

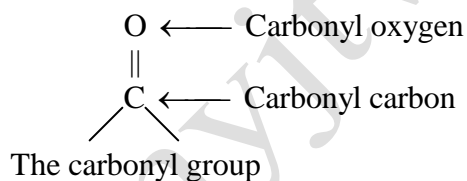
CHAPTER	7
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ALDEHYDES AND KETONES

Carbonyl compounds: The organic compounds which contain a carbonyl functional group are called carbonyl compounds. Examples of carbonyl compounds are,

- | | |
|------------------------|--------------|
| (i) Aldehydes | (ii) Ketones |
| (iii) Carboxylic acids | (iv) Esters |
| (v) Acid halides | (vi) Amides |
| (vii) Acid anhydrides | |

The carbonyl group consist of carbon atom doubly bonded to an oxygen atom. This unit ($>C=O$) is referred to as the carbonyl group.



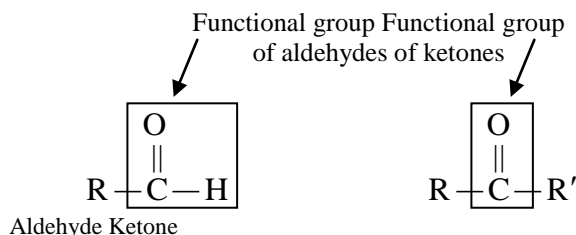
Both aldehydes and ketones contain a carbon-oxygen double bond ($>C=O$) which is carbony functional group, so aldehydes and ketones are collectively called carbonyl compounds.

Aldehydes: Aldehydes are organic compound that contain a carbonyl carbon which is bonded to at least one hydrogen atom.



The functional group of aldehyde is known as formyl group. Formaldehyde, HCHO, in which the carbonyl carbon is bonded to two hydrogen atoms, is an exception.

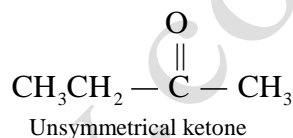
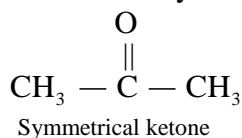
Ketones: The carbonyl compounds in which the carbonyl C is always bonded to two alkyl groups are called ketones. These alkyl groups may be same or different. The two groups may be alkyls or aryls or one may be alkyl and other aryl. The ketone functional group is called keto group and is represented as $-\text{CO}-$.



Types of ketones: On the basis of nature of the alkyl or aryl groups ketones may be of two types.

Symmetrical ketones: When both the alkyls/aryls are the same then the ketones are called symmetrical.

Unsymmetrical ketones: When both the alkyls/aryls are different from one another then the ketones are called unsymmetrical.



Nomenclature of Aldehydes

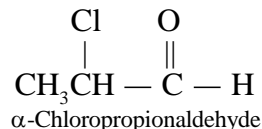
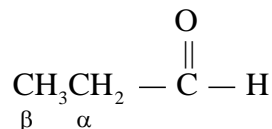
There are two systems of naming aldehydes.

(1) Common System: Common names for aldehydes are obtained from the names of the corresponding carboxylic acids. The aldehyde name is obtained by replacing the ending *-ic acid* of the acid name with *-aldehyde*.

CARBOXYLIC ACID	ALDEHYDE
$\begin{array}{c} \text{O} \\ \\ \text{H} - \text{C} - \text{OH} \end{array}$ <p>Formic acid</p>	$\begin{array}{c} \text{O} \\ \\ \text{H} - \text{C} - \text{H} \end{array}$ <p>Formaldehyde</p>
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{OH} \end{array}$ <p>Acetic acid</p>	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{H} \end{array}$ <p>Acetaldehyde</p>
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{OH} \end{array}$ <p>Propionic acid</p>	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{H} \end{array}$ <p>Propionaldehyde</p>
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{OH} \end{array}$ <p>Butyric acid</p>	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{H} \end{array}$ <p>Butyraldehyde</p>

While naming substituted aldehydes, the position of substituents on the parent chain is indicated by Greek letters α , β , γ , etc. The carbon atom adjacent to the carbonyl group in an aldehyde is called the α -carbon, the next one along the chain is

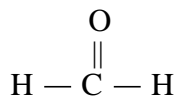
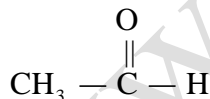
the β -carbon, and so forth.



(2) **IUPAC System:** IUPAC names for aldehydes are obtained by replacing the ending $-e$ of the corresponding alkane with $-al$. Since the aldehyde functional group is always at the end of the chain, there is no need to specify its position. However, when other substituents are present, the carbonyl carbon is assigned number 1.

For naming aldehyde following rules must be learned.

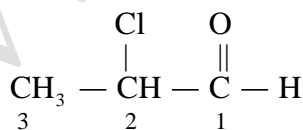
- Select the longest continuous chain of carbon containing aldehydic group.
- Name the longest continuous chain of carbon as alkane on the basis of number of carbon atoms.
- Replace the ending “e” of alkane by “al”. So alkane will become alkanal, and methane to methanal etc.
- As the aldehydes have their functional group at terminal position so there is no need to write its position.
- The position, name and number of other substituents are written before the name of the parent aldehyde.

Methanal (*Methane* $-e + al$)

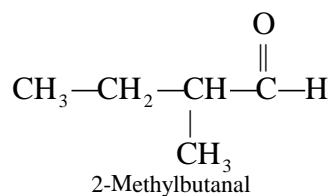
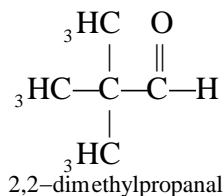
Ethanal

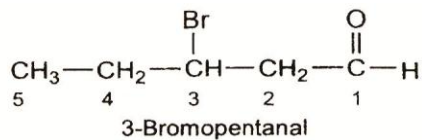
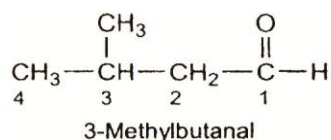
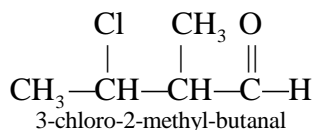


Propanal

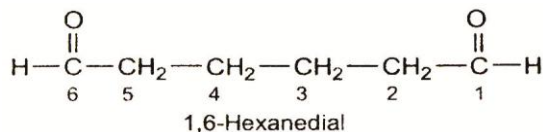


2-Chloropropanal





- (6) When there are two aldehydic groups in a molecule, it is named as **Alkanedial**. Notice that *-e* of the corresponding alkane name is retained.



Chemistry Joke:

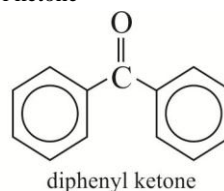
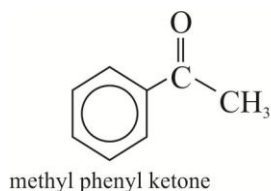
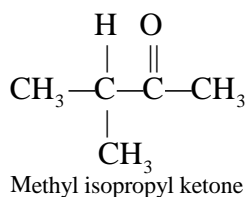
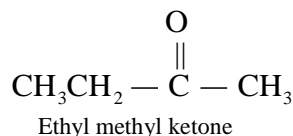
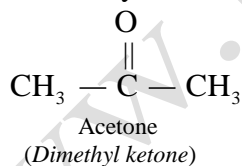
Q: What's the difference between kajol and kajal?

Chemist answer: As kajol has "ol" at the end so it is an alcohol while kajal has "al" at the end so it is an aldehyde.

Nomenclature of Ketones

There are two systems of naming ketones.

- (1) **Common System:** Common names of ketones are obtained by simply naming the two alkyl groups attached to the carbonyl group and adding the word *ketone*. The simplest ketone, dimethyl ketone, is usually referred to as *acetone*.



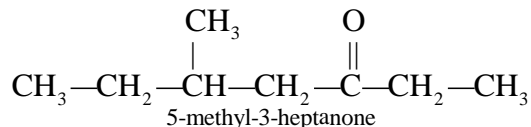
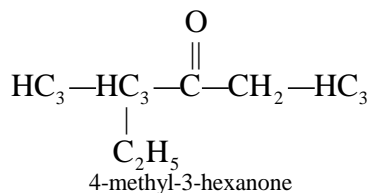
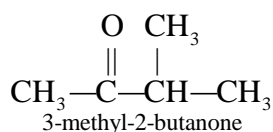
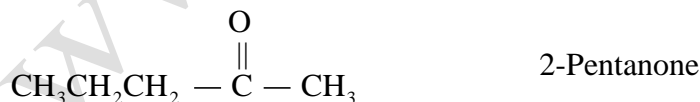
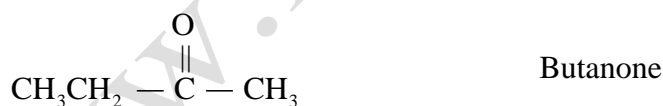
- (2) **IUPAC System:** IUPAC names for ketones are obtained by replacing the ending "e" of the corresponding alkane with "one". The chain is then numbered to give the

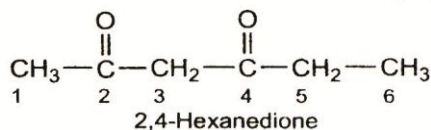
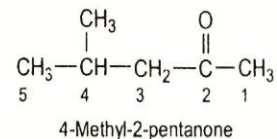
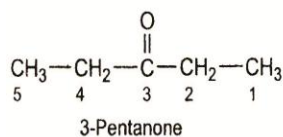
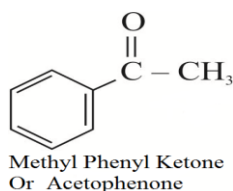
carbonyl carbon the *lowest* possible number. This number is then used to designate the position of the carbonyl group.

Rules for naming ketones are:

1. Select the longest continuous chain of carbon having ketonic functional group.
2. Name the longest continuous carbon chain as alkane on the basis of number of carbon atoms.
3. Replace the ending “e” of alkane by “one” so alkane will become alkanone and propane to propanone etc.
4. Number the longest continuous carbon chain from the side to which the ketonic group is nearer.
5. The position of the functional group must be mentioned before the name of the parent chain.
6. The position name and number of the other substituents must be written before the name of parent chain.
7. When there are two carbonyl groups in a molecule, it is named as **Alkanedione**. Notice that *-e* of the corresponding alkane name is retained.

