Aldehydes and Ketones
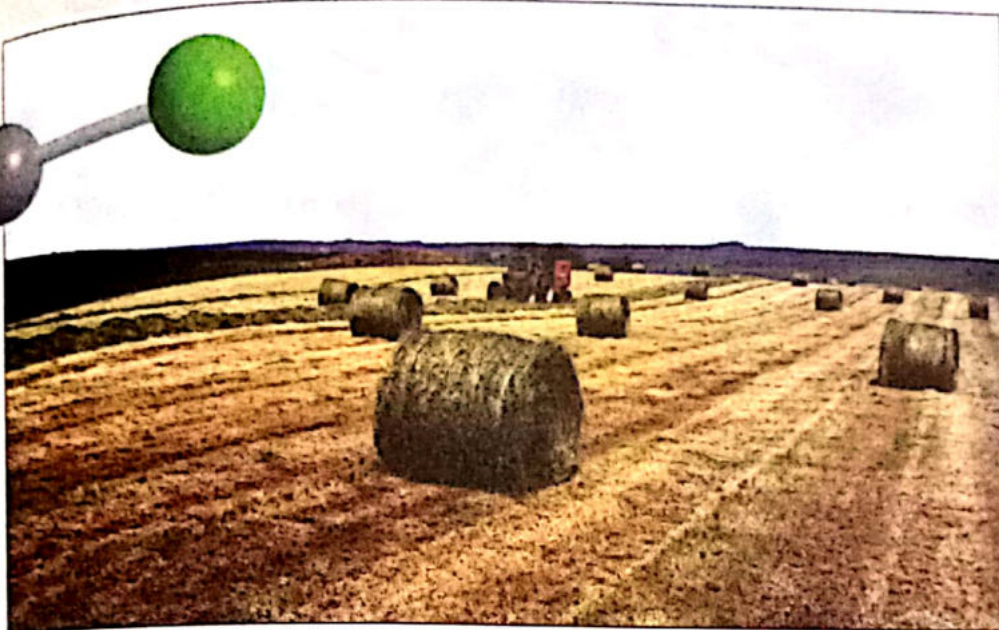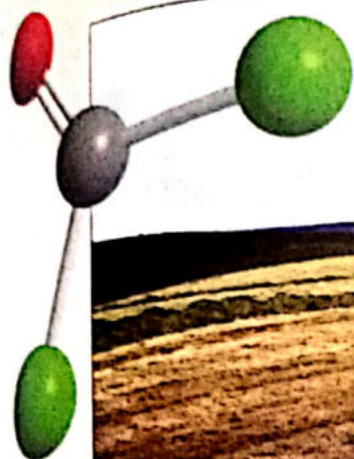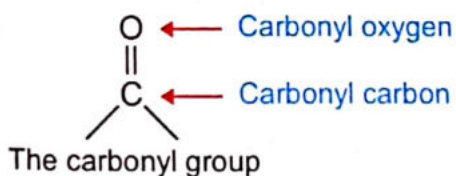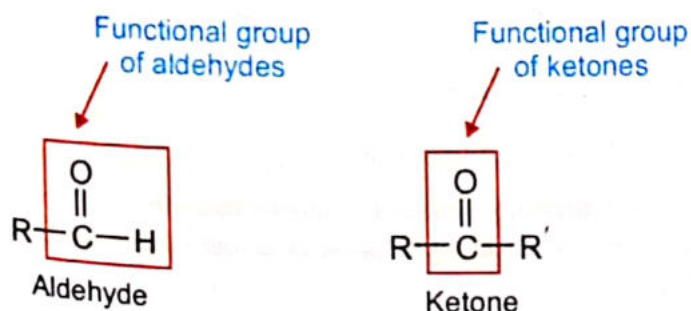
Many compounds with pleasant smells have carbonyl groups. The smell of phosgene and of coumarin are similar to that of newmown hay. While the former is highly toxic, the latter is not.

Both aldehydes and ketones contain a carbon-oxygen double bond (>C=O). This unit is referred to as the **Carbonyl Group**.

$$O \leftarrow \text{Carbonyl oxygen}$$
$$\underset{\text{The carbonyl group}}{C \leftarrow \text{Carbonyl carbon}}$$

Aldehydes and ketones are collectively called **Carbonyl Compounds**. In aldehydes, the carbonyl carbon is bonded to one hydrogen and one alkyl group. Formaldehyde, HCHO, in which the carbonyl carbon is bonded to two hydrogen atoms is an exception. In ketones, the carbonyl carbon is always bonded to two alkyl groups. These alkyl groups may be same or different.

Functional group of aldehydes

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Aldehyde

Functional group of ketones

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

Ketone

The carbonyl group, like the carbon-carbon double bond of alkenes, is composed of one σ and one π bond.
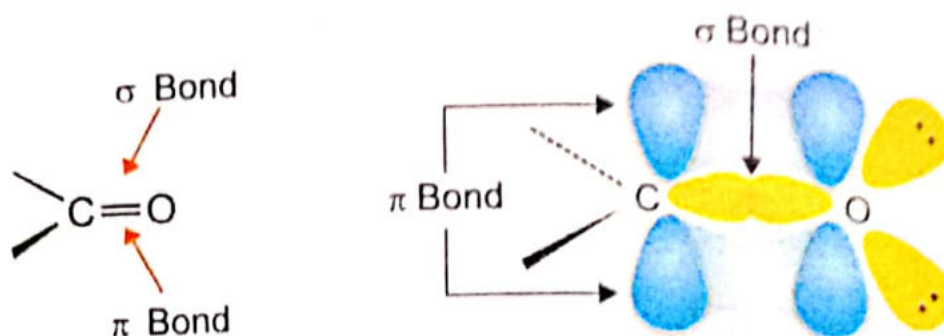
Both the carbon and oxygen are sp^2 hybridized. The σ bond is formed by the overlap of an sp^2 orbital of carbon and an sp^2 orbital of oxygen. The π bond is formed by the overlap of unhybridized p orbitals of the two atoms. The two unshared electron pairs of oxygen occupy the sp^2 hybrid orbitals of oxygen. Because the carbonyl carbon is sp^2 hybridized, the three atoms attached to it lie in the same plane. The bond angles between the attached atoms are approximately 120° (Fig. 19.1).
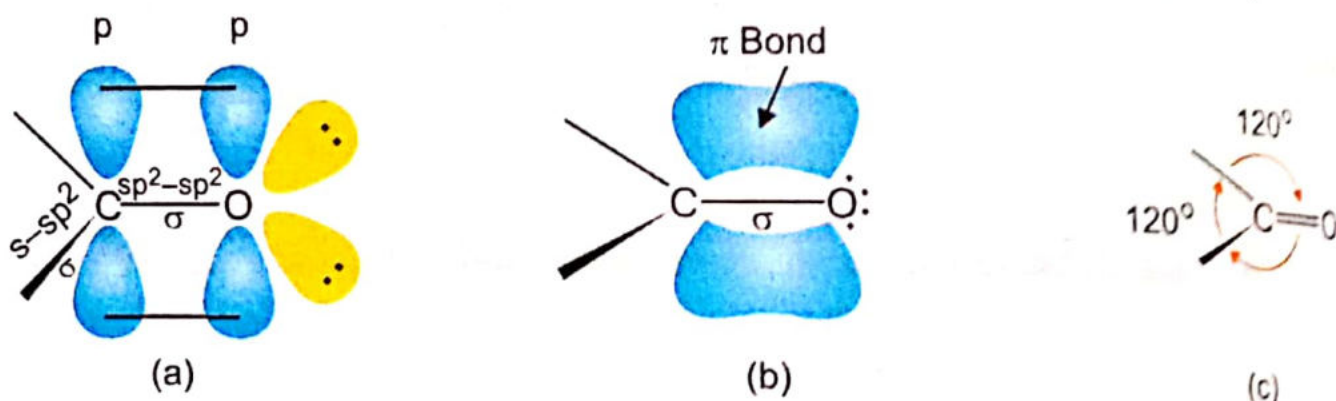

Fig. 19.1. The carbon-oxygen double bond in aldehydes and ketones is composed of a σ bond and a π bond. (a) The σ bond is formed by the overlap of an sp^2 orbital of carbon and an sp^2 orbital of oxygen ; (b) The π bond is formed by the overlap of the unhybridized p orbitals ; (c) Geometry of the carbonyl group.

The electrons in the π bond of the carbonyl group are *not* equally shared. In fact, they are pulled more toward the more electronegative oxygen atom. As a result, the bond is polarized, with the oxygen atom being slightly negative (δ_) and the carbon atom being slightly positive (δ₊). This is often indicated as :
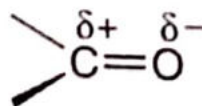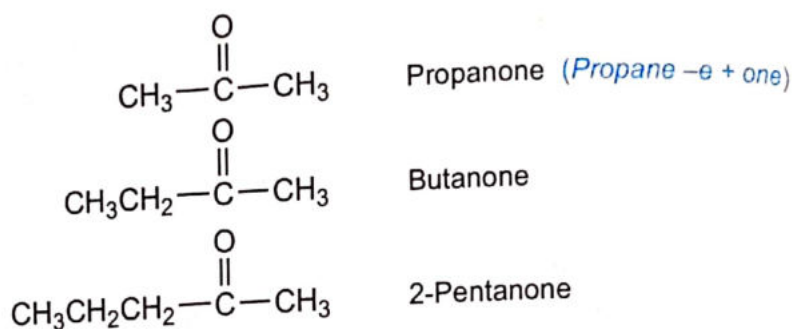

Alternatively, the polar nature of the carbonyl group can also be indicated by the following resonance structures :

NOMENCLATURE OF ALDEHYDES

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Acetone
(*Dimethyl ketone*)

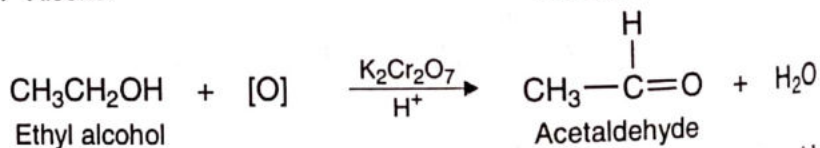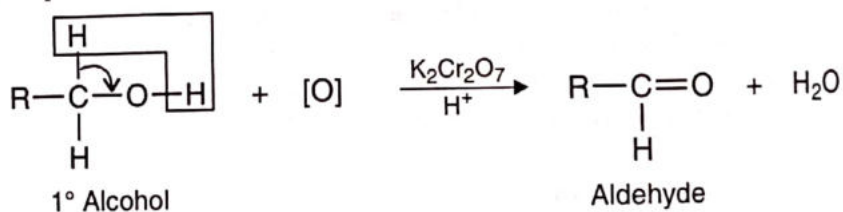$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Ethyl methyl ketone
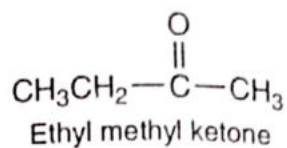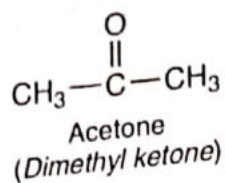
(2) **IUPAC System**. IUPAC names for ketones are obtained by replacing the ending -e of the corresponding alkane with -*one*. The chain is then numbered to give the carbonyl carbon the lowest possible number. This number is then used to designate the position of the carbonyl group. The IUPAC names of some ketones are given below :
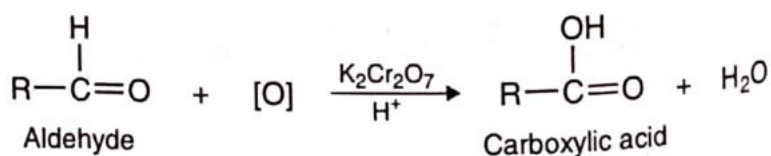
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \qquad \text{Propanone} \;(\textit{Propane} -e + one)$$

$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \qquad \text{Butanone}$$

$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \qquad \text{2-Pentanone}$$

METHODS OF PREPARATION

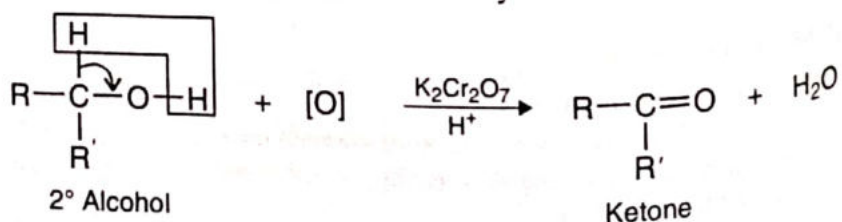Aldehydes and ketones may be prepared by the following methods :

(1) **Oxidation of Alcohols**. Aldehydes and ketones can be prepared by the controlled oxidation of primary and secondary alcohols using an acidified solution of potassium dichromate or permanganate. Primary alcohols produce aldehydes.

