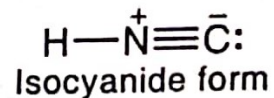
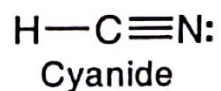


Alkyl nitriles or alkyl cyanides: Structure, Nomenclature and Preparation

Definition

Hydrogen cyanide exists as a tautomeric mixture as shown below



The alkyl derivatives of the cyanide form are called **Alkyl cyanides** or **Nitriles**, while those of the isocyanide form are referred to as **Alkyl isocyanides** or **Isonitriles**.



Cyanides

**(bonding of alkyl
through carbon)**

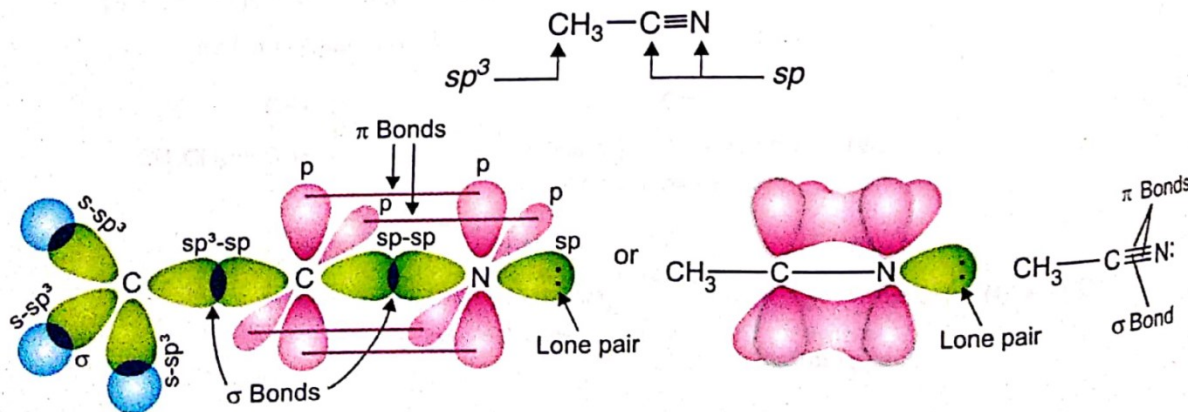


Isocyanides

**(bonding of alkyl
through nitrogen)**

Structure

Structure of nitrile compound is explained by taking acetonitrile as example. The carbon and nitrogen atom of the triple bond are sp hybridized.



If the diagram appears complicated you can draw only the right portion

Fig: Molecular orbital structure of Acetonitrile

The σ bonds result from $s-sp^3$, sp^3-sp , and $sp-sp$ overlaps. The π bonds result by the overlap of p orbitals from the sp hybridized atoms of the carbon-nitrogen triple bond (as in alkynes). The carbon-nitrogen triple bond is made up of one σ bonds and two π bonds (Fig.24.1). The H-C-H and H-C-C bonds angles are $109^\circ 28'$. The C-C-N angle is 180° . The lone-pair of electrons on nitrogen resides in the sp hybrid orbital of nitrogen.

Nomenclature

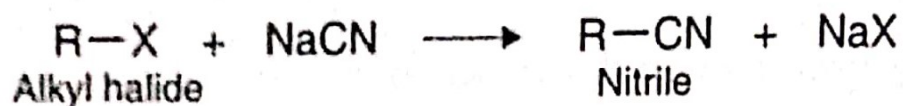
There are three ways of naming alkyl cyanide compounds. The first way is referred as cyan System, the second is the common name (just like your nick name), and the third is the IUPAC name

Structure	Cyan Name	Common Name	IUPAC Name
CH_3-CN	Methyl cyanide	Acetonitrile	Ethanenitrile
$\text{CH}_3\text{CH}_2-\text{CN}$	Ethyl cyanide	Propionitrile	Propanenitrile
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{CN}$	Propyl cyanide	Butyronitrile	Butanenitrile
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CN} \end{array}$	Isopropyl cyanide	Isobutyronitrile	2-Methylpropanenitrile

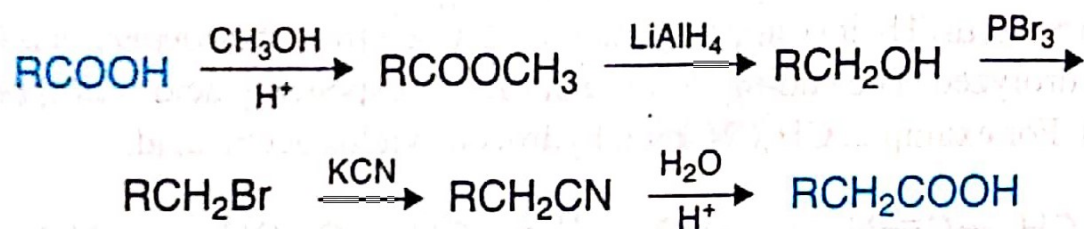
Preparation

2. Preparation by action of metal cyanides of alkyl halides

(1) Action of Metal cyanides on Alkyl halides. Nitriles can be prepared conveniently by heating an alkyl halide with sodium or potassium cyanide in aqueous-ethanolic solution.

