CHAPTER 19

ALDEHYDES AND KETONES

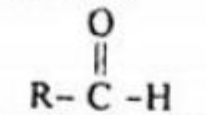
After completing this lesson, you will be able to:

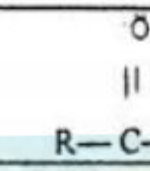
- Explain nomenclature and structure of aldehydes and ketones. (Applying)
- Discuss the preparation of aldeydes and ketones by ozonlysis of alkene, hydration of lkynes, oxidation of alcohols and Friedal Craft's acylation of armatics. (Applying)
- Describe reactivity of aldeydes and ketones and their comparison. (Analyzing)
- Describe acid and base catalysed nucleophlic addition reaction of aldehydesa nd ketones. (Applying)
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrcarbns, alcohols, by using carbons nucleophiles, nitrogen nucleophies oxygen nucleophiules. (Applying)
- Describe oxidation reactions of aldehydesa nd ketones. (Applying)
- Describe isomerism in aldehydes and ketones, (Understanding)

Q1. What are aldehydes and ketones?

Answer

Organic compounds containing the carbonyl functional group are called aldehydes and ketones.

Aldehydes	Ketones
(1) Functional Group	
In aldehydes, the C-atom of carbonyl group is directly attached to at least One H-atom.	In ketones, the C-atom of carbonyl group is bonded to twp carbon atoms called ketonic group.
(2) General Formula	
The homologous series of aldehydes have general formula $C_nH_{2n}O$.	The homologous series of ketones have general formula $C_nH_{2n}O$.
(3) General Formula Structure	
An aldehyde may be represented by the general formula structure 	A ketone may be represented by the general formula structure

	
(4) 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.
(5) Examples	
(i) H-CHO (Formaldehyde) (ii) CH_3-CHO (Acetaldehyde)	 Acetone (ii) Methyl ethyl ketone

Q2. Give nomenclature of aldehydes and ketons.

Answer

a) Common names

An aldehydes is named after the name of carboxylic acid obtained on its oxidation, the ending –ic acid is replaced by "aldehyde", e.g.,

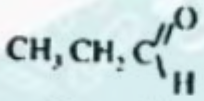
For naming substituted aldehyde, the chain is labeled by using α, β, γ … etc. the carbon next to carbon of the carbonyl group is indicated by 'α' and so on.

b) IUPAC Names

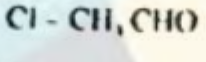
1. The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon.
2. The ending e of the alkane is replaced y al
3. The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number 1.

4. The position of the substituent is indicated by numbers which is written before their number.

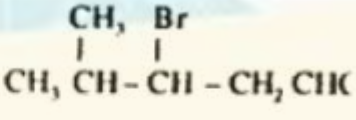
Examples:



Propanal



2-chloro ethanal

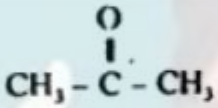


(3-bromo-4-methyl pentanal-1)

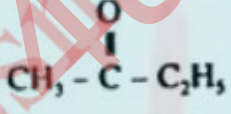
Ketones:

a) Common names:

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

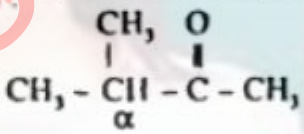


Dimethyl Ketone (Acetone)

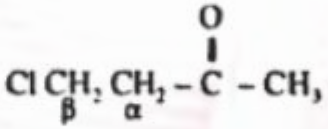


Ethyl methyl Ketone

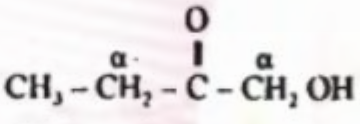
Substituted ketones are named by labeling the chain using α, β, γ … etc, the carbon next to carbon of carbonyl group is indicated by 'α' and so on, e.g.



Methyl α-methyl ethyl Ketone



Methyl β-chloroethyl ketone



α-hydroxyl-methyl ethyl ketone.

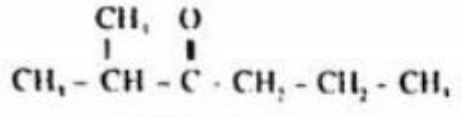
(b) IUPAC Names:

The longest chain containing the carbonyl group is taken a parent hydrocarbon.

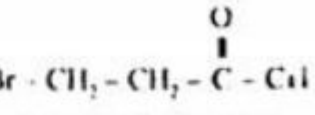
The ending e of hydrocarbon is replaces by one

The numbering starts from the end that gives the carbonyl carbon the lower number. In cyclic ketones, carbonyl carbon is number 1

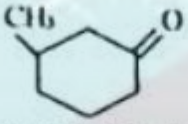
The positions of substituent are indicated by numbers before their names.