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle H}{C}}-O-H \;+\; [O] \quad \xrightarrow[\text{H}^+]{K_2Cr_2O_7} \quad R-\overset{\displaystyle H}{\underset{\displaystyle |}{C}}=O \;+\; H_2O$$

1° Alcohol   Aldehyde

$$CH_3CH_2OH \;+\; [O] \quad \xrightarrow[\text{H}^+]{K_2Cr_2O_7} \quad CH_3-\overset{\displaystyle H}{\underset{\displaystyle |}{C}}=O \;+\; H_2O$$

Ethyl alcohol   Acetaldehyde

The aldehydes formed in the above reaction are very easily oxidized to carboxylic acids if allowed to remain in the reaction mixture.

$$R-\overset{\displaystyle H}{\underset{\displaystyle |}{C}}=O \;+\; [O] \quad \xrightarrow[\text{H}^+]{K_2Cr_2O_7} \quad R-\overset{\displaystyle OH}{\underset{\displaystyle |}{C}}=O \;+\; H_2O$$

Aldehyde   Carboxylic acid

Ketones are prepared by the oxidation of secondary alcohols.

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle R'}{C}}-O-H \;+\; [O] \quad \xrightarrow[\text{H}^+]{K_2Cr_2O_7} \quad R-\overset{\displaystyle |}{\underset{\displaystyle R'}{C}}=O \;+\; H_2O$$

2° Alcohol   Ketone

$$
\underset{\substack{\text{2-Propanol}\\\text{(Isopropyl alcohol)}}}{\overset{\displaystyle \overset{OH}{|}}{CH_3-CH-CH_3}} + [O] \xrightarrow[H^+]{K_2Cr_2O_7} \underset{\text{Acetone}}{CH_3-\overset{\displaystyle \overset{O}{\|}}{C}-CH_3} + H_2O
$$
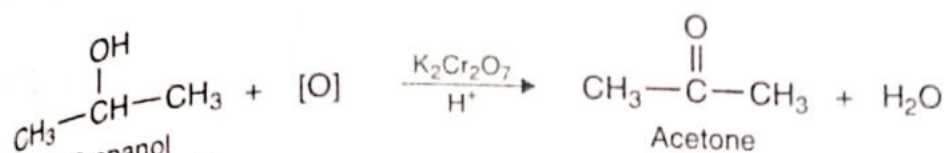
Ketones are not easily oxidized further and can be obtained in high yield by this method. Alternatively, ketones can be obtained from secondary alcohols by **Oppenauer Oxidation**. In this process, the appropriate secondary alcohol is refluxed with excess of acetone in the presence of aluminium tertiary-butoxide, AlOC(CH$_3$)$_3$, catalyst.

$$
\underset{\substack{\text{2° Alcohol}}}{\overset{R}{\underset{R'}{\Large{>}}}CHOH} + \underset{\text{Acetone}}{\overset{CH_3}{\underset{CH_3}{\Large{>}}}C=O} \xrightarrow[\Delta]{AlOC(CH_3)_3} \underset{\text{Ketone}}{\overset{R}{\underset{R'}{\Large{>}}}C=O} + \underset{\text{2-Propanol}}{\overset{CH_3}{\underset{CH_3}{\Large{>}}}CHOH}
$$
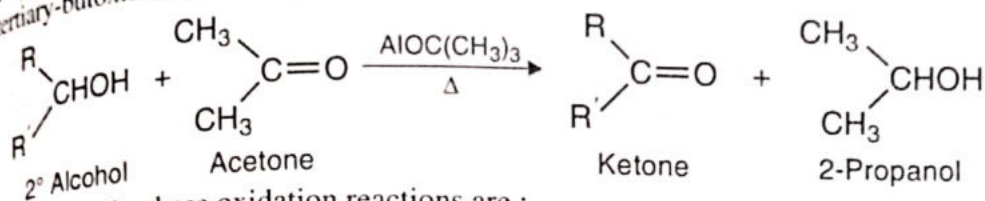
Other agents used for these oxidation reactions are :

(a) Alkaline potassium permanganate : KMnO$_4$/$\overline{O}$H

(b) Chromic acid : H$_2$Cr$_2$O$_7$
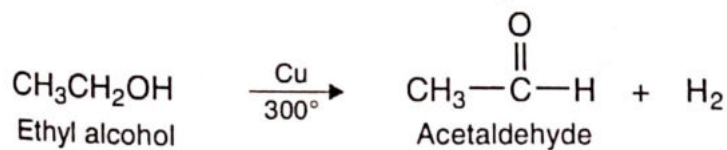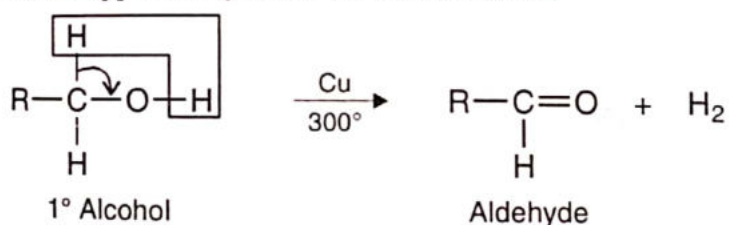
This reagent is prepared *in situ* from CrO$_3$ or Na$_2$Cr$_2$O$_7$ with dilute sulfuric acid.

(c) Pyridine chlorochromate (PCC), C$_5$H$_6$NCrO$_3$Cl, in dichloromethane solvent.
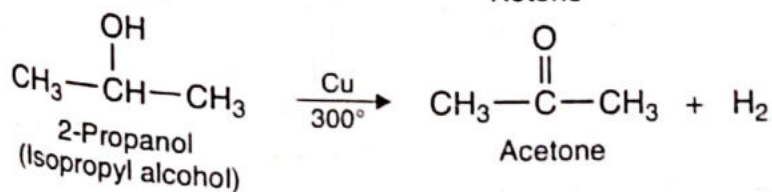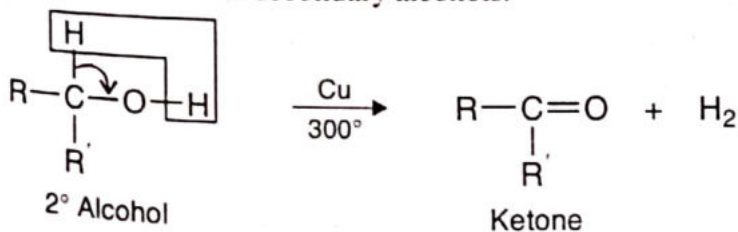
PCC in dichloromethane is a special oxidizing agent. It is used to convert primary alcohols to aldehydes. This reagent does not oxidize aldehydes to carboxylic acids.

$$
\underset{\text{1-Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[CH_2Cl_2]{PCC} \underset{\text{Butanal}}{CH_3CH_2CH_2-\overset{\displaystyle \overset{O}{\|}}{C}-H}
$$
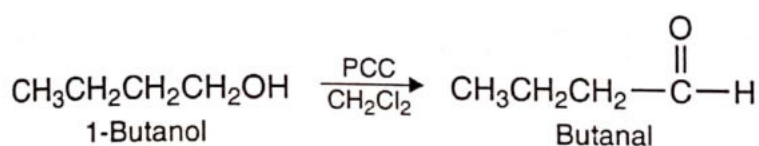
2. **Catalytic Dehydrogenation of Alcohols**. Aldehydes may be prepared by passing the vapors of primary alcohols over a copper catalyst heated to about 300°C.

$$
\underset{\text{1° Alcohol}}{\overset{\displaystyle H}{\underset{\displaystyle H}{R-\overset{|}{\underset{|}{C}}\!\!-O\!-\!H}}} \xrightarrow[300°]{Cu} \underset{\text{Aldehyde}}{\overset{\displaystyle }{\underset{\displaystyle H}{R-\overset{|}{C}=O}}} + H_2
$$

$$
\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°]{Cu} \underset{\text{Acetaldehyde}}{CH_3-\overset{\displaystyle \overset{O}{\|}}{C}-H} + H_2
$$

Similarly ketones are produced from secondary alcohols.

$$
\underset{\text{2° Alcohol}}{\overset{\displaystyle H}{\underset{\displaystyle R'}{R-\overset{|}{\underset{|}{C}}\!\!-O\!-\!H}}} \xrightarrow[300°]{Cu} \underset{\text{Ketone}}{\overset{\displaystyle }{\underset{\displaystyle R'}{R-\overset{|}{C}=O}}} + H_2
$$

$$
\underset{\substack{\text{2-Propanol}\\\text{(Isopropyl alcohol)}}}{\overset{\displaystyle \overset{OH}{|}}{CH_3-CH-CH_3}} \xrightarrow[300°]{Cu} \underset{\text{Acetone}}{CH_3-\overset{\displaystyle \overset{O}{\|}}{C}-CH_3} + H_2
$$

(3) **Oxidation of Alkenes (Ozonolysis)** Aldehydes and ketones can be obtained by ozonolysis of alkenes. This involves the treatment of the alkenes with ozone to give ozonides. The ozonides are not isolated because they are often explosive in dry state. They are decomposed with $Zn+H_2O$ to give aldehydes and ketones.
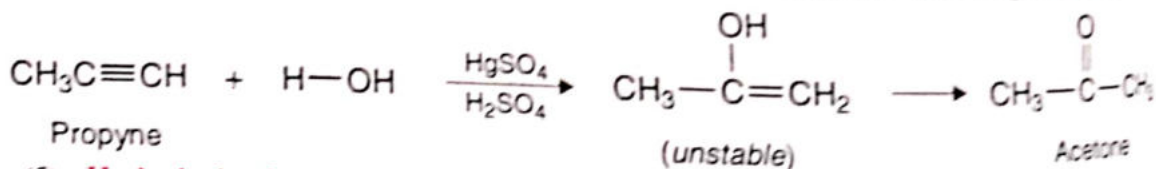

2-Pentene → Propanal + Acetaldehyde
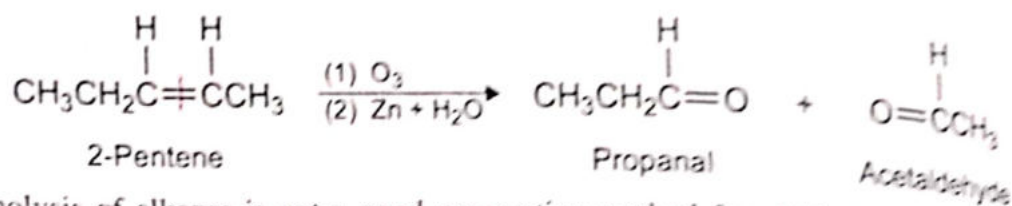
Ozonolysis of alkenes is not a good preparative method for aldehydes and ketones. This is because a mixture of carbonyl compounds is often produced. However, if the starting alkene is symmetrical, only one carbonyl compound will be obtained. For example,

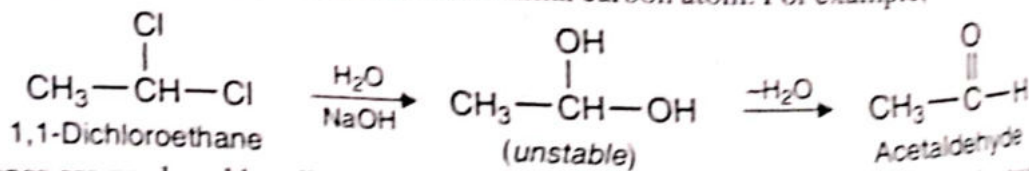2-Butene → Acetaldehyde + Acetaldehyde
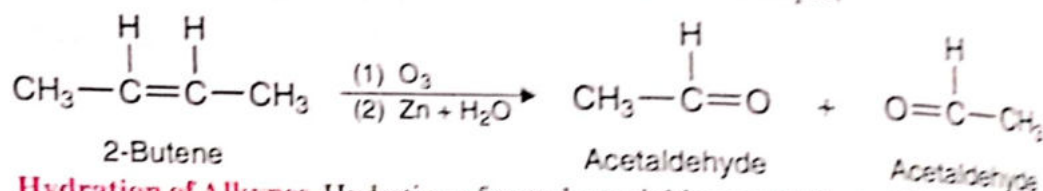
(4) **Hydration of Alkynes.** Hydration of acetylene yields acetaldehyde. Water adds to acetylene in the presence of mercuric sulfate and sulfuric acid to form an unstable enol-intermediate. This intermediate rearranges to give acetaldehyde.

