CHAPTER 19

ALDEHYDES AND KETONES

Introduction

Organic compounds containing the carbonyl functional group ($-\overset{O}{\overset{||}{C}}-$) are called aldehydes and ketones.

Aldehydes	Ketones
Functional Group	
In aldehyde, the C-atom of carbonyl group is directly attached to at least one H-atom.	In ketone, the C-atom of carbonyl group is bonded to two carbon atoms.
Position of Functional Group	
Carbonyl functional group lies at one end of the chain.	Carbonyl functional group lies within the chain.
General Formula	
The homologous series of aldehydes have general formula $C_nH_{2n}O$.	The homologous series of ketones have general formula $C_nH_{2n}O$.
General Formula Structure	
An aldehyde may be represented by the general formula structure $R-\overset{:\ddot{O}}{\overset{||}{C}}-H$	A ketone may be represented by the general formula structure $R-\overset{:\ddot{O}}{\overset{||}{C}}-R$
Occurrence	
Aldehyde groups are present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavors.	Ketonic group is present in camphor and fructose.
Examples	
(i) H-CHO (Formaldehyde) (ii) CH_3-CHO (Acetaldehyde)	$CH_3-\overset{O}{\overset{||}{C}}-CH_3$ Acetone $CH_3-\overset{O}{\overset{||}{C}}-C_2H_5$ Methyl ethyl ketone

NOMENCLATURE

Aldehydes

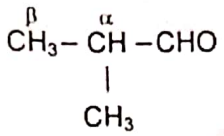
(i) Common Names

- An aldehyde is named after the name of carboxylic acid obtained on its oxidation. The ending –ic acid is replace by "aldehyde" e.g.

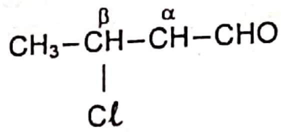
Carboxylic Acid	Aldehyde
Formic acid ($H-\overset{O}{\overset{||}{C}}-OH$)	Formaldehyde ($H-\overset{O}{\overset{||}{C}}-H$)
Acetic acid ($CH_3-\overset{O}{\overset{||}{C}}-OH$)	Acetaldehyde ($CH_3-\overset{O}{\overset{||}{C}}-H$)

Propionic acid ($CH_3-CH_2-\overset{O}{\overset{\|\|}{C}}-OH$)	Propionaldehyde ($CH_3-CH_2-\overset{O}{\overset{\|\|}{C}}-H$)

- For naming substituted aldehydes, the chain is labeled by using α, β, γ ... etc. The carbon next to carbon of the carbonyl group is indicated by 'α' and so on.



(α-methyl propionaldehyde)

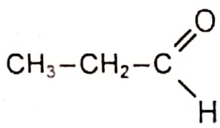


(β-chloro butyraldehyde)

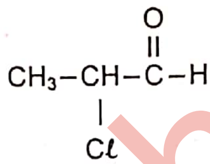
(b) IUPAC Names

1. The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon.
2. The ending 'e' of the alkane is replaced by 'al'.
3. The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number 1.
4. The position of the substituent is indicated by numbers which is written before their names.

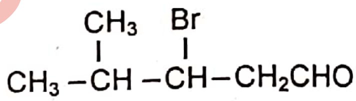
Examples:



Propanal



2-Chloropropanal

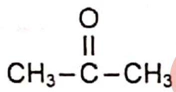


(3-Bromo-4-methylpentanal)

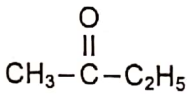
Ketones

(a) Common Names

- Ketones are named by adding the word ketone after writing the names of alkyl or aryl group linked to carbonyl carbon in alphabetical order.

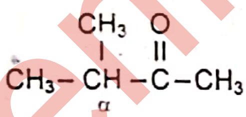


Dimethyl ketone (Acetone)

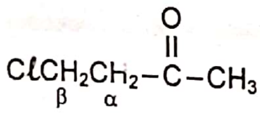


Ethyl methyl ketone

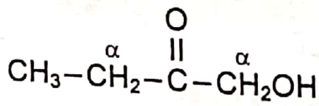
- Substituted ketones are named by labeling the chain using α, β, γ ... etc. The carbon next to carbon of carbonyl group is indicated by 'α' and so on, e.g.



Methyl α-methyl ethyl ketone



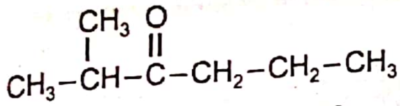
Methyl β-chloroethyl ketone



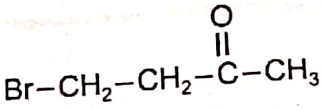
α-hydroxyl-methyl ethyl ketone

(b) IUPAC Names

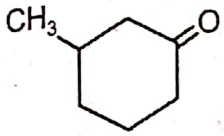
1. The longest chain containing the carbonyl group is taken as the parent hydrocarbon.
2. The ending 'e' of hydrocarbon is replaced by 'one'.
3. The numbering starts from the end that gives the carbonyl carbon the lower number. However, in cyclic ketones, carbonyl carbon is number 1.
4. The positions of substituents are indicated by numbers before their names.



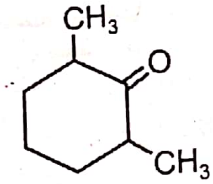
2-Methyl-3-hexanone



4-Bromo-2-butanone



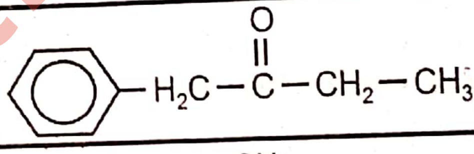
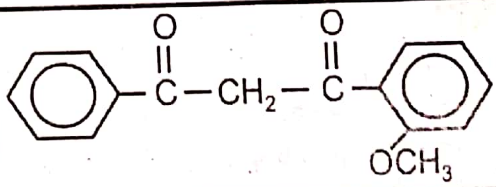
3-Methylcyclohexanone



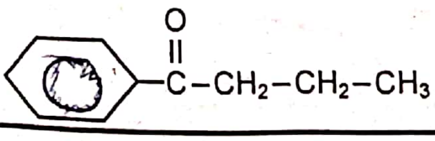
2, 6-Dimethylcyclohexanone

QUICK QUIZ

Write the structures of the following compounds:

No.	Compound Name	Structure
(a)	2-Hexanone	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_3$
(b)	Pentanal	$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$
(c)	2,4-Hexanedione	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$
(d)	1-Phenyl-2-butanone	
(e)	4-Methyl-2-pentanone	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{\|}{CH}}-CH_3$
(f)	1-Phenyl-3-(2-methoxyphenyl)-1,3-propanedione	

Give the IUPAC names of the followings:

No.	Structure	IUPAC Name
(a)	$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$	Butanal
(b)	$CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$	3-Pentanone
(c)		1-Cyclohexyl 1-butanone
(d)	$OCH-CH_2-CH_2-CHO$	1,4-Butanedial

(e)	$CH_3-C(CH_3)=CH-C(=O)-HC=C(CH_3)_2$	2,6-Dimethyl-2,5-heptadien-4-one

Physical Properties

- The polar nature of the C=O (due to the electronegativity difference of the atoms) means dipole-dipole interactions will occur.
- Though C=O cannot hydrogen-bond to each other, the C=O can accept hydrogen bonds from hydrogen bond donors (e.g. water, alcohols).

Class	Compound	Structure	B.Pt
Alkane	Butane	$CH_3-CH_2-CH_2-CH_3$	0°C
Aldehyde	Propanal	$CH_3-CH_2-C(=O)-H$	50°C
Ketone	Acetone	$CH_3-C(=O)-CH_3$	56°C
Alcohol	Propanol	$CH_3-CH_2-CH_2-OH$	97°C

The implications of these effects are:

- ➢ higher melting and boiling points compared to analogous alkanes.
- ➢ lower boiling points than analogous alcohols.
- ➢ more soluble than alkanes but less soluble than alcohols in aqueous media.

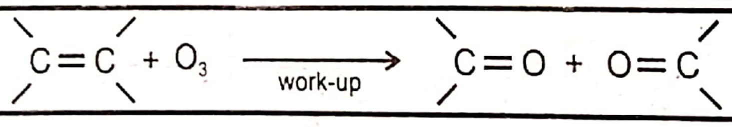
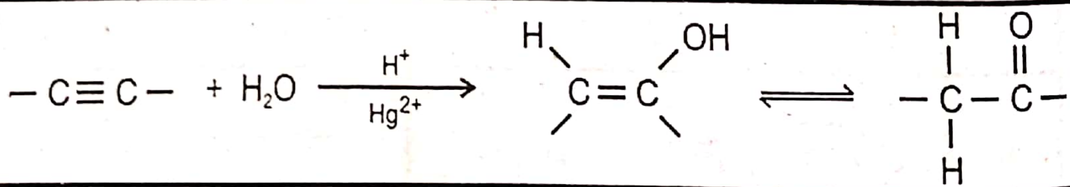
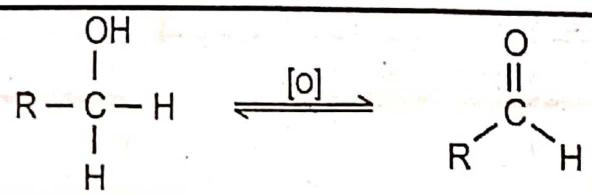
Q. Explain why the boiling point of Alcohol is greater than ketones and aldehydes?

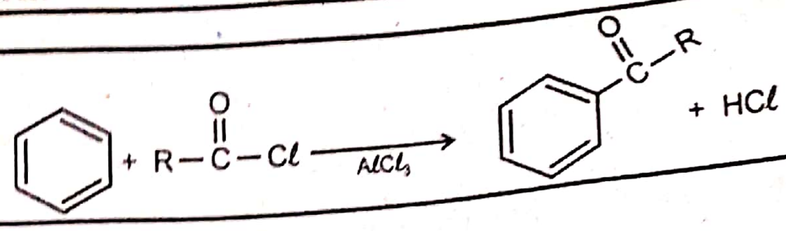
Ans. An alcohol contains OH group allowing for hydrogen bonding which is stronger than other intermolecular forces. Aldehydes and ketones have C = O but no H bond to the oxygen (therefore no hydrogen bonding). Therefore boiling points of alcohols are greater than carbonyl compounds.

Structure

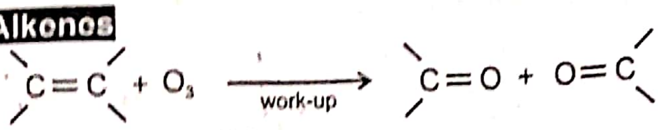
The carbonyl group consists of an O atom bonded to a C atom via a double bonds via an sp^2 hybridization model similar to that of ethene. As oxygen is more electronegative, it tends to attract the π electrons to itself. This attraction makes the carbonyl group a polar group. The oxygen atom has a partial negative charge on it and is nucleophilic, whereas the carbon atom has a partial positive charge and is electrophilic. $>\overset{\delta+}{C}=\overset{\delta-}{O}$

PREPARATIONS OF ALDEHYDES AND KETONES

Ozonolysis of Alkenes	
Hydration of Alkynes	
Oxidation of Alcohols	

Friedel-Crafts Acylation of Aromatics	

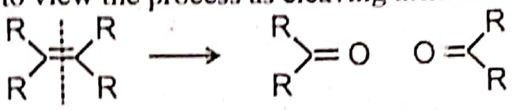
(1) Ozonolysis of Alkenes



Reaction type: Electrophilic Addition

Elaboration

- Overall transformation : **C = C** to **2C = O**
- Reagents: ozone, O_3, followed by a reducing work-up, usually Zn in acetic acid.
- It is convenient to view the process as cleaving the alkene into two carbonyl compounds:

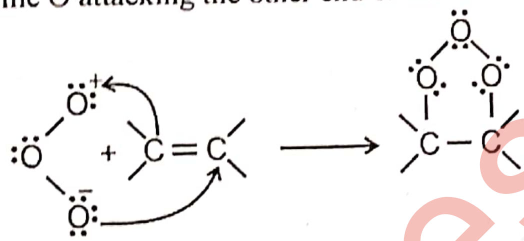


- The substituents on the **C = O** depend on the substituents on the **C = C**.

Mechanism for Reaction of Alkenes with O_3

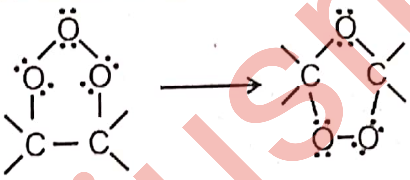
Step 1:

The Pi(π) electrons act as the nucleophile, attacking the ozone at the electrophilic terminal O. A second C–O is formed by the nucleophilic O attacking the other end of the C = C.



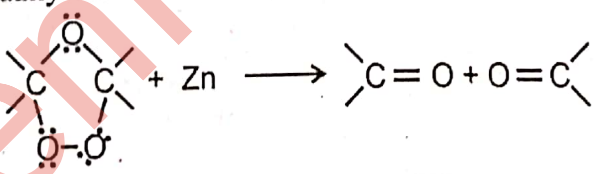
Step 2:

The cyclic species called the molozonide rearranges to the ozonide.