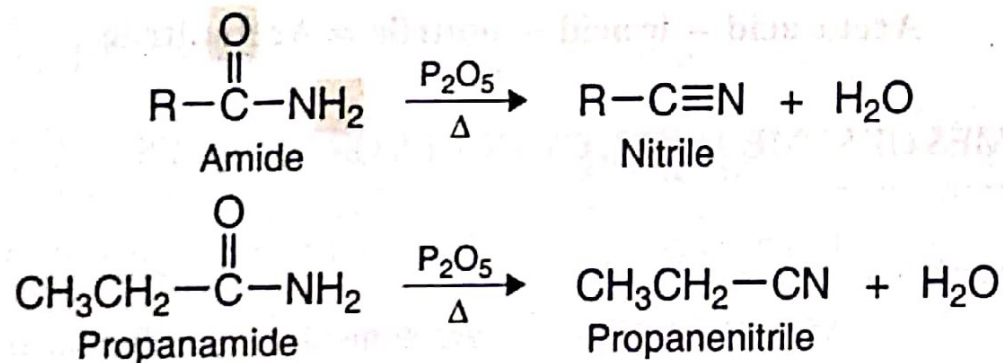


When nitriles are prepared from alkyl halides by this method, an extra carbon atom is introduced. This is the key step for ascending the series of carboxylic acids (or 1° alcohols)



2. Dehydration of Amides or Ammonium Salts of Carboxylic Acids

(2) **Dehydration of Amides or Ammonium salts of Carboxylic acids.** Simple amides on drastic dehydration by heating with phosphorus pentoxide yield nitriles.

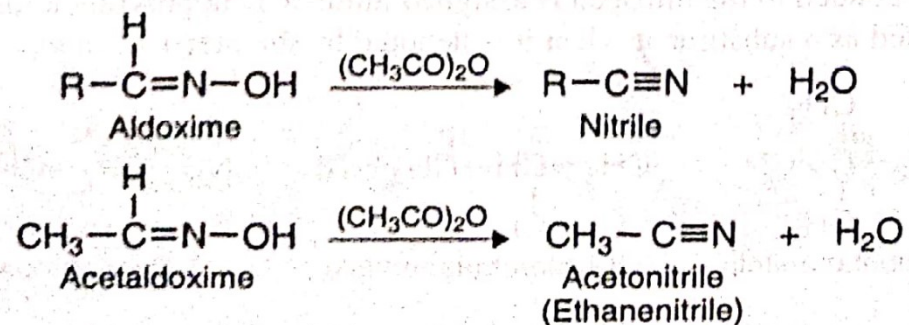


Higher molecular weight amides may be dehydrated by heating alone.

Ammonium salts of carboxylic acids dehydrate first to form amide, which on loss of a molecule of water yields nitrile. Thus when carboxylic acid vapors mixed with ammonia are passed over heated alumina at 500°C, a nitrile results. (*Industrial method*)

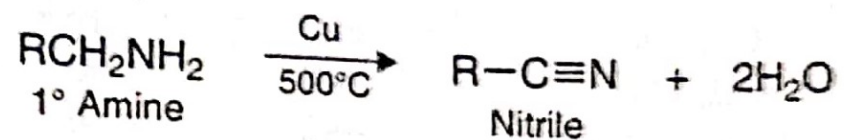
3. Dehydration of Aldoximes

(3) **Dehydration of Aldoximes.** Aldoximes on dehydration with acetic anhydride or phosphorus pentoxide yield nitriles.



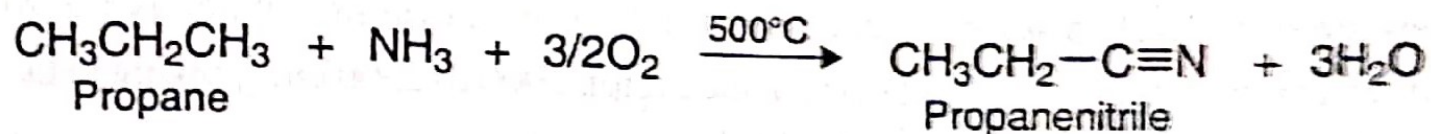
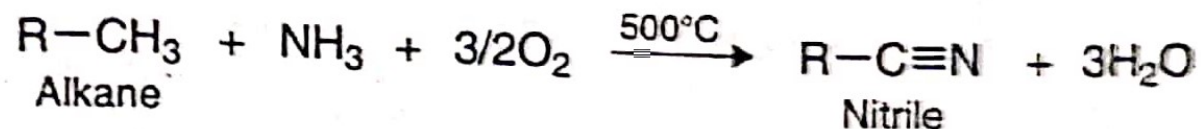
4. Dehydrogenation of Higher Amines

(4) **Dehydrogenation of Higher Amines.** Higher amines get dehydrogenated by passing their vapor over a Cu or Ni catalyst at high temperature.

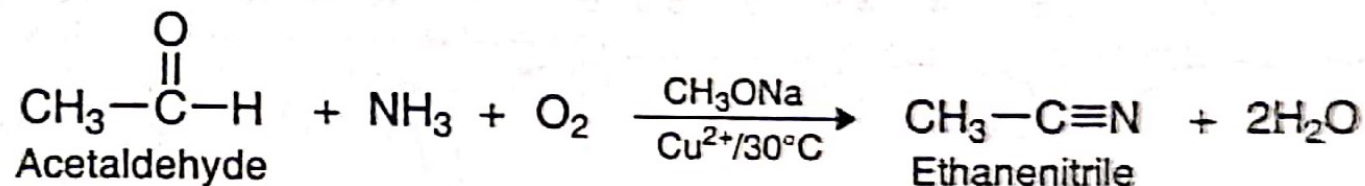


5. Amoxidation of Alkanes or Aldehydes

(5) **Amoxidation of Alkanes or Aldehydes.** An alkane having a terminal methyl group is oxidized at high temperature (500-600°C) over a catalyst in the presence of ammonia to form a nitrile.