$HC\equiv CH$ + $H-OH$ $\xrightarrow[H_2SO_4]{HgSO_4}$ (unstable) → Acetaldehyde
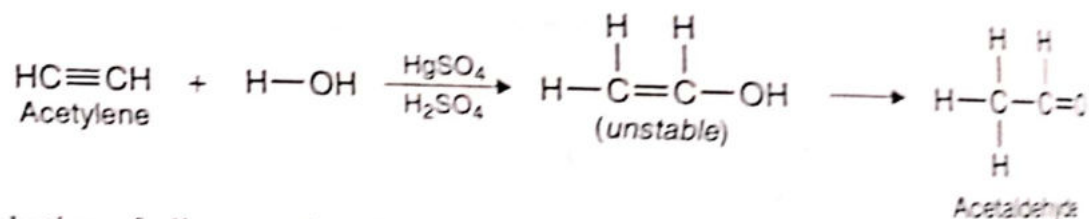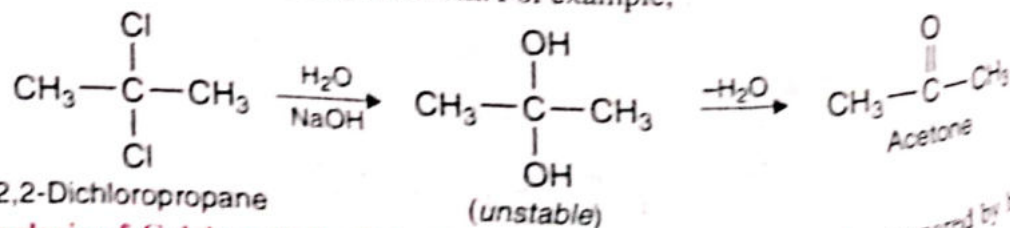
Hydration of alkynes, other than acetylene, gives ketones. Water adds according to the *Markovnikov rule* to give an unstable enol-intermediate. This intermediate rearranges to form ketone.

$CH_3C\equiv CH$ + $H-OH$ $\xrightarrow[H_2SO_4]{HgSO_4}$ $CH_3-\overset{OH}{C}=CH_2$ → $CH_3-\overset{O}{C}-CH_3$
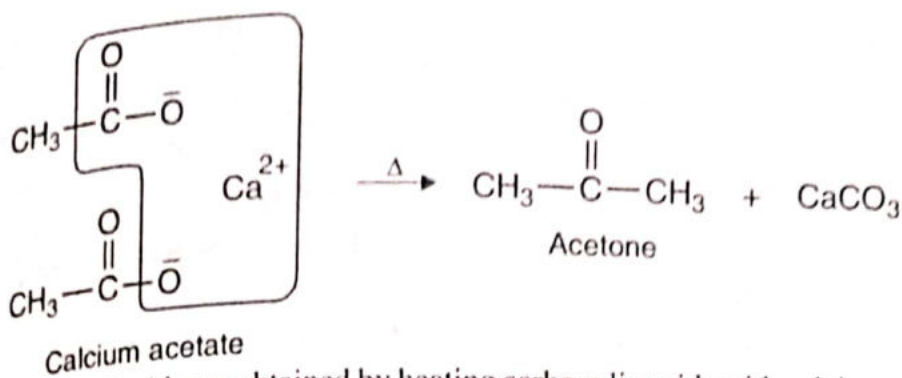Propyne (unstable) Acetone

(5) **Hydrolysis of gem-Dihalides.** A *gem*-dihalide is a compound that has two halogen atoms attached to the same carbon. Aldehydes are prepared by alkaline hydrolysis of those *gem*-dihalides in which two halogen atoms are attached to the terminal carbon atom. For example,

$CH_3-\overset{Cl}{\underset{Cl}{CH}}$ $\xrightarrow[NaOH]{H_2O}$ $CH_3-\overset{OH}{CH}-OH$ $\xrightarrow{-H_2O}$ $CH_3-\overset{O}{C}-H$
1,1-Dichloroethane (unstable) Acetaldehyde

Ketones are produced by alkaline hydrolysis of those *gem*-dihalides in which the two halogen atoms are attached to a non-terminal carbon atom. For example,

$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3$ $\xrightarrow[NaOH]{H_2O}$ $CH_3-\overset{OH}{\underset{OH}{C}}-CH_3$ $\xrightarrow{-H_2O}$ $CH_3-\overset{O}{C}-CH_3$
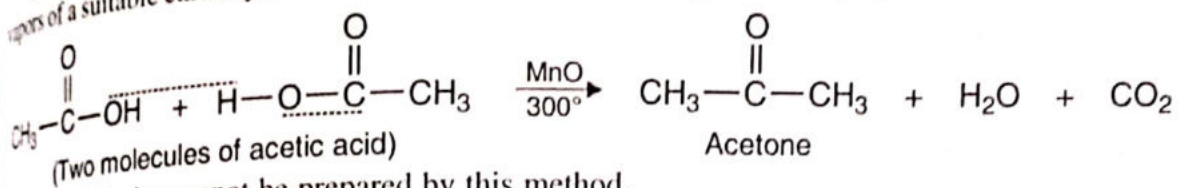2,2-Dichloropropane (unstable) Acetone

(6) **Pyrolysis of Calcium Salts of Acids.** Symmetrical ketones may be prepared by heating calcium salts of acids at 400°C. For example,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{O} \Big\rangle Ca^{2+} \overset{\Delta}{\longrightarrow} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CaCO_3$$
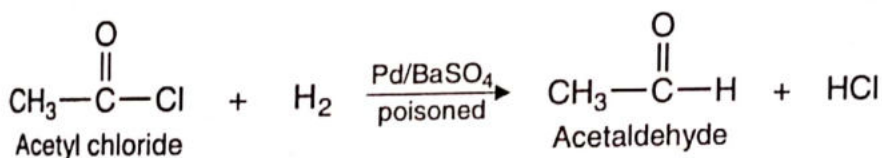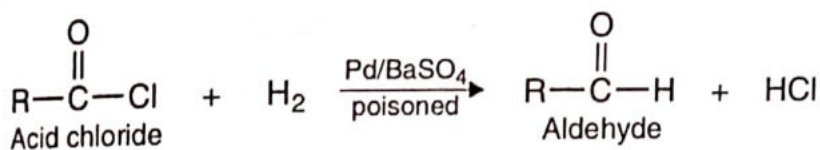
Calcium acetate

Acetone

The calcium salts of acids are obtained by heating carboxylic acids with calcium oxide.
Aldehydes cannot be prepared by this method.

(7) **Catalytic Decomposition of Acids.** Symmetrical ketones can also be prepared by passing the vapors of a suitable carboxylic acid over heated MnO or ThO_2. For example,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[300°]{MnO} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O + CO_2$$

(Two molecules of acetic acid)

Acetone

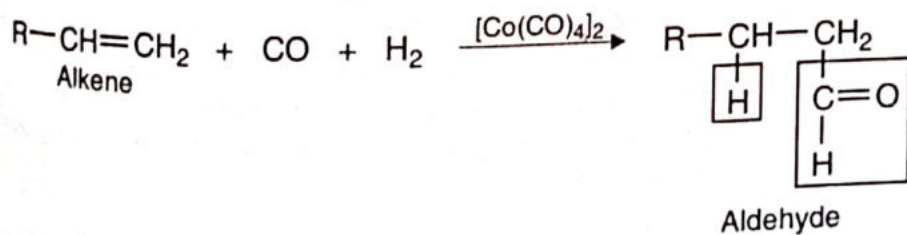Aldehydes cannot be prepared by this method.

(8) **Reduction of Acid Chlorides.** Aldehydes can be prepared by the hydrogenation of acid chlorides in the presence of palladium supported over barium sulfate.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow[poisoned]{Pd/BaSO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCl$$

Acid chloride

Aldehyde

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow[poisoned]{Pd/BaSO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCl$$

Acetyl chloride

Acetaldehyde

Normally the aldehyde would be further reduced to a primary alcohol. In this case the catalyst Pd/BaSO₄ is 'poisoned' with sulfur to deactivate it partially and prevent the reduction of the aldehyde to an alcohol. This reaction is called **Rosenmund Reduction**.
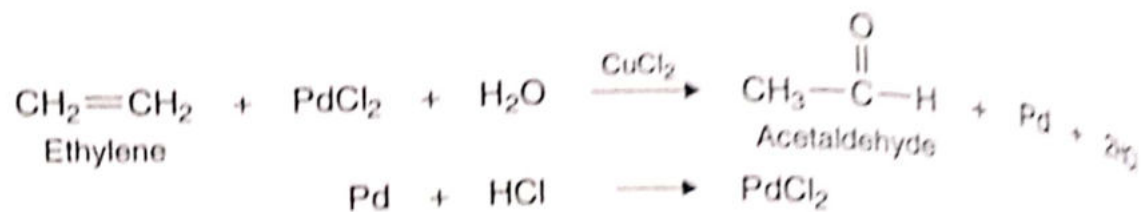
Ketones cannot be prepared by this method.

(9) **Oxo Process.** The Oxo process is an industrially important method for producing aldehydes. It involves the treatment of an alkene with carbon monoxide and hydrogen in the presence of cobalt carbonyl catalyst. High temperatures and pressures are used.

$$R-CH=CH_2 + CO + H_2 \xrightarrow{[Co(CO)_4]_2} R-CH-CH_2$$
$$\overset{|}{H} \quad \overset{|}{\underset{|}{\overset{\displaystyle C=O}{H}}}$$

Aldehyde

The net reaction appears to be an *anti*-Markovnikov addition of formaldehyde to the alkene.
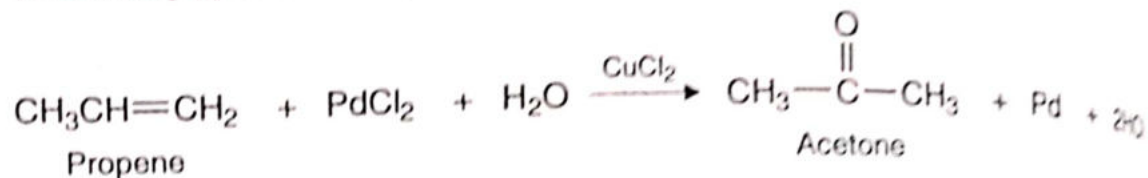
Ketones cannot be prepared by this method.

(10) **Wacker Process.** Both aldehydes and ketones can be prepared by this method. This process involves the treatment of an alkene with an acidified aqueous solution of palladium chloride and cupric chloride. For example,

$$CH_2=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3-\overset{\overset{O}{\|}}{C}-H + Pd + 2HCl$$
Ethylene   Acetaldehyde

$$Pd + HCl \longrightarrow PdCl_2$$

The cupric chloride promotes the second reaction, enhancing the reconversion of the palladium back into palladium chloride.

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

Acetone is prepared similarly from propene.

$$CH_3CH=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + Pd + 2HCl$$
Propene   Acetone

PHYSICAL PROPERTIES

(1) Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C. Other lower aldehydes and ketones are colorless liquids.

(2) Lower aldehydes possess rather unpleasant, pungent smells whereas the ketones have pleasant, sweet odors.

(3) Density of aldehydes and ketones is less than that of water.

Table 19.1	BOILING POINTS OF SOME ALDEHYDES AND KETONES	
Name	Formula	bp°C
ALDEHYDES		
Formaldehyde	HCHO	-21
Acetaldehyde	CH_3CHO	20
Propionaldehyde	CH_3CH_2CHO	49
n-Butyraldehyde	$CH_3CH_2CH_2CHO$	76
KETONES		
Acetone	CH_3COCH_3	56
Butanone	$CH_3COCH_2CH_3$	80
2-Pentanone	$CH_3COCH_2CH_2CH_3$	102
3-Pentanone	$CH_3CH_2COCH_2CH_3$	101

(4) **Boiling Points of Aldehydes and Ketones** (Table 19.1). Because of the polarity of the carbonyl group, aldehydes and ketones are polar compounds. The polar character of the molecules gives rise to intermolecular attractions. These attractive forces, called **dipole-dipole attractions**, occur between the partial negative charge on the carbonyl oxygen of one molecule and the partial positive charge on the carbonyl carbon of another molecule.
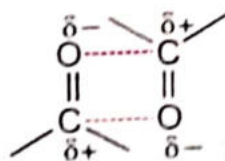
Dipole-dipole attractions among carbonyl compounds

Dipole-dipole attractions, although important, are not as strong as interactions due to hydrogen bonding. As a result, the boiling points of aldehydes and ketones are higher than those of nonpolar

...but lower than those of alcohols, of comparable molecular weights. For example,

CH₃CH₃
Ethane
(mol wt. 30, bp –89°C)

$$H-\overset{\overset{\displaystyle O}{\parallel}}{C}-H$$
Formaldehyde
(mol wt. 30; bp –21°C)

CH₃OH
Methyl alcohol
(mol wt. 32; bp 64.5°C)

$$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3CHCH_3}{|}}$$
Isobutane
(mol wt. 58; bp –12°C)

$$CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}CH_3$$
Acetone
(mol wt. 58; bp 56°C)

$$\overset{\displaystyle OH}{\underset{\displaystyle CH_3CHCH_3}{|}}$$
Isopropyl alcohol
(mol wt. 60; bp 82.5°C)
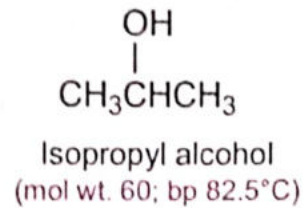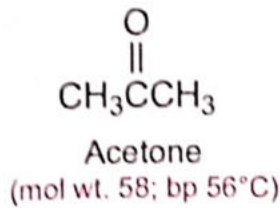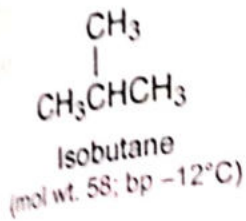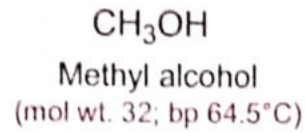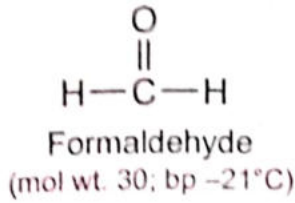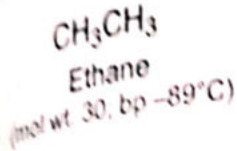
Solubility in Water. The lower aldehydes and ketones are soluble in water because aldehydes and ketones form hydrogen bonds with water, even though they are incapable of intermolecular hydrogen bonding with themselves.