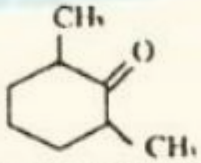
2-methyl-3- hexanone



4-bromo-2-butanone



3-Methyl Cyclo hexanone



2, 6 dimethyl cycl hexanone

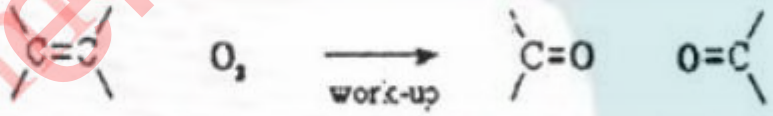
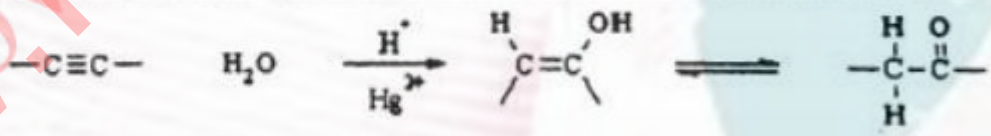
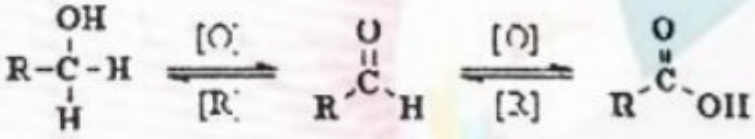
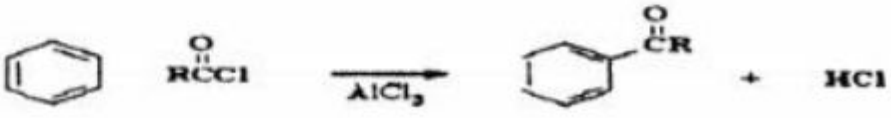
Q3. Give Physical Properties of aldehydes of ketones.

Answer

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

Q4. Give Preparations of Aldehydes and Ketones.

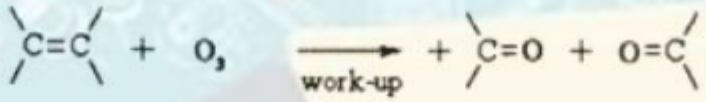
Answer

Ozonolysis of Alkenes	
Hydration of Alkynes	
Oxidation of Alcohols	
Friedel-Crafts Acylation of Aromatics	

Q5. Give reactions of ethane with ozone alongwith mechanism.

Answer

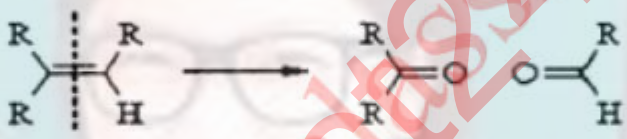
Ozonolysis of Alkenes



Reaction type: Electrophilic Addition

Elaboration

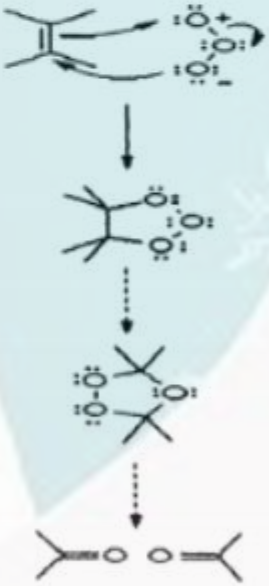
1. Overall transformation : **C=C** to **2C=O**
2. Reagents: ozone, O_3, followed by a reducing work-up, usually Zn in acetic acid.
3. It is convenient to view the process as cleaving the alkene into two carbonyl compounds:
4. The substituents on the **C=O** depend on the substituents on the **C=C**.



MECHANISM FOR REACTION OF ALKENES WITH O_3

Step 1:

The 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 malozonide decomposes to give two carbonyl compounds.

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.,

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$$HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_2 = CH \cdot OH \longrightarrow$$

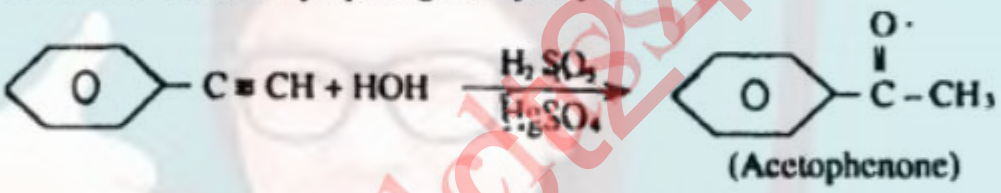
Vinyl alcohol

$$CH_3 - \underset{\underset{H}{|}}{C} = O$$ (Acetaldehyde)