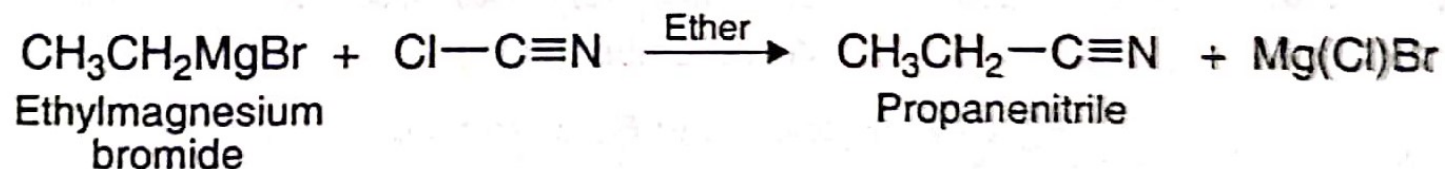
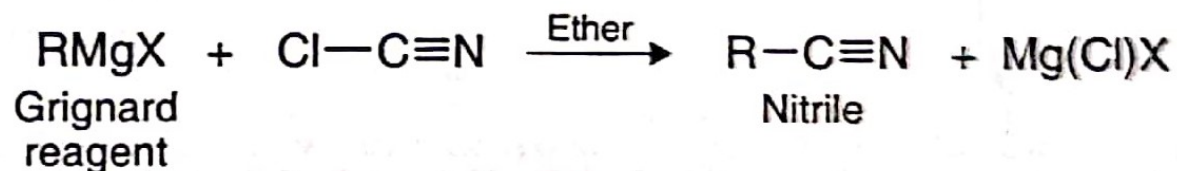


An aldehyde gives a similar reaction in the presence of sodium methoxide (CH_3ONa) and Cu^{2+} ion at 30°C.



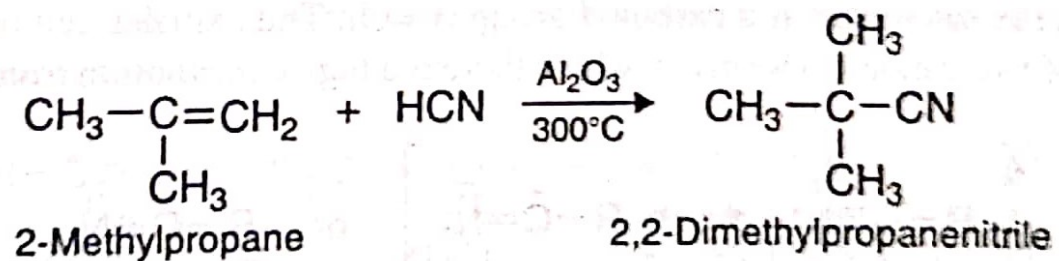
6. By action of Grignard reagents with cyanogen chloride

(6) **Action of Grignard reagents with Cyanogen chloride.** Grignard reagents react with cyanogen chloride ($\text{Cl}-\text{C}\equiv\text{N}$) to form nitriles.



7. Preparation by addition of HCN to alkenes

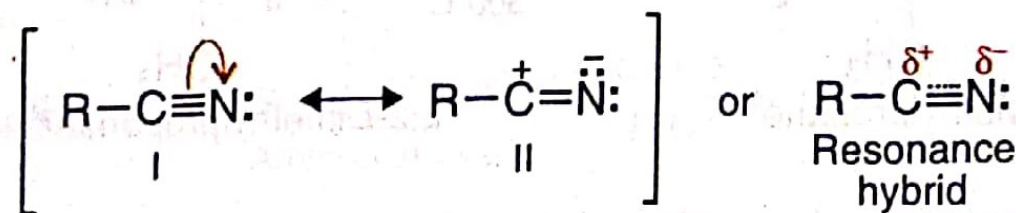
(7) **Addition of HCN to Alkenes.** Hydrogen cyanide adds to terminal alkenes in the gaseous phase at 300°C in presence of alumina to give nitriles.



Alkyl nitriles or alkyl cyanides: **Chemical Properties**

Types of reactions that can take place on nitriles

The CN group in nitrile is polarized as indicated by the high dipole moment, 4.0 D. It is Polar in the same way as a carbonyl group (C=O). Thus nitriles can be represented as a resonance hybrid of two canonical forms, in which there is a high contribution from the dipolar form.

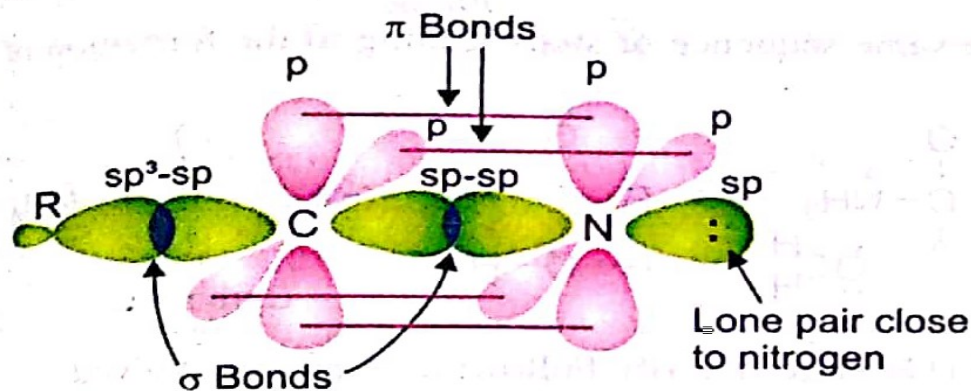


Because of the dipole, a nitrile is subject to electrophilic attack on nitrogen and to nucleophilic attack on carbon. The cyan group being electron attracting activates the α hydrogen which can be easily removed as a proton by strong bases. In fact the cyan group could be compared to the carbonyl group in its chemical behavior. Thus nitriles give the addition reactions just like aldehydes and ketones.