Intermolecular hydrogen bonding between water and aldehydes

Intermolecular hydrogen bonding between water and ketones
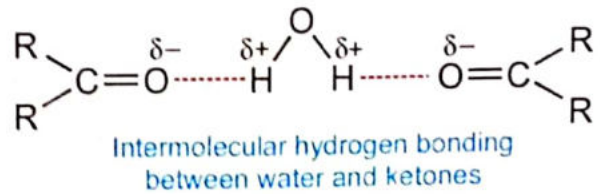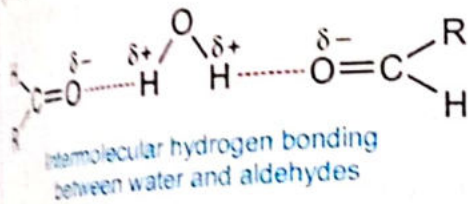
As the hydrocarbon portion of the molecule increases, the solubility in water decreases rapidly. Aldehydes and ketones with more than six carbons are essentially insoluble in water. However, the higher as well as the lower aldehydes and ketones are soluble in organic solvents such as benzene, ether and carbon tetrachloride.
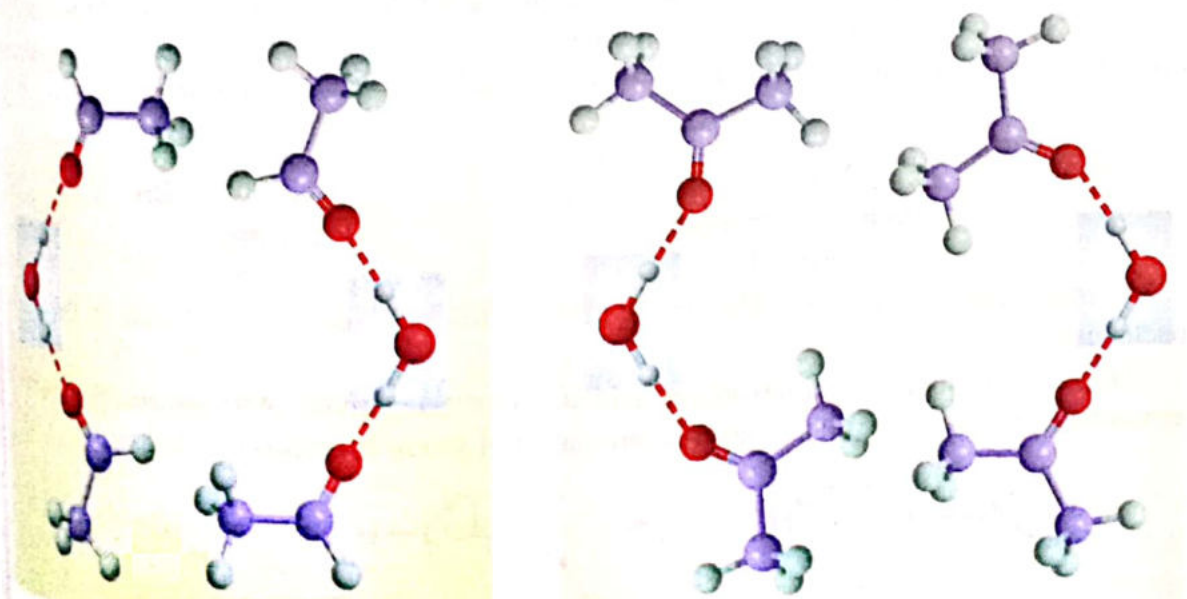
CHEMICAL PROPERTIES

Nucleophilic Addition Reactions. The carbonyl group of aldehydes and ketones is a highly p̶
group. It may be represented as :

$$>C\overset{\curvearrowright}{=}O \longleftrightarrow >\overset{+}{C}-\overset{-}{O} \equiv >\overset{\delta+}{C}=\overset{\delta-}{O}$$

The positively charged carbon is readily attacked by electron-rich nucleophiles. The nega̶
charged oxygen is attacked by electron-deficient electrophiles.

$$\overset{\delta-}{:O:} \longleftarrow \text{Nucleophilic oxygen reacts with acids and electrophiles}$$

$$\overset{\delta+}{C} \longleftarrow \text{Electrophilic carbon reacts with bases and nucleophiles}$$

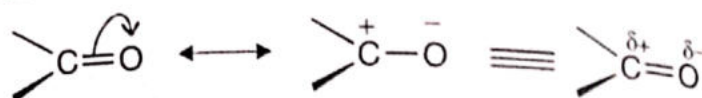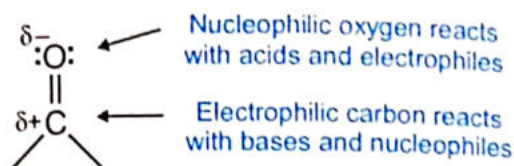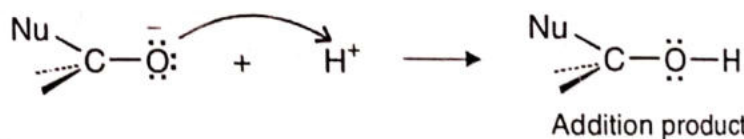Aldehydes and ketones undergo nucleophilic addition reactions by the following ge̶
mechanism.

Step 1. The nucleophile (Nu:⁻) attacks the positively charged carbonyl carbon to form a ̶
bond. As the new bond is formed, π-bond between the carbon and oxygen is broken. The electron̶
goes to oxygen, which acquires a negative charge.

$$Nu:^- + \underset{\delta+}{>}C\overset{\curvearrowright}{=}\underset{\cdot\cdot\delta-}{O:} \longrightarrow Nu\underset{\cdots}{>}C-\overset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^-$$

Step 2. The electrophile (*e.g.*, H⁺) attacks the negatively charged oxygen to form the add̶
product.

$$Nu\underset{\cdots}{>}C-\overset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^- + H^+ \longrightarrow Nu\underset{\cdots}{>}C-\overset{\cdot\cdot}{O}-H$$

Addition product

The nucleophilic addition reactions of carbonyl compounds may be catalyzed by acids or b̶

Base-catalyzed addition. Bases convert a weak neutral nucleophile to a strong one by remo̶
a proton. The strong nucleophile then adds to the carbonyl group as shown above.

$$Nu\overset{\curvearrowleft}{-}H + :B^- \longrightarrow Nu:^- + BH$$

Neutral nucleophile	Nucleophile
(*weak*)	(*strong*)
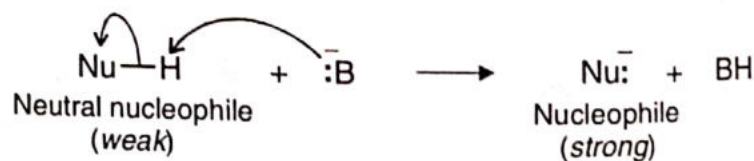
Acid-catalyzed addition. The acid-catalyzed nucleophilic addition occurs by the follo̶
mechanism :

Step 1. The hydrogen ion from the acid attacks the negatively charged carbonyl oxygen to̶
protonated carbonyl group. The protonated carbonyl group is resonance stabilized.

$$>\overset{\delta+}{C}=\overset{\delta-}{\underset{\cdot\cdot}{O}}: + H^+ \longrightarrow >C\overset{\curvearrowright}{=}\overset{+}{\underset{\cdot\cdot}{O}}-H \longleftrightarrow >\overset{+}{C}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$$

Protonated carbonyl group
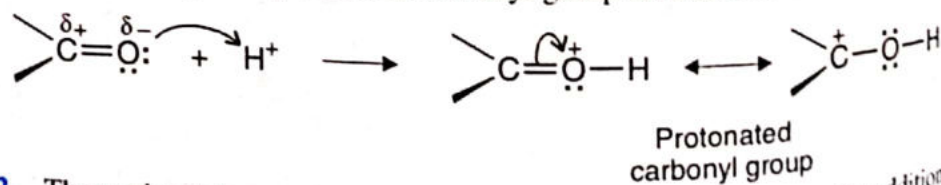
Step 2. The nucleophile attacks the protonated carbonyl group to form the addition pr̶

$$>\overset{+}{C}-\overset{\cdot\cdot}{O}-H + Nu:^- \longrightarrow Nu\underset{\cdots}{>}C-\overset{\cdot\cdot}{O}-H$$
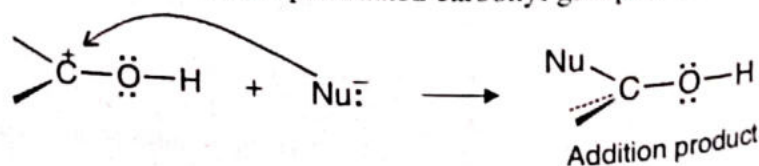
Addition product

Notice that the addition product is the same whether the reaction is acid-catalyzed or base-catalyzed. The nucleophile always adds to the carbonyl carbon and the proton (electrophile), to the oxygen. Generally ketones are less reactive than aldehydes in nucleophilic addition reactions.

Acidity of α-Hydrogens. A carbon atom next to the carbonyl group is called an α-carbon. A hydrogen attached to an α-carbon is referred to as an α-hydrogen. The α-hydrogens of aldehydes and ketones are acidic in nature. The acidity is due to the fact that the anion, which results from the removal of an α-hydrogen by a base B:⁻, is stabilized by resonance. The resonance-stabilized anion is called **Enolate Ion.**

Removal of H
by base

Resonance-stabilized
enolate ion
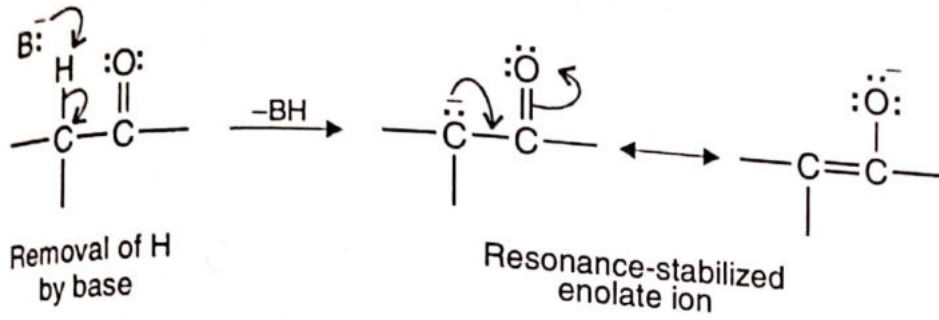
The α-carbon of the enolate ion is negatively charged. It can act as a nucleophile. The formation of the enolate ion followed by its addition to a carbonyl group is the process involved in all the condensation reactions of aldehydes and ketones.
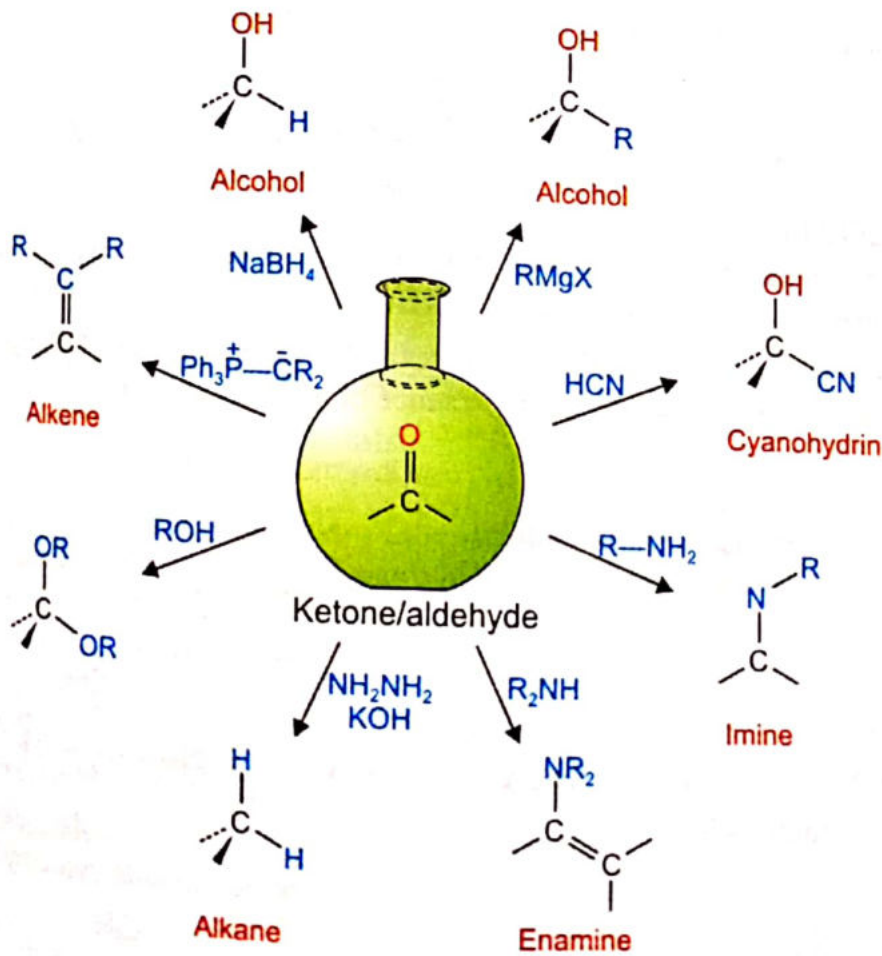
Important reactions of Carbonyl compounds