Propyne gives acetone:

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

This reaction is useful for preparing methyl aryl ketones



(Acetophenone)

Oxidation of Primary and Secondary Alcohols

Primary alcohols are oxidized to aldehydes by (i) warming with acidic dichromate solution (ii) Jone reagent (CrO_3 + dil. H_2SO_4 + acetone) (iii) Sarett reagent (CrO_3 in pyridine)

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

Butanol — Butanal

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

$$n-C_7H_{15}CH_2OH \xrightarrow[reagent]{Jone} n-C_7H_{15}CHO$$

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

$$CH_3 - \underset{\underset{CH_3}{|}}{C}HOH \xrightarrow{[O]} CH_3 - \underset{\underset{CH_3}{|}}{C} = O$$

Q6. Friedel-Crafts Acylation of Benzene

Answer

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

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

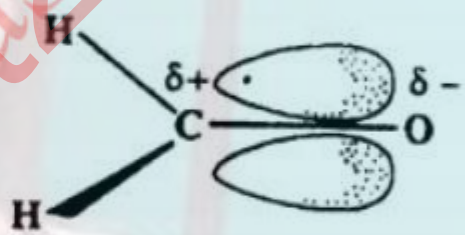
(Alkyl aryl ketone)

$AlCl_3$ generates acylenium ion (electrophile) which is substituted in the aromatic ring

$$R-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \rightleftharpoons R-\overset{\overset{O}{\|}}{C}_{(+)} + AlCl_4^-$$

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 to 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.

Q7. Give different reactions of aldehydes and ketones.

Answer

Nucleophilic Addition

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

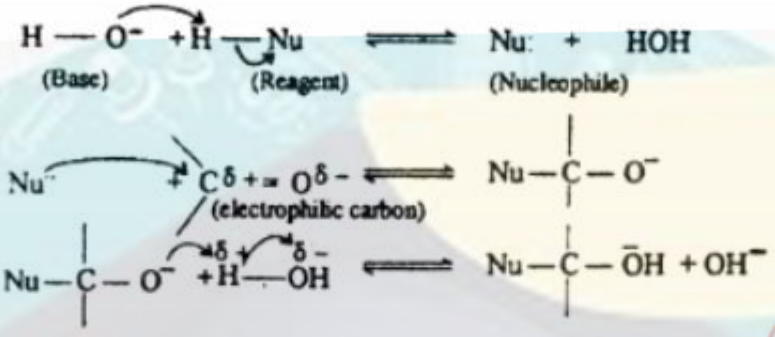
i) Base catalysed nucleophilic addition reaction

ii) Acid catalysed nucleophilic addition reaction

i) Base Catalysed

A base catalysed nucleophilic addition reaction takes place with a strong nucleophilic reagent. The base reacts with the reagent ad 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

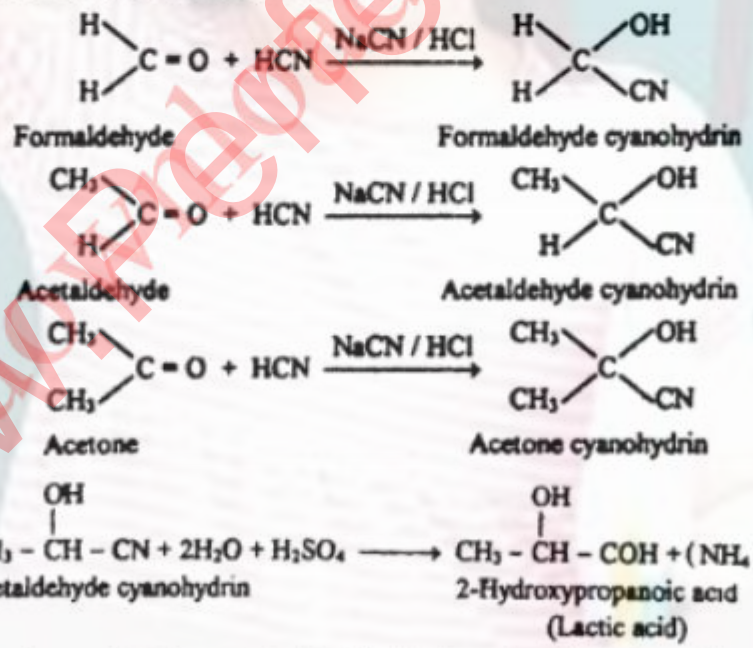


There are five types of base catalysed nucleophilic addition reactions of carbonyl compounds.