Weak Basic character of nitriles

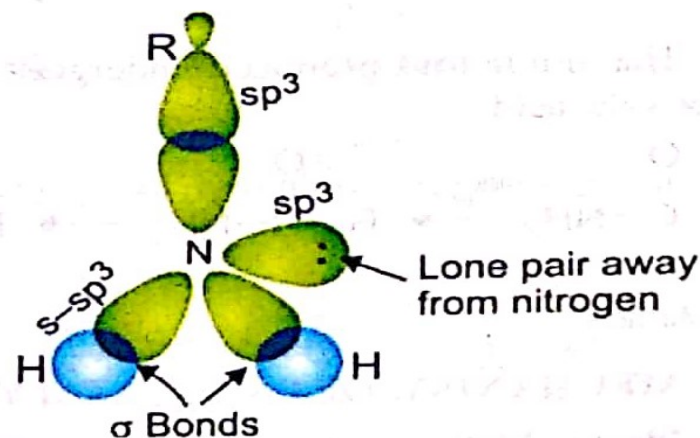
(1) **Weak Basic Character.** Despite the presence of an unshared pair of electrons at the nitrogen atom, the nitriles are not basic enough to form salts with aqueous acids. They are, therefore, less basic than amines and ammonia. However, they form addition compounds with strong acids in the absence of water.

The weak basic character of nitriles has been associated with a greater s character of the orbital containing the unshared electron pair. Unlike amines where the lone pair of electrons is in sp^3 orbital, the lone pair of N atom in nitriles resides in an sp orbital. This orbital (sp) has greater s character than sp^3 orbital. Therefore, the lone pair of nitrogen in nitriles is less readily available and they are much weaker bases than amines.



NITRILE

Lone pair held closer to the N atom in sp orbital is less readily available; hence nitriles are **Less Basic**.

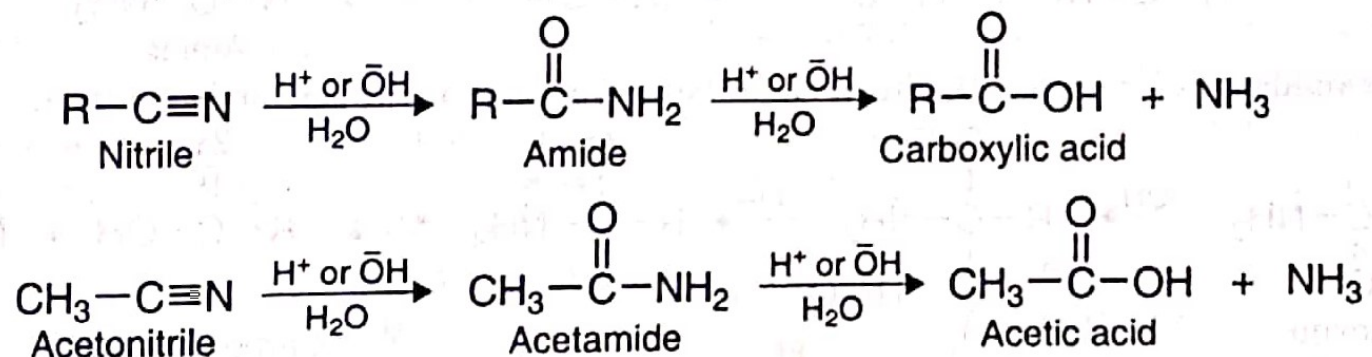


PRIMARY AMINE

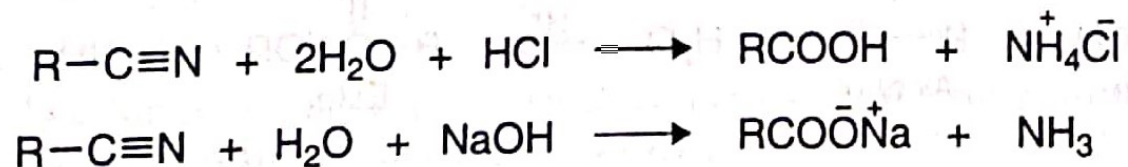
Lone pair lying relatively away from the N atom in sp^3 orbital is more readily available; hence amines are **More Basic**.

Hydrolysis reaction of nitriles

(2) **Hydrolysis.** On boiling with aqueous mineral acid or aqueous alkali, nitriles are hydrolyzed to a carboxylic acid and ammonia. This reaction takes place through the formation of an amide, which is then hydrolyzed to a carboxylic acid.



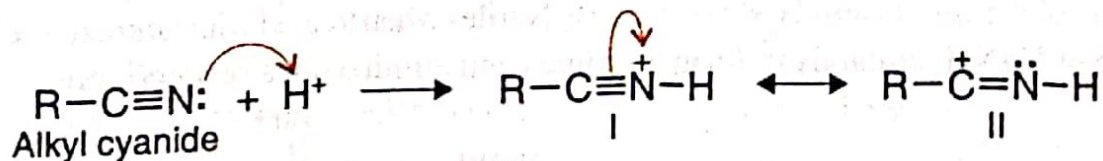
When a mineral acid (say HCl) is used for hydrolysis, the product is a carboxylic acid and ammonia. On the other hand, if an alkali (say NaOH) is used, the hydrolysis results in the formation of sodium salt of the carboxylic acid.