Some of the important reactions of aldehydes and ketones are described below :

ADDITION REACTIONS

Addition of Sodium Bisulfi...

$$\underset{}{-\overset{\displaystyle O}{\overset{\|}{C}}-} \ + \ NaHSO_3 \ \longrightarrow \ -\overset{\displaystyle OH}{\underset{\underset{SO_3Na}{|}}{\overset{|}{C}}}-$$

Bisulphite
addition compound

$$\underset{Acetaldehyde}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H} \ + \ NaHSO_3 \ \longrightarrow \ CH_3-\overset{\displaystyle OH}{\underset{\underset{SO_3Na}{|}}{\overset{|}{C}}}-H$$
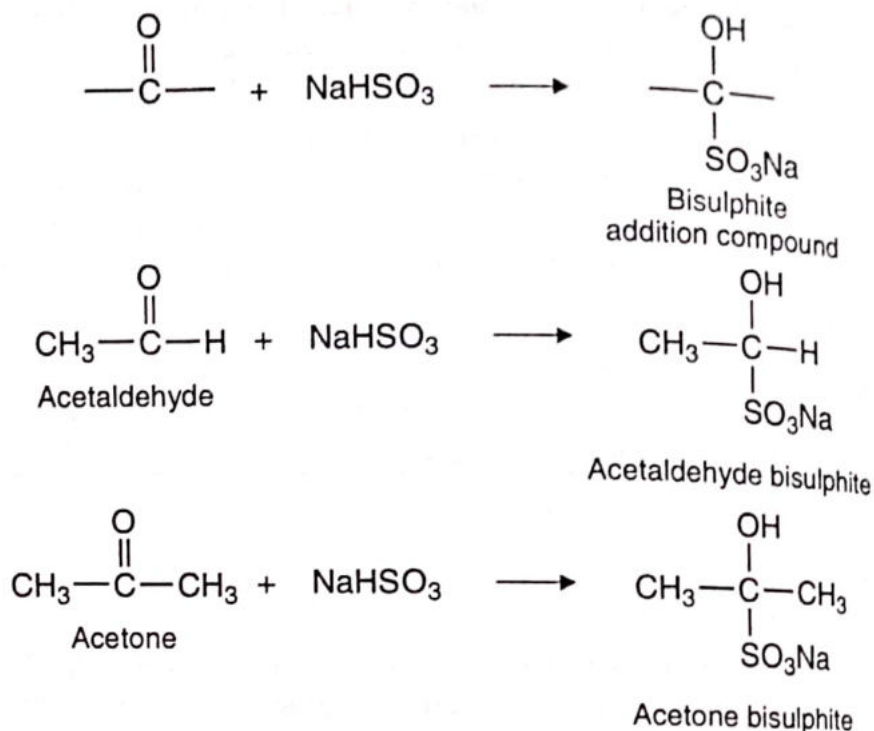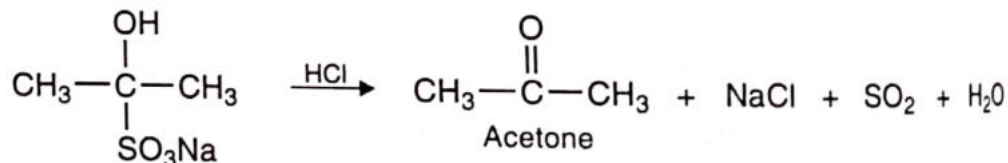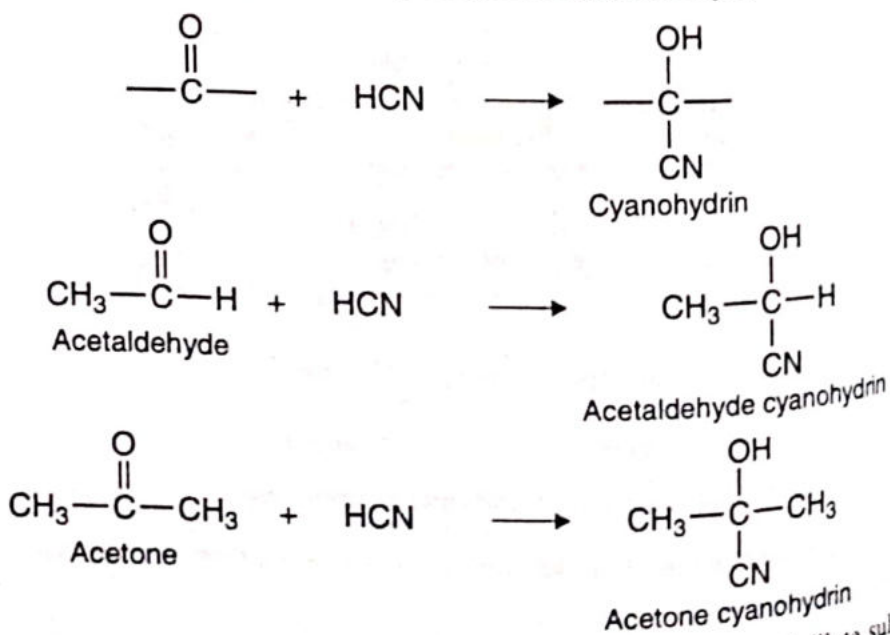
Acetaldehyde bisulphite

$$\underset{Acetone}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \ + \ NaHSO_3 \ \longrightarrow \ CH_3-\overset{\displaystyle OH}{\underset{\underset{SO_3Na}{|}}{\overset{|}{C}}}-CH_3$$

Acetone bisulphite

The bisulfite addition compounds can be decomposed with dilute acids or bases to rege
the carbonyl compound. For example,

$$CH_3-\overset{\displaystyle OH}{\underset{\underset{SO_3Na}{|}}{\overset{|}{C}}}-CH_3 \ \xrightarrow{HCl} \ \underset{Acetone}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \ + \ NaCl \ + \ SO_2 \ + \ H_2O$$

Therefore, the formation and decomposition of bisulfite addition compounds is used
purification and separation of carbonyl compounds from mixtures.

(2) **Addition of Hydrogen Cyanide**. Aldehydes and ketones react with hydrogen cyanide
Cyanohydrins. The reaction is carried in the presence of a basic catalyst.

$$\underset{}{-\overset{\displaystyle O}{\overset{\|}{C}}-} \ + \ HCN \ \longrightarrow \ -\overset{\displaystyle OH}{\underset{\underset{CN}{|}}{\overset{|}{C}}}-$$

Cyanohydrin

$$\underset{Acetaldehyde}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H} \ + \ HCN \ \longrightarrow \ CH_3-\overset{\displaystyle OH}{\underset{\underset{CN}{|}}{\overset{|}{C}}}-H$$

Acetaldehyde cyanohydrin

$$\underset{Acetone}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \ + \ HCN \ \longrightarrow \ CH_3-\overset{\displaystyle OH}{\underset{\underset{CN}{|}}{\overset{|}{C}}}-CH_3$$
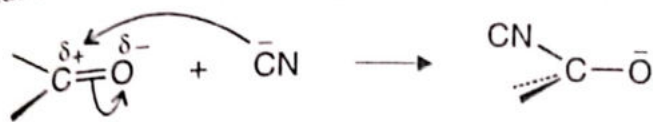
Acetone cyanohydrin

HCN is a very poisonous gas. It is produced *in situ* by the action of dilute sulfuric
potassium cyanide.

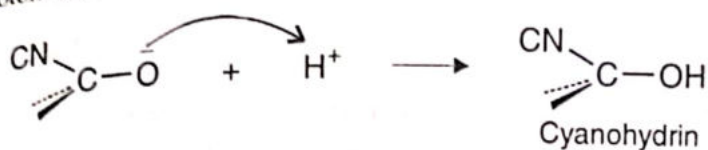**MECHANISM.** The mechanism involves the following steps :

Step 1. The base removes a proton from hydrogen cyanide to produce cyanide ions.

$$HCN + \overset{-}{O}H \longrightarrow H_2O + \overset{-}{C}N$$
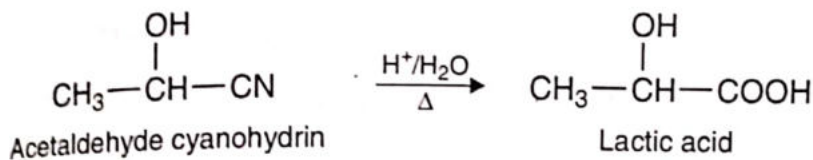$$\text{Nucleophile}$$

Step 2. The cyanide ion attacks the carbonyl carbon to form an anion.

Step 3. The proton from the solvent (usually water) combines with the anion to give cyanohydrin.

Cyanohydrin

Like other nitriles, cyanohydrins can be hydrolysed to give α-hydroxy carboxylic acids. For example.

$$\underset{\text{Acetaldehyde cyanohydrin}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CN} \xrightarrow[\Delta]{H^+/H_2O} \underset{\text{Lactic acid}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-COOH}$$

3. Addition of Grignard Reagents. Aldehydes and ketones react with Grignard reagents to give addition product which can be hydrolysed with dilute acid to yield an alcohol.
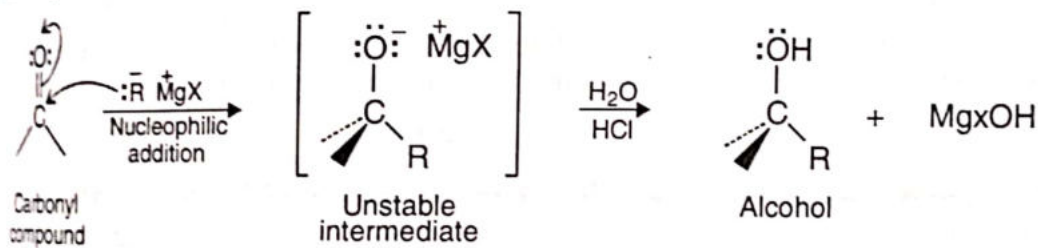
The reaction provides a convenient way of preparing alcohols that contain a larger carbon chain than the starting materials. Formaldehyde reacts with Grignard reagents to produce primary alcohols. Other aldehydes give secondary alcohols. Ketones react with Grignard reagents to produce tertiary alcohols. For example,
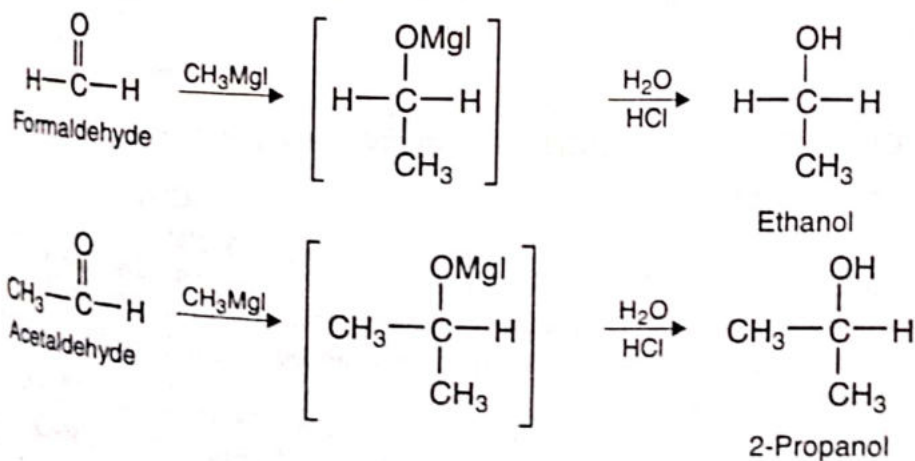
(4) Addition of Ammonia. Aldehydes ~~(~~ ~~aldehyde ammonias.~~ For example,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \ + \ NH_3 \ \longrightarrow \ CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-H$$

Acetaldehyde   Acetaldehyde ammonia
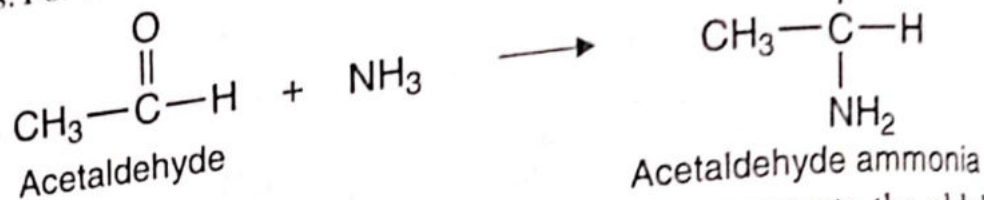
The aldehyde ammonias when heated with dilute acids, regenerate the aldehydes. ~~r~~ formation and decomposition of these compounds is used for purification of aldehydes.