Step 3:

On work-up (usually Zn / acetic acid) the ozonide decomposes to give two carbonyl compounds.



(2) Hydration of Alkynes

Water adds on to alkynes in the presence of dil. H_2SO_4 and $HgSO_4$ to produce an aldehyde or ketone. Enol forms as intermediate which isomerizes into aldehydes or ketones. e.g.

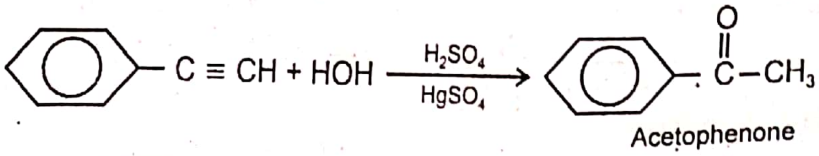
$$HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Vinyl alcohol}}{CH_2 = CH-OH} \xrightarrow{\text{Rearrangement}} \underset{\text{Acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}} = O}$$

Propyne gives acetone:

$$CH_3-C\equiv CH + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\overset{OH}{\overset{|}{C}} = CH_2 \xrightarrow{\text{Rearrangement}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetone

This reaction is useful for preparing methyl aryl ketones



(3) Oxidation of Primary and Secondary Alcohols

Primary alcohols are oxidized to aldehydes by:

(i) Warming with acidic dichromate solution

$$CH_3CH_2CH_2CH_2OH \xrightarrow[Na_2Cr_2O_7]{Conc.H_2SO_4} CH_3CH_2CH_2CHO$$

Butanol — Butanal

(ii) Jone reagent (CrO_3 + dil. H_2SO_4 + acetone)

(iii) Sarett reagent (CrO_3 in pyridine)

$$C_6H_5CH_2OH \xrightarrow[\text{reagent}]{\text{Sarett}} C_6H_5CHO$$

Benzyl alcohol — Benzaldehyde

- Non-aqueous solvents are employed to avoid further oxidation.
- Secondary alcohols are oxidized to ketones.

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{HC}}}-OH \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2-Propanol — Acetone (Propanone)

(4) Friedel-Crafts Acylation of Benzene

It is the substitution of acyl group in an organic compound in the presence of $AlCl_3$ or some other Lewis acids.

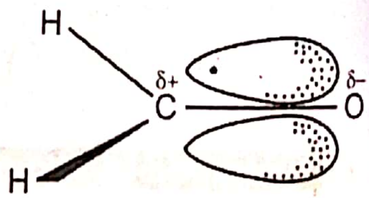
$$C_6H_6 + R-\underset{O}{\underset{\|}{C}}-Cl \xrightleftharpoons{AlCl_3} C_6H_5COR + HCl$$

(Alkyl aryl ketone)

$AlCl_3$ generates acylenium ion ($R-\overset{O}{\overset{\|}{C}}{}^{+}$) (electrophile) which is substituted in the aromatic ring.

Reactivity

The double bond of the carbonyl group has a σ-bond and a π-bond. As oxygen is more electronegative, it attracts the π-electrons towards itself. This attraction makes the carbonyl group a polar group.



The oxygen atom has a partial negative charge on it and the carbon atom has partial positive charge. The π e'ectron cloud is pulled more strongly by the oxygen atom than the carbon atom. It makes oxygen atom nucleophile and carbon atom becomes electrophile.

REACTIONS OF ALDEHYDES AND KETONES

Nucleophilic Addition Reactions

There are two types of nucleophilic addition reactions of carbonyl compounds:

1. Base catalysed nucleophilic addition reaction
2. Acid catalysed nucleophilic addition reaction

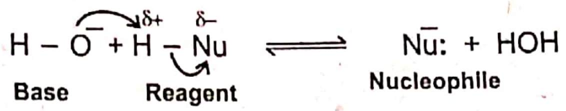
The characteristic reactions of carbonyl compounds are nucleophilic addition reactions.

(1) BASE-CATALYSED ADDITION REACTIONS

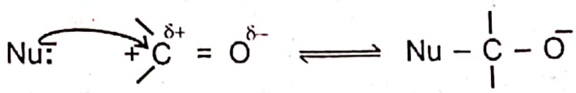
A base-catalysed nucleophilic addition reaction will take place with a strong nucleophilic reagent. The base reacts with the reagent and generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reaction is as follows:

General mechanism

Step-I:



Step-II:

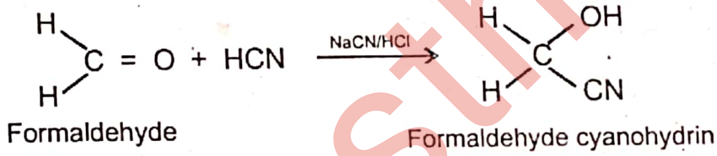


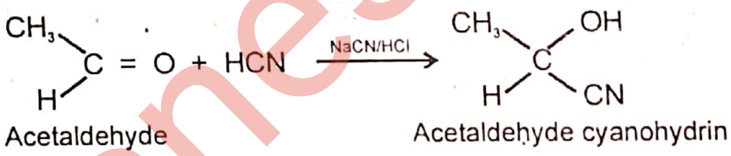
Step-III:

The base catalysed nucleophilic addition reactions of aldehydes and ketones are as follow:

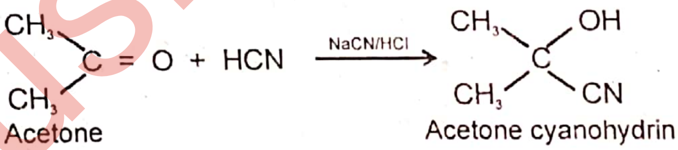
(i) Addition of Hydrogen Cyanide

Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The acid generates HCN form sodium cyanide in HCℓ.





Q. How would you convert Acetaldehyde into lactic acid?



The cyano group, –CN is hydrolysed by an aqueous acid into a carboxylic acid through an acid amide.

$$CH_3-\underset{}{\overset{OH}{\overset{|}{CH}}}-CN + 2H_2O + H_2SO_4 \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-COOH + NH_4HSO_4$$

Acetaldehyde cyanohydrin → **2-Hydroxypropanoic acid (Lactic acid)**

Use of the reaction

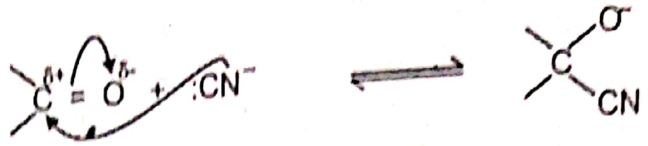
The reaction is used in the synthesis of α-hydroxy acids that contain one carbon atom more than number of carbon atoms in the starting aldehydes or ketones.

Mechanism

The reaction is base-catalysed because HCN has no lone pair of electrons on its carbon. The base (OH^-) generate cyanide ion which acts as nucleophile. The mechanism of the reaction is as follows:

Step-I:

Step-II:



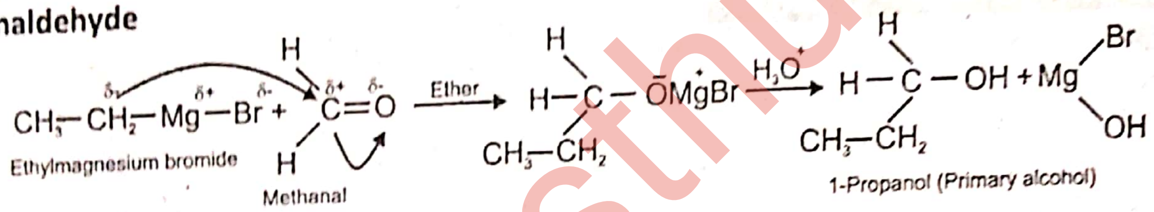
Step-III:

The hydroxide ion liberated in the formation of cyanohydrin reacts with undissociated hydrogen cyanide and roduces more cyanide ions which in turn react with more carbonyl compound.

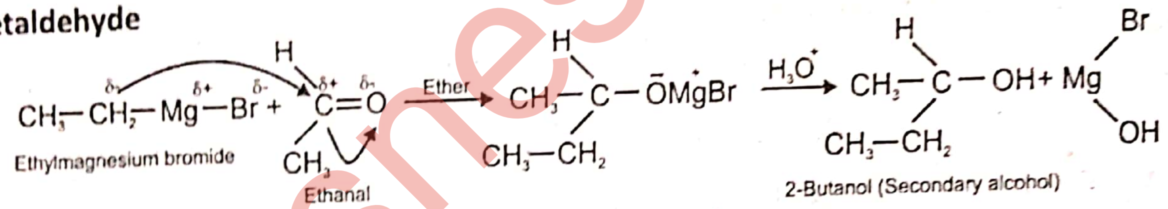
ii) Addition of Grignard Reagents

Grignard reagents add to aldehydes and ketones to form adducts which on hydrolysis with a dilute mineral acid HCℓ, H_2SO_4) give alcohols.

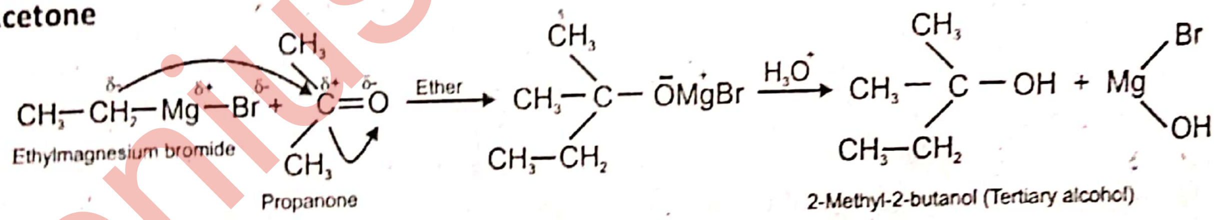
(i) With Formaldehyde



(ii) With Acetaldehyde

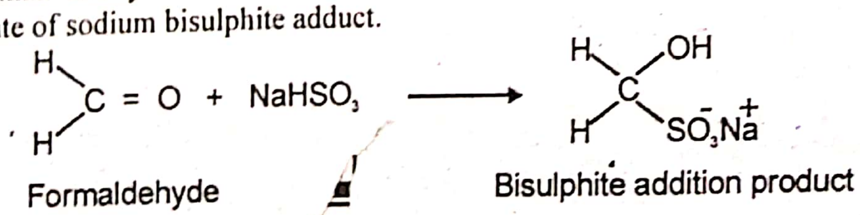


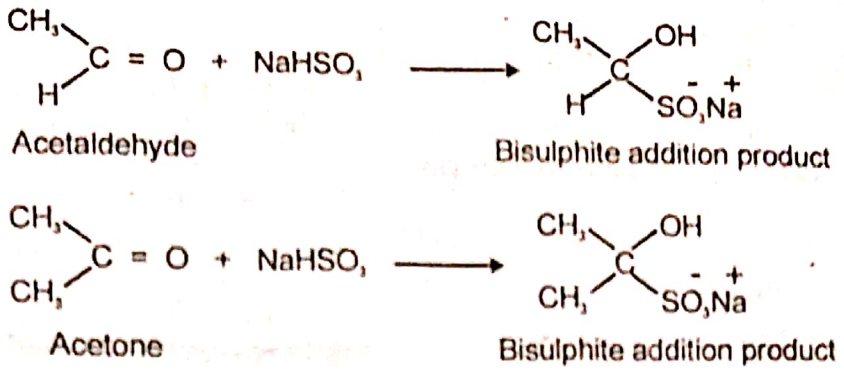
(iii) With Acetone



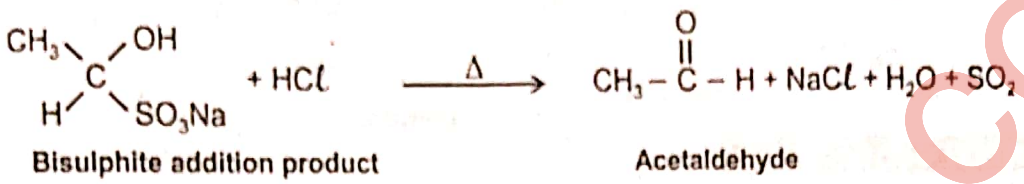
iii) Addition of Sodium Bisulphite

Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphite to form a crystalline white precipitate of sodium bisulphite adduct.





Bisulphite on heating with a dilute mineral acid (HCl or H_2SO_4) regenerates the parent aldehyde or ketone.



Use of the reaction

The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

(iv) Condensation Reaction

"The reactions, in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H_2O or NH_3, are called condensation reactions."

Exercise: Q.3(iv) Define and explain aldol condensation along with mechanism.

ALDOL CONDENSATION

"Aldol condensation is a reaction in which two molecules of same or different carbonyl compounds containing α-hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to form aldol or ketol, which usually loses water molecule."