1) Addition of hydrogen cyanide
2) Addition of Grignard's reagent
3) Addition of sodium bisulphate
4) Condensation reactions
5) Holoform reactions

1) Addition of hydrogen cyanide

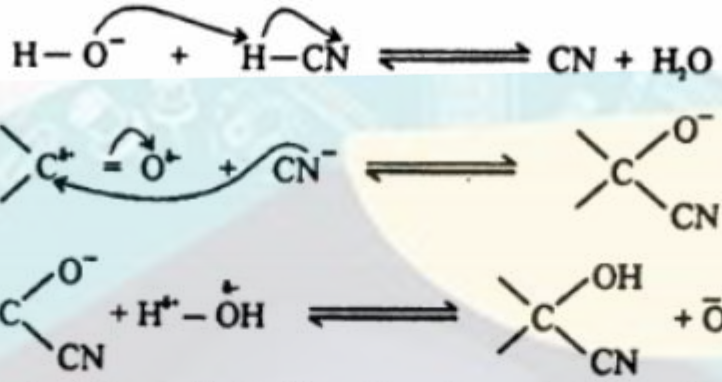
Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The acid generates HCN form sodium cyanide in HCl.



The reaction is used in the synthesis of α hydroxyl acid that contains one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.

Mechanism

The reaction is base catalysed. The base (OH^-) generates cyanide ions which act as nucleophile. The mechanism of the reaction is as follows:



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

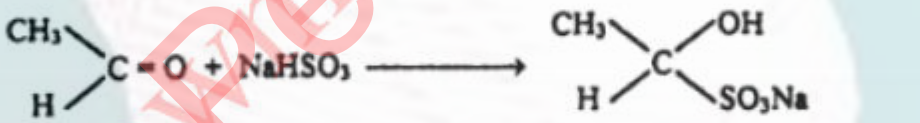
1) Addition of Grignard's reagent

Grignard's reagents add to aldehydes and ketones to form adduct which on hydrolysis with a dilute mineral acid give alcohols. (Chapter 17)

2) Addition of sodium bisulphate

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

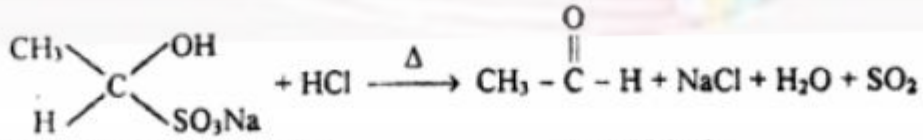
Formaldehyde — Bisulphite addition product



Acetaldehyde — Bisulphite addition product

Acetone — Bisulphite addition product

Bisulphate on heating a dilute mineral acid (HCl or H_2SO_4) regenerates the parent aldehydes or ketone.



Bisulphite addition product — Acetaldehyde

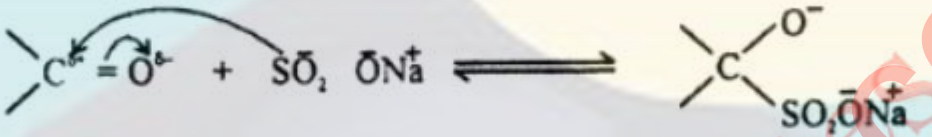
The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

Mechanism

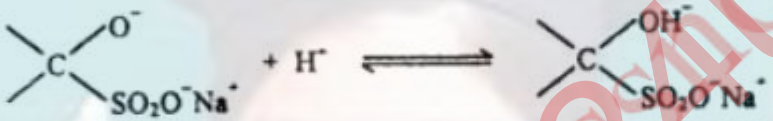
Sodium bisulphate ionizes to form sulphate ions.

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

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



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



Bisulphite addition product

Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite.

1) Condensation reactions

The reaction 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.

a) ALDOL CONDENSATION

Definition:

Aldol condensation is a reaction in which two molecules of same or different carbonyl compound containing a-hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to from 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:

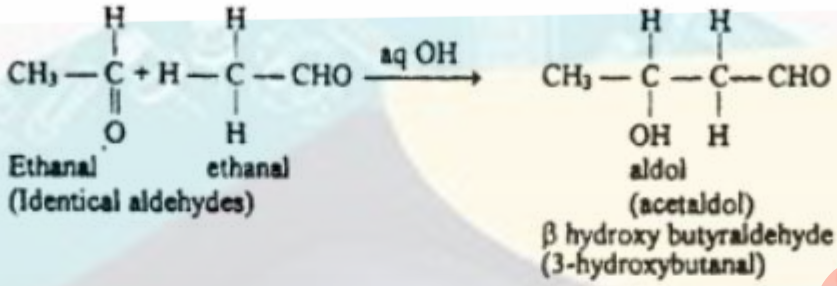
i) Between two aldehydes (identical or different)

ii) Between an aldehyde and a ketone

iii) Between two ketone (identical or different)