Formaldehyde and ketones do not form addition compounds with ammonia, but inste complex condensation products. For example,

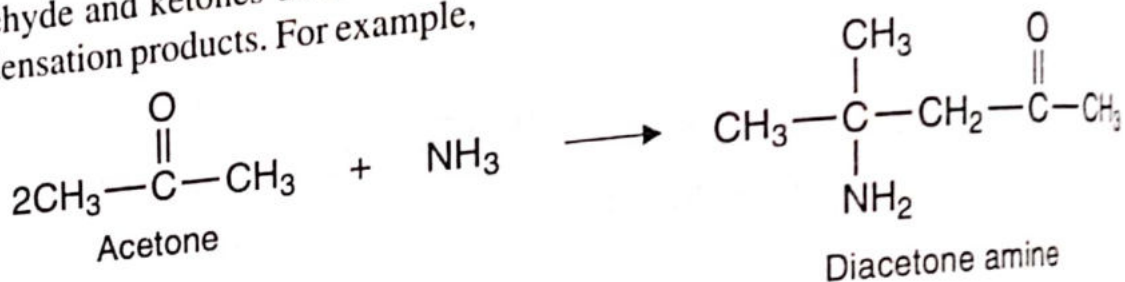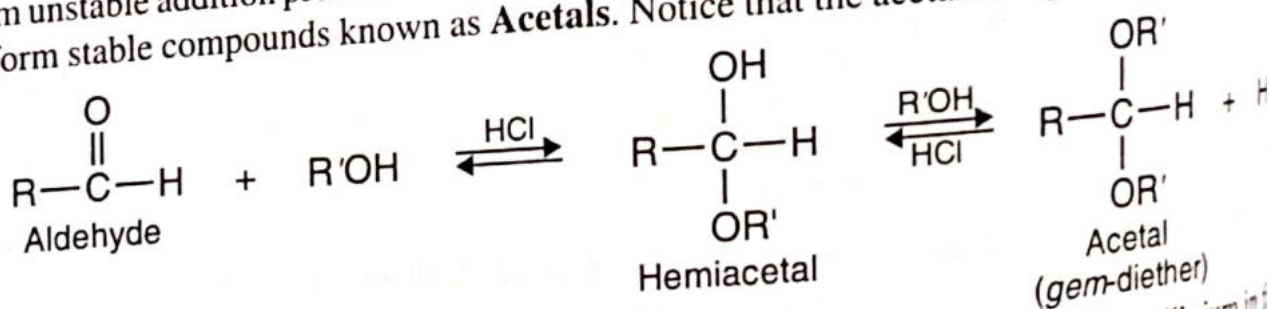$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \ + \ NH_3 \ \longrightarrow \ CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Acetone   Diacetone amine
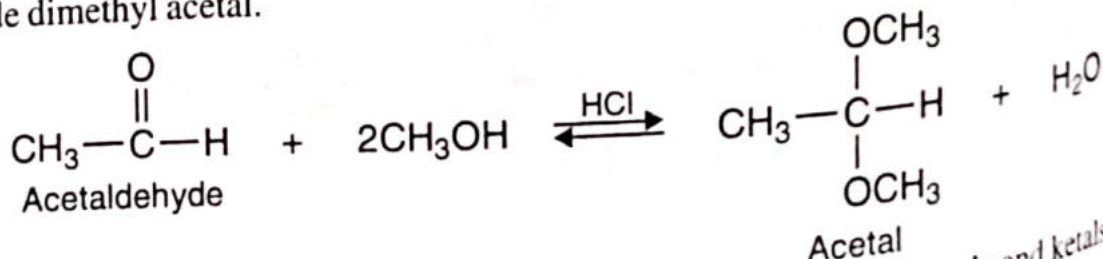
B. ADDITION REACTIONS FOLLOWED BY LOSS OF WATER

(5) Addition of Alcohols. Alcohols react with aldehydes in the presence of anhydrous form unstable addition products known as **Hemiacetals.** These hemiacetals react further with to form stable compounds known as **Acetals.** Notice that the acetals are *gem*-diethers.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \ + \ R'OH \ \underset{}{\overset{HCl}{\rightleftharpoons}} \ R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-H \ \underset{HCl}{\overset{R'OH}{\rightleftharpoons}} \ R-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-H \ + \ H$$

Aldehyde   Hemiacetal   Acetal
                                                 (*gem*-diether)

The reaction is reversible. A large excess of alcohol is used to shift the equilibrium in i acetal formation. The reaction of acetaldehyde with methyl alcohol results in the form acetaldehyde dimethyl acetal.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \ + \ 2CH_3OH \ \overset{HCl}{\rightleftharpoons} \ CH_3-\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{C}}-H \ + \ H_2O$$

Acetaldehyde   Acetal

Ketones do not react with alcohols to form the corresponding hemiketals and ketals.

(6) Reaction with Ammonia Derivatives. Some ammonia derivatives (NH_2-Z) react with al and ketones to form compounds containing carbon-nitrogen double bonds, together w elimination of a water molecule.

$$\diagup \!\!\!\!\diagdown C=\ddot{O} \ + \ H_2N-Z \ \longrightarrow \ \diagup \!\!\!\!\diagdown C=N-Z \ + \ H_2O$$

The reaction products are usually crystalline solids whose melting points can be used to identify aldehydes and ketones, most of which are liquids.

MECHANISM. The mechanism of the above reaction involves the following steps :

Step 1. Ammonia derivatives (NH_2-Z) behave as nucleophilic reagents since they have an unshared electron-pair on nitrogen. They add to the carbonyl group in aldehydes and ketones.
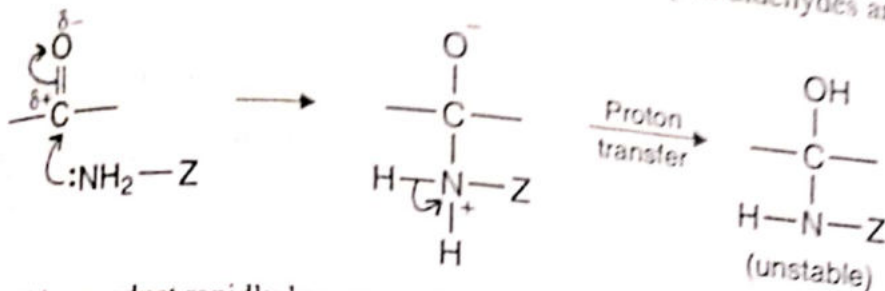
Step 2. Addition product rapidly loses a molecule of water to give the final product.
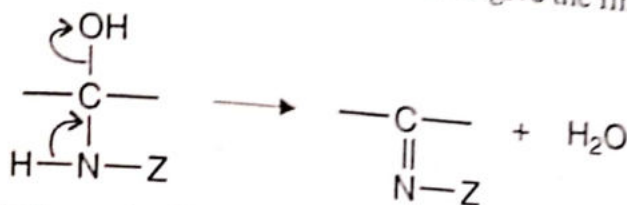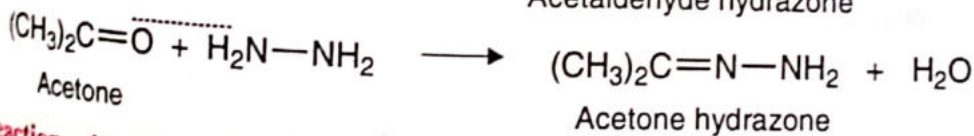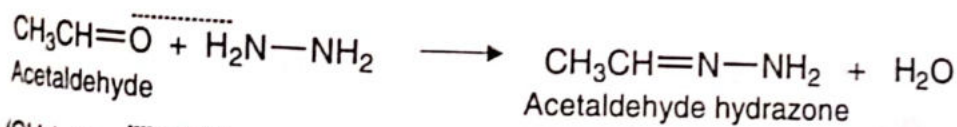

The ammonia derivatives which react in this way are : hydroxylamine, hydrazine, phenylhydrazine, dinitrophenylhydrazine, and semicarbazide.
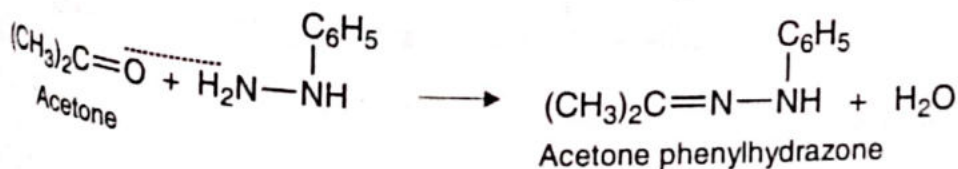
a) **Reaction with Hydroxylamine.** Aldehydes and ketones react with hydroxylamine (NH_2OH) to form oximes. For example,

$$CH_3CH{=}O + H_2N{-}OH \longrightarrow CH_3CH{=}N{-}OH + H_2O$$
Acetaldehyde   Acetaldehyde oxime

$$(CH_3)_2C{=}O + H_2N{-}OH \longrightarrow (CH_3)_2C{=}N{-}OH + H_2O$$
Acetone   Acetone oxime

b) **Reaction with Hydrazine.** Aldehydes and ketones react with hydrazine (NH_2NH_2) to form hydrazones. For example,

$$CH_3CH{=}O + H_2N{-}NH_2 \longrightarrow CH_3CH{=}N{-}NH_2 + H_2O$$
Acetaldehyde   Acetaldehyde hydrazone

$$(CH_3)_2C{=}O + H_2N{-}NH_2 \longrightarrow (CH_3)_2C{=}N{-}NH_2 + H_2O$$
Acetone   Acetone hydrazone

c) **Reaction with Phenylhydrazine.** Aldehydes and ketones react with phenylhydrazine ($NH_2NHC_6H_5$) to form phenylhydrazones. For example,

$$CH_3CH{=}O + H_2N{-}\underset{\underset{\displaystyle C_6H_5}{|}}{NH} \longrightarrow CH_3CH{=}N{-}\underset{\underset{\displaystyle C_6H_5}{|}}{NH} + H_2O$$
Acetaldehyde   Acetaldehyde phenylhydrazone

$$(CH_3)_2C{=}O + H_2N{-}\underset{\underset{\displaystyle C_6H_5}{|}}{NH} \longrightarrow (CH_3)_2C{=}N{-}\underset{\underset{\displaystyle C_6H_5}{|}}{NH} + H_2O$$
Acetone   Acetone phenylhydrazone
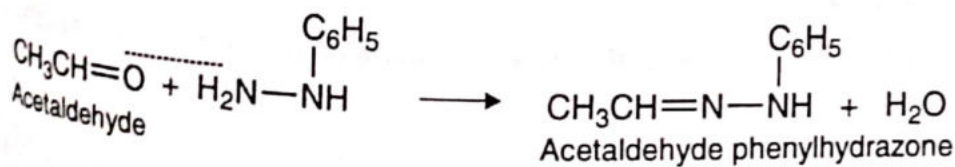
(d) **Reaction with 2,4-Dinitrophenylhydrazine.** Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones. For example,

$$(CH_3)_2C=O \ + \ H_2NNH-\!\!\!\bigcirc\!\!\!-NO_2 \quad \xrightarrow{-H_2O} \quad (CH_3)_2C=NNH-\!\!\!\bigcirc\!\!\!-NO_2$$