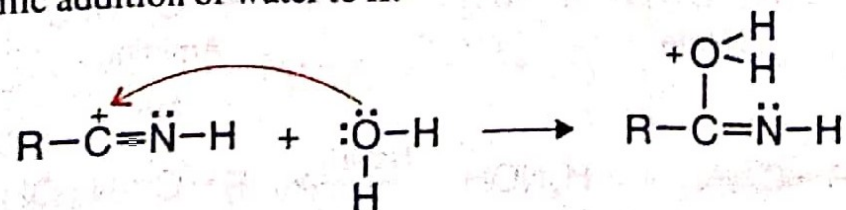
Mechanism of acid hydrolysis of nitriles

MECHANISM OF ACID-CATALYZED HYDROLYSIS. Following steps are involved :

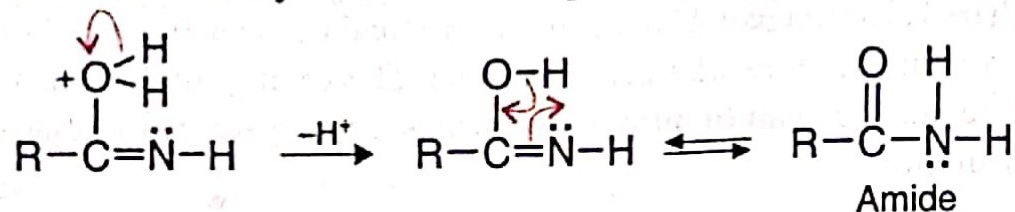
Step 1. Protonation of nitrile.



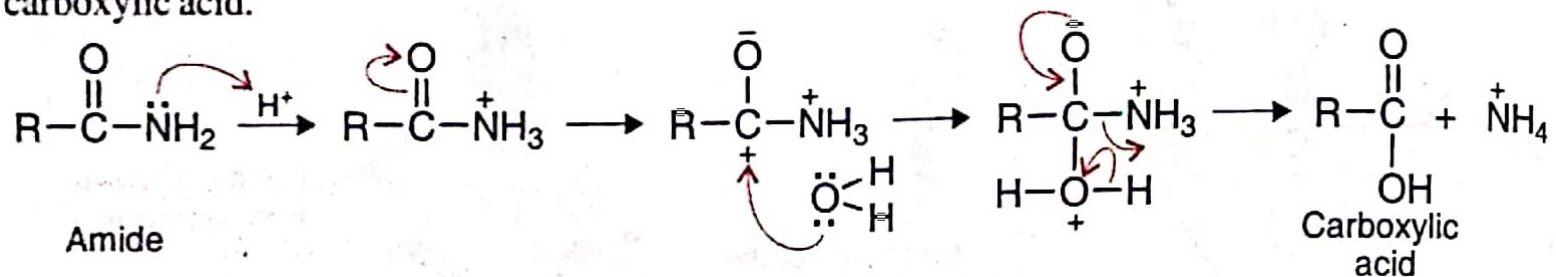
Step 2. Nucleophilic addition of water to II.



Step 3. Proton loss followed by tautomeric arrangement.



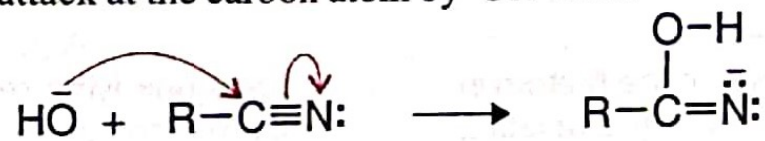
The amide thus produced undergoes the same sequence of steps leading to the formation of carboxylic acid.



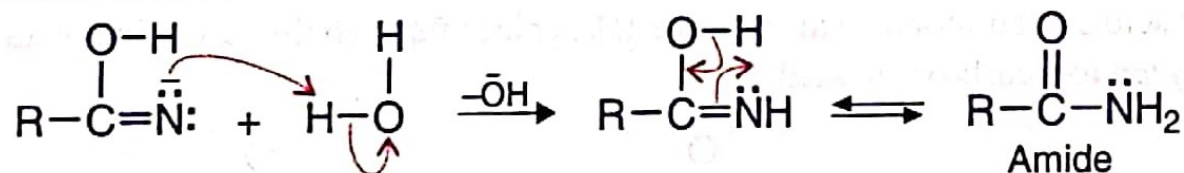
Mechanism of base catalyzed hydrolysis of nitriles

MECHANISM OF BASE-CATALYZED HYDROLYSIS. Following steps are involved :

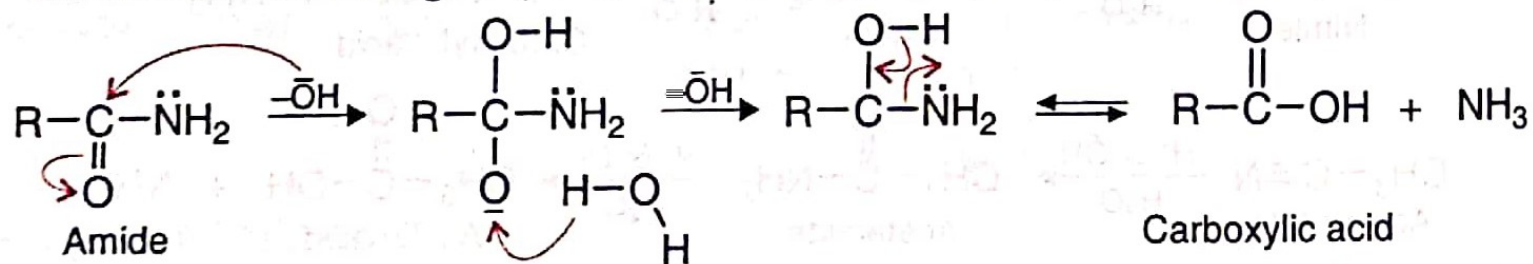
Step 1. Nucleophilic attack at the carbon atom by $\bar{\text{O}}\text{H}$ ions.