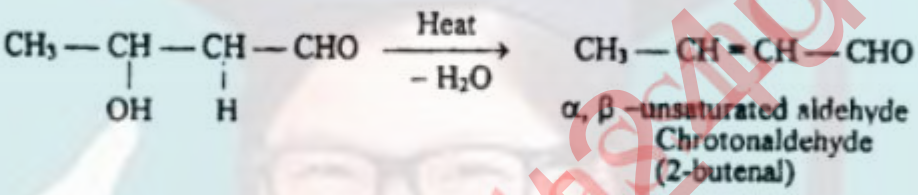
i) Condensation between two aldehydes:

(a)

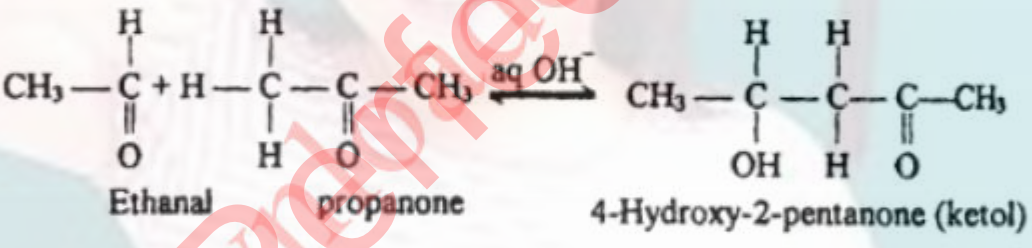


On heating aldol loses a molecule of water to form α, β–unsaturated aldehyde

(b)



(ii) Condensation between aldehyde and ketone:



Mechanism of Aldol Condensation:

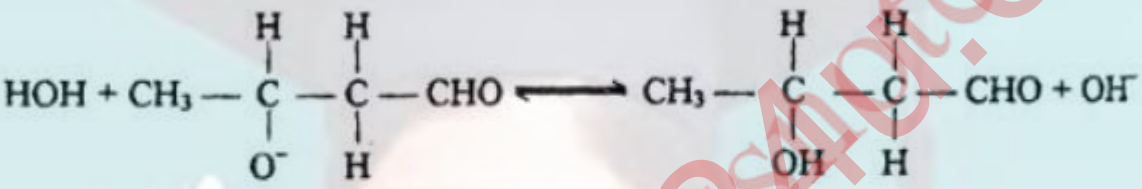
Following steps are involved in aldol condensation.

1) Removal of a proton from α–carbon of aldehyde/ketone by base:
(Formation of nucleophile)

2) Attack of nucleophile on carbonyl carbon to form alkoxide ion:

(Formation of alkoxide ion)

3) Removal of proton from water by alkoxide ion:
(Formation of aldol)

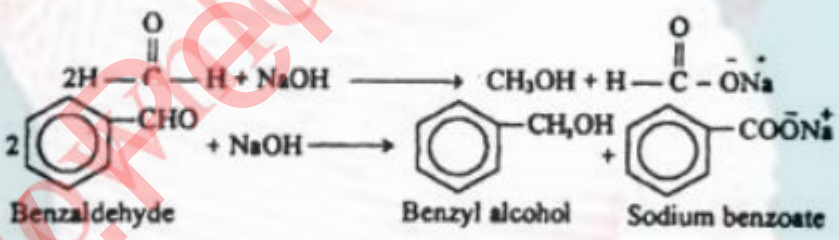


b) Cannizzaro's Reaction:

Aldehydes having no α-hydrogen atoms undergo Canizzaro's reaction. It is a disproportionate (self oxidation-reduction) reaction.

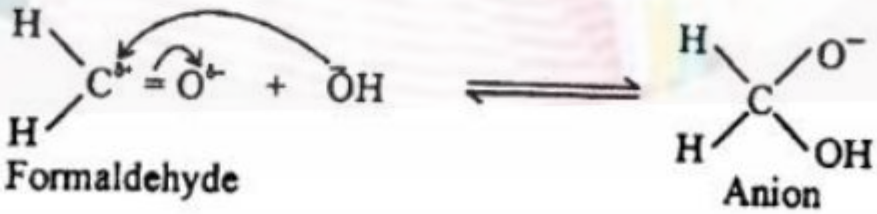
Two molecules of the aldehyde are involved.