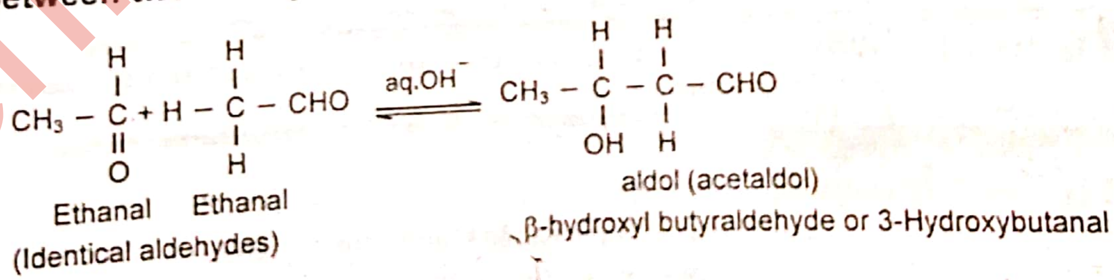
Mild Alkaline conditions

Aldol condensation takes place under mild alkaline conditions, for example in the presence of sodium carbonate, sodium bicarbonate, barium hydroxide, dilute sodium hydroxide or an alkoxide in low concentration.

Types

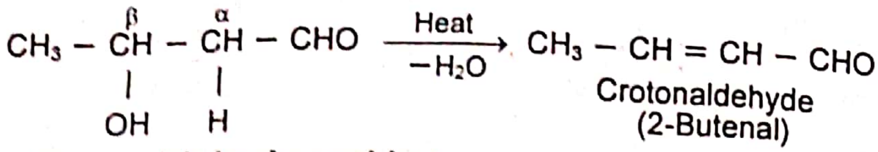
Aldol condensation can occur in following combinations:

(i) Condensation between two aldehydes:

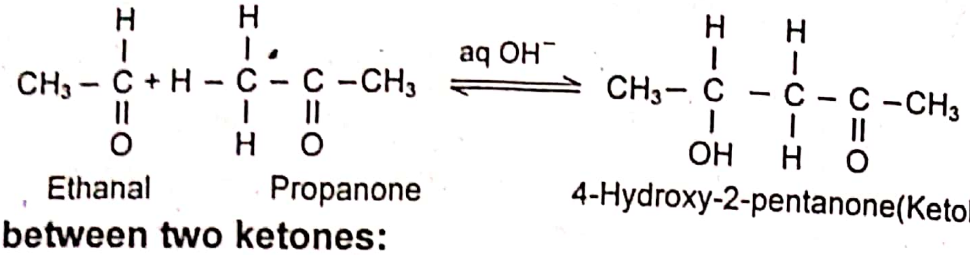


Conversion into Crotonaldehyde

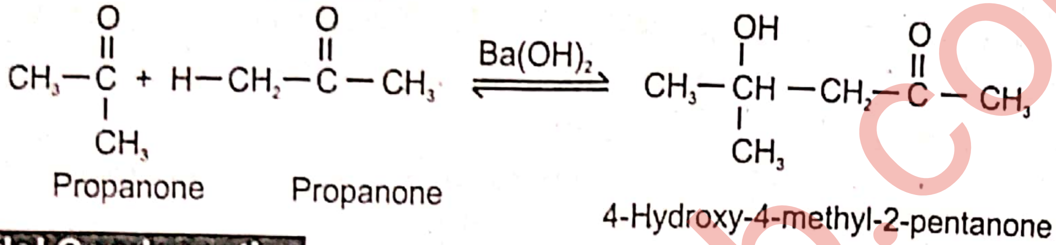
The aldol compound readily loses water on heating in ... oform ... sence of dilute acid to form α, β-unsaturated carbonyl compound. A carbon-carbon double bond is formed betw... α-and β-carbon atoms.



(ii) Condensation between aldehyde and ketone:



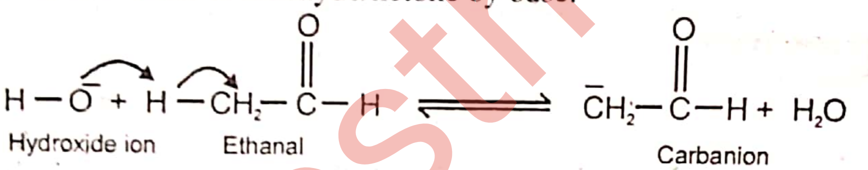
(iii) Condensation between two ketones:



Mechanism of Aldol Condensation

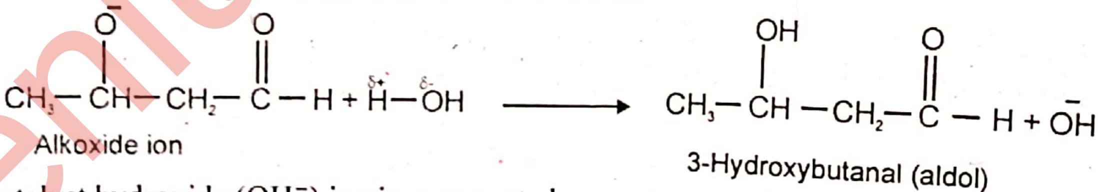
Following steps are involved in aldol condensation:

- **Formation of nucleophile**
  Removal of a proton from α-carbon of aldehyde/ketone by base:



- **Formation of alkoxide ion**
  Attack of nucleophile on carbonyl carbon to form alkoxide ion.

- **Protonation:**
  The alkoxide ion removes a proton from water to form aldol.

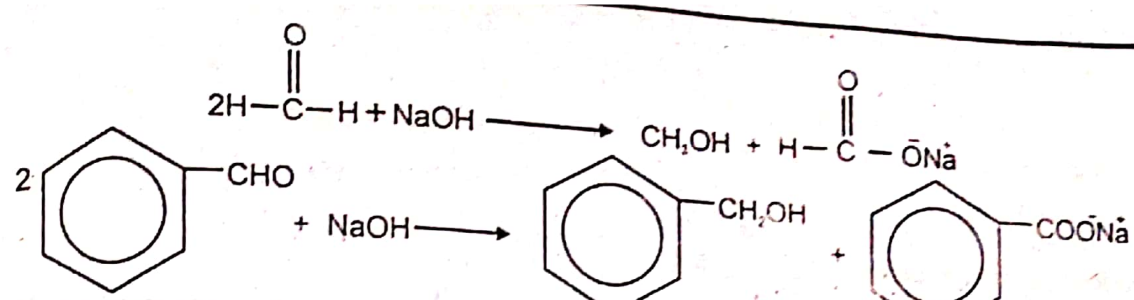


The basic catalyst hydroxide (OH^-) ion is regenerated.

Exercise: Q.3(viii) Which type of aldehydes give Cannizzaro's reaction? Explain with mechanism.

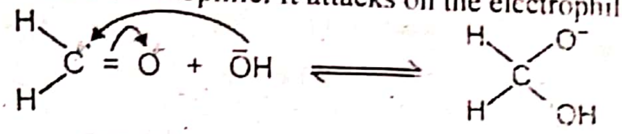
(v) Cannizzaro's Reaction

- Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction.
- It is a disproportionate (self oxidation-reduction) reaction.
- Two molecules of the aldehyde are involved. One molecule is reduced into corresponding alcohol and the other is oxidized into acid (in the salt form).
- The reaction is carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.



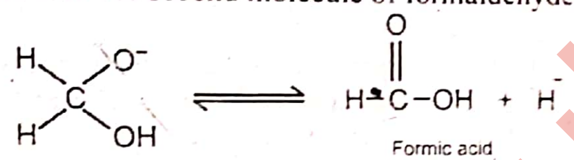
Mechanism

- **Step I:**
The hydroxide ion acts as a nucleophile. It attacks on the electrophilic carbonyl carbon to form a complex anion.



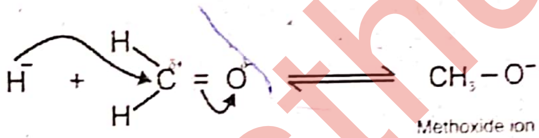
CH_3OH (Reduced product)
Reduction ↑ Addition of Hydrogen
HCHO
Oxidation ↓ Addition of oxygen
HCOOH (oxidized product)

- **Step II:**
The anion transfers a hydride ion to second molecule of formaldehyde.

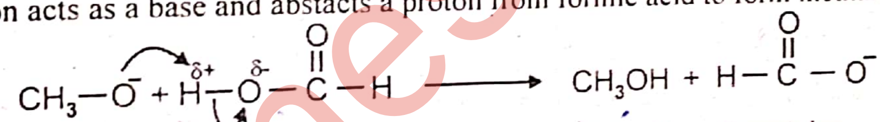


The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.

- **Step III:**



- **Step IV:**
The methoxide ion acts as a base and abstacts a proton from formic acid to form methanol and formate ion.



- **Step V:**
The formate ion in the presence of alkali gives a salt of the acid.

$$H-\overset{O}{\overset{||}{C}}-O^- + NaOH \longrightarrow H-\overset{O}{\overset{||}{C}}-O^-Na^+ + \overset{-}{O}H$$

Exercise: Q.3(v) Give detail of haloform reaction. Why it is called so?

(vi) Haloform Reaction

Only acetaldehyde and methyl ketones react with halogens (Cl_2, Br_2, I_2) in the presence of sodium hydroxide to give haloform and sodium salt of the acid. The term haloform is used for the reaction because a haloform (chloroform, bromoform or iodoform) is one of the products.

$$R-\overset{O}{\overset{||}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

R = alkyl, aryl or hydrogen; Halogen; Haloform; Sod. carboxylate

(i) Acetaldehyde is the only aldehyde which undergoes iodoform reaction.

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \underset{\text{Iodine}}{3I_2} + 4NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3} + \underset{\text{sod. formate}}{HCOONa} + 3NaI + 3H_2O$$

(ii) All secondary ketones undergo iodoform reaction.

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + \underset{\text{Iodine}}{3I_2} + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. acetate}}{CH_3COONa} + 3NaI + 3H_2O$$

(iii) Ethanol is the only primary alcohol that gives this reaction.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. formate}}{HCOONa} + 5NaI + 5H_2O$$

(iv) Secondary alcohols containing the methyl group also undergo this reaction.

$$\underset{\text{Secondary alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. carboxylate}}{RCOONa} + 5NaI + 5H_2O$$

From a synthetic point of view, the haloform reaction affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than the parent compound.

Iodoform Test

"The haloform reaction using iodine and aqueous sodium hydroxide is called the iodoform test." It results in the formation of water insoluble iodoform which is a yellow solid.

Use of Iodoform Test

Iodoform test is used to distinguish:

- Methyl ketones from other ketones.
- Ethanol from methanol and other primary alcohols.
- Acetaldehyde from other aldehydes.

MCQ's

Which of the following give positive iodoform test?

(a) 1 – Pentanol
(b) 2 – Pentanone
(c) 3 – Pentanone
(d) Pentanal

(2) ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

These reactions will take place with a weak nucleophilic reagent. The addition is initiated by the proton (H^+) liberated by the acid. The proton combines with the carbonyl oxygen atom and increases the electrophilic character of the carbonyl carbon. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.

Mechanism:

The general mechanism of the reaction is as follows.

Step-I:

$$>\overset{\delta+}{C}=\overset{\delta-}{O} + H^+ \rightleftharpoons\ >C=O^+-H$$

Step-II:

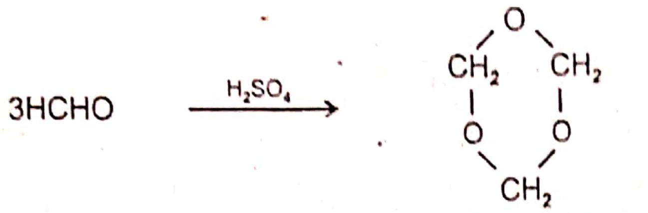
$$Nu^- + >C=O^+-H \rightleftharpoons Nu-\overset{|}{\underset{|}{C}}-OH$$

The acid-catalysed nucleophilic addition reactions of aldehydes and ketones are the following:

1. Polymerization

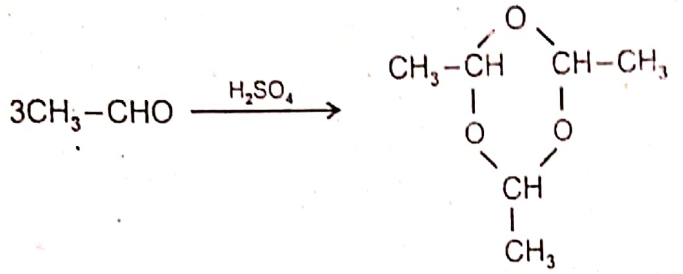
Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde respectively.

Metaformaldehyde is a white solid having melting point 62°C.



Metaformaldehyde

Paraldehyde is a cyclic trimer and is used as a hypnotic and soporific (sleep producing).

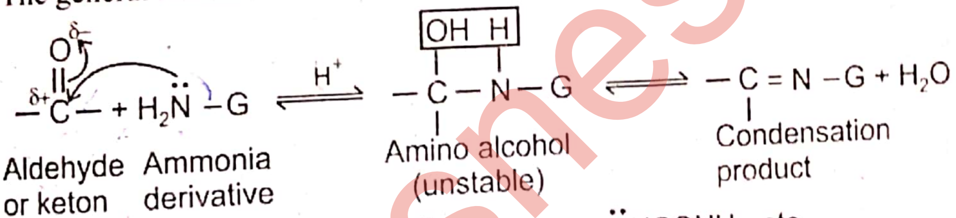


Paraldehyde

2. Addition of Ammonia Derivatives

Aldehydes and ketones react with ammonia derivatives, $G-NH_2$ to form compounds containing the group, $>C=N-G$ and water. The reaction is known as condensation reaction or addition-elimination reaction because water is lost after addition occurs. The reaction is acid catalyzed.

The general reaction is:



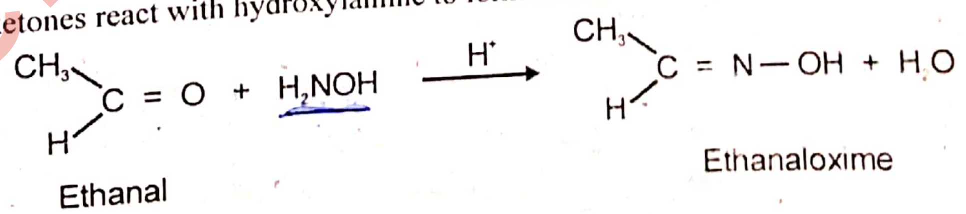
Where G = $\ddot{O}H$, $-\ddot{N}H_2$, $-\ddot{N}HC_6H_5$, $-\ddot{N}HCONH_2$, etc.

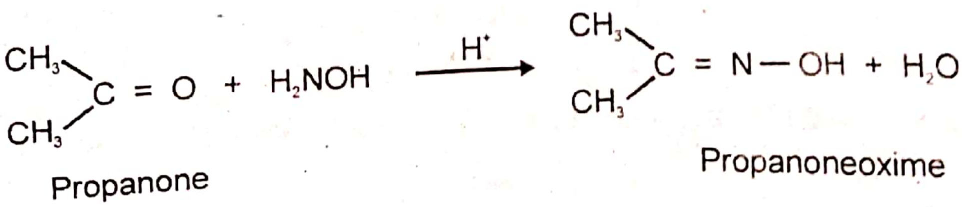
Some commonly used ammonia derivatives are hydroxylamine, NH_2OH, hydrazine, NH_2NH_2, phenylhydrazine, $C_6H_5NHNH_2$, semicarbazide, $NH_2NHCOHN_2$ and 2, 4, dinitrophenylhydrazine, $NH_2NHC_6H_3(NO_2)_2$.

The reactions of the above stated ammonia derivatives with aldehydes and ketones are as follow.

(i) Reaction with Hydroxylamine

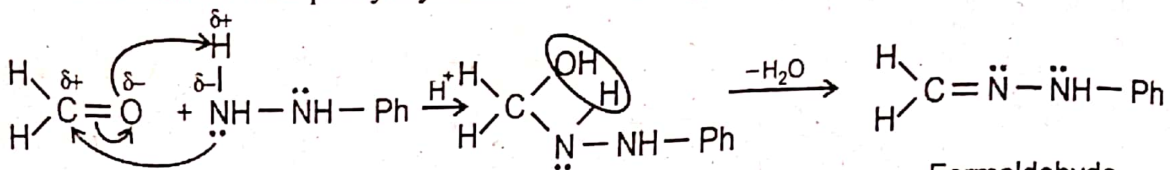
Aldehyes and ketones react with hydroxylamine to form oximes in the presence of an acid.



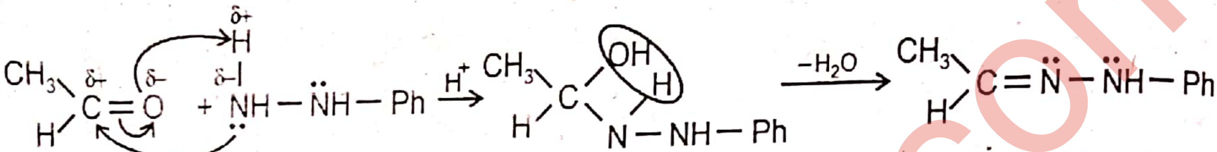


(ii) Reaction with Phenylhydrazine ($\ddot{N}H_2 - \ddot{N}H - C_6H_5$) ($C_6H_5$ = phenyl group = Ph−)

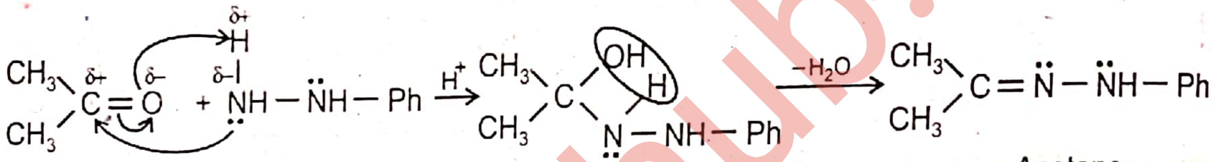
Aldehydes and ketones react with phenyl hydrazine to form phenylhydrazones in the presence of an acid.



Formaldehyde (Methanal) → Formaldehyde Phenylhydrazone



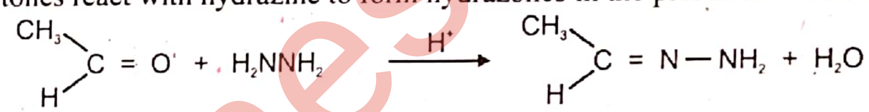
Acetaldehyde (Ethanal) → Acetaldehyde Phenylhydrazone



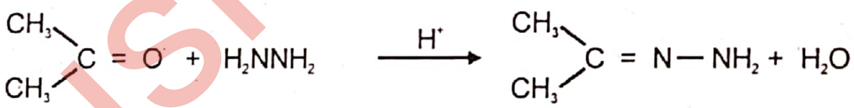
Acetone (Propanone) → Acetone Phenylhydrazone

(iii) Reaction with Hydrazine

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



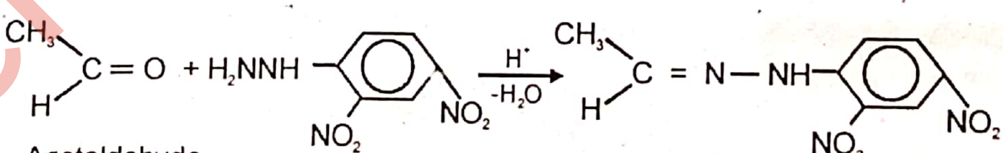
Acetaldehyde → Acetaldehyde hydrazone



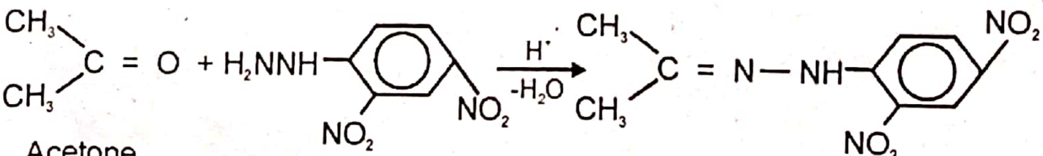
Acetone → Acetone hydrazone

(iv) Reaction with 2, 4-Dinitrophenylhydrazine [2, 4-DNPH]

Aldehydes and ketones react with 2, 4-dinitrophenyhydrazine to form 2, 4-dinitrophenylhyrazones in the presence of an acid.



Acetaldehyde + 2,4-DNPH → Acetaldehyde 2,4-DNPH



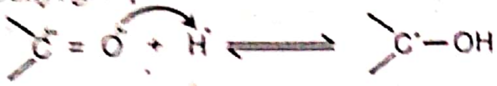
Acetone + 2,4-DNPH → Acetone 2,4-DNPH

The reactions can be used for the identification of aldehydes and ketones because 2, 4-Dinitrophenylhydrazones are usually yellow or orange crystalline solids.

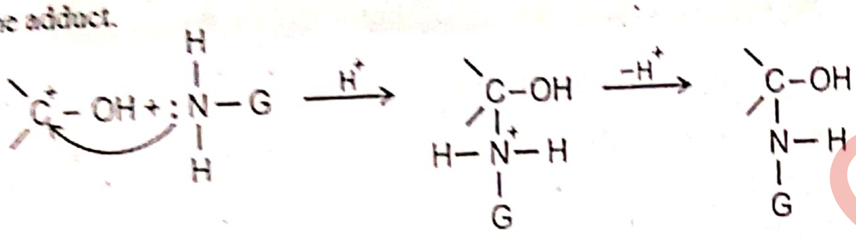
Q.3(vii) What is the mechanism for addition of ammonia derivatives to carbonyl group?

Ans: **Mechanism of the Reaction of Ammonia Derivatives**

Step I: Protonation of oxygen of the carbonyl group.

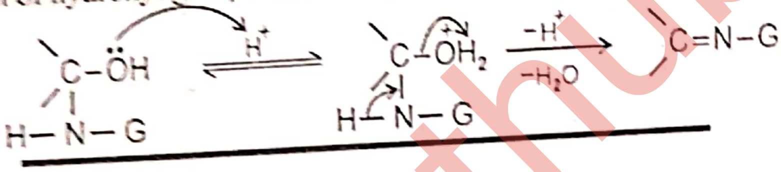


Step II: Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



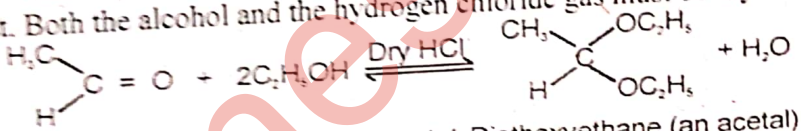
Adduct

Step III: Protonation of oxygen of hydroxyl group followed by the removal of water



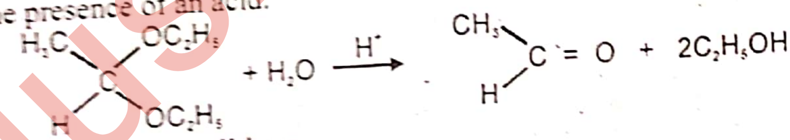
3. Addition of Alcohols

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride gas acts as a catalyst. Both the alcohol and the hydrogen chloride gas must be dry.



1,1-Diethoxyethane (an acetal)

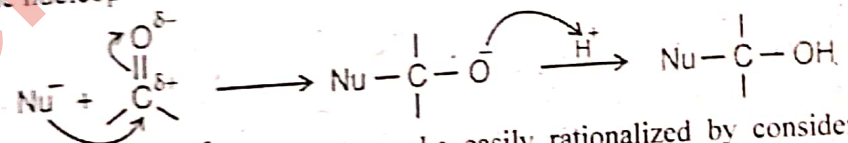
The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.



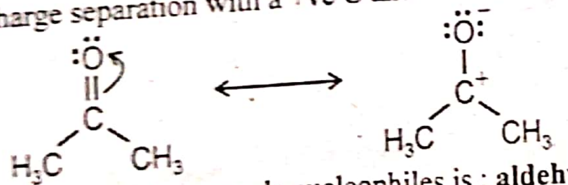
Note: Ketones do not react under these conditions.

Relative Reactivity

Overall a simple nucleophilic addition can be represented with curly arrows as follows:



The reactivity of aldehydes and ketones can be easily rationalized by considering the important resonance contributor which has charge separation with a +ve C and −ve O.

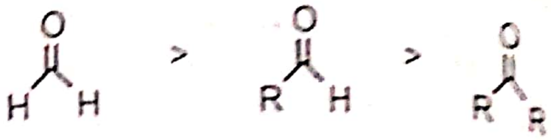


In general the reactivity order towards nucleophiles is : **aldehydes > ketones**

The substituents have two contributing factors on the reactivity at the carbonyl C:

(i) Size of the substituents attached to the C=O

Larger groups will tend to sterically hinder the approach of the **Nucleophile**.



(ii) The electronic effect of the substituent

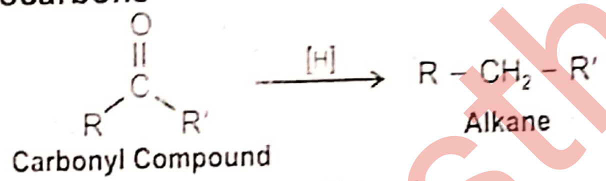
Alkyl groups are weakly electron donating so they make the C in the carbonyl less electrophilic and therefore less reactive towards nucleophiles.

These trends are supported by the trends in the equilibrium data for the formation of hydrate.

Carbonyl Compound	K / M^{-1}	% Hydrate
Carbonyl	41	99.96
Methanal	1.8×10^{-2}	50
Ethanal	4.1×10^{-3}	19
2,2-Dimethylpropanal	2.5×10^{-5}	0.14

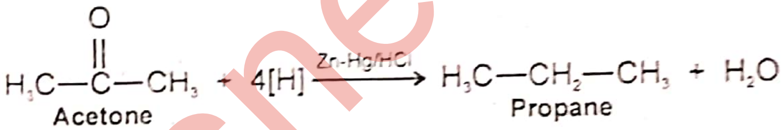
REDUCTION OF ALDEHYDES AND KETONES

Reduction to Hydrocarbons



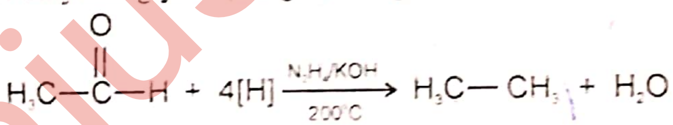
Clemmensen Reduction (acidic conditions)

Zn(Hg) in HCl reduced the C=O into $-CH_2-$ (Methylene)



Wolf-Kishner Reduction (basic conditions)

NH_2NH_2 / KOH / ethylene glycol (a high boiling solvent) reduces the C=O into $-CH_2-$

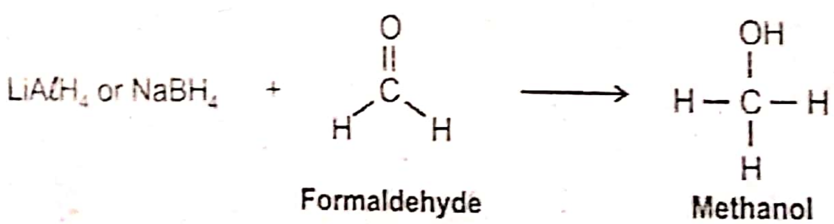


Overview

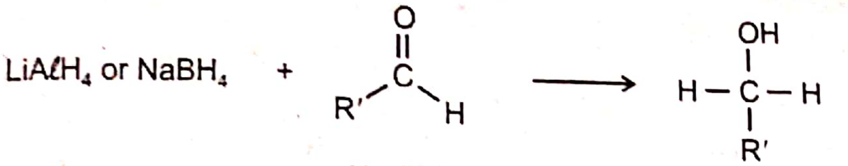
- These reduction methods do not reduce C=C, C ≡ C or $-CO_2H$
- The choice of method should be made based on the tolerance of other functional groups to the acidic or basic reaction conditions.

Hydride Reductions of Aldehydes and Ketones

- Reduction of methanal (formaldehyde) gives methanol.

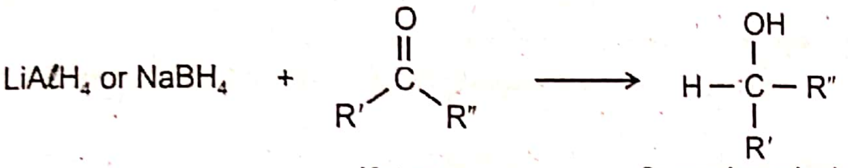


- Reduction of other aldehydes gives **primary** alcohols.



Aldehyde — Primary alcohol

- Reduction of ketones gives **secondary** alcohols.

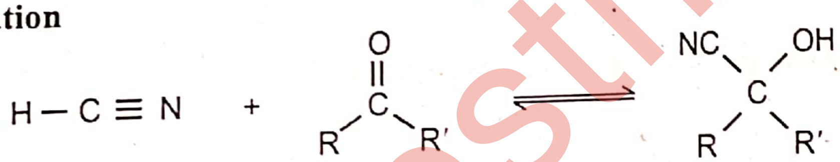


Ketone — Secondary alcohol

- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents like $LiA\ell H_4$ and $NaBH_4$ act as a source of $4H^-$ (hydride ion).
- Overall 2 H atoms are added across the **C=O** to give **H−C−O−H.**
- A hydride reacts with the carbonyl group, **C=O**, in aldehydes or ketones to give alcohols.
- The substituents on the carbonyl tell the nature of the product alcohol.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction.

Using Carbon Nucleophiles

Cyanohydrin Formation

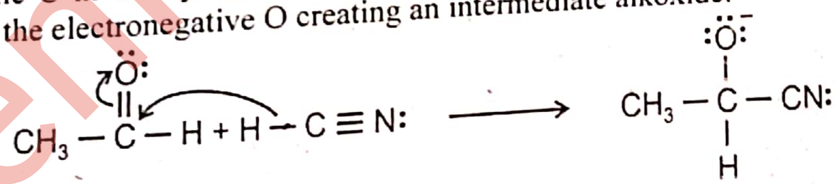


- Cyanide adds to aldehydes and ketones to give a cyanohydrin.
- The reaction is usually carried out using NaCN or KCN with $HC\ell$.
- HCN is a fairly weak acid, but **very toxic.**
- The reaction is useful since the cyano group can be converted into other useful functional groups ($-CO_2H$ or $-CH_2NH_2$)

Nucleophilic addition of cyanide to an aldehyde

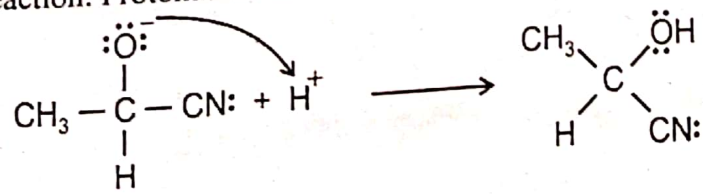
Step 1:

The nucleophilic C in the cyanide adds to the electrophilic C in the polar carbonyl group. Electrons from the C = O move to the electronegative O creating an intermediate alkoxide.



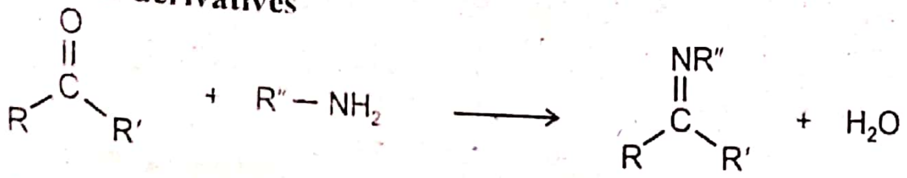
Step 2:

An acid/base reaction. Protonation of the alkoxide oxygen creates the cyanohydrin product.



Using Nitrogen Nucleophiles

Reactions of Primary Amine derivatives

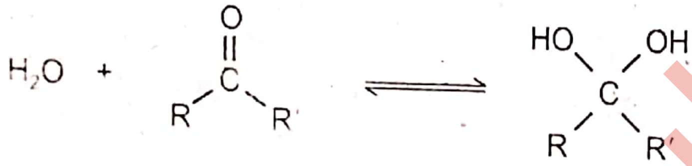


imine

- Primary amines, **R−NH₂** or **ArNH₂**, undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.
- The reactions are usually carried out in an acidic buffer to activate the C=O and facilitate dehydration but without inhibiting the nucleophile.
- Systems of the general type **Z−NH₂** undergo this type of reaction.

Using Oxygen Nucleophiles

Formation of Hydrates



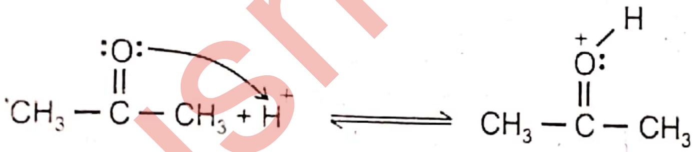
hydrate

- Aldehydes and ketones react with water to give 1,1-geminal diols known as **hydrates**.
- In general, hydrates are not stable enough to be isolated as the equilibrium shifts back to starting materials.
- However, hydrates are the reactive species in the oxidation of aldehydes to acids.
- Understanding the mechanism is useful before looking at the very closely related reactions of alcohols.

Mechanism for the Acid Catalyzed Formation of Hydrates

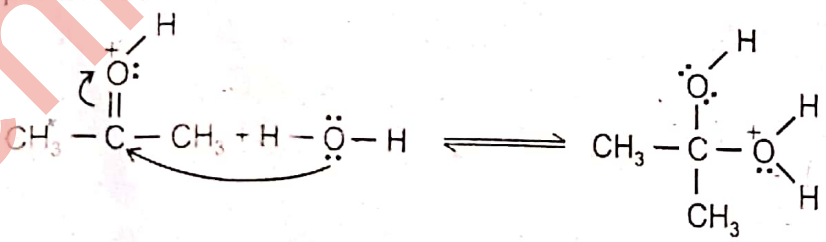
Step 1:

An acid/base reaction. Since there is only a weak nucleophile we need to activate the carbonyl by protonating on O.



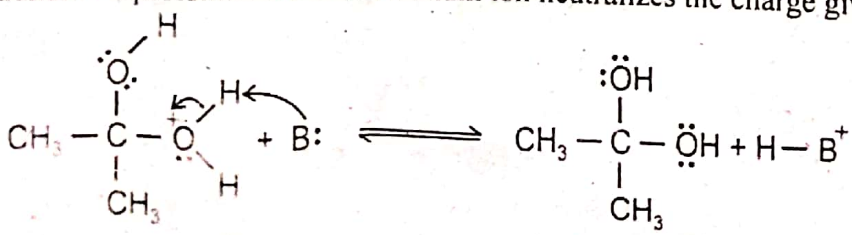
Step 2:

The nucleophilic O in the water attacks the electrophilic C in the C = O, breaking the π bond and giving the electrons to the positive O.



Step 3:

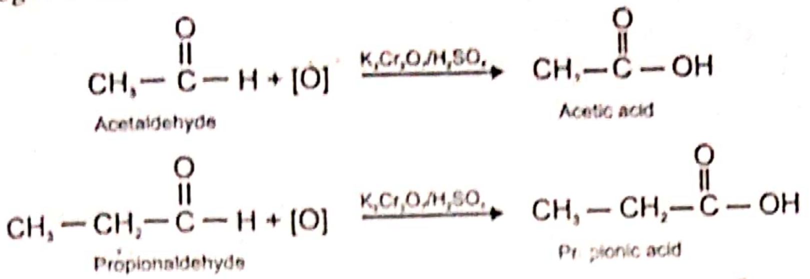
An acid/base reaction. Deprotonation of the oxonium ion neutralizes the charge giving the hydrate.



OXIDATION REACTIONS

(i) Oxidation of Aldehydes

- Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids. They are also oxidized by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4, $KMnO_4$ / H_2SO_4 and dilute nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidised to – OH group.



Mild oxidizing agents	Strong oxidizing agents
• Tollen's reagent	• conc. HNO_3
• Fehling's solution	• $K_2Cr_2O_7/H_2SO_4$
• Benedict's solutions	• $KMnO_4/H_2SO_4$

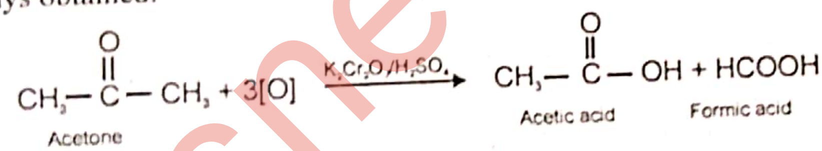
The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

(ii) Oxidation of Ketones

- Ketones do not undergo oxidation easily because they require breaking of strong carbon-carbon bond.
- They give no reaction with mild oxidizing agent. They are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and con. HNO_3.
- In oxidation of ketones, only the carbon atoms adjacent to the carbonyl group are attacked. The carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized.

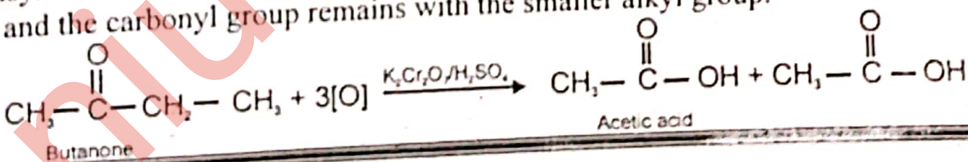
Symmetrical ketones

In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and a mixture of two carboxylic acids is always obtained.



Unsymmetrical ketones

In case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atom is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



Society Science Technology

Sugars: Glucose and Fructose (Naturally occurring carbonyl compounds)

- Sugars are sweet tasting soluble carbohydrates. Carbohydrates derive their name for the fact that they are composed of carbon, hydrogen and oxygen with H and O in the ratio of 2:1 as in water.
- Monosaccharides such as glucose are usually pentoses or hexoses, i.e. they contain 5 or 6 carbon atoms in their molecules.

- Disaccharides such as sucrose consist of two monosaccharide molecules joined by the elimination of a molecule of water.
- Polysaccharides such as starch are made up of many monosaccharides units joined together.

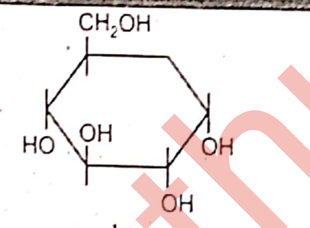
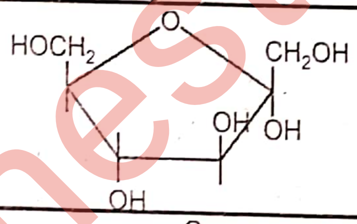
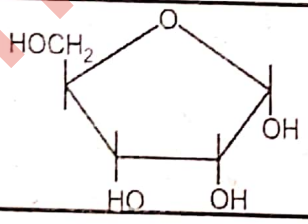
Notice that the Monosaccharides all have asymmetric molecules. They therefore exhibit optical isomerism.

Structure of Carbohydrates

The most obvious feature of the structure of the monosaccharides and disaccharides is the presence of large number of – OH groups. These give them a large capacity for hydrogen bonding, so they are non-volatile solids, soluble in water. The presence of – OH groups on several adjacent carbon atoms in the molecule is thought to be responsible for the sweet taste of sugars.