Acetone ⟶ Acetone 2,4-dinitrophenylhydrazone
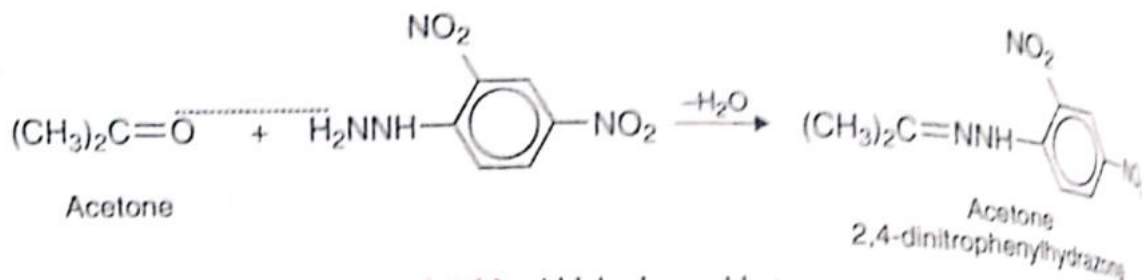
(e) **Reaction with Semicarbazide.** Aldehydes and ketones react with semicarbazides to form semicarbazones. For example,

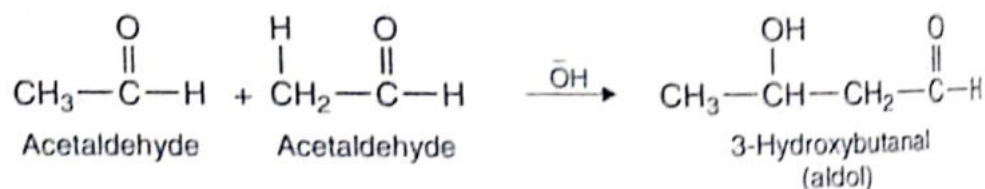$$CH_3CH=O + H_2N-NHCNH_2 \longrightarrow CH_3CH=N-NHCNH_2 + H_2O$$

Acetaldehyde ⟶ Acetaldehyde semicarbazone

$$(CH_3)_2C=O + H_2N-NHCNH_2 \longrightarrow (CH_3)_2C=N-NHCNH_2 + H_2O$$
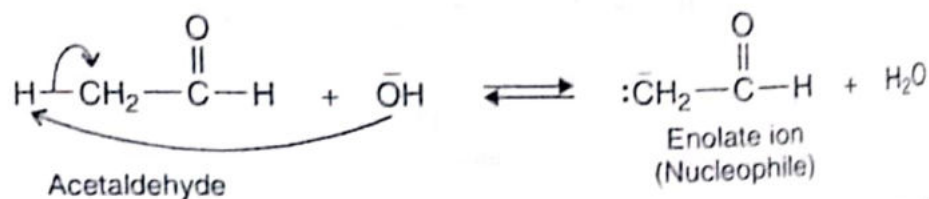
Acetone ⟶ Acetone semicarbazone
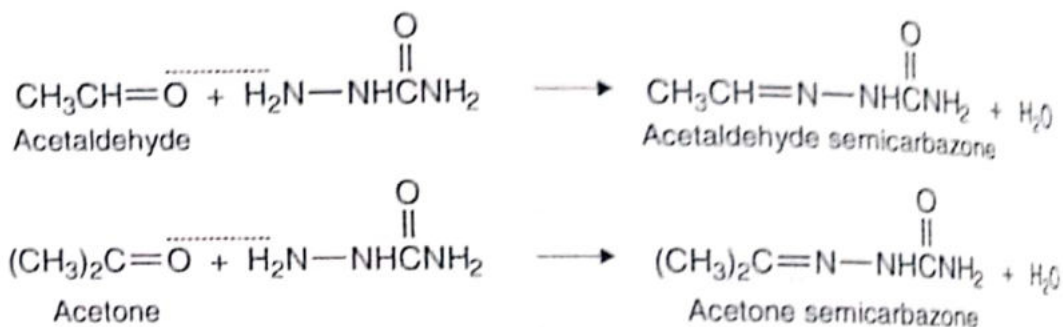
C. REACTIONS INVOLVING ALKYL GROUPS

(7) Aldol Condensation. Aldehydes containing α-hydrogens undergo self-addition in presence of a base to form products called **Aldols**. The reaction is called *Aldol Condensation*. The term aldol is derived from the combination of the words Aldehyde and Alcohol, the two functional groups present in the product. For example, two molecules of acetaldehyde combine with each other in the presence of dilute NaOH to form 3-hydroxybutanal.

$$CH_3-\overset{O}{\overset{\|}{C}}-H \ + \ \overset{H}{\overset{|}{C}}H_2-\overset{O}{\overset{\|}{C}}-H \quad \xrightarrow{\overline{O}H} \quad CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H$$

Acetaldehyde Acetaldehyde ⟶ 3-Hydroxybutanal (aldol)

MECHANISM. The reaction is reversible and involves the following steps:

Step 1. The enolate ion is formed

$$H\overset{\curvearrowleft}{-}CH_2-\overset{O}{\overset{\|}{C}}-H \ + \ \overline{O}H \ \rightleftharpoons \ :CH_2-\overset{O}{\overset{\|}{C}}-H \ + \ H_2O$$

Acetaldehyde ⟶ Enolate ion (Nucleophile)

Step 2. The enolate ion attacks the carbonyl carbon of another unionized aldehyde molecule

$$CH_3-\underset{\delta+}{\overset{\overset{\delta-}{O}}{\overset{\|}{C}}}-H \ + \ :CH_2-\overset{O}{\overset{\|}{C}}-H \ \rightleftharpoons \ CH_3-\overset{\overline{O}}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H$$

Acetaldehyde Enolate ion
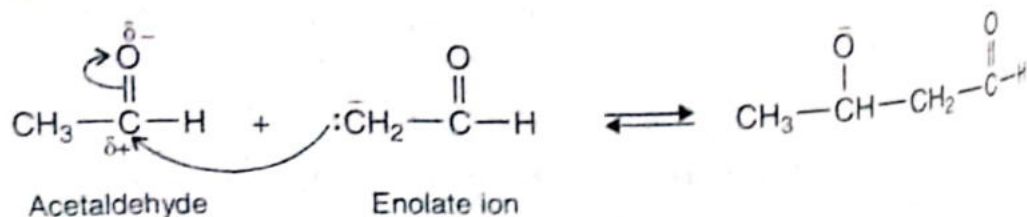
Step 3. The negative oxygen in the product accepts a proton from water to give aldol.

$$HO-H$$

$$CH_3-\overset{O}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-H \rightleftharpoons CH_3-\overset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-H + \overset{-}{O}H$$

3-Hydroxybutanal
(aldol)
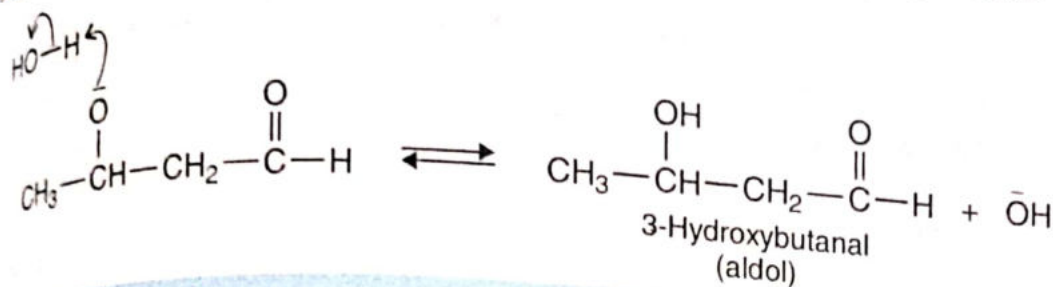
The product in all aldol condensations has several common structural characteristics

1. The product is a larger molecule that contains a newly formed carbon-carbon bond.
2. The newly formed C–C bond occurs between the α carbon of one aldehyde molecule and what was originally the carbonyl carbon of the second aldehyde molecule.
3. The product contains two functional groups: one carbonyl group and one hydroxyl group.
4. The hydroxyl group is always attached to the beta carbon (β carbon), which is two carbons away from the carbonyl group.

Aldols are easily dehydrated either by heating or by treatment with dilute acid to form β-unsaturated aldehydes. For example,

$$CH_3-\overset{OH}{\underset{|}{CH}}-\overset{H}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-H \xrightarrow{\Delta} CH_3-CH=CH-\overset{O}{\overset{||}{C}}-H + H_2O$$

3-Hydroxybutanal   2-Butenal
                        (Crotonaldehyde)
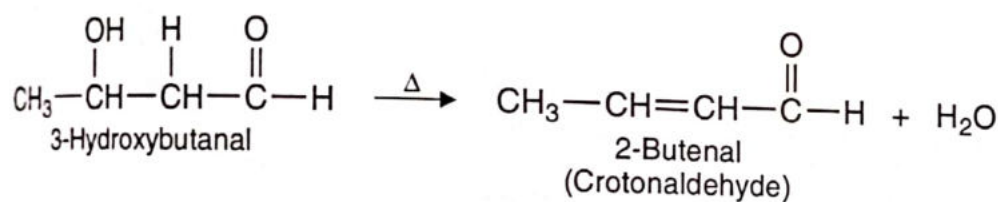
Ketones containing α-hydrogens also undergo aldol condensation to form **Ketols**. For example, two molecules of acetone combine with each other in the presence of barium hydroxide to form 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol).
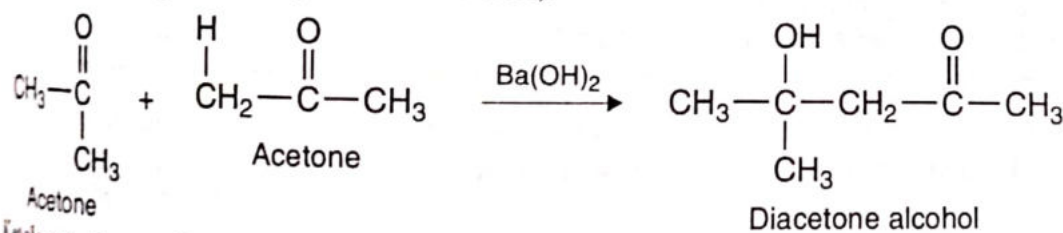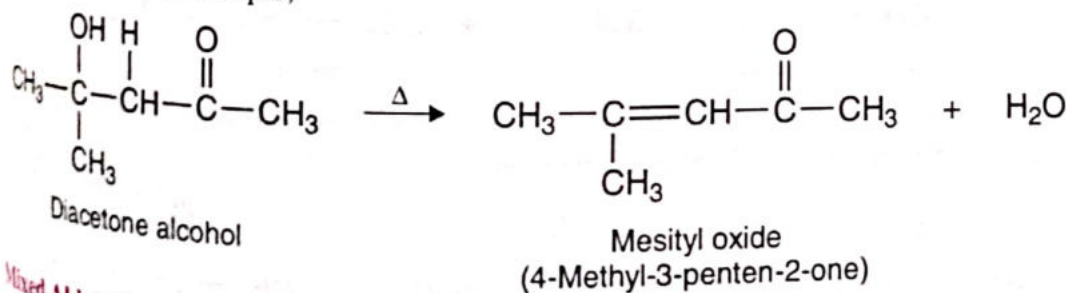
$$CH_3-\overset{O}{\underset{\underset{CH_3}{|}}{\overset{||}{C}}} + \overset{H}{\underset{|}{CH_2}}-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{Ba(OH)_2} CH_3-\overset{OH}{\underset{\underset{CH_3}{|}}{\overset{|}{C}}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$$

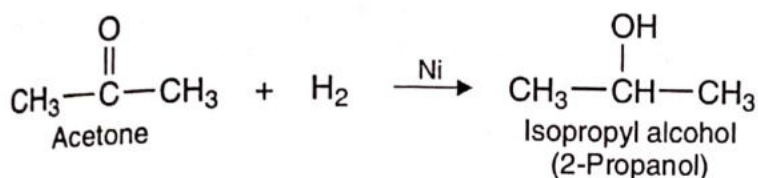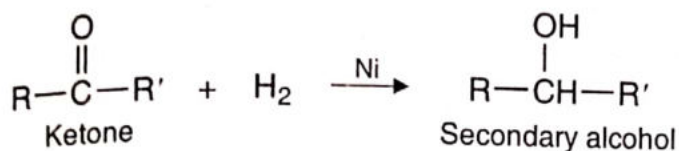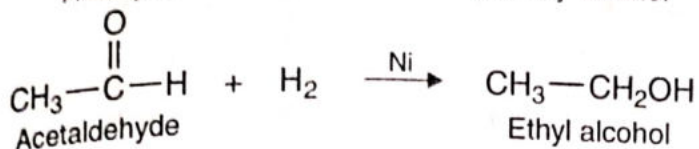Acetone   Acetone   Diacetone alcohol

Ketols are also easily dehydrated by heating or by treatment with dilute acid to form α,β-unsaturated ketones. For example,

$$CH_3-\overset{OH}{\underset{\underset{CH_3}{|}}{\overset{|}{C}}}-\overset{H}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{\Delta} CH_3-\overset{}{\underset{\underset{CH_3}{|}}{C}}=CH-\overset{O}{\overset{||}{C}}-CH_3 + H_2O$$

Diacetone alcohol   Mesityl oxide
                              (4-Methyl-3-penten-2-one)

Mixed Aldol Condensation. The reaction of two different carbonyl compounds (one of which must have an α-H) in the presence of a base is known as mixed aldol condensation. For example, acetaldehyde reacts with benzaldehyde (which has no α-H) in the presence of a base to form cinnamaldehyde.