The IUPAC names of some ketones are given below:





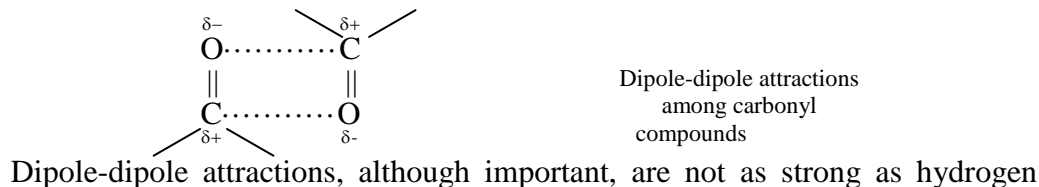
Physical Properties

- (1) Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C. Other lower aldehydes and ketones are colourless liquids.
- (2) Lower aldehydes possess rather unpleasant, pungent smells whereas the ketones have pleasant, sweet odours.
- (3) Density of aldehydes and ketones is less than that of water.

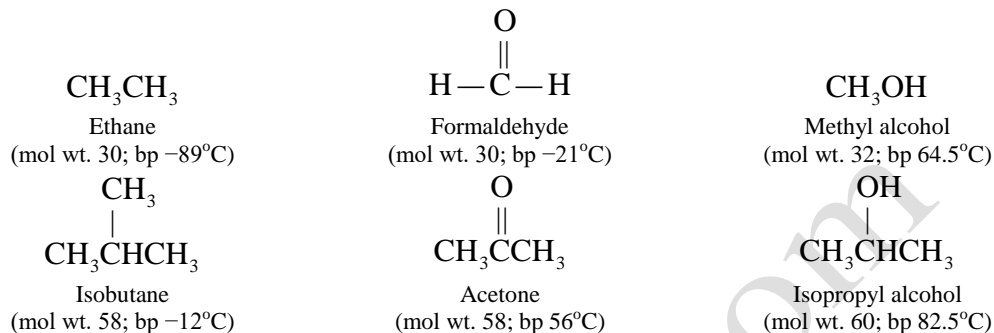
Boiling Points of Some Aldehydes and Ketones

Name	Formula	bp °C
Aldehydes		
Formaldehyde	HCHO	-21
Acetaldehyde	CH ₃ CHO	20
Propionaldehyde	CH ₃ CH ₂ CHO	49
<i>n</i> -Butyraldehyde	CH ₃ CH ₂ CH ₂ CHO	76
Ketones		
Acetone	CH ₃ COCH ₃	56
Butanone	CH ₃ COCH ₂ CH ₃	80
2-Pentanone	CH ₃ COCH ₂ CH ₂ CH ₃	102
3-Pentanone	CH ₃ CH ₂ COCH ₂ CH ₃	101

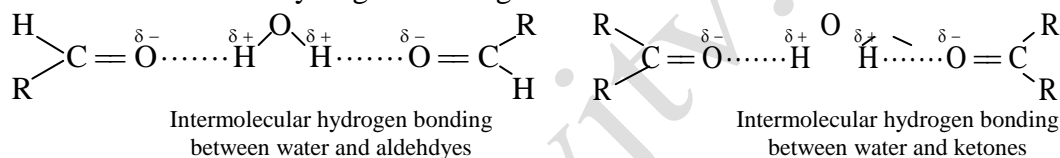
- (4) Because of the polarity of the carbonyl group, aldehydes and ketones are polar compounds having high dipole moment values. The polar character of the molecules gives rise to intermolecular attractions. These attractive forces, called dipole-dipole attractions, occur between the partial negative charge on the carbonyl oxygen of one molecule and the partial positive charge on the carbonyl carbon of another molecule.



bonding. As a result, the boiling points of aldehydes and ketones are higher than those of nonpolar alkanes, but lower than those of alcohols, of comparable molecular weights. For example,



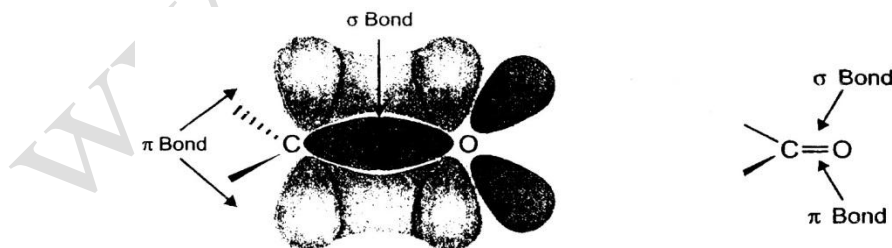
- (5) The lower aldehydes and ketones are soluble in water because aldehydes and ketones form hydrogen bonds with water, even though they are incapable of intermolecular hydrogen bonding with one another.



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.

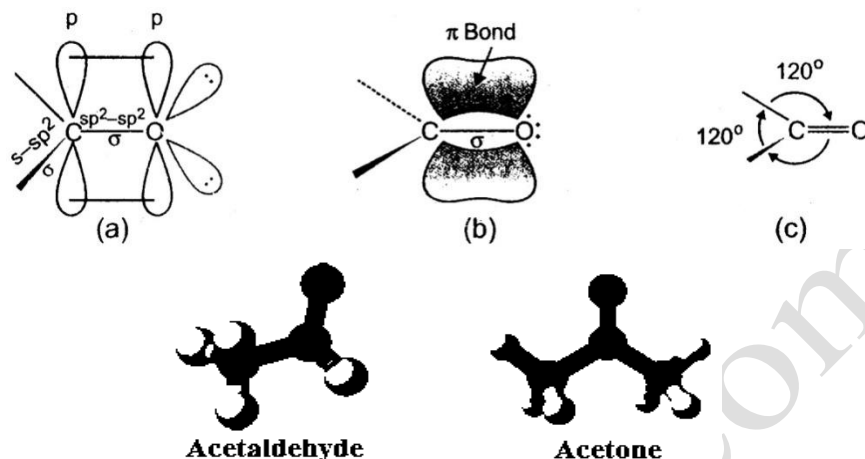
Structure of the Carbonyl Group

The carbonyl group, like the carbon-carbon double bond of alkenes, is composed of one σ bond 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_z orbitals of the two atoms. The two unshared electron pairs of oxygen occupy the sp^2 hybridized 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

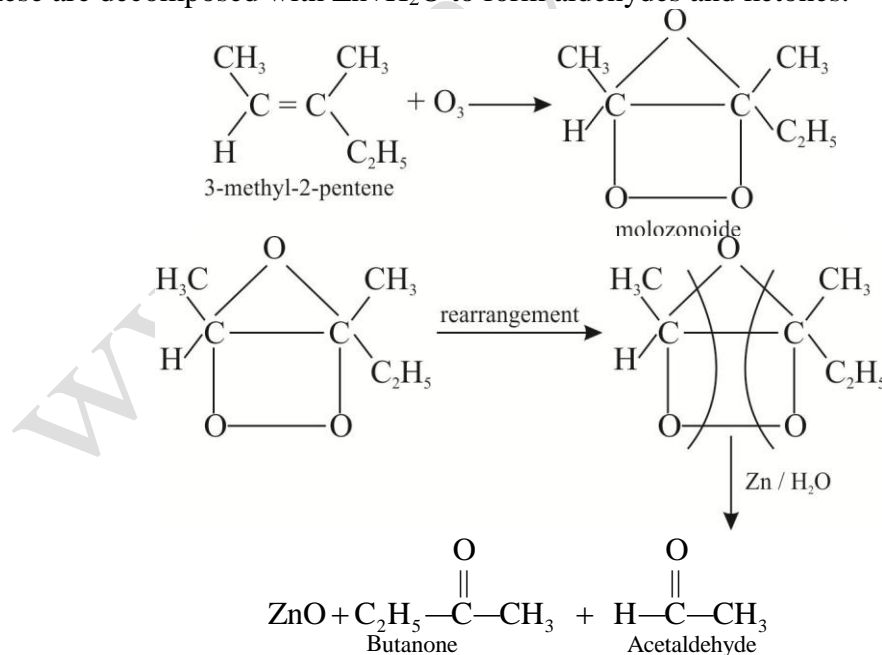
between the attached atoms are approximately 120° . The C=O bond distance is 1.23\AA shorter than C–O bond distance in alcohols and ether (1.43\AA).



Methods of Preparation

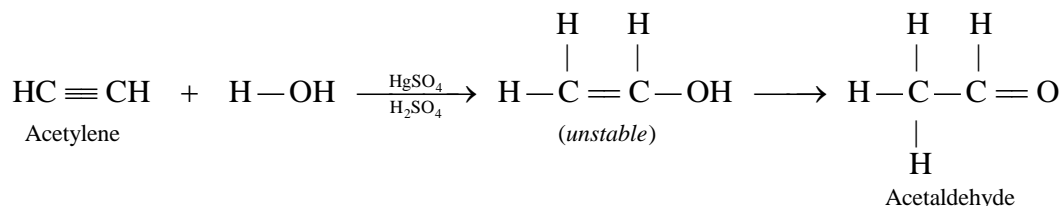
Aldehydes and ketones may be prepared by the following methods:

(1) 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 these are often explosive in dry state. These are decomposed with $\text{Zn} + \text{H}_2\text{O}$ to form aldehydes and ketones.

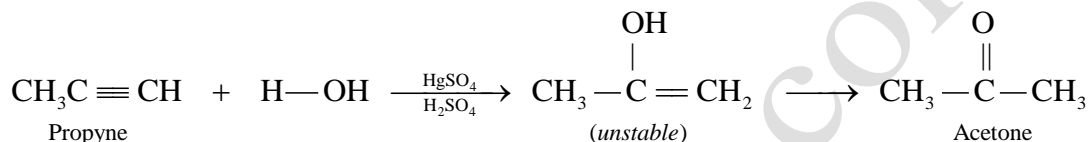


(2) Hydration of Alkynes: Hydration of acetylene yields acetaldehyde. Water adds to acetylene in the presence of mercuric sulphate and sulphuric acid to form an

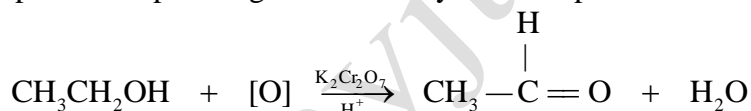
unstable enol-intermediate. This intermediate rearranges to give acetaldehyde.



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 ketones.

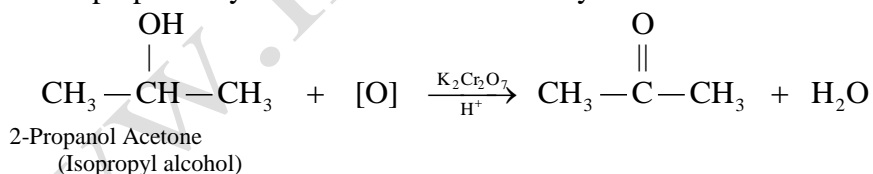


(3) Oxidation of Alcohols: Aldehydes and ketones can be prepared by the controlled oxidation of primary and secondary alcohols using an acidified solution of potassium dichromate or potassium permanganate. Primary alcohols produce aldehydes.

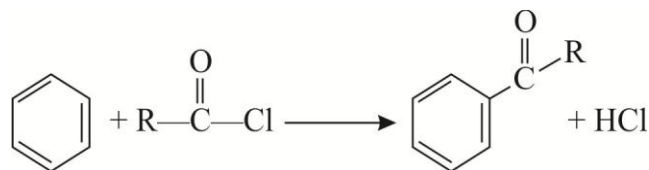


Ethyl alcohol Acetaldehyde

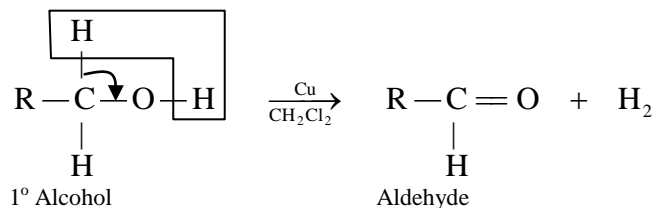
Ketones are prepared by the oxidation of secondary alcohols.



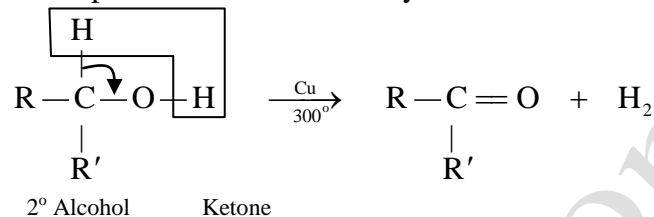
(4) Friedel Craft Acylation of benzene: Introduction of acyl group to an aromatic ring in the presence of acetyl halide and anhydrous AlCl_3 catalysis is called Friedel craft acylation.



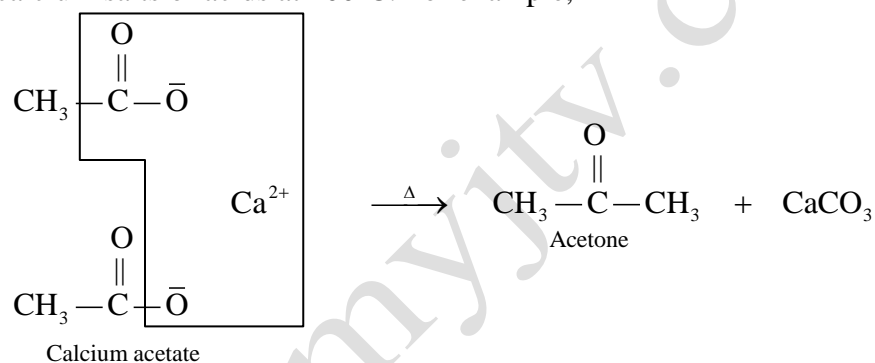
(5) Catalytic Dehydrogenation of Alcohols: Aldehydes may be prepared by passing the vapours of primary alcohols over a copper catalyst heated to about 300°C .



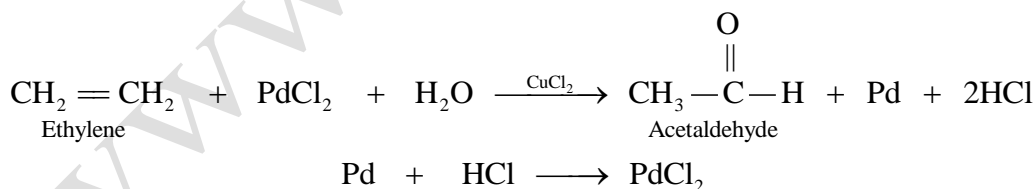
Similarly ketones are produced from secondary alcohols.



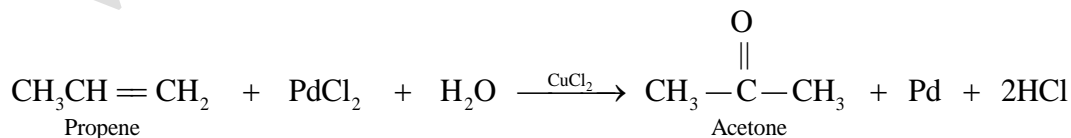
(6) **Pyrolysis of Calcium Salts of Acids:** Symmetrical ketones may be prepared by heating calcium salts of acids at 400°C . For example,



(7) **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,



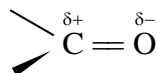
Acetone is prepared similarly from propene.



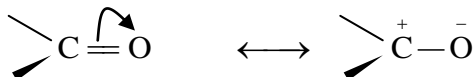
Reactivity of the Carbonyl Group

The electrons of the carbonyl group are *not* equally shared. In fact, these 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:

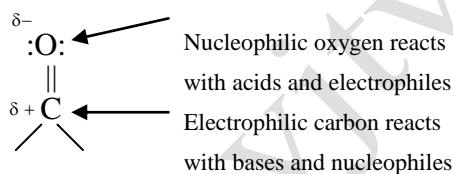


Alternatively, the polar nature of the carbonyl group can also be indicated by the following resonance structures:



As a result of this polarization, most carbonyl reactions involve nucleophilic attacks at the carbonyl carbon often accompanied by addition of a proton to the oxygen. The aldehydes and ketones usually undergo nucleophilic addition reactions. The nucleophilic addition in carbonyl compounds is shown as follows.

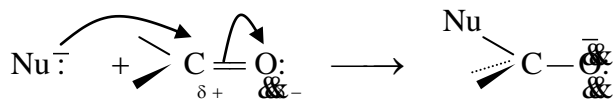
The positive charged carbon is readily attacked by electron-rich nucleophiles. The negatively charged oxygen is attached by electron-deficient electrophiles.



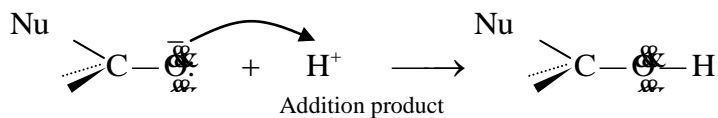
In these reactions, the nucleophilic end (negative part) of the reagent combines with the electrophilic carbon of carbonyl group while the electrophilic end (positive part) of the reagent, usually a proton goes to the oxygen, these reactions are catalyzed either by an acid or by a base. The presence of base increases the electrophilic character of the reagent while the presence of acid increase the electrophilic character of the carbonyl carbon atom.

Aldehydes and ketones undergo nucleophilic addition reaction by the following general mechanism.

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



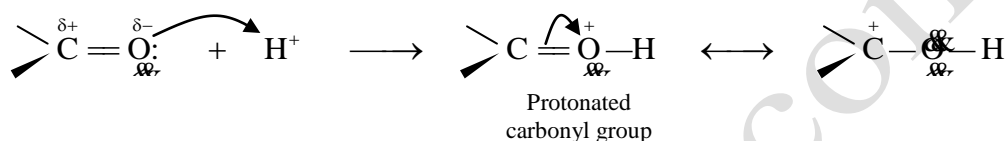
Step 2. The electrophile (*e.g.*, H^+) attacks the negatively charged oxygen to form the addition product.



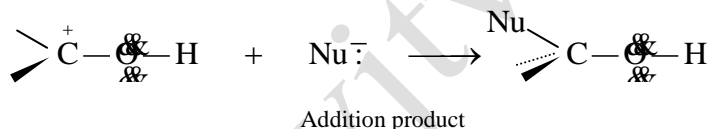
The nucleophilic addition reactions of carbonyl compound may be catalyzed by acids or bases.

Acid-catalyzed addition: The acid-catalysed nucleophilic addition occurs by the following mechanism:

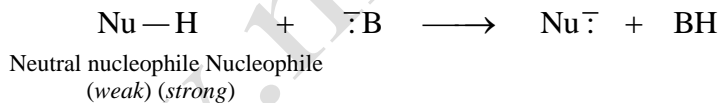
Step 1. The hydrogen ion from the acid attacks the negatively charged carbonyl oxygen to give protonated carbonyl group (oxonium ion). The protonated carbonyl group is resonance stabilized.



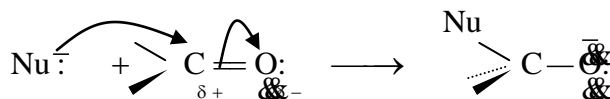
Step 2. The nucleophile attacks the protonated carbonyl group to form the addition product.



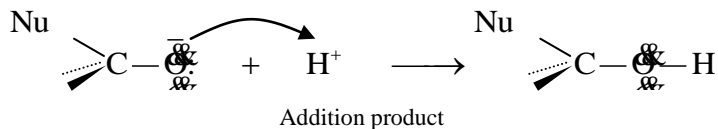
Base-catalyzed addition: Bases convert a weak neutral nucleophile to a strong one by removing a proton.



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



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

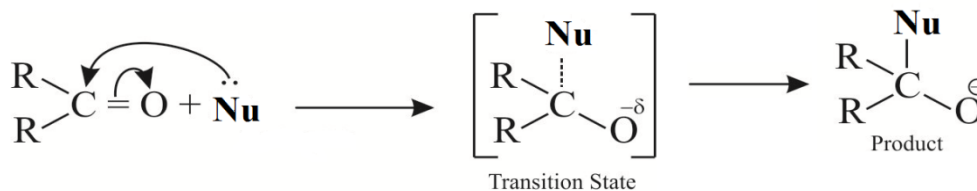
the proton (electrophile) to the oxygen. The carbonyl carbon which is sp^2 hybridized in aldehyde or ketones become tetrahedral and sp^3 hybridized in product and bond angle changes from 120° to 109.5° .

Relative Reactivity

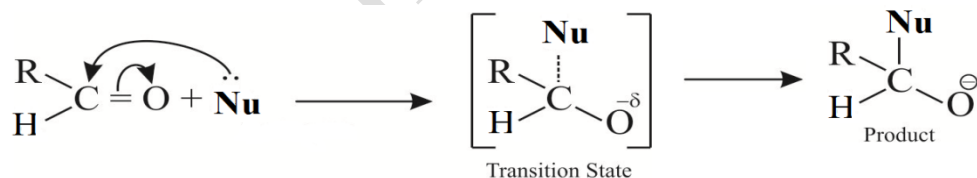
Generally aldehydes are more reactive towards nucleophilic addition reactions than ketones for the following reasons.

1. Steric hindrance: Steric hindrance plays an important role in the reactivity of aldehyde and ketones. The carbonyl carbon of ketones is more crowded than aldehydes. In nucleophilic addition the attached groups come enough closer because in the product the hybridization changes from sp^2 to sp^3 and the bond angle decreases from 120° to 109.5° . So ketones are less reactive due to steric hindrance of bulky alkyl groups which do not stabilize the transition state formed during the reaction. While in case of aldehyde no such hindrance is present due to which the transition state is more stable in aldehydes.

In Ketones:



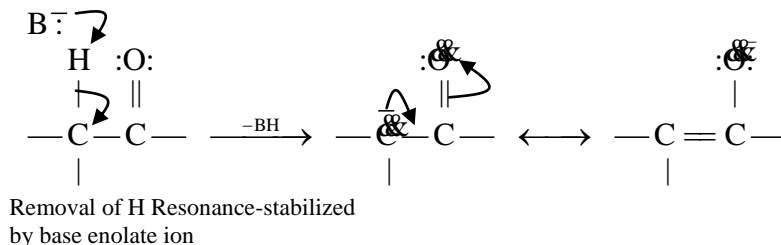
In Aldehydes:



2. Electronic effect: Electron releasing effect of alkyl groups also play an important role in the reactivity of carbonyl compounds. In case of ketone two bulky alkyl groups are attached with carbonyl carbon which increases electron density on electropositive carbon making it difficult to be attacked by nucleophile. While in aldehydes only one electron releasing alkyl group is attached therefore it will not increase electron density on carbon that much so a nucleophile can easily attack that's why aldehydes are more reactive towards nucleophilic addition reactions than ketones.

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**.



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.

Chemical reactions of aldehydes and ketones

1. Reduction of aldehydes and ketones or Addition reactions

Addition of hydrogen to aldehydes and ketones is called reduction. Following are some of the reduction reactions of aldehydes and ketones.

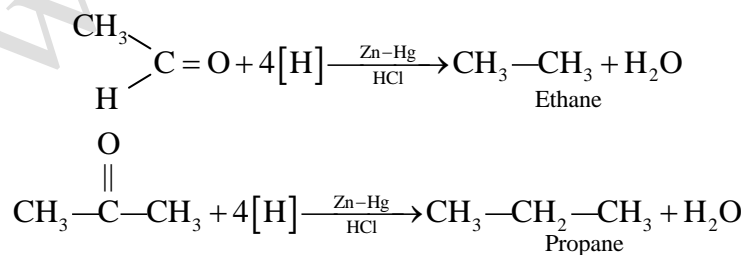
I. Reduction of carbonyl compounds

Addition of hydrogen to carbonyl compounds is called reduction. The increase in hydrogen content of a compound is called reduction. Aldehyde and ketones both undergo reduction in many ways.

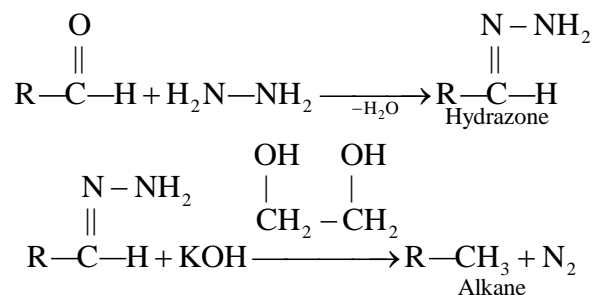
Reduction of carbonyl compounds to hydrocarbons

Aldehydes and ketones can be reduced to saturated hydrocarbons by the following two processes.

- i. **Clemmenson reduction:** The type of reduction in which aldehyde except formaldehyde can easily undergo reduction using amalgamated Zn and HCl mixture.



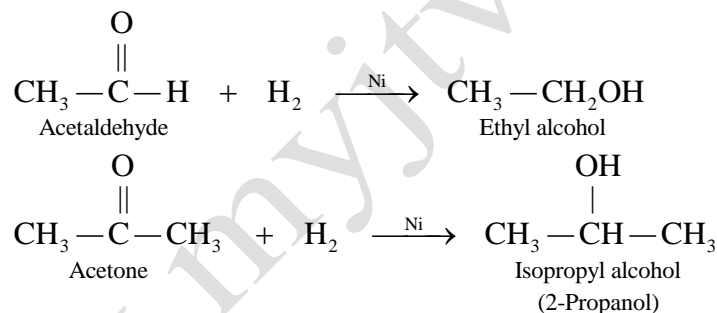
- ii. **Wolf-Kishner reduction:** In this reaction when an aldehyde or ketone is treated with hydrazine (N_2H_4), it give hydrazone (an intermediate) which upon reaction with KOH and Glycol yield corresponding alkane. KOH act as catalyst provide OH^- ion which remove H^+ ion from the amine group.



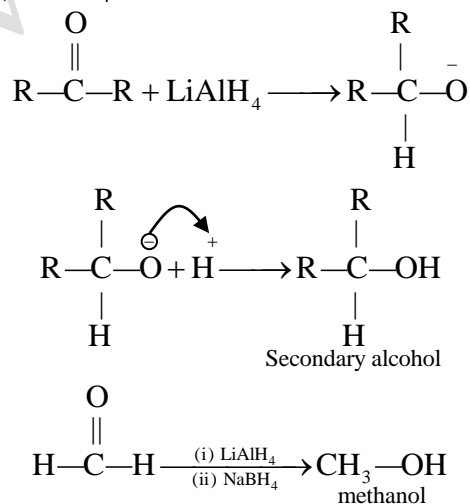
II. Reduction by hydrogen and hydrides: Formation of alcohols

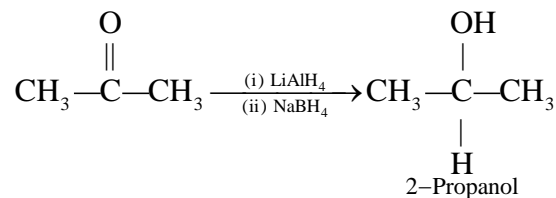
This is another very important and common method used for reduction of aldehydes and ketones. The aldehydes can easily reduce to primary alcohol while ketones into secondary alcohols by using metal hydrides as reducing agents.

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.



The most common metal hydrides used are lithium aluminium hydride, LiAlH_4 and sodium borohydride, NaBH_4 .

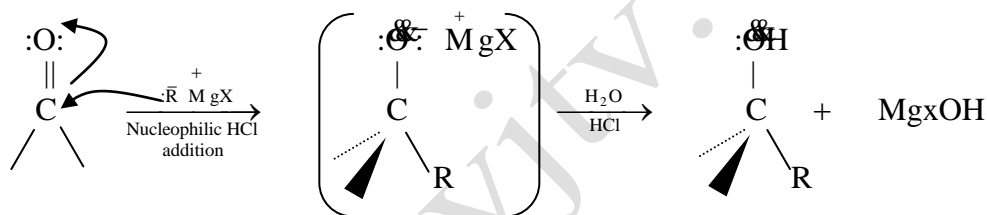




III. Reduction by using carbon nucleophiles

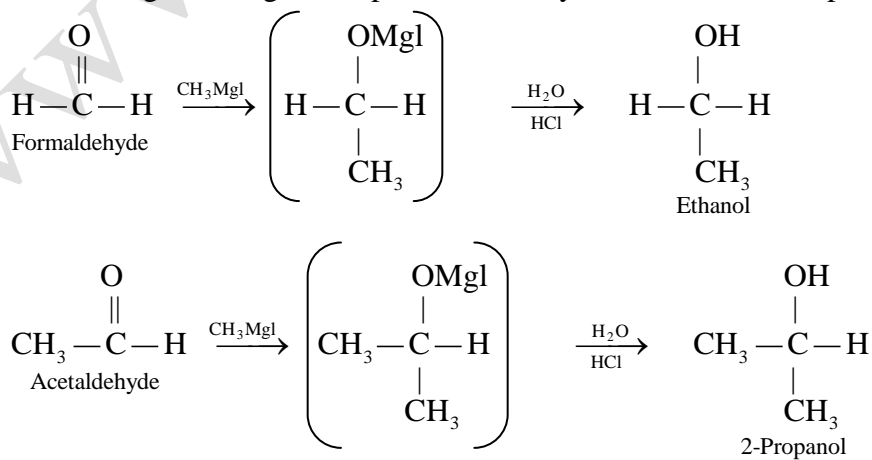
Carbanion (carbon having negative charge) are excellent nucleophiles to attack the electrophilic center in carbonyl compounds. Organometallic compounds (Grignard Reagent) and hydrogen cyanide both have carbon that can act as nucleophile and can reduce aldehydes and ketones by nucleophilic addition.

- i. **Reduction by using Grignard reagent:** Aldehydes and ketones react with Grignard reagents to give an addition product which can be hydrolysed with dilute acid to yield an alcohol.

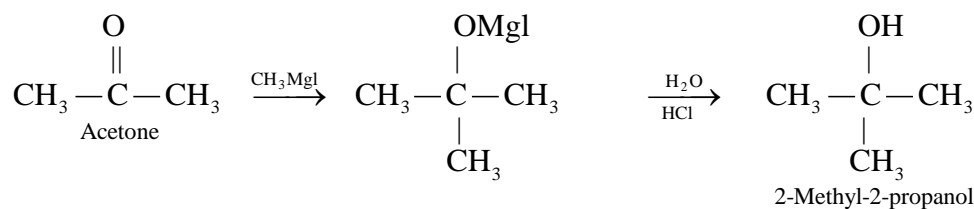


Carbonyl compound Unstable intermediate Alcohol

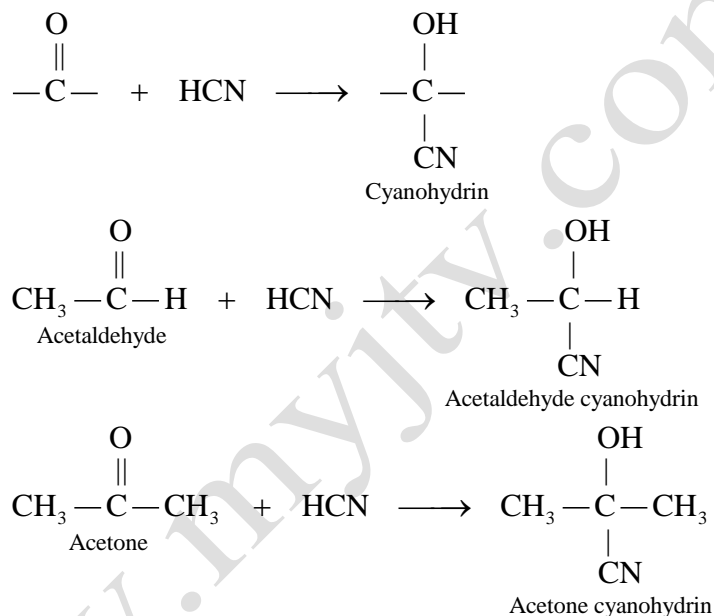
The reaction provides a convenient way of preparing alcohols that contain a large carbon chain than the starting materials. Formaldehyde reacts with Grignard reagents to produce primary alcohols. Other aldehydes give secondary alcohols. Ketones react with Grignard reagents to produce tertiary alcohols. For example,



(365)



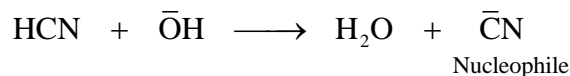
- ii. **Reduction by using HCN:** Aldehydes and ketones react with hydrogen cyanide to form **Cyanohydrins**. The reaction is carried in the presence of a basic catalyst.



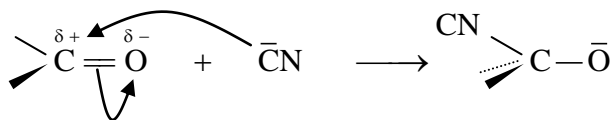
HCN is a very poisonous gas. It is produced *in situ* by the action of dilute sulphuric acid on potassium cyanide.

Mechanism: The mechanism involves the following steps:

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

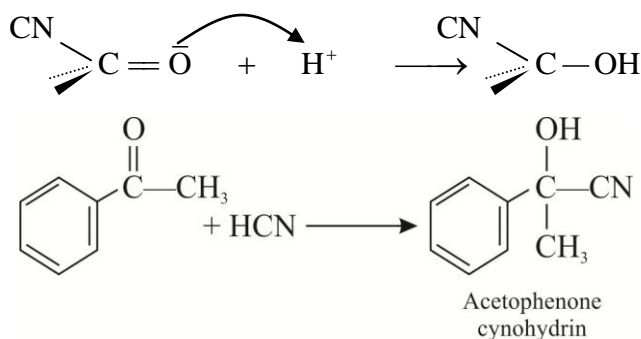


Step 2. The cyanide ion attacks the carbonyl carbon to form an anion.



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

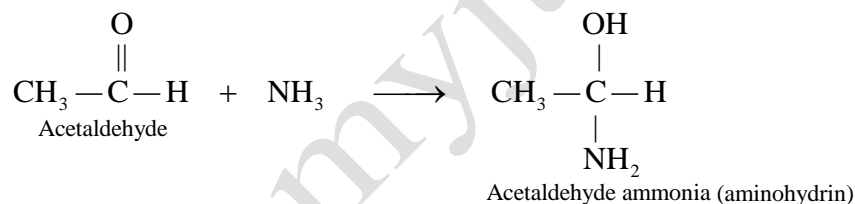
give cyanohydrin.



IV. Reduction by using nitrogen nucleophiles

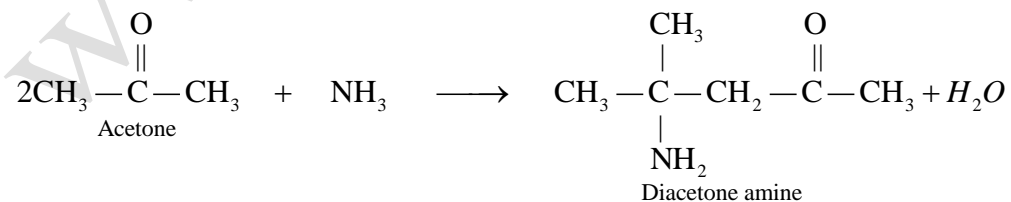
Nitrogen containing compounds (ammonia, amines, hydrazine, phenylhydrazine, hydroxylamine, semicarbazide) can also act as reducing agent due to presence of lone pair of electrons on nitrogen atom and therefore act as nucleophiles towards carbonyl carbon atom.

- i. **Reaction with ammonia:** Aldehydes (except formaldehyde) react with ammonia to form solid aldehyde ammonias. For example,



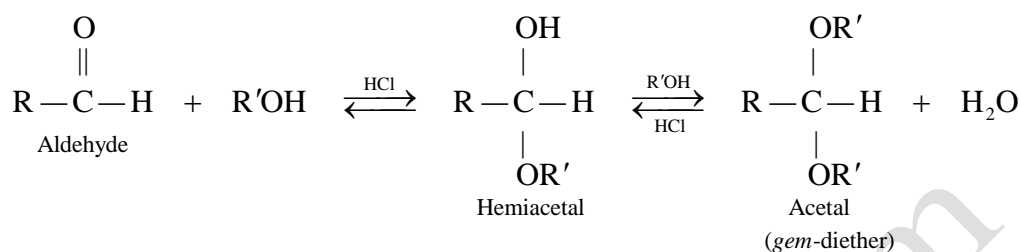
The aldehyde ammonia is when heated with dilute acids, regenerate the aldehydes. Thus the formation and decomposition of these compounds is used for purification of aldehydes.

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

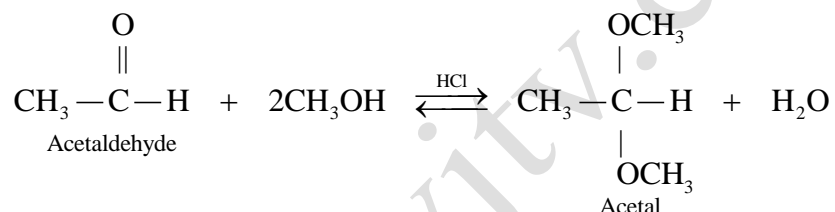


- ii. **Reaction with alkyl amines:** Both aldehydes and ketones react with alkyl amine to form an unstable intermediate which loses water to form an imine.

the same carbon. These hemiacetals react further with alcohols to form stable compounds known as **Acetals**. Notice that the acetals are *gem*-diethers. Acetals has two ether functional groups.



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

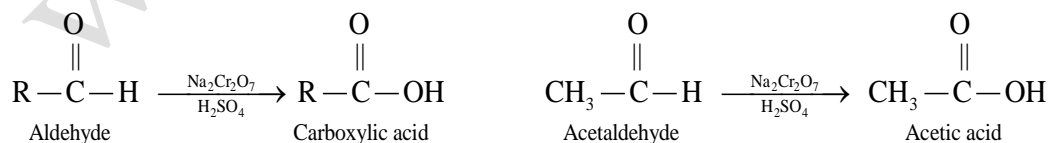


Ketones do not react with alcohols to form the corresponding hemiketals and ketals.

2. Oxidation reactions of aldehydes and ketones

Although the chemical reactivity of aldehydes and ketones is very similar, their behaviour toward oxidizing agents is quite different. Aldehydes are easily oxidized. Ketones are oxidized only under drastic conditions.

I. Oxidation of aldehydes: Aldehydes can be oxidized with sodium (or potassium) dichromate in acidic medium or acidified potassium permanganate or Ag_2O to form carboxylic acids containing the same number of carbon atoms. Actually the hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group.

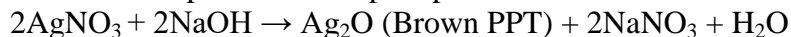


Aldehydes can be oxidized by much milder oxidizing agents such as *Tollens' reagent*, *Fehling's solution* and *Benedict's solution*, these three reagents can be used to distinguish aldehydes from ketones as ketones are not oxidized by these reagents.

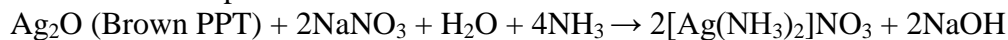
i. Oxidation by Tollen's reagent

Tollens' Reagent/Silver mirror test: Tollen's reagent is a solution of silver nitrate, sodium hydroxide and ammonia.

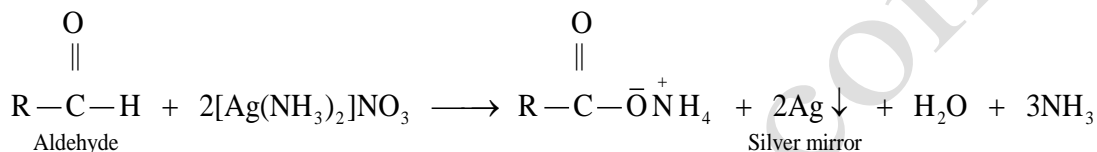
In the first step silver oxide precipitate is formed.



In the second step ammonia is added to dissolve the brown PPT.

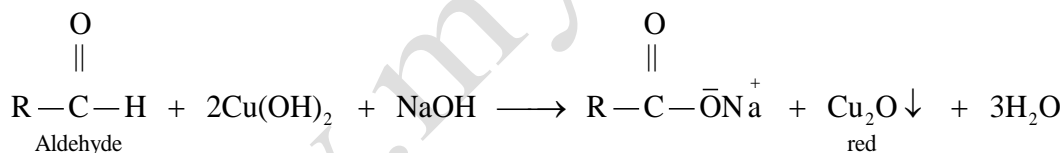


Tollens' reagent is used to oxidize an aldehyde, silver ion is reduced to metallic form and if the reaction is carried out in a clean test tube, it deposits on the inner surface of the tube and result in the formation of a *mirror*. The mirror formation indicates the presence of an aldehyde group in a molecule.



ii. Oxidation by fehling's solution

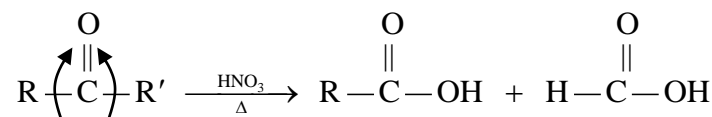
Fehling's Solution: Fehling's solution is an alkaline solution of cupric ion complexed with sodium potassium tartrate ions. When Fehling's solution is used to oxidise an aldehyde, the complexed cupric ion (*deep blue*) is reduced to cuprous oxide (*red*). The presence of the red precipitate of cuprous oxide serves as an indication of an aldehyde group in a molecule.



Benedict's solution is an alkaline solution of cupric ion complexed with citrate ions. It is a mixture of sodium carbonate, sodium citrate and copper sulphate. It reacts in the same way as Fehling's solution.

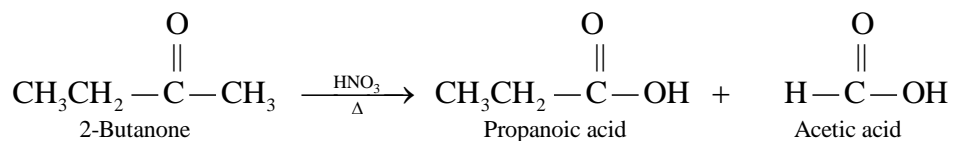
II. Oxidation of ketones

Ketones having alpha hydrogen atom can be oxidized by strong oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, $\text{KMnO}_4/\text{H}_2\text{SO}_4$ 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.



Either of these
bonds can break

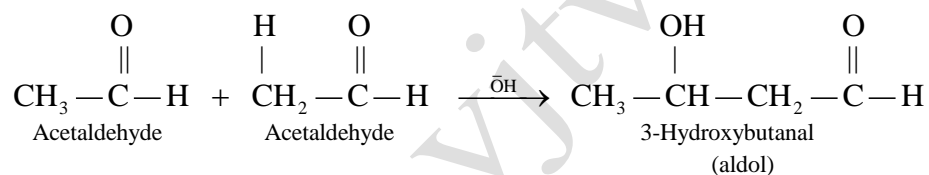
Carboxylic acids



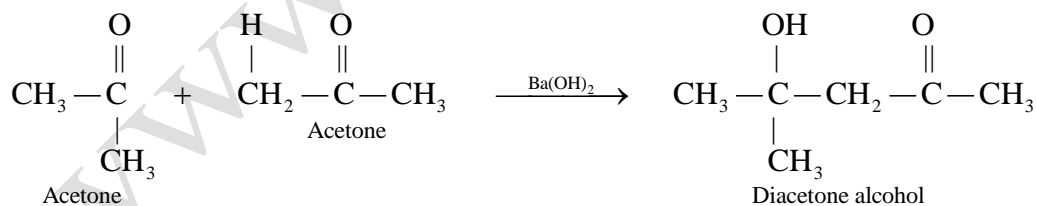
In case of unsymmetrical ketones, the carbonyl group remains with smaller alkyl group as oxidation takes place at this site. Ketones do not react with Tollens' reagent, Fehling's solution, or Benedict's solution.

3. Miscellaneous reactions

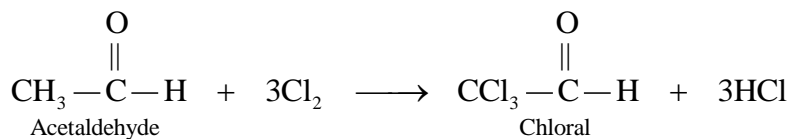
(I) Aldol Condensation: Aldehydes containing α -hydrogens undergo self-addition in the presence of a base to form products called **Aldols**. The reaction is called *Aldol Condensation*. The term aldols is derived from the combination of the words Aldehyde and Alcohol, the two functional groups present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



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).

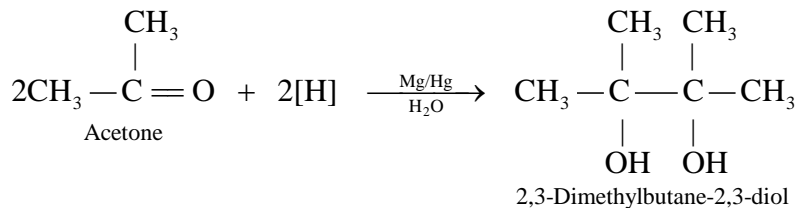


(II) Chlorination: Under suitable conditions, chlorine will successively replace the α -hydrogens in aldehydes and ketones. For example, when chlorine is bubbled through acetaldehyde, chloral (trichloroethanal) is obtained.



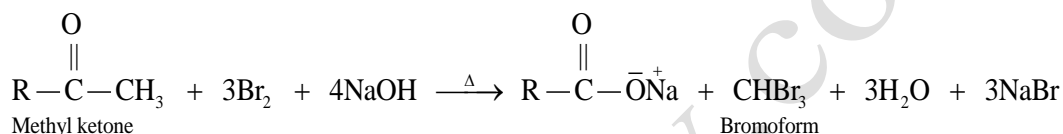
(III) Reduction to Pinacols: Ketones when reduced in neutral or alkaline medium,

form pinacols (symmetrical 1,2-diols). For example, acetone undergoes reduction with magnesium amalgam to form 2,3-dimethylbutane-2,3-diol.

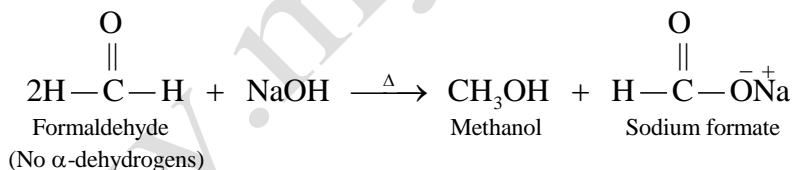


Aldehydes do not give this reaction.

(IV) 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,



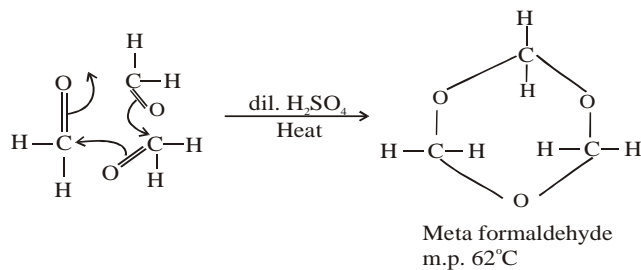
(V) Cannizzaro Reactions: Aldehydes which lack an α -hydrogen, when heated with concentrated NaOH , undergo a disproportionation reaction. One half of the aldehyde molecules are oxidized to a carboxylic acid and one half are reduced to an alcohol. This reaction is known as *Cannizzaro Reaction*. (Remember: Aldehydes with α -hydrogens do not undergo this reaction. Under these conditions, they undergo an Aldol condensation reaction). For example,



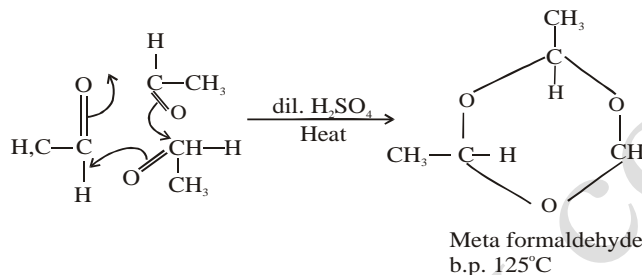
(VI) Schiff's Test: Dilute solutions of aldehydes when added to Schiff's reagent (Rosaniline hydrochloride dissolved in water and its red colour decolourized by passing sulphur dioxide) restores its red colour. This is known as Schiff's test for aldehydes. Ketones do not give this test.

(VII) Polymerization: The first few members of the aldehyde series readily undergo polymerization to give a variety of products. Ketones, however, are not much susceptible to polymerization.

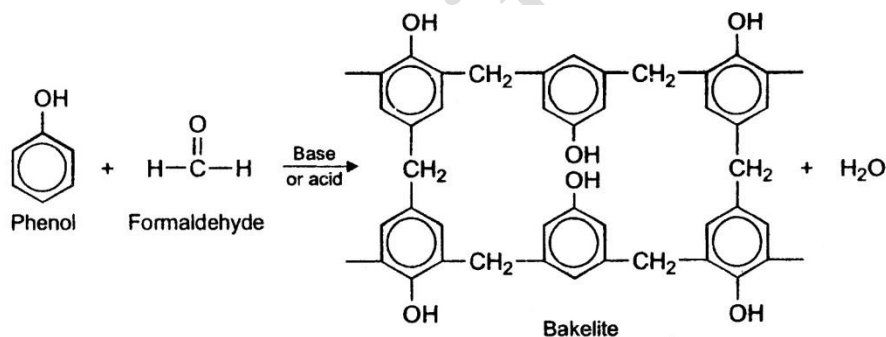
Formaldehyde polymerizes in the presence of dilute H_2SO_4 , on heating, forming meta formaldehyde.



In case of acetaldehyde, polymerization yields paraldehyde.



Formaldehyde condenses with phenol to give a synthetic plastic **Bakelite**. Phenol is refluxed with formalin and ammonia (catalyst)



When an oil separates. The oily liquid is transferred to an open vessel and heated until a test sample, on cooling in water, is found to be hard and brittle. It is then left to cool to give Bakelite.

Testing of Ketones

- Sodium nitroprusside test:** When alkaline sodium nitroprusside solution is added drop by drop to ketones, the appearance of wine red coloration confirms the presence of ketones. Aldehydes do not give any colour with sodium nitroprusside solution.
- Brady's test:** Ketones form red precipitate on heating with 2,4-dinitrophenyl hydrazine (Brady's reagent). Aldehyde do not give any colour on heating with Brady's reagent.

EXERCISE

Q.1. Choose the correct answer.

- (i) The carbon of the carbonyl group is
 (a) sp^3 – hybridized (b)✓ trigonal planar
 (c) Pyramidal in geometry (d) tetrahedral in geometry

The C atom is sp^2 hybridized and the geometry is trigonal planar.

- (ii) The reduction of $>C=O$ to $>CH_2$ is carried out with
 (a) Catalytic reduction (b)✓ Zn-Hg and conc. HCl
 (c) Wolff Kishner reduction (d) $LiAlH_4$

Carbonyl compounds can be converted into alkanes by all the above processes but very easily by using Zn-Hg and conc. HCl which is Clemmenson reduction technique.

- (iii) A compound $C_4H_{10}O$ yields a compound C_4H_8O on oxidation. The compound $C_4H_{10}O$ is.
 (a) An aldehyde (b)✓ An alcohol
 (c) A ketone (d) An acid
- (iv) Formaldehyde gives an additive product with methyl magnesium iodide which on hydrolysis gives,
 (a) n –propyl alcohol (b) Iso propyl alcohol
 (c) Methyl alcohol (d)✓ Ethyl alcohol
- (v) Which of the following compounds can react with ammonical silver nitrate solution to form silver mirror?
 (a) Acetone (b) Ethanol
 (c) Ether (d)✓ Ethanal
- (vi) Which of the following compounds precipitates Cu_2O from Fehling's reagent but does not react with sodium metal?
 (a) C_2H_5OH (b)✓ C_2H_5CHO
 (c) $CH_3CH(OH)CH_3$ (d) CH_3COCH_3
- (vii) When propanal is heated with Fehling's solution there is.
 (a) A colour change from green to orange.
 (b)✓ A colour change from blue to red.
 (c) A negative test with Tollen's reagent
 (d) No colour change.

SHORT QUESTIONS

Q.2. Short Questions:

(i) Aldehyde contains the carbonyl group, ketones, carboxylic acids and esters also contain carbonyl group. What distinguishes these later compounds from an aldehyde?

Ans. Aldehydes can be easily oxidized even by a mild oxidizing agent due to presence of hydrogen atom directly attached with carbonyl carbon. While no such hydrogen is there in all other carbonyl compounds. Tollen's test, Fehling solution test and Benedict's test are positive for aldehydes while other compounds cannot be identified by such tests. The reaction of aldehyde with Grignard's reagent yield primary or secondary alcohols while ketone give tertiary alcohols.

(ii) The mechanism of nucleophilic addition to a carbonyl compound.

Ans. Given in the theory.

(iii) Aldehydes and ketones undergo nucleophilic addition while alkenes undergo electrophilic addition.

Ans. Aldehydes and ketones undergo nucleophilic addition reactions whereas alkene undergoes electrophilic addition reaction. This is because in case of aldehyde and

ketones the $\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$ bond is more polar due to greater electronegativity of oxygen atom which creates an electrophilic carbon therefore a nucleophile can easily attack the electrophilic carbon. Whereas double bond in alkene ($\text{C} = \text{C}$) is not that much polar due to which electron density is equally distributed between the two carbon atoms hence an electrophile can be easily attacked the electron density, hence they undergo electrophilic addition reactions easily rather than nucleophilic addition reaction.

(iv) Aldehydes are oxidized easily than ketones.

Ans. Aldehydes can be easily oxidized because of presence of hydrogen atom directly attached with carbonyl carbon due to which an aldehyde can be easily oxidized as compared to ketone. The C-H bond in aldehydes is weak and can easily be broken during oxidation compared to the C-C bond which is strong and stable.

(v) Ketones are somewhat less reactive than aldehydes towards nucleophile.

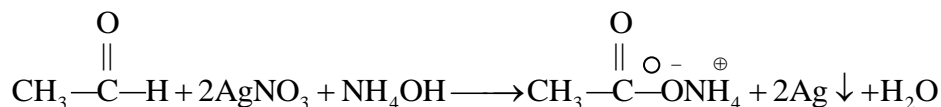
Ans. Given in the theory.

(vi) Which test can be used for the identification of aldehydes from ketones in laboratory?

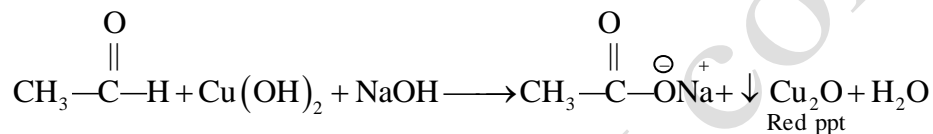
Ans. The following two tests are used to distinguish between aldehydes and ketones.

(i) Tollen's test

(ii) Fehling Solution Test

(1) Tollen's Test/Silver mirror test:Reagents: $\text{AgNO}_3 / \text{NH}_4\text{OH}$ 

The atomic silver formed deposits at the inner walls of the test tube and mirror formation takes place in case of aldehydes but not in ketones.

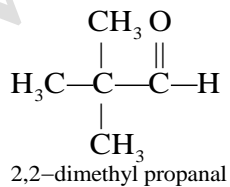
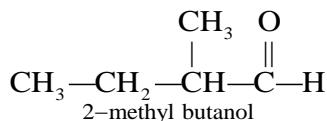
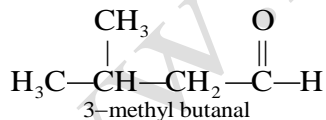
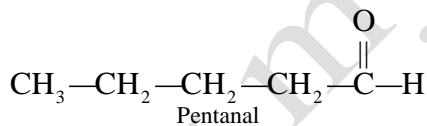
(2) Fehling Solution Tests:Reagent: $\text{Cu}(\text{OH})_2 / \text{NaOH}$ 

This test is also not given by ketones.

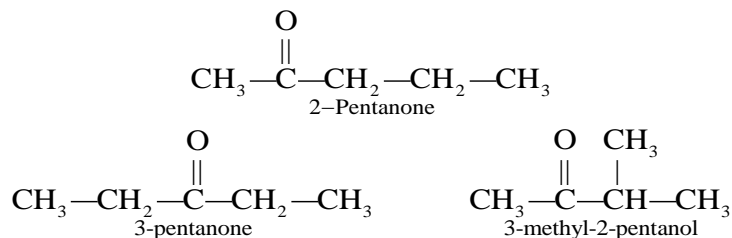
Q.3. Write the structural formulae and give IUPAC names for all aldehyde and ketone isomers of the molecular formula $\text{C}_5\text{H}_{10}\text{O}$.

Ans. Molecular formula $\text{C}_5\text{H}_{10}\text{O}$

Possible isomeric structures for aldehydes from the above formula



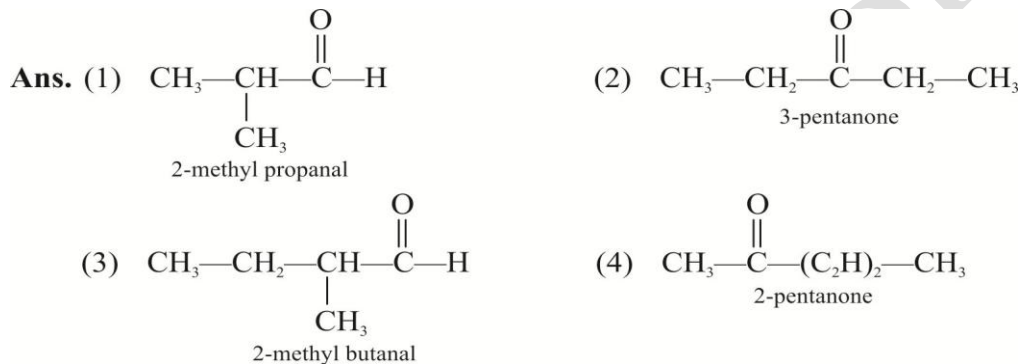
Possible isomeric structures of ketones for the above formula



Q.4. Explain the structure and reactivity of carbonyl compounds.

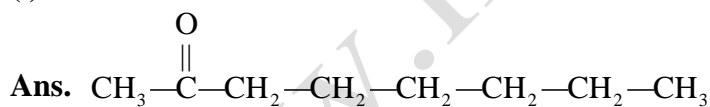
Ans. Given in the theory.

Q.5. Name each of the following compounds according to IUPAC system.

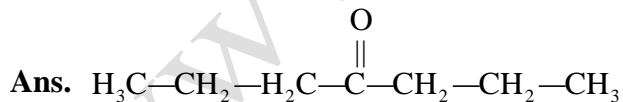


Q.6. Write structural formula for each of the following.

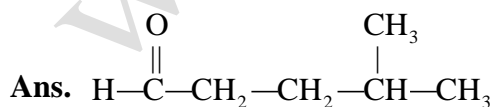
(i) 2-octanone



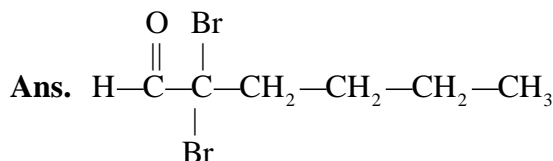
(ii) di-n-propyl ketone/4-heptanone



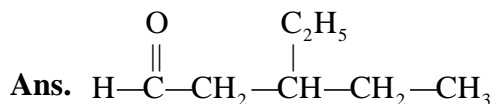
(iii) 4-methyl pentanal



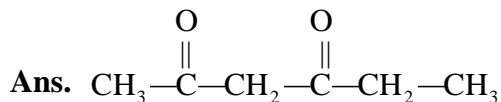
(iv) 2,2-dibromohexanal



(v) 3-ethyl pentanal



(vi) Hexane-2,4-dione/2,4-hexanedione



Q.7. Give a reaction to prepare each of the following.

(i) Cyanohydrin

(ii) Oxime

(iii) Imine

(iv) Hydrazone

(v) Acetal

Ans. Given in the theory.

Q.8. Using Grignard reagent and the appropriate aldehyde or ketone how each of the following can be prepared?

(i) 1-butanol

(ii) Ethyl alcohol

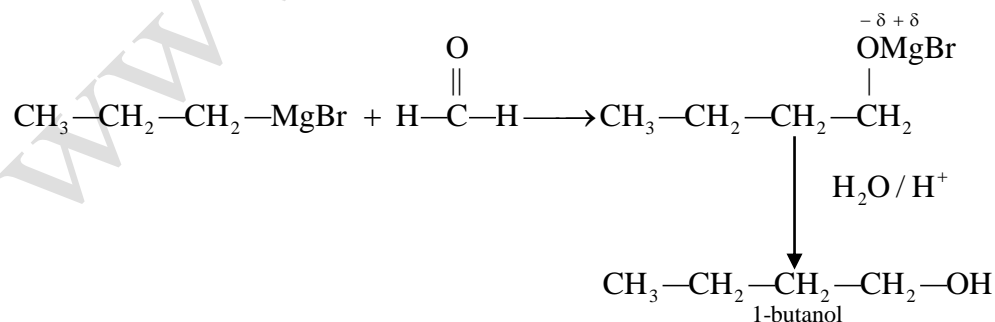
(iii) 2-butanol

(iv) 2-methyl-2-butanol

(v) 3-methyl-3-pentanol

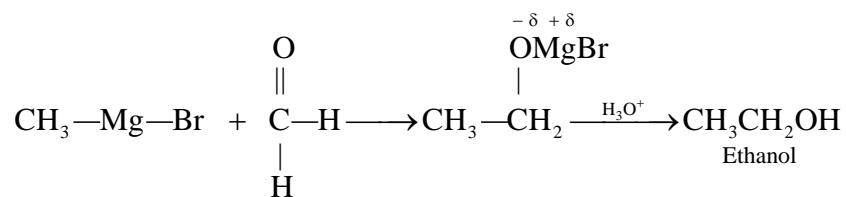
(i) 1-butanol

Ans. When propyl magnesium bromide is treated with formaldehyde we get 1-butanol.

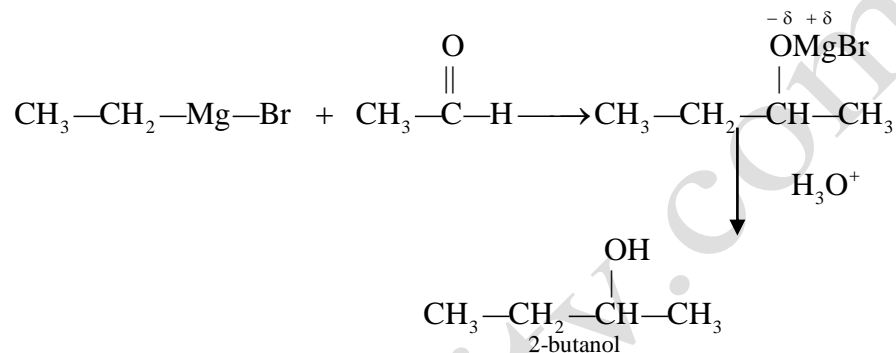


(ii) Ethyl alcohol

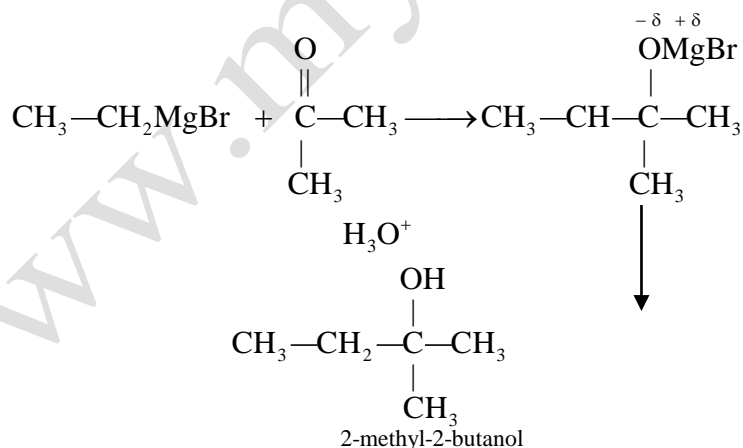
Ans. When Methyl Magnesium Bromide is treated with formaldehyde we get ethyl alcohol.

**(iii) 2-butanol**

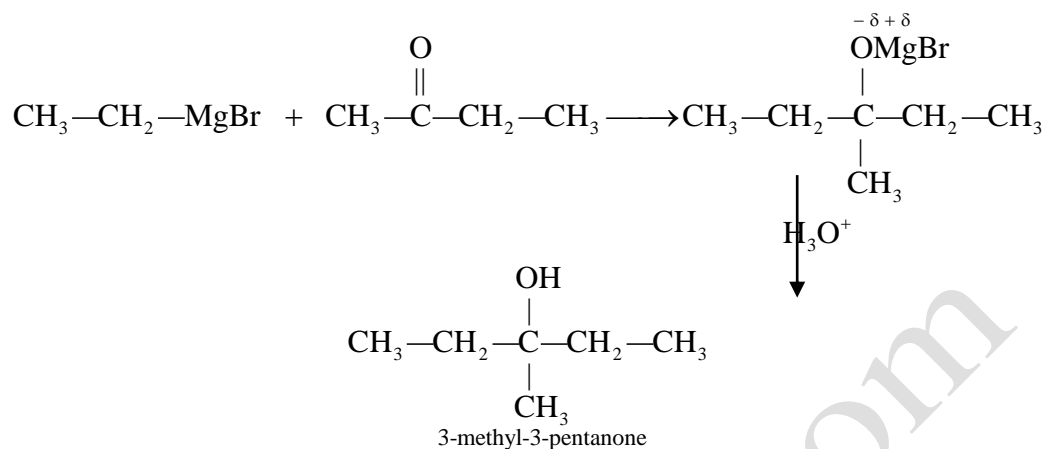
Ans. When $\text{C}_2\text{H}_5\text{MgBr}$ is treated with Acetaldehyde we get 2-butanol.

**(iv) 2-methyl-2-butanol**

Ans. When $\text{C}_2\text{H}_5\text{MgBr}$ is treated with acetone is given 2-methyl-2-butanol.

**(v) 3-methyl-3-pentanol.**

Ans. When $\text{C}_2\text{H}_5\text{-MgBr}$ is treated with butanone it gives 3-methyl-3-pentanol.



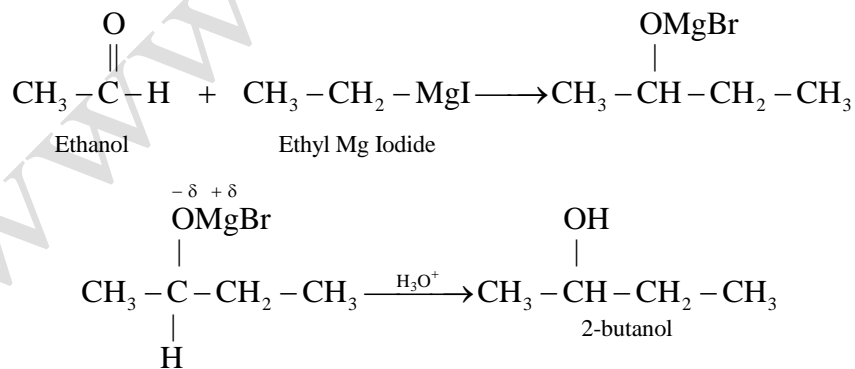
- Q.9. (a) Write any three methods for preparation of acetaldehyde.**
- (b) How does ethanol react with the following reagents?**
- Ethyl magnesium iodide
 - Zinc – mercury amalgam and HCl
 - Lithium Aluminium hydride
 - Acidified $\text{K}_2\text{Cr}_2\text{O}_7$

- (a) Write any three methods for preparation of acetaldehyde.**

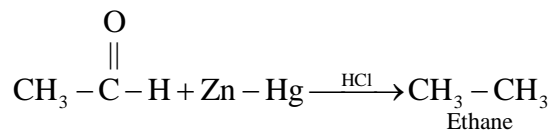
Ans. Given in the theory.

- (b) How does ethanal react with the following reagents?**

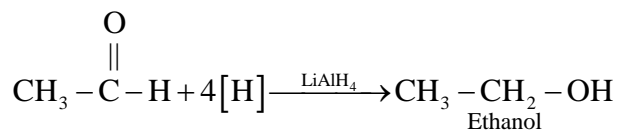
Ans. (i) Ethyl magnesium iodide



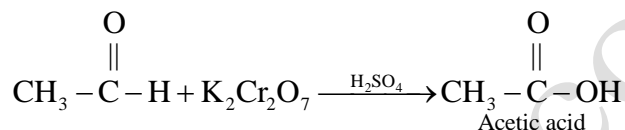
- (ii)** Zinc-Mercury amalgam & HCl



(iii) Lithium Aluminium Hydride



(iv) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$



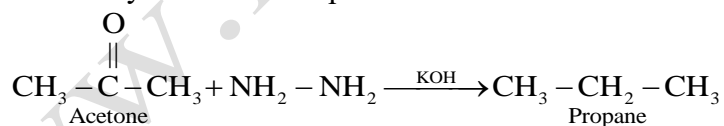
- Q.10. (a) How aromatic ketones are prepared by Friedel-craft acylation?**
(b) Starting from acetone, how will you prepare each of the following.
- | | |
|----------------------------------|-------------------------------|
| (i) Propane | (ii) 2-propanol |
| (iii) Acetone cyanohydrin | (iv) Acetone hydrazone |
| (v) A hemiketal | (vi) Acetic acid |

(a) How aromatic ketones are prepared by Friedel-Craft reactions.

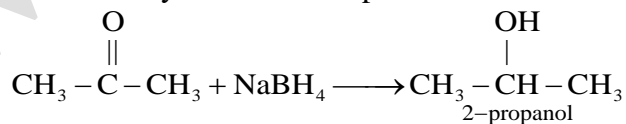
Ans. Given in the theory.

(b) Starting from acetone, how will you prepare each of the following.

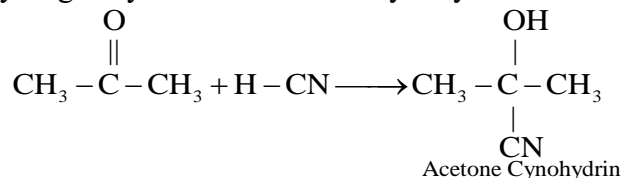
Ans. (i) Acetone + hydrazine \rightarrow Propane



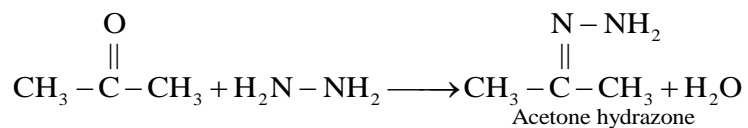
(ii) Acetone + sodium borohydride \rightarrow 2-Propanol



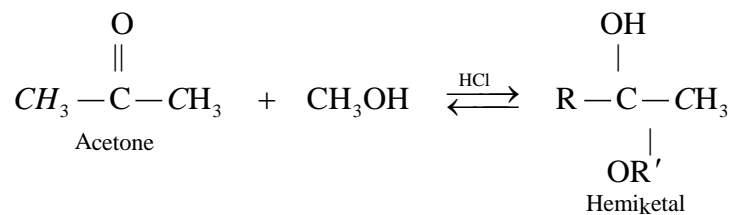
(iii) Acetone + hydrogen cyanide \rightarrow Acetone cynohydrine



(iv) Acetone + hydrazine \rightarrow Acetone hydrazone



(v) Acetone + alcohol → Hemiketal



(vi) Acetone + Acidified potassium dichromate → Acetic acid