Step 2. Nucleophilic N atom takes up a proton from water regenerating $\bar{\text{O}}\text{H}$ ion. The product rearranges to produce stable amide.

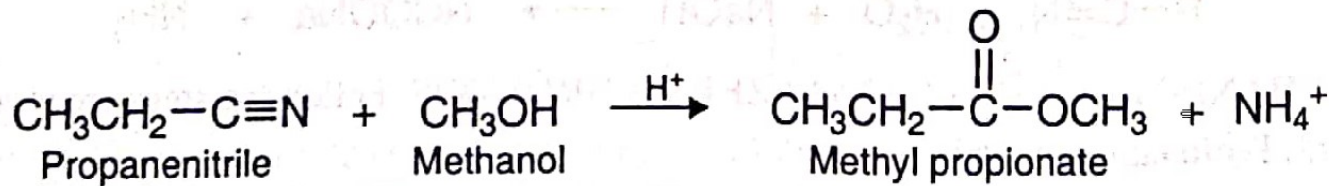
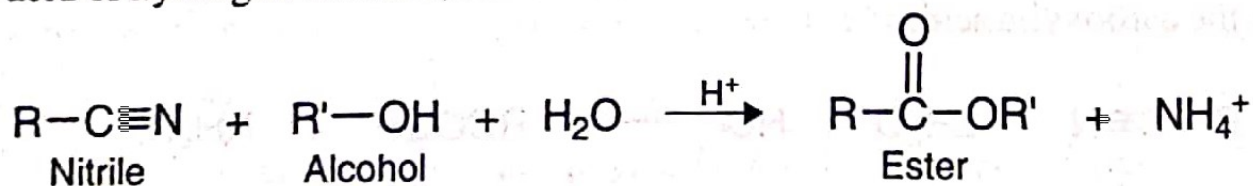


The amide thus formed gets hydrolyzed further to give carboxylic acid and ammonia.



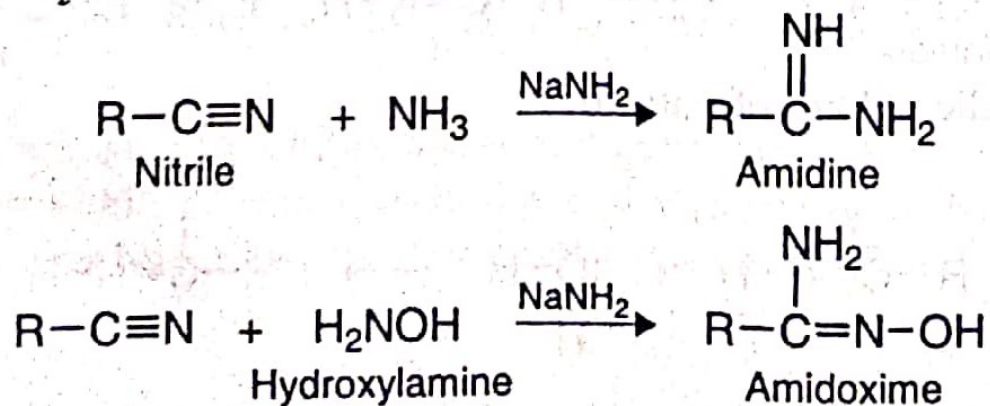
2) Alcoholysis of nitriles

(2) **Alcoholysis.** Nitriles on boiling with excess of alcohol in the presence of concentrated sulfuric acid or hydrogen chloride, form esters.

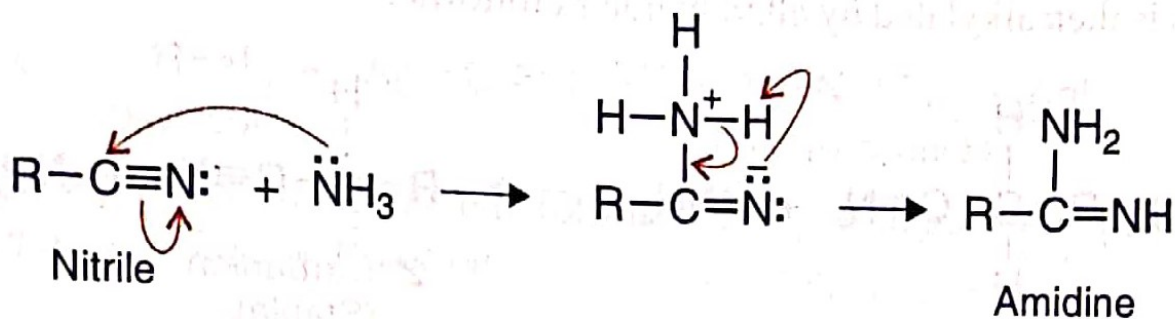


3) Addition of Ammonia and Hydroxylamine

(3) **Addition of Ammonia and Hydroxylamine.** Nitriles when treated with ammonia or hydroxylamine in the presence of NaNH_2 as catalyst, form amidines and amidoximes respectively.