One molecule is reduced into corresponding alcohol and the other is oxidized into the acid (in the salt form). The reaction carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

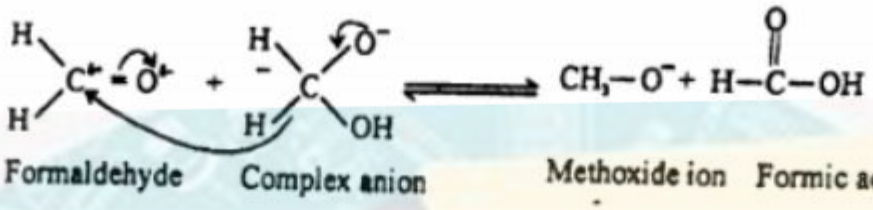


Mechanism of Cannizzaro's Reaction:

The hydroxide ion acts as a nucleophile. It attaches on the electrophilic carbonyl carbon to form a complex anion.

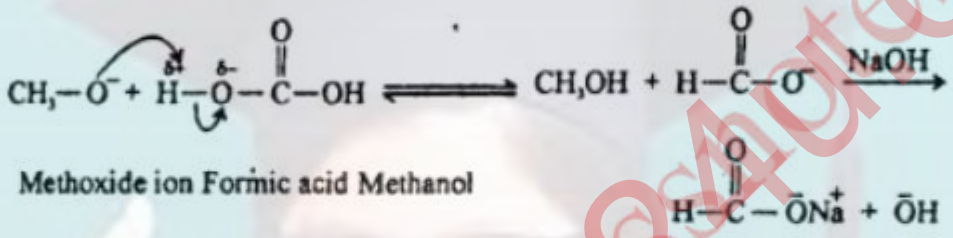


The anion transfers a hydride ion to second molecule of formaldehyde.



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

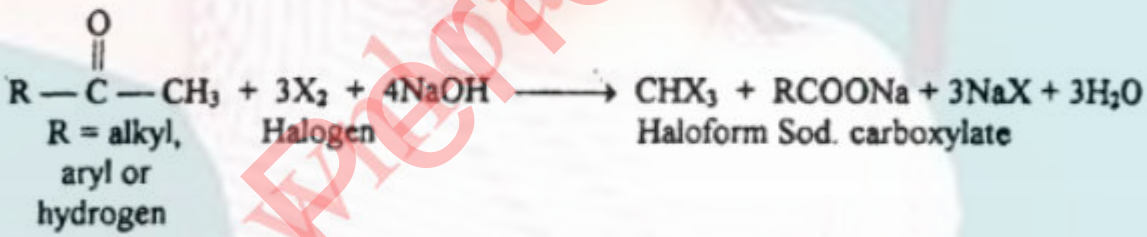
The methoxide ion acts as a base and abstracts a proton from formic acid to form methanol and formate ion.

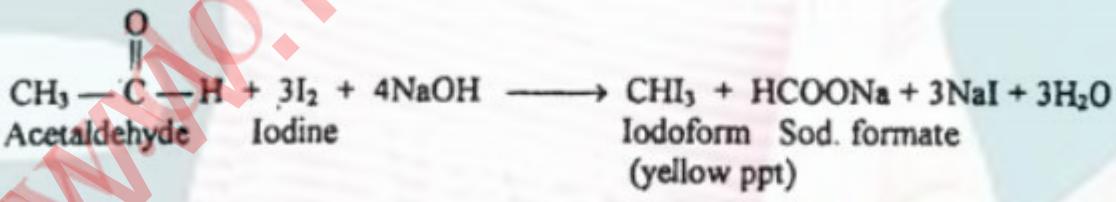


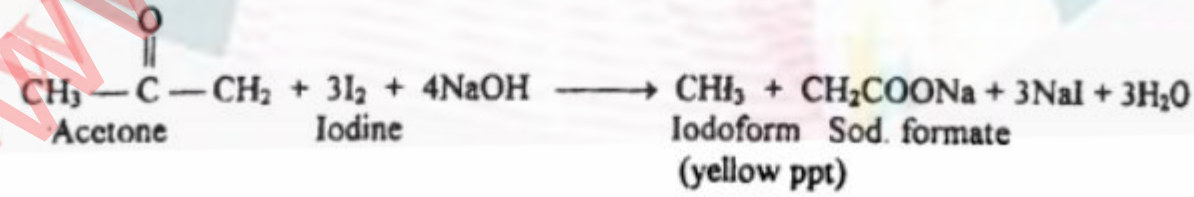
The formate ion in the presence of alkali gives a salt of acid.

