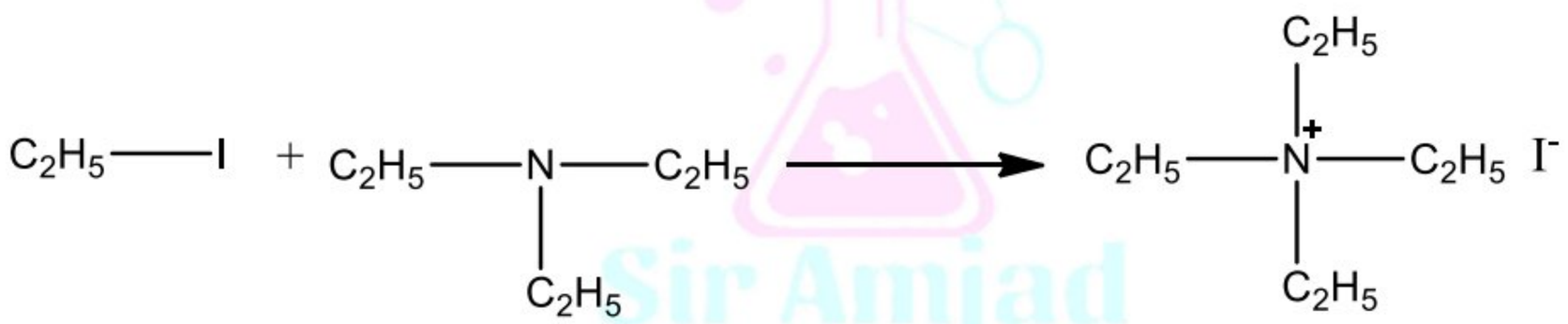
1.By the reaction of Alkyl Halides with ammonia

When an alcoholic solution of ammonia is heated with an alkyl halide in a sealed tube at 100°C, a mixture of prim-,sec-, ter- amines and a quaternary ammonium salt is obtained.









At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts, but the quaternary salt is unaffected.

The three types of amines are separated by fractional distillation.

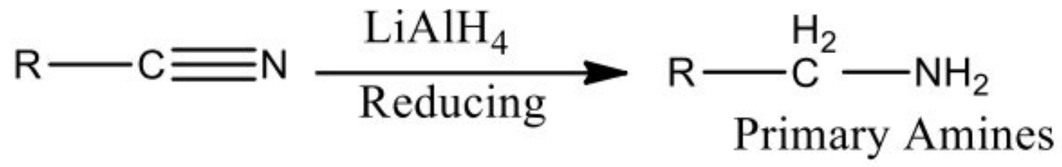
2. By the reductions of nitrogen containing functional groups:

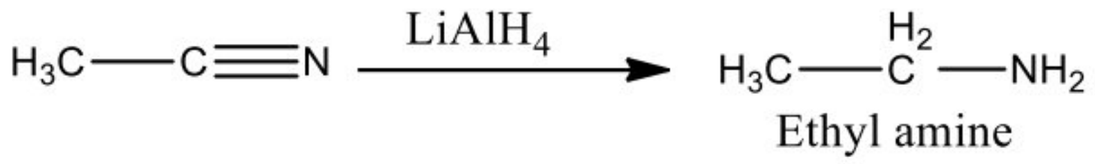
Nitrogen containing functional such as nitriles, amides, and nitro are reduced to amino group by various reducing agents.

a. Reduction of Nitriles

Reduction of alkyl or aryl nitriles gives primary amines.

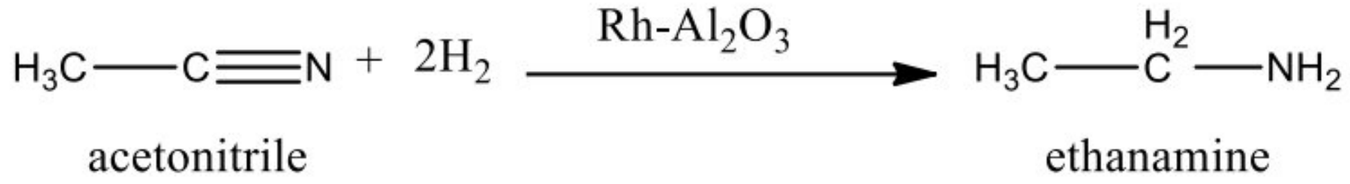
Reducing agent i.e. LiAlH4, or sodium in ethanol.