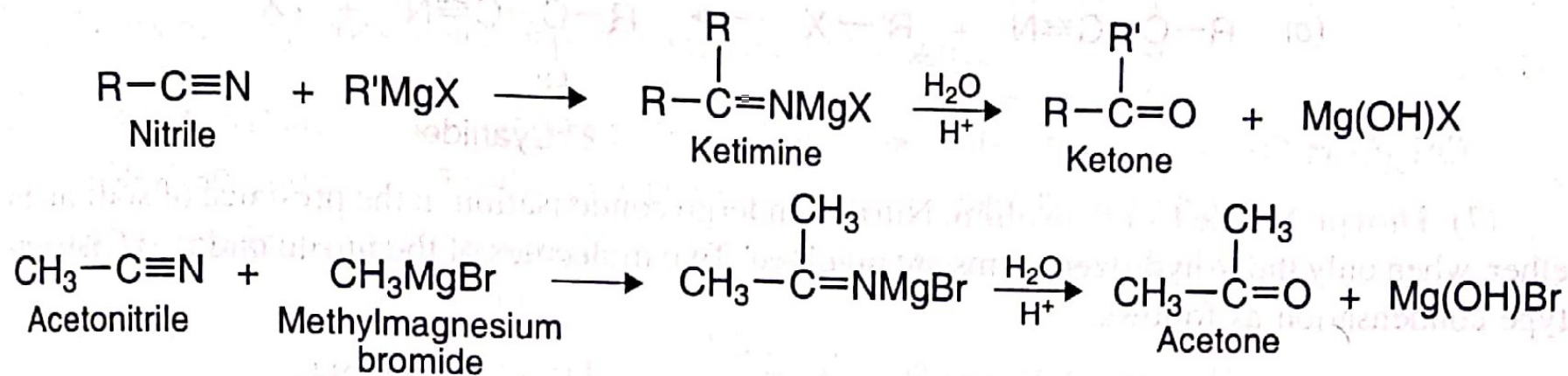


MECHANISM. Both these reagents add by nucleophilic addition mechanism similar to those in case of carboxyl compounds.



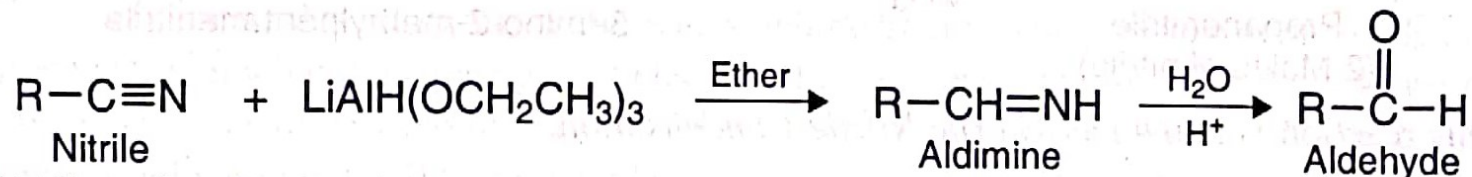
4) Addition of Grignard reagents

(4) **Addition of Grignard reagents.** Nitriles react with Grignard reagents to form ketimines, which on hydrolysis yield ketones.

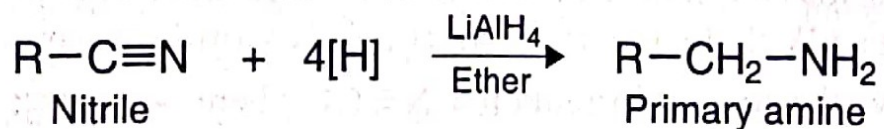


5) Reduction of Nitriles

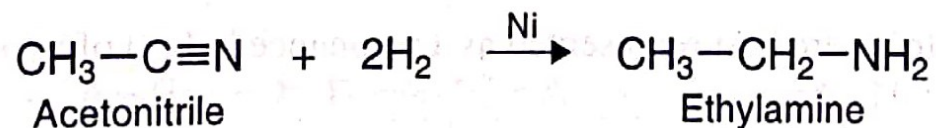
(5) **Reduction.** (a) **Partial reduction.** When nitriles are reduced with lithium triethoxyaluminium hydride, $\text{LiAlH}(\text{OCH}_2\text{CH}_3)_3$, in ether, aldimine is first produced. This on subsequent hydrolysis yields an aldehyde.



(b) **Complete Reduction to primary amines.** On treatment with lithium aluminium hydride, LiAlH_4 , nitriles undergo complete reduction to yield primary amines.

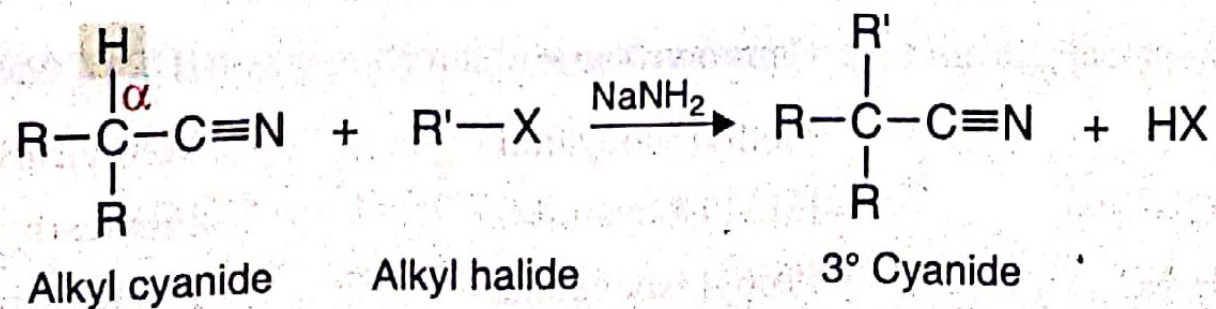
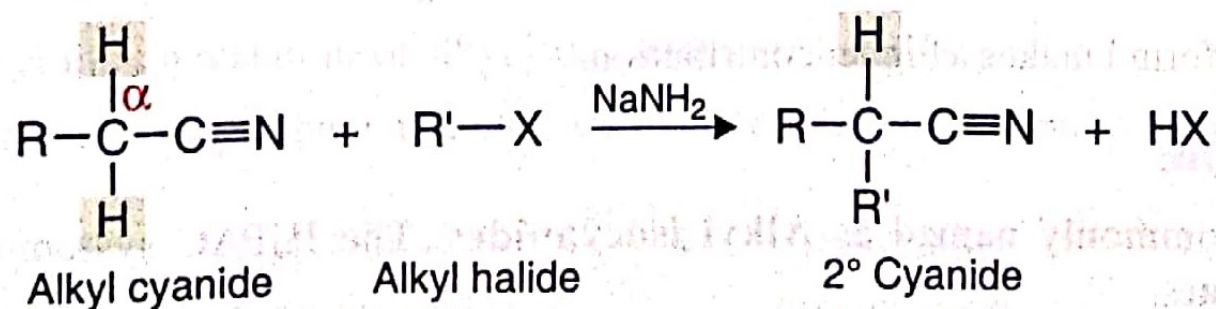