1) Haloform Reaction

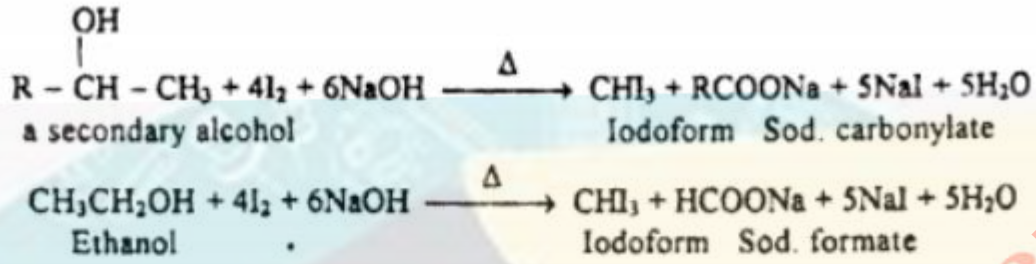
Only acetaldehyde and methyl ketones react with halogens (Cl, Br, I) in the presence of sodium hydroxide to give haloform (chloroform, bromoform or iodoform) and sodium salt of the acid.







Secondary alcohols containing the methyl group also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.



Halogen reaction, affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than parent compound.

Iodoform Test:

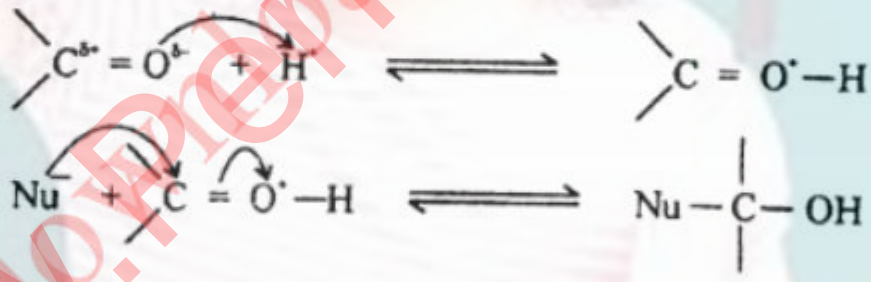
It is halofrom reaction in which iodine and aqueous sodium hydroxide form water insoluble iodoform (a yellow solid). Iodoforum test is used for distinguishing methyl ketones from other ketones. It is also used to distinguish ethanol form methanol and other primary alcohols. It can be used to distinguish acetaldehyde from other aldehydes.

ii) ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

Acid Catalysed Addition Reactions

The addition is initiated by the proton liberated by the acid, which combines with the carbonyl oxygen. It increases the electrophilic character of the carbonyl carbon and the attack of the weaker nucleophile on the electrophilic carbon becomes easy.

The general mechanism of the reaction is as fallows.



There are three types:

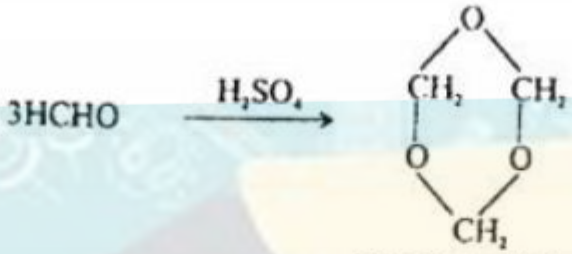
Polymerization

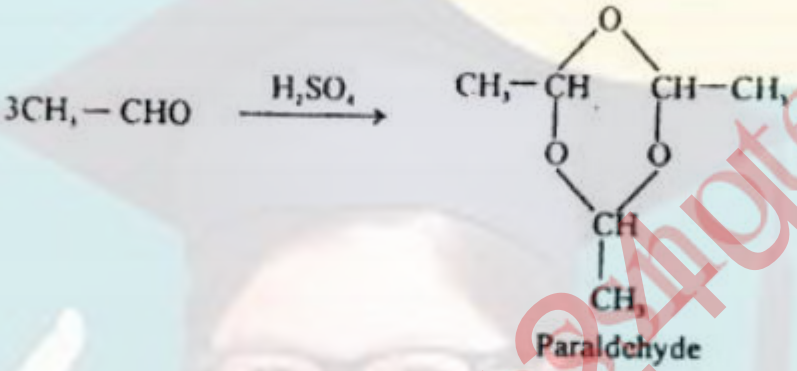
Addition of ammonia derivatives

Addition of alcohols

Polymerization

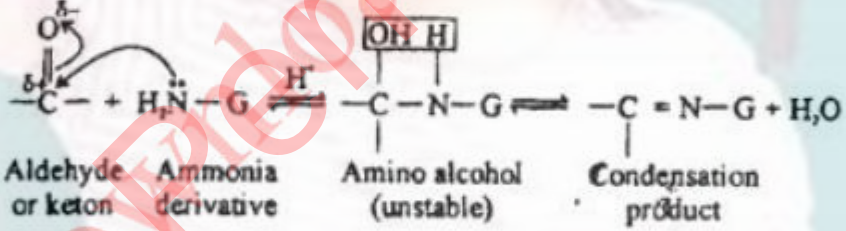
Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde.