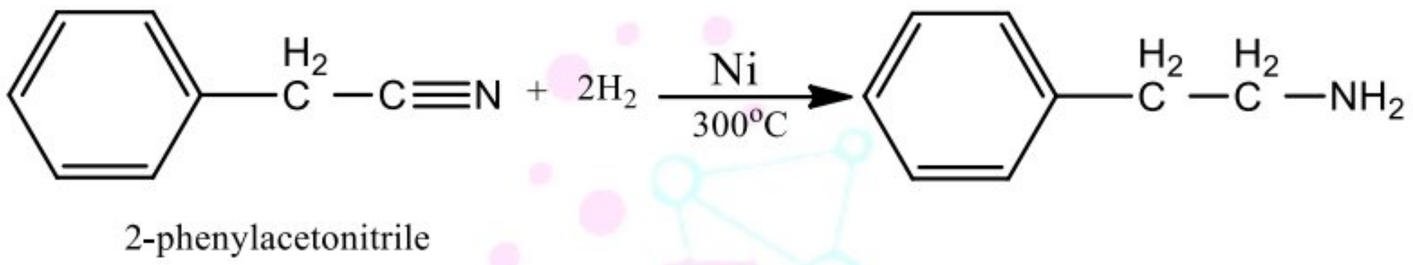




b. Catalytic Reduction

Nitriles on reaction with hydrogen gas in the presence of catalysts such as Rh-Al2O3, Pt or Raney nickel gives primary amines.





d. Reduction of Amides

When an amide is treated with reducing agent LiAlH4, -CO group of amide is reduced to -CH2 and primary amine is formed.

Basicity of Amines

Structure and Basic Nature

- In amines, the nitrogen atom is sp^3-hybridized and has a tetrahedral geometry.
- It forms three σ-bonds with atoms or groups and has one lone pair of electrons on nitrogen.
- This lone pair can accept a proton (H^+), making amines basic in nature.

Reaction with water:

$$RNH_2 + H_2O \rightleftharpoons [RNH_3]^+ + OH^-$$

- The formation of hydroxide ions (OH^-) makes the solution alkaline.
- Therefore, aqueous solutions of amines are basic.
- Amines are more basic than ammonia (NH_3) because alkyl groups increase electron density on nitrogen.

Relative Basicity of Aqueous Ammonia, Ethylamine, and Phenylamine

Base	pKb	Basic Strength
Ethylamine ($CH_3CH_2NH_2$)	3.27	Strongest
Ammonia (NH_3)	4.75	Moderate
Phenylamine ($C_6H_5NH_2$)	9.36	Weakest

Rule: The lower the pKb, the stronger the base.

Explanation

1. Ethylamine ($CH_3CH_2NH_2$)

- The ethyl group ($-C_2H_5$) is an electron-donating group (+I effect).
- It increases electron density on nitrogen, making the lone pair more available for protonation.
- The ethylammonium ion formed is also stabilized because the alkyl group disperses the positive charge.

Therefore, ethylamine is more basic than ammonia.

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2. Ammonia (NH_3)

- Ammonia has only hydrogen atoms (no electron-donating group).
- The lone pair is less electron-rich than in alkyl amines.
- It can accept a proton, but less readily than ethylamine.

So, ammonia is less basic than ethylamine.

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3. Phenylamine (Aniline, $C_6H_5NH_2$)

- **The lone pair on nitrogen is delocalized into the benzene ring through resonance.**

- **This makes the lone pair less available for bonding with a proton (H^+).**
- **Hence, phenylamine is much less basic than ammonia.**

Phenylamine is the weakest base.

Order of Basic Strength

$$Phenylamine < Ammonia < Ethylamine$$

Formation of Nitriles

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1. From Halogenoalkanes (Alkyl Halides)

Reaction:
When a halogenoalkane (alkyl halide) is heated with potassium cyanide (KCN) in ethanol, it produces a nitrile (alkyl cyanide).

$$\mathrm{R{-}X + KCN \xrightarrow[\text{Heat}]{\text{Ethanol}} R{-}CN + KX}$$

Examples:

1. **From methyl bromide:**

$$\boldsymbol{CH_3Br + KCN \rightarrow CH_3CN + KBr}$$

Product: Methyl cyanide (Ethanenitrile)

2. **From ethyl bromide:**

$$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$$

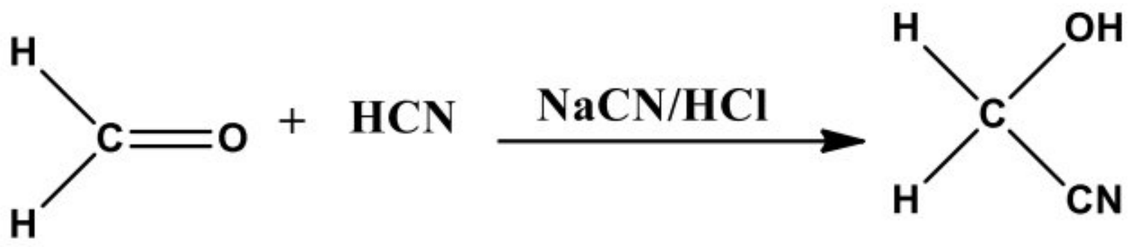
Product: Ethyl cyanide (Propanenitrile)
This reaction increases the length of the carbon chain by one carbon atom, since the –CN group adds an extra carbon.
Hence, it's commonly used in organic synthesis to extend carbon chains.