This reduction may also be carried with sodium and ethanol (*Mendius Reaction*), or with hydrogen and metal catalyst (Raney nickel).



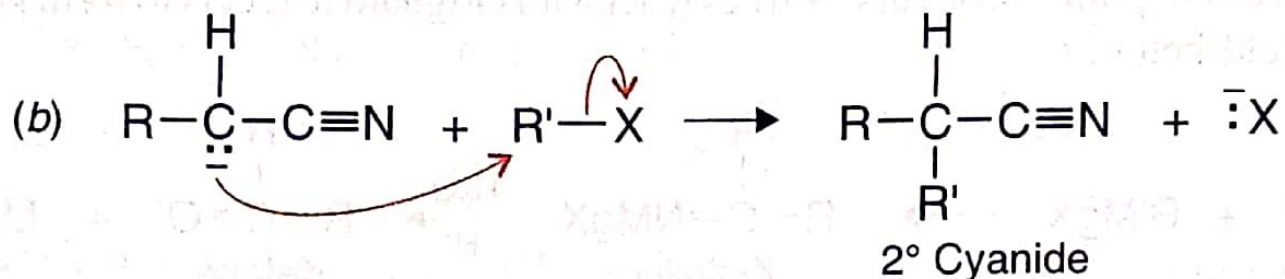
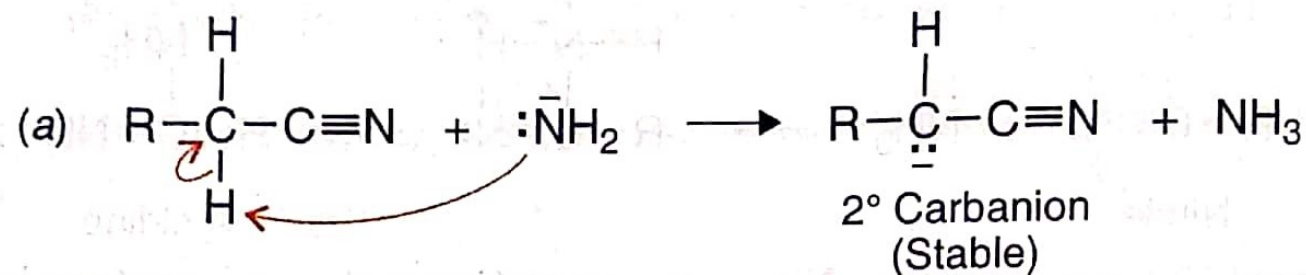
6) Alkylation of nitriles

(6) **Alkylation.** Nitriles having α -hydrogen atoms are alkylated readily when heated with an alkyl halide in the presence of sodium amide (NaNH_2).



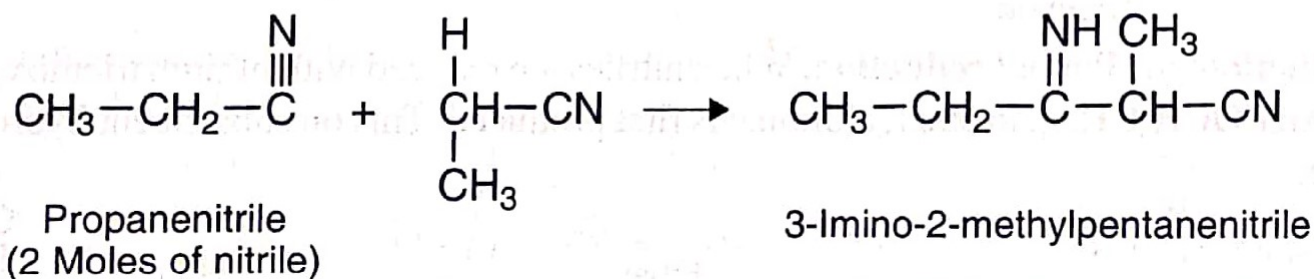
Mechanism is in next page

MECHANISM. The base $:\bar{\text{N}}\text{H}_2$ furnished by sodium amide initiates the reaction producing carbanion, which is then alkylated by alkyl halide as follows :



7) Thorpe Nitrile Condensation

(7) **Thorpe Nitrile Condensation.** Nitriles undergo condensation in the presence of sodium in ether, when only the α -hydrogen atoms are involved. Two molecules of the nitrile undergo Claisen-type condensation as follows



This reaction is known as *Thorpe Nitrile Condensation*.