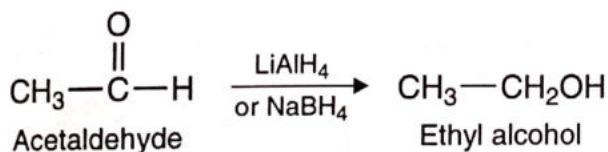*Reduction to Alcohols.* Aldehydes and ketones can be reduced to alcohols by treatment with *hydrogen and Ni or Pt catalyst.* Aldehydes give primary alcohols. Ketones give secondary alcohols.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \ + \ H_2 \xrightarrow{\ Ni\ } R-CH_2OH$$
Aldehyde   Primary alcohol

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \ + \ H_2 \xrightarrow{\ Ni\ } CH_3-CH_2OH$$
Acetaldehyde   Ethyl alcohol

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \ + \ H_2 \xrightarrow{\ Ni\ } R-\overset{\overset{\displaystyle OH}{|}}{C}H-R'$$
Ketone   Secondary alcohol

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \ + \ H_2 \xrightarrow{\ Ni\ } CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$$
Acetone   Isopropyl alcohol
(2-Propanol)
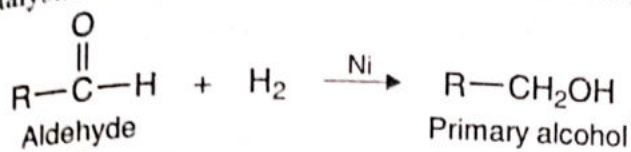
The same results can be achieved with chemical reducing agents such as lithium aluminium hydride $(LiAlH_4)$ or sodium borohydride $(NaBH_4)$. For example,

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2OH$$
Acetaldehyde   Ethyl alcohol

(*ii*) **Reduction to Alkanes.** Aldehydes and ketones can be reduced to alkanes by either the Clemmensen reduction or the Wolf-Kishner reduction.
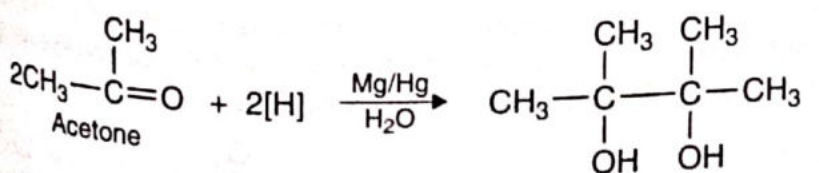
(*a*) **Clemmensen Reduction.** This involves the use of zinc-mercury amalgam in hydrochloric acid as the reducing agent.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \xrightarrow[HCl]{Zn/Mg} R-CH_2-R'$$
       Alkane
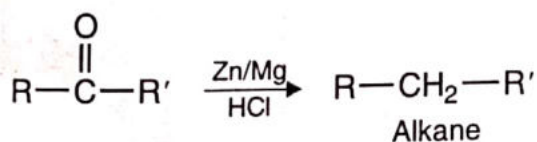
(*b*) **Wolf-Kishner Reduction.** This involves the use of a basic solution of hydrazine as the reducing agent.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \xrightarrow[NH_2NH_2]{NaOH} R-CH_2-R'$$
       Alkane
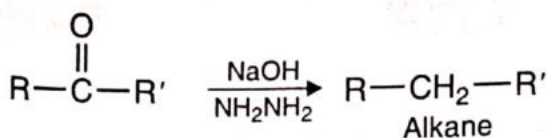
(*iii*) **Reduction to Pinacols.** Ketones when reduced in neutral or alkaline medium, form pinacols (*symmetrical 1,2-diols*). For example, acetone undergoes reduction with magnesium amalgam to form 2,3-dimethylbutane-2,3-diol.

$$2CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O \ + \ 2[H] \xrightarrow[H_2O]{Mg/Hg} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$$
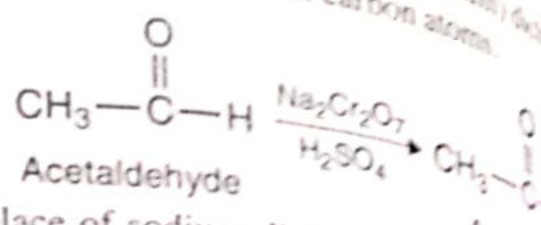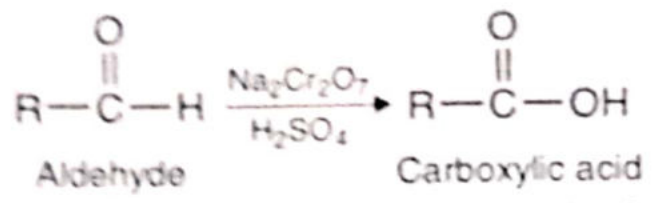Acetone   2,3-Dimethylbutane-2,3-diol
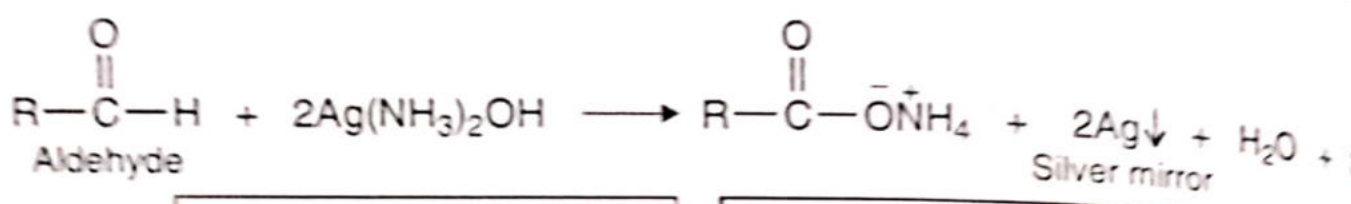
Aldehydes do not give this reaction.

oxidizing agents is quite different. Aldehydes are easily oxidized. Ketones are oxidized ~~is very similar, their beh~~

drastic conditions.

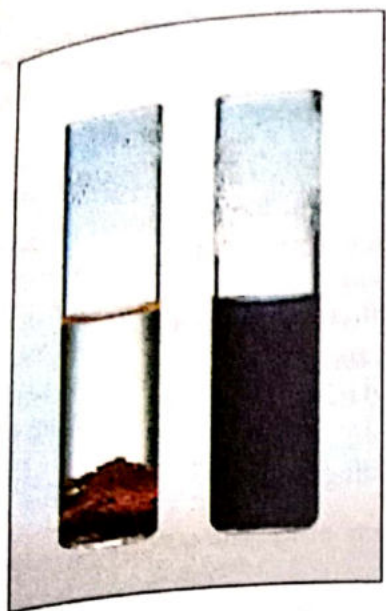**(12) Oxidation of Aldehydes.** Aldehydes can be oxidized with sodium (or potassium) in acidic medium to form carboxylic acids containing the same number of carbon atoms.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[\text{H}_2\text{SO}_4]{\text{Na}_2\text{Cr}_2\text{O}_7} R-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Aldehyde   Carboxylic acid

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[\text{H}_2\text{SO}_4]{\text{Na}_2\text{Cr}_2\text{O}_7} CH_3-$$

Acetaldehyde

Potassium permanganate can also be used in place of sodium dichromate. Aldehydes oxidized by much milder oxidizing agents such as *Tollens' reagent, Fehling's solution and* solution.

Tollens' Reagent. Tollen's reagent is an ammoniacal solution of silver oxide. It is obtain adding ammonia to a precipitate of silver oxide present in a solution of silver nitrate and hydroxide. When Tollens' reagent is used to oxidize an aldehyde, the silver ion is reduced to me form and if the reaction is carried out in a clean test tube, deposits as a *mirror*. The silver mirror indicates the presence of an aldehyde group in a molecule.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-H + 2Ag(NH_3)_2OH \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 + 2Ag\downarrow + H_2O + 3$$

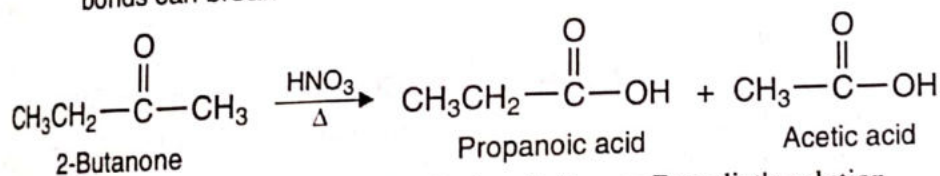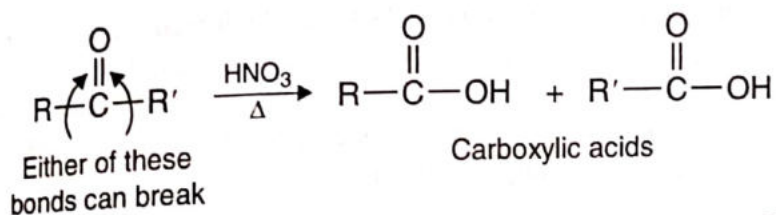Aldehyde   Silver mirror
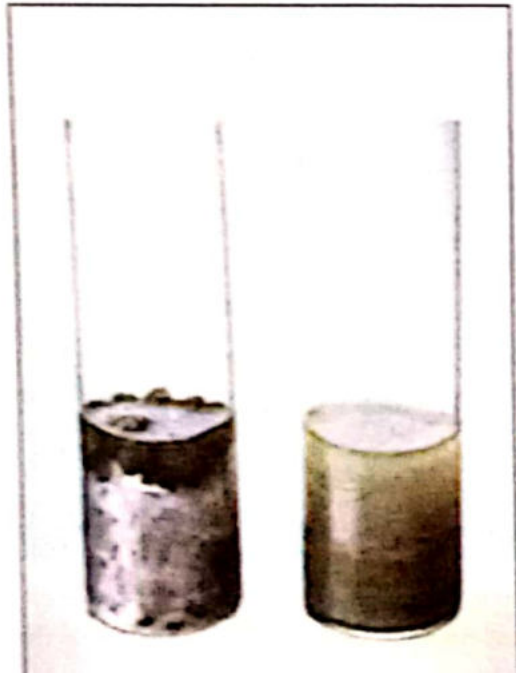
The presence of an aldehyde group in a molecule is shown by the formation of a brick-red precipitate of copper (I) oxide in the Fehling's test.

Benedict's solution is an alkaline solution of cupric ion complexed with citrate ions. It reacts in the same way as Fehling's solution.
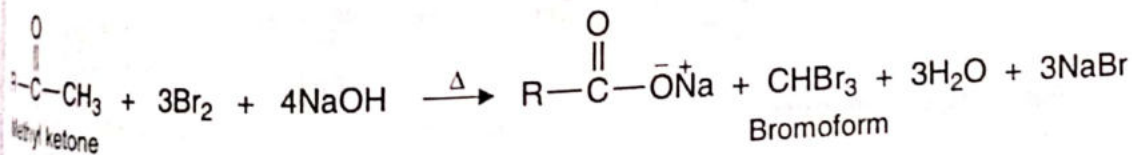
(13) Oxidation of Ketones. Ketones can be oxidized by strong oxidizing agents such as alkaline $KMnO_4$ or hot concentrated HNO_3 to form two carboxylic acids with fewer carbon atoms than the original ketone. This is because the ketone is broken into two fragments by attack on either side of the carbonyl group.

$$R\overset{O}{\underset{\text{Either of these bonds can break}}{\overset{\|}{-}C-}}R' \xrightarrow[\Delta]{HNO_3} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$

Carboxylic acids

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{HNO_3} CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

2-Butanone   Propanoic acid   Acetic acid

Ketones do not react with Tollens' reagent, Fehling's solution, or Benedict's solution.

SOME OTHER IMPORTANT REACTIONS

(14) Haloform Reaction. Acetaldehyde and methyl ketones react rapidly with halogen (Cl_2, Br_2, or I_2) in the presence of alkali to form haloform. For example,

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 4NaOH \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O\overset{+}{N}a + CHBr_3 + 3H_2O + 3NaBr$$

Methyl ketone   Bromoform

This reaction, called the *Haloform reaction*, takes place in two steps.

Step 1. Three hydrogen atoms on the α-carbon are successively replaced by halogen atoms.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 3NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-CBr_3 + 3H_2O + 3NaBr$$

Methyl ketone α,α,α-Tribromoketone