2. From Aldehydes and Ketones (Cyanohydrin Formation)

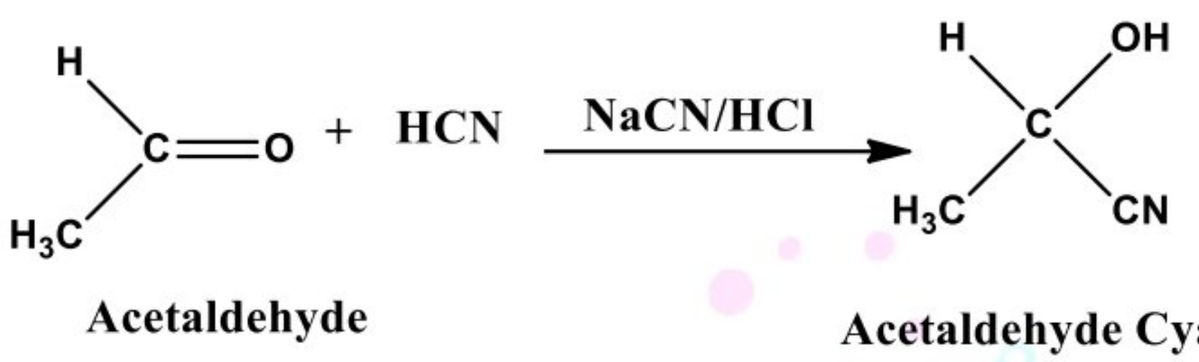
Reaction:
Aldehydes and ketones react with hydrogen cyanide (HCN) to form cyanohydrins.

However, since HCN is a highly toxic gas, the reaction is carried out using a mixture of KCN and dilute HCl:

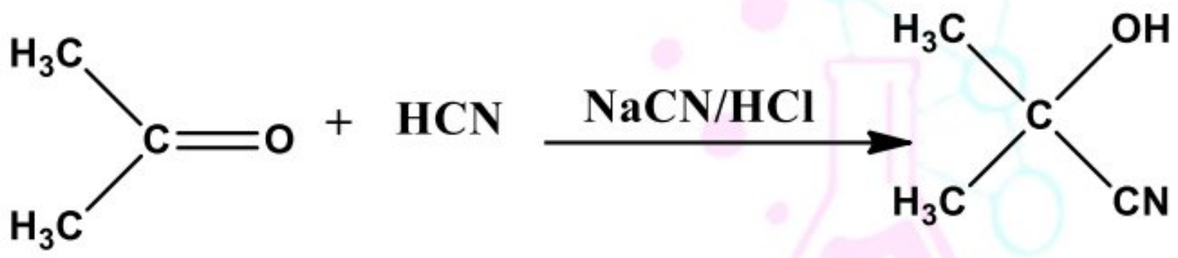
- $KCN + HCl \rightarrow HCN + KCl$
- The free cyanide ions (CN^-) act as a catalyst and help the addition reaction.



Formaldehyde **Formaldehyde cyanohydrin**



Acetaldehyde **Acetaldehyde Cyanohydrin**



Acetone **Acetone cynanohydrin**

Importance of the Reaction

- Used to prepare nitriles (R–CN).
- Increases carbon chain length by one carbon atom.
- Useful in synthesis of higher homologs (homologation reactions)

Hydrolysis of nitriles

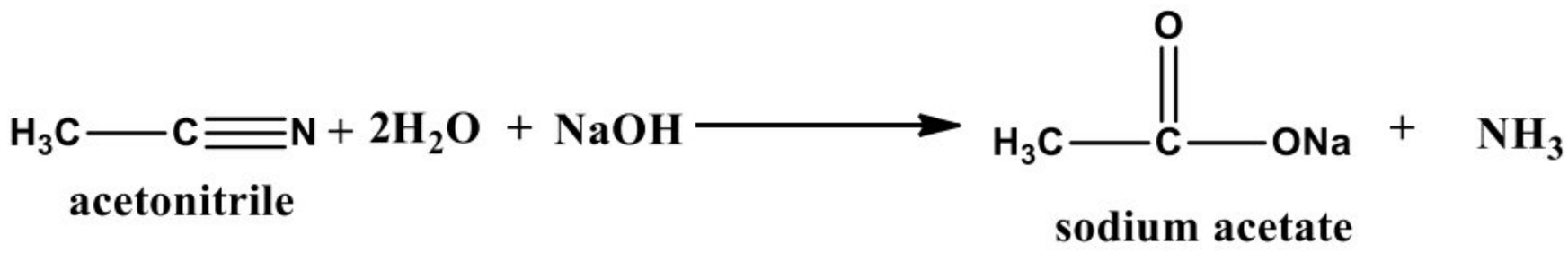
Hydrolysis of nitriles can occur with both dilute acid or dilute alkali.