Addition of ammonia derivatives

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



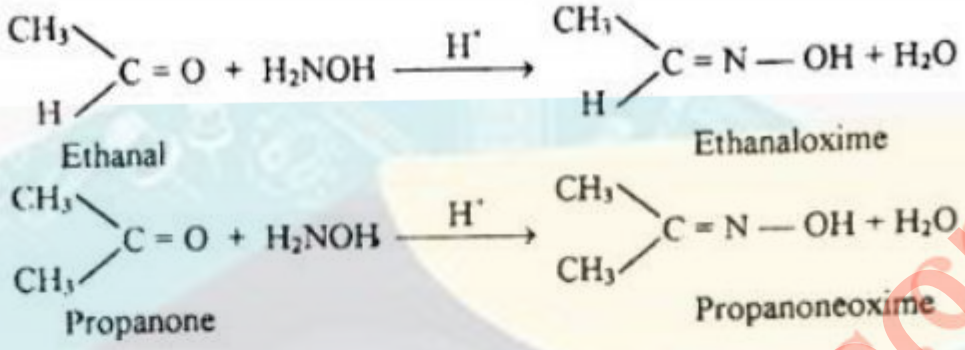
Where G = $\ddot{O}H$, — $\ddot{N}H_2$ — $\ddot{N}HC_6H_5$, — $\ddot{N}HCON_2$, etc

Specific Examples:

Some commonly used ammonia derivatives are hydroxylamine, NH_2OH, hydrazine, NH_2NH_2, phenylhydrazine, $C_6H_6NHNH_2$, semicarbazide, $NH_2NHCONH_2$, and 2,4-dinitrophenylhydrazine, $NH_2NHC_6H_3(NO_2)_2$.

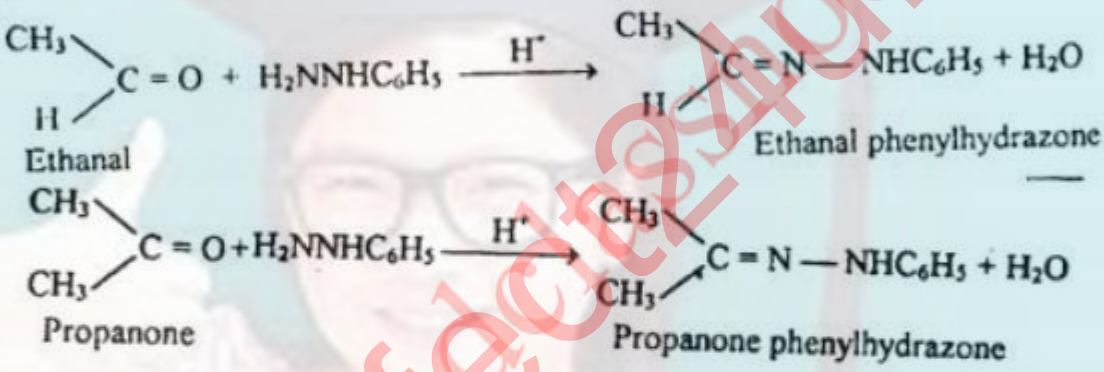
Reaction with hydroxylamine

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



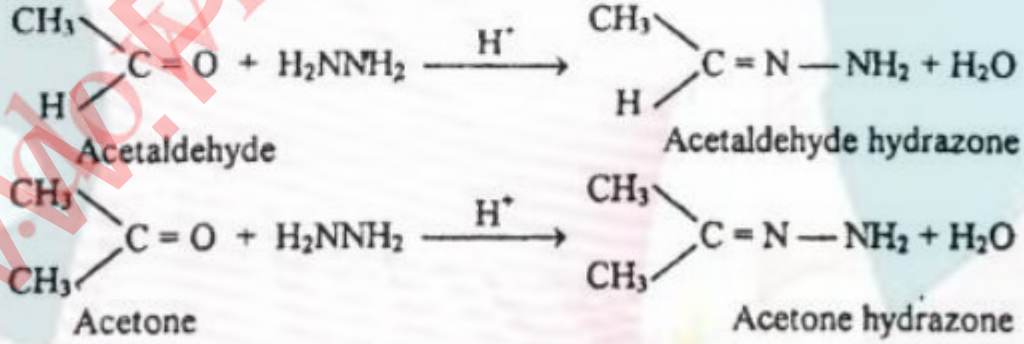
Reaction with Phenylhydrazine

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