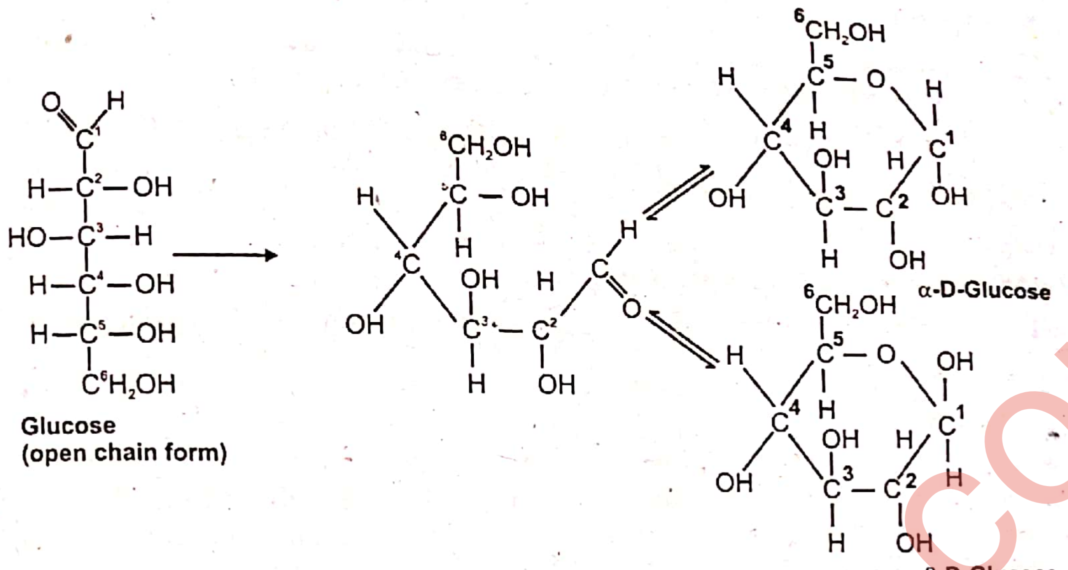
Properties of Carbohydrates

As well as showing the properties of polyhydroxy compounds, sugars show many properties in solution that are typical of carbonyl compounds. For example, glucose gives a crystalline condensation compound with 2,4-dinitrophenylhydrazine. This is surprising since the structure of glucose contains no carbonyl group in ring structure.

Name	Type	Structure	Occurrence
Glucose	Monosaccharide, aldose, hexose	 α-glucose	Occurs abundantly in plants and animals
Fructose	Monosaccharide, ketose, hexose		In fruits and honey
Ribose	Monosaccharide, aldose, pentose		Component of the molecules of ribonucleic acid (RNA) and vitamin B12
Sucrose	Disaccharide	Sucrose $\xrightarrow{H_2O}$ Glucose + Fructose	Sugar cane, sugar beet (commonly simply called, 'sugar')
Maltose	Disaccharide	Maltose $\xrightarrow{H_2O}$ Glucose + Glucose	Malt
Lactose	Disaccharide	Lactose $\xrightarrow{H_2O}$ Glucose + Galactose	Milk
Starch	Polysaccharide	Chains of α-D glucose units	Plant storage organs, e.g. Potato, wheat grain, rice, barley, maize etc.
Cellulose	Polysaccharide	Chains of β-D glucose units (linked differently to those in starch)	Structural material of plants.

The carbonyl properties possessed by glucose arise from the fact that in addition to its normal ring form it can exist as an open chain form.

Glucose – An example of aldehyde



Glucose (open chain form)

α-D-Glucose

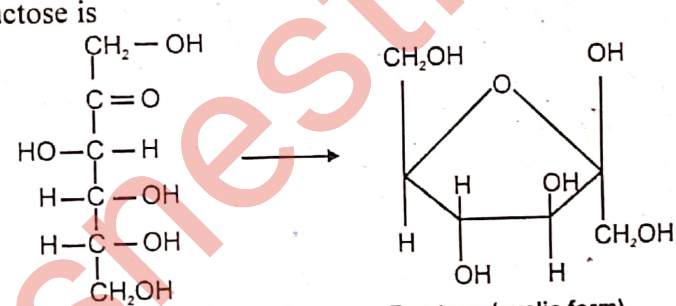
β-D-Glucose

(Glucose (cyclic form)

The two forms are readily inter-converted and in aqueous solution about 1% of glucose molecules exist in the open chain form. This form carries an aldehyde group, so glucose has several properties typical of an aldehyde. It is some time called an aldose. Thus, in addition to the condensation reaction already mentioned, glucose shows the reducing properties typical of an aldehyde. The reduction of Fehling's solution (or Benedict's solution) is a standard test for glucose and other reducing sugars.

Fructose – An example of Ketone

The open chain form of fructose is



Fructose (open chain form) Fructose (cyclic form)

Fructose is therefore a ketose.

Q. Why does the open chain form of glucose and other sugars change to the ring form?

Ans. It is a result of the tendency of the carbonyl group to undergo nucleophilic addition. The nucleophile involved is the oxygen atom of one of the –OH group of the same molecule. An internal nucleophilic addition reaction occurs, forming a ring.

Do You Know?

- 40% aqueous solution of formaldehyde is known as formalin, which is used in the preservation of biological specimens and sterilizing surgical instruments.
- Acetone is widely used as solvents in industry, the laboratory and at home.
- Formaldehyde is used as decolourizing agent in vat dyeing.
- Formaldehyde and acetaldehyde are used in silvering of mirrors.

QUICK QUIZ

1. What is functional group of carbonyl compounds? Write their general formula?

Ans.
- The functional group of carbonyl compounds is $-\overset{O}{\overset{\|}{C}}-$.
- Their general formula is $C_nH_{2n}O$.

2. What types of aldehydes used in Cannizzaro's reactions

Ans. Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction. e.g. Formaldehyde, benzaldehyde etc.

3. What is Cannizzaro's reaction?

Ans. Cannizzaro's reaction:

Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction. Two molecules of the aldehyde are involved, one molecule being converted into the corresponding alcohol (the reduced product) and the other into the acid in the salt form (the oxidation product). The reaction is carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

$$2H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow CH_3OH + H-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{Na}$$

4. Which types of carbonyl compound condense to form an aldol?

Ans. Aldehydes and ketones possessing α-hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as aldols. e.g. acetaldehyde, acetone etc.

5. What are haloform reactions?

Ans. Haloform reactions:

The carbonyl compounds react with halogens in the presence of sodium hydroxide to give haloform and sodium salt of the acid. The term haloform is used for the reaction because a haloform (chloroform, bromoform or iodoform) is one of the products.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + \underset{\text{Halogen}}{3X_2} + 4NaOH \longrightarrow \underset{\text{Haloform}}{CHX_3} + \underset{\text{Sod. carboxylate}}{RCOONa} + 3NaX + 3H_2O$$

R = alkyl, aryl or hydrogen

6. Give the oxidation reactions of aldehydes.

Ans. Oxidation reactions of aldehydes:

Aldehydes are easily oxidized to carboxylic acids by:

- Mild oxidizing agents (Tollen's reagent, Fehling's solution or Benedict's solution).
- Strong oxidizing agents ($K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ or dilute nitric acid).

The hydrogen atom attached to the carbonyl group in aldehydes is oxidised to – OH group.

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

KEY POINTS

- Primary alcohols can be oxidized to aldehydes (or further to carboxylic acids).
- Secondary alcohols can be oxidized to ketones.
- Tertiary alcohols cannot be oxidized (no carbinol C−H).
- The protonation of a carbonyl gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.
- Organolithium or Grignard reagents react with the carbonyl group, C=O, in aldehydes or ketones to give alcohols.
- The carbonyl group, −C=O, is present in aldehydes and ketones. In aldehydes it is in a terminal position in the carbon chain. In ketones it is in a non – terminal position.
- Aldehydes and ketones are named using the suffixes –al and –one, respectively.
- Aldehydes are prepared by oxidising primary alcohols, ketones by oxidizing secondary alcohols.
- The carbonyl group readily undergoes nucleophilic addition. This is sometime followed by the elimination of a molecule of water, resulting in a condensation reaction.
- Aldehydes are generally more reactive then ketones.
- The tendency of aldehydes to undergo nucleophilic addition makes them polymerize readily.
- Aldehydes can be oxidized to carboxylic acids by a variety of reagents. Ketones are not readily oxidized.
- The carbonyl group activates the hydrogen atoms on neighbouring carbon atoms, making them more readily substituted then those in alkanes.

EXERCISE

Q1. Multiple Choice Questions. Encircle the correct answer:

- Read the question carefully.
- Try to answer the question yourself before reading the answer choices.
- Guess only if you can eliminate one or more answer choices.
- Drawing a picture can help.
- Don't spend too much time on any one question.
- In-depth calculations are not necessary; approximate the answer by rounding.

(1) The carbon atom of a carbonyl group is
(a) sp hybridized (b) sp^2 hybridized (c) sp^3 hybridized (d) none of these

(2) Ketones are prepared by the oxidation of
(a) primary alcohol (b) secondary alcohol (c) tertiary alcohol (d) none of these

(3) Acetone reacts with HCN to form a cyanohydrins. It is an example of
(a) electrophilic addition (b) electrophilic substitution
(c) nucleophilic addition (d) nucleophilic substitution

(4) Cannizzaro's reaction is not given by
(a) formaldehyde (b) acetaldehyde (c) benzaldehyde (d) trimethylacetaldehyde

(5) Which of the following reagents will react with both aldehydes and ketones?
(a) Grignard reagent (b) Tollen's reagent (c) Fehling's reagent (d) Benedict's reagent

(6) Aldehydes are the oxidation product of
(a) p-alcohols (b) s-alcohols (c) ter-alcohols (d) carboxylic acids

(7) Which of the following compounds will not give iodoform test on treatment with I_2/ NaOH.
(a) acetaldehyde (b) acetone (c) butanone (d) 3-pentanone

(8) **Aldehydes and ketones are carbonyl compounds. Which of them react both with $NaBH_4$ and with Tollen's reagent.**

(a) both aldehydes and ketones (b) aldehydes only

(c) ketones only (d) neither aldehydes nor ketones

(9) **Which one of the following can undergo Aldol condensation reaction?**

(a) formaldehyde (b) acetaldehyde (c) benzeldehyde (d) trimethylacetaldehyde

(10) **Aldol condensation is not successful with compounds**

(a) having no α-hydrogen (b) having α-hydrogen (c) having α-methyl group (d) none

(11) **Phenyl hydrazine on treatment with carbonyl compounds form.**

(a) hydroxyl amines (b) phenyl hydrazone (c) oximes (d) none

(12) **Formaldehyde react with NH_3 to give?**

(a) tetraethylene hexamine (b) tetraethylene tetramine

(c) hexamethylene tetraamine (d) cyclonite

(13) **General formula of aldehyde and ketone is**

(a) $C_nH_{2n}O$ (b) $C_nH_{2n+1}O$ (c) C_nH_nO (d) $C_nH_{2n+2}O$

(14) **Which of the following can be prepared in the laboratory by dry distillation of $(HCOO)_2Ca$?**

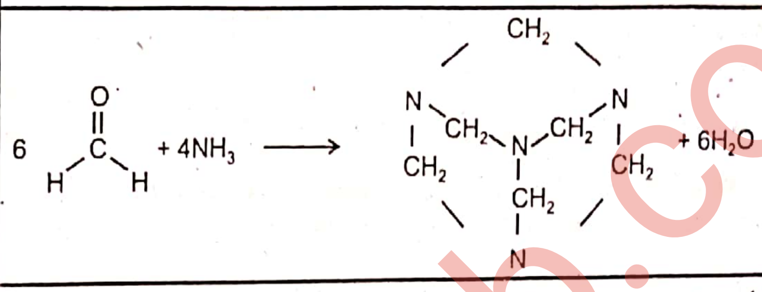
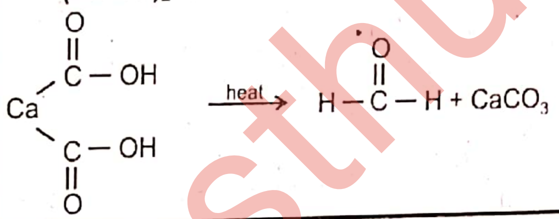
(a) $H_2C = CH_2$ (b) HCHO (c) CH_3OH (d) CH_3CHO

(15) **The colour of Iodoform is**

(a) white (b) black (c) yellow (d) blue

SOLVED EXERCISE MCQs

Q. No	Answer	Reason
(1)	(b) sp^2 hybridized	>C = O, double bond shows sp^2 character of carbonyl group.
(2)	(b) secondary alcohol	$(CH_3)_2CH-OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (CH_3)_2C=O + H_2O$
(3)	(c) nucleophilic addition	Because CN^- from HCN act as nucleophile that attack on carbonyl carbon. So HCN addition is Nucleophilic addition.
(4)	(b) acetaldehyde	Because Cannizzaro's reaction is given by those compounds which have no α-hydrogen but acetaldehyde has α-hydrogen.
(5)	(a) Grignard Reagent	Tollen, Fehling and Benedict's reagents do not react with ketones because they are not strong oxidizing agents.
(6)	(a) p-alcohol	Because primary alcohol is oxidized to aldehyde while secondary alcohol is oxidized to ketone.
(7)	(d) 3-Pentanone	Iodoform test is given by methyl ketones i.e. the ketones which have methyl group adjacent to carbonyl group. Since 3-Pentanone has no methyl group adjacent to carbonyl group it will not give iodoform test.
(8)	(b) Aldehyde only	Because aldehyde are reduced to primary alcohol by $NaBH_4$ and are oxidized by Tollen's reagent.

(9)	(b) Acetaldehyde	Because for Aldol condensation α-hydrogen is required so acetaldehyde has α-hydrogen.
(10)	(a) Having no α-hydrogen	Because for aldol condensation α-hydrogen is required.
(11)	(b) Phenyl hydrozone	Phenyl hydrazine on treatment with carbonyl compound form phenyl hydrazine. $\underset{\text{Ethanal}}{CH_3(H)C=O} + H_2NNHC_6H_5 \xrightarrow{H^+} \underset{\text{Ethanal phenylhydrazone}}{CH_3(H)C=N-NHC_6H_5} + H_2O$
(12)	(c) Hexamethylene tetraamine	
(13)	(a) $C_nH_{2n}O$	Since two hydrogen atoms are removed and one oxygen atom is added.
(14)	(b) HCHO	$(HCOO)_2Ca \xrightarrow{heat} HCHO + CaCO_3$ 
(15)	(c) Yellow	see table below

Haloform	Formula	Appearance
Fluoroform	CHF_3	Colourless gas
Chloroform	$CHCl_3$	Colourless liquid
Bromoform	$CHBr_3$	Colourless liquid
Iodoform	CHI_3	Bright yellow crystals

SHORT ANSWERS QUESTIONS

2. Give brief answers for the following questions.

(i) How is formaldehyde prepared industrially?

Ans. In industry, a mixture of methanol vapour and air is passed over iron oxide-molybdenum oxide or Ag catalyst at 500°C

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[500^\circ C]{FeO,\ MoO_3} H-\overset{O}{\overset{\|}{C}}-H + H_2O$$

(ii) Describe briefly the nucleophilic addition mechanism to the carbonyl compound.

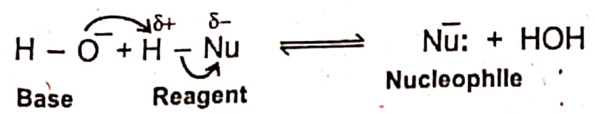
Ans. In carbonyl compounds nucleophilic addition reaction mechanism is of following two types:

(i) **Base-catalysed nucleophilic addition reaction**

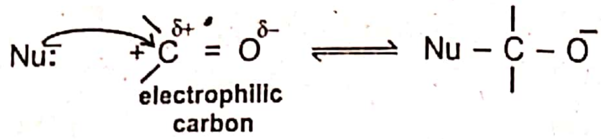
It will take place with a strong nucleophilic reagent. The base reacts with the reagent and generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reaction is as follows:

General mechanism

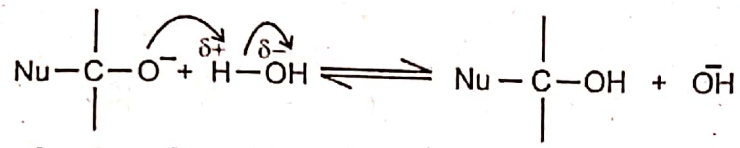
Step-I:



Step-II:



Step-III:



(ii) Acid-catalysed nucleophilic addition reaction

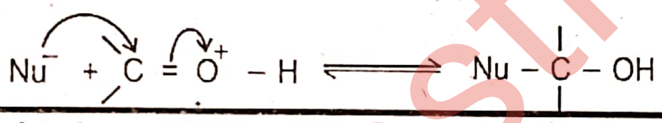
The addition is initiated by the proton (H^+) liberated by the acid. The proton combines with the carbonyl oxygen atom and increases the electrophilic character of the carbonyl carbon. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.

Mechanism:

The general mechanism of the reaction is as follows.

Step-I:

Step-II:

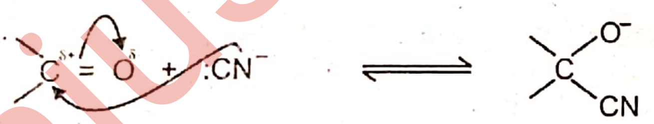


(iii) What is the mechanism of HCN addition to carbonyl compounds?

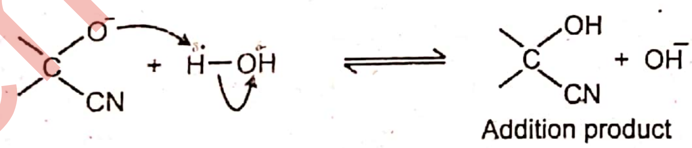
Ans. The reaction is base-catalysed because HCN has no lone pair or electrons on its carbon. The base (OH^-) generates cyanide ions which acts as nucleophiles. The mechanism of the reaction is as follows:

Step-I:

Step-II:



Step-III:

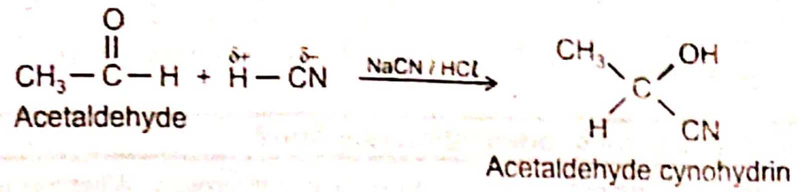


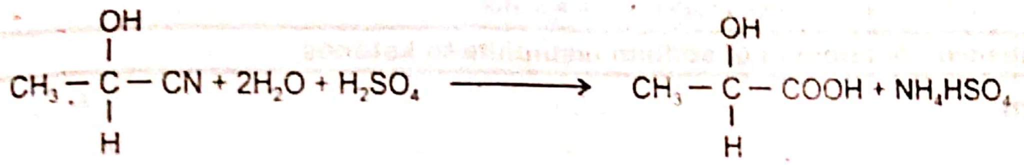
(iv) How is ethanol converted to lactic acid?

Ans. Conversion of Ethanol into Lactic acid:

$$CH_3CH_2 - OH + [O] \xrightarrow[\text{Conc } H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Ethanol   Acetaldehyde



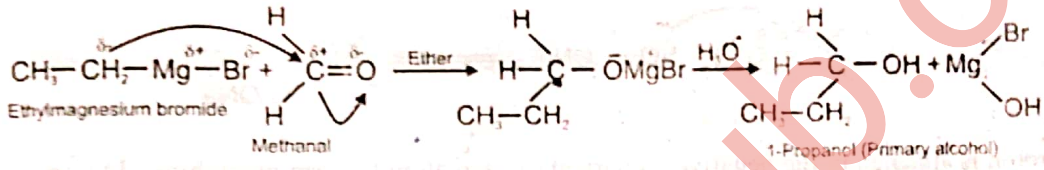


2-Hydroxy Propanoic acid (Lactic acid)

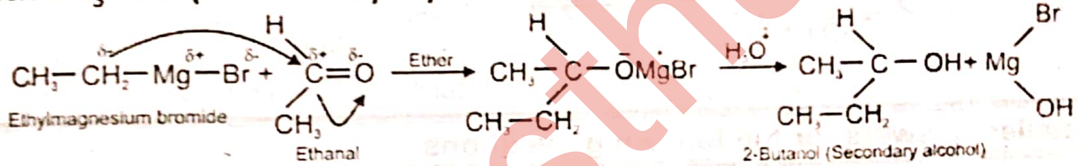
(v) What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?

Ans.

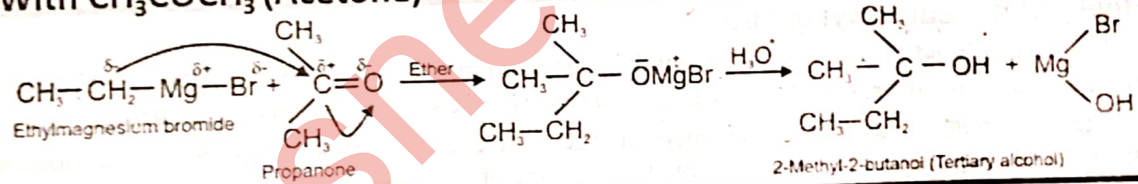
(i) With HCHO (Formaldehyde)



(ii) With CH_3CHO (Acetaldehyde)



(iii) With CH_3COCH_3 (Acetone)



(vi) What is Haloform reaction?

Ans. Acetaldehyde, ethanol, methyl ketones and secondary alcohols with methyl group at α-carbon, react with halogens in the presence of sodium hydroxide to give haloform and sodium salt of acid. This reaction is known as **haloform** reaction.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

(vii) Which types of alcohols undergo iodoform reaction?

Ans. Alcohols containing methyl group on α carbon give positive iodoform reaction.

- Ethanol is the only primary alcohol that gives this reaction.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. formate}}{HCOONa} + 5NaI + 5H_2O$$

- Secondary alcohols containing the methyl group also undergo this reaction.

$$\underset{\text{Secondary alcohol}}{R-\overset{OH}{\overset{|}{C}}H-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. carboxylate}}{RCOONa} + 5NaI + 5H_2O$$

(ix) Why formaldehyde do not give aldol condensation reaction?

Ans. For aldol condensation reaction, the carbonyl compound must have α-hydrogen. Where as in formaldehyde, there is no α-hydrogen so it does not give aldol condensation reaction.

(x) Give the mechanism of addition of sodium bisulphite to ketones.

Ans. **Mechanism**

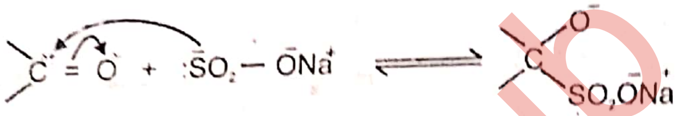
Step-I:

Sodium bisulphite ionizes to form sulphite ions.

$$NaHSO_3 \rightleftharpoons \bar{S}O_2-O^- + H^+ + Na^+$$

Step-II:

The sulphite ion acts as a nucleophile, since the sulphur atom is more nucleophilic than oxygen, a C – S bond is formed.



Step-III:

Proton is attached to the negatively charged oxygen atom to form bisulphite addition product.

Bisulphite addition product

Q3. Give detailed answers for the following questions.

Q3.(i) What is the reactivity of the carbonyl group?

Ans. **Reactivity of the carbonyl group**

The double bond of the carbonyl group has a σ-bond and a π-bond. As oxygen is more electronegative, it attracts the π-electrons towards itself. This attraction makes the carbonyl group a polar group.

The oxygen atom has a partial negative charge on it and the carbon atom has partial positive charge. The π electron cloud is pulled more strongly by the oxygen atom than the carbon atom. It makes oxygen atom nucleophile and carbon atom becomes electrophile.

Q3.(ii) How will you prepare formaldehyde and acetaldehyde on industrial scale?

Ans. **Industrial Preparation of Formaldehyde**

Formaldehyde is manufactured by passing a mixture of methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500 °C.

$$CH_3OH + \frac{1}{2}O_2 \xrightarrow[500^\circ C]{FeO,\ Mo_2O_3} H-\overset{O}{\overset{||}{C}}-H + H_2O$$

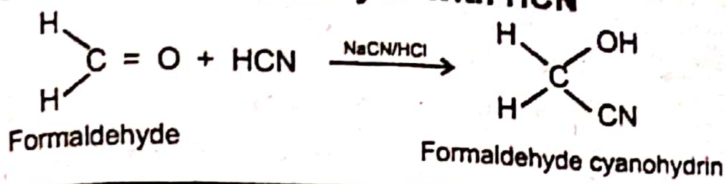
Industrial Preparation of Acetaldehyde

Acetaldehyde is prepared industrially by air oxidation of ethylene using palladium chloride catalyst with a cupric chloride promoter.

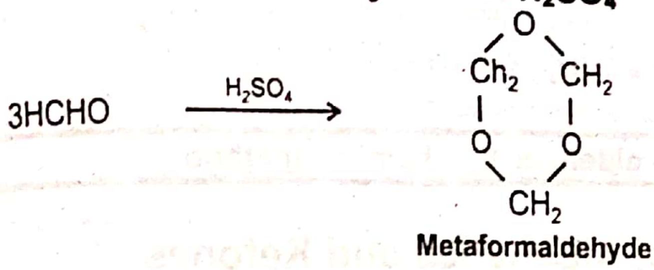
$$\underset{\text{Ethylene}}{2CH_2=CH_2} + O_2 \xrightarrow[H_2O]{PdCl_2 + CuCl_2} \underset{\text{Acetaldehyde}}{2CH_3-\overset{O}{\overset{||}{C}}-H}$$

Q3.(iii) How formaldehyde reacts with following? (i) HCN (ii) H_2SO_4 (iiii) $NaHSO_3$

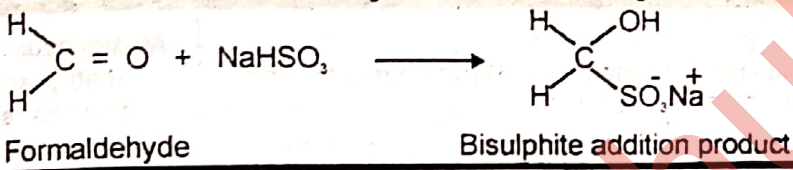
Ans. (i) Reaction of Formaldehyde with HCN



(ii) Reaction of Formaldehyde with H_2SO_4



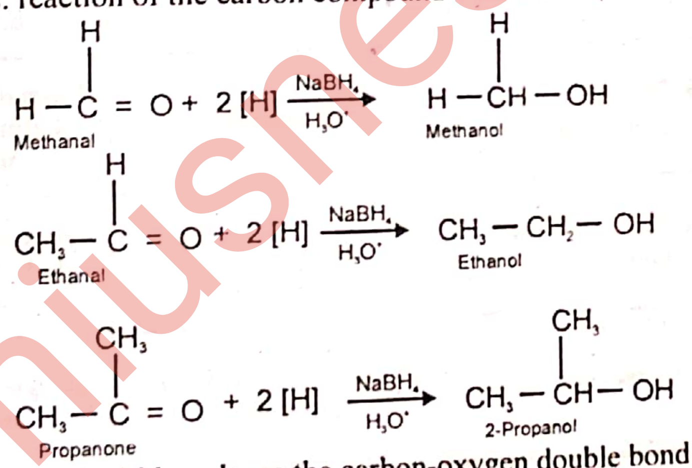
(iii) Reaction of Formaldehyde with $NaHSO_3$



Q3.(vi) Give the following reductions of aldehydes and ketones along with mechanism.
(i) $NaBH_4$ (ii) Catalytic reduction

Ans: (i) Reductions of aldehydes and ketones with $NaBH_4$

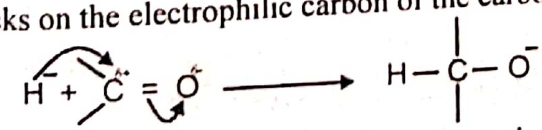
Aldehydes and ketones are reduced to alcohols with sodium borohydride, $NaBH_4$. The reaction is carried out in two steps: reaction of the carbon compound with $NaBH_4$ under anhydrous conditions and then **hydrolysis.**



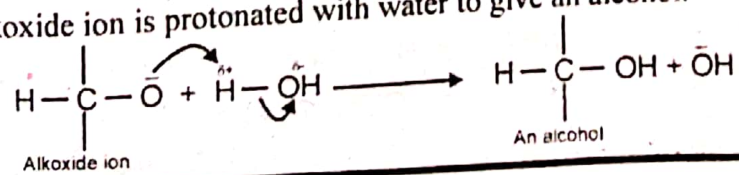
Sodium borohydride reduces the carbon-oxygen double bond but not the carbon-carbon multiple bond.

Mechanism

The tetrahydridoborate (III) ion BH_4^- is source of hydride ion, H^-. The hydride ion acts as a nucleophile. It attacks on the electrophilic carbon of the carbonyl group to give an alkoxide ion.

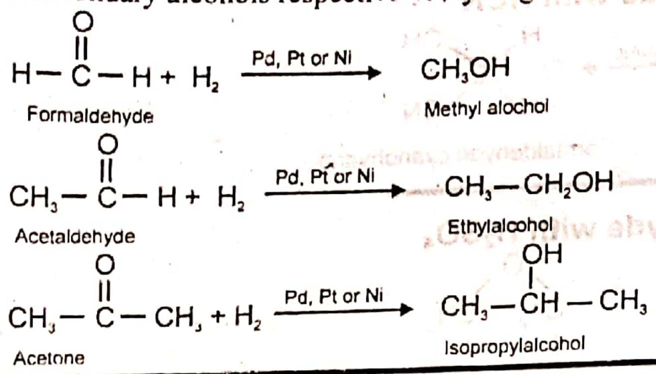


The alkoxide ion is protonated with water to give an alcohol.



(ii) Catalytic Reduction

Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt, or Ni form primary and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



Q3.(ix) How do you distinguish a ketone and an aldehyde by chemical method?

Ans.

Distinction Tests of Aldehydes and Ketones

Chemical reaction	Aldehyde	Ketone	Exception
Sodium bisulphite Test ($NaHSO_3$)	White ppt is formed	White ppt is formed	All aldehydes but only methyl ketones give this reaction
2, 4 DNPH Test (2, 4 - Dinitrophenylhydrazine)	Yellow Red ppt is formed	Yellow Red ppt is formed	is used for both aldehydes and ketones
Tollen's Test Ammonical silver nitrat solution	A silver mirror (Ag) is formed	no reaction	Both aliphatic and aromatic aldehydes give this reaction but not ketones
Fehling's solution Test (An alkaline solution containing a cupric tartrate complex ion)	Brick Red ppt of Cu_2O is formed	no reaction	Aromatic aldehydes and ketones do not give this reaction
Benedict's solution Test (An alkaline solution containing a cupric citrate complex ion)	Brick Red ppt of Cu_2O is formed	no reaction	Aromatic aldehydes and ketones do not give this reaction
Sodium Nitroprusside Test $Na_2[Fe(CN)_5NO]$	no reaction	A wine red or Orange red colouration	Aldehydes do not give this reaction

Q3.(x) How will you differentiate between acetophenone and benzophenone?

Ans. Acetophenone and benzophenone can be distinguished using the iodoform test. For iodoform test the main criteria is the presence of free methyl group on carbonyl carbon.

Since acetophenone contains a free methyl group therefore it will give a positive iodoform test.

$$C_6H_5COCH_3 + 4NaOH + 3I_2 \longrightarrow C_6H_5COONa + \underset{\text{Yellow ppt of iodoform}}{CHI_3} + 3NaI + 3H_2O$$

However, benzophenone does not contain any free methyl group therefore it will give a negative iodoform test.

$$C_6H_5COC_6H_5 + 4NaOH + 3I_2 \longrightarrow \text{No reaction}$$

Skill Activity

(i) Predict the formulas of the products of the following reaction

(a) $CH_3COCH_2CH_3 + H_2 \longrightarrow$

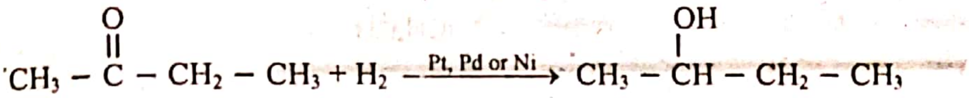
(b) $C_6H_5COCH_3 + NH_2OH \longrightarrow$

(c) $CH_3CH_2COCH_2CH_3 + HCN \longrightarrow$

(d) $C_6H_5CHO + KMnO_4 \longrightarrow$

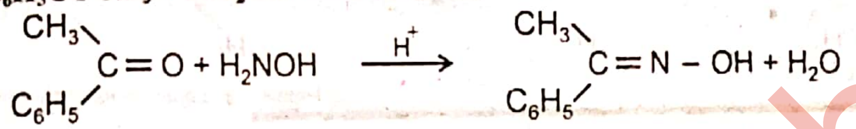
(e) $CH_3CH_2CHO + Cl_2 \longrightarrow$

Ans. **(a)** $CH_3COCH_2CH_3 + H_2 \longrightarrow$



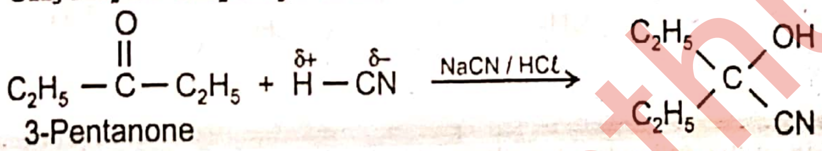
2-Butanone 2-Butanol (Secondary alcohol)

(b) $C_6H_5COCH_3 + NH_2OH \longrightarrow$



Actetophenone Actetophenone oxime

(c) $CH_3CH_2COCH_2CH_3 + HCN \longrightarrow$



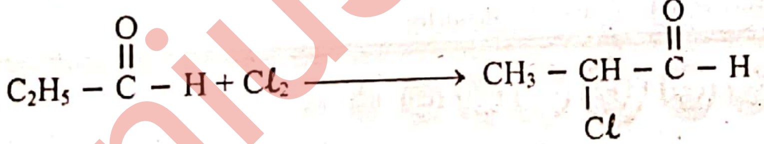
3-Pentanone

3-Pentanone cynohydrin

(d) $C_6H_5CHO + KMnO_4 \longrightarrow$

Benzaldehyde Benzoic acid

(e) $CH_3CH_2CHO + Cl_2 \longrightarrow$



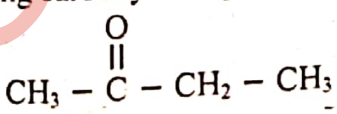
2-Chloropropanal

Propanal

(ii) Write structural formulas for all compounds of molecular formula C_4H_8O containing a carbonyl group.

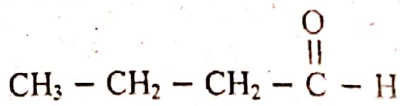
Ans. Following carbonyl compounds contain molecular formula C_4H_8O:

(i)



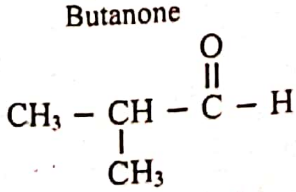
Butanone

(ii)



Butanal (Butyraldehyde)

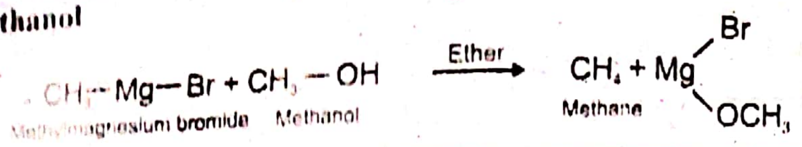
(iii)



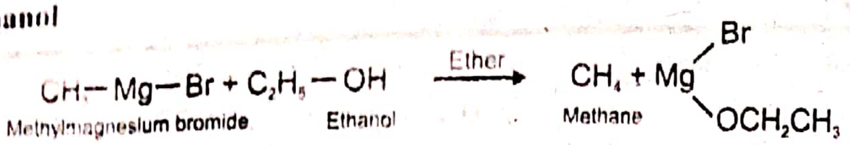
Iso-butyraldehyde

(iii) Predicts the formulas of the compounds formed when the following are treated with the Grignard's reagent methyl magnesium bromide, followed by water.
(a) Methanol (b) Ethanol (c) Propanone (d) Carbon dioxide

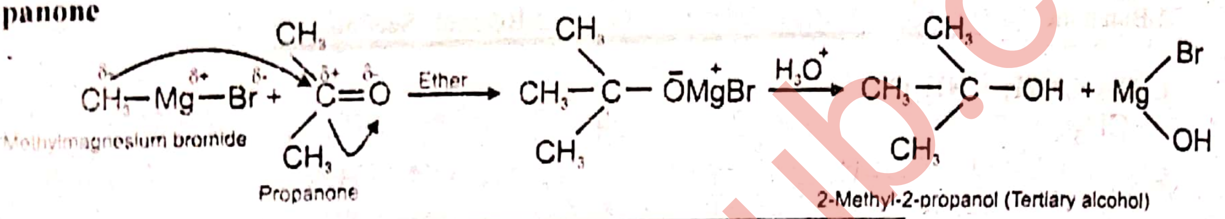
Ans. (a) Methanol



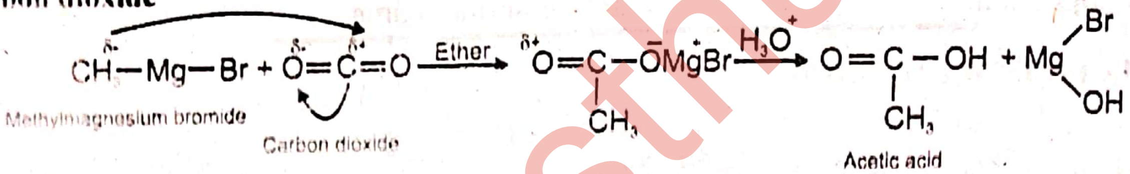
(b) Ethanol



(c) Propanone



(d) Carbon dioxide



Skill Activity

(i) Predict the formulas of the products of the following reaction

$CH_3COCH_2CH_3 + H_2 \longrightarrow$

$C_6H_5CHOCH_3 + NH_2OH \longrightarrow$

$CH_3CH_2COCH_2CH_3 + HCN \longrightarrow$

$C_6H_5CHO + KMnO_4 \longrightarrow$

$CH_3CH_2CHO + Cl_2 \longrightarrow$

(ii) Write structural formulas for all compounds of molecular formula C_4H_8O containing a carbonyl group.

(iii) Predicts the formulas of the compounds formed when the following are treated with the Grignard's reagent methyl magnesium bromide, followed by water.
(a) Methanol (b) Ethanol (c) Propanone (d) Carbon dioxide