1. Acid hydrolysis of nitriles

When a nitrile is heated with a dilute acid such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic acid is formed.

2. Alkaline hydrolysis of nitriles

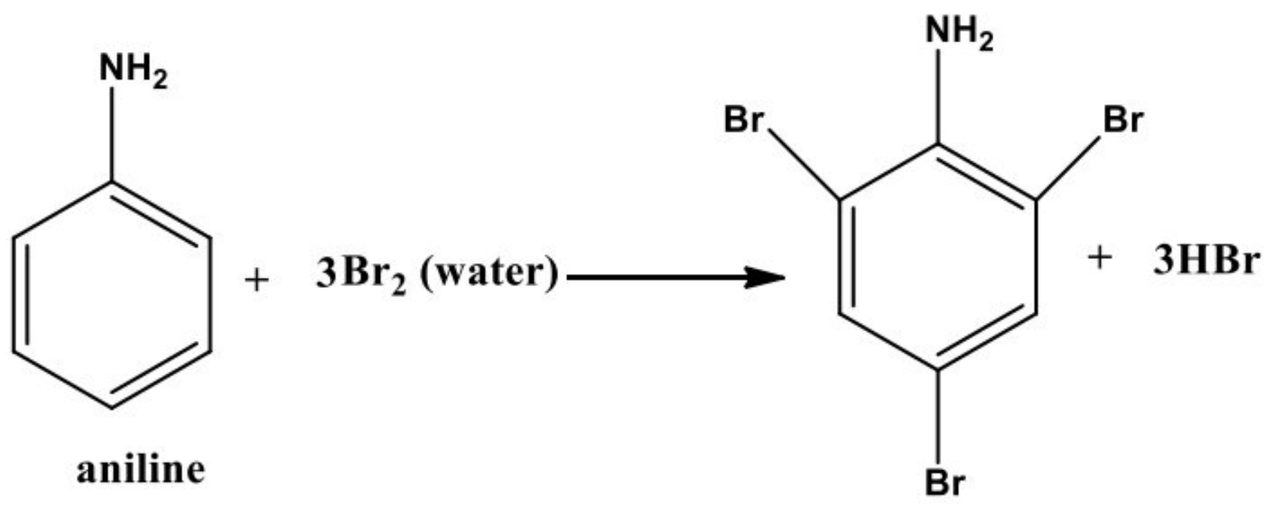
When a nitrile is heated with a dilute sodium hydroxide solution, a salt of carboxylic acid is produced, which on acidification with dilute hydrochloric acid gives free carboxylic acid.



Phenylamine and Azo Compounds

(a) Reaction of phenylamine with bromine water

When bromine water is added to an aqueous solution of phenylamine at room temperature, the reddish-brown colour of bromine is decolourized and a white precipitate of 2,4,6-tribromophenylamine is produced.



(b) Reaction of Phenylamine with HNO_2 / $NaNO_2$

(Preparation of Diazonium Salts)

Step 1: Reactants and Conditions

- Phenylamine (aniline) is dissolved in dilute hydrochloric acid to form anilinium chloride.
- The solution is cooled below 5°C (in ice).
- A cold solution of sodium nitrite ($NaNO_2$) is prepared separately and also kept below 5°C.

Step 2: Formation of Nitrous Acid (in situ)
Inside the reaction mixture, sodium nitrite reacts with hydrochloric acid to produce nitrous acid (HNO_2):

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

Step 3: Diazonium Salt Formation
The nitrous acid then reacts with phenylamine at a temperature below 5°C to form benzene diazonium chloride ($C_6H_5N_2Cl$):

Benzene diazonium chloride

Product: Benzene diazonium chloride
(Also written as Phenyl diazonium chloride)

Step 4: Temperature Control

- The temperature must be below 5°C.
- Above 10°C, diazonium salts decompose because they are unstable.

Step 5: Decomposition on Warming
When the diazonium salt solution is warmed, it decomposes to form phenol:

$$C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 \uparrow + HCl$$

For More Information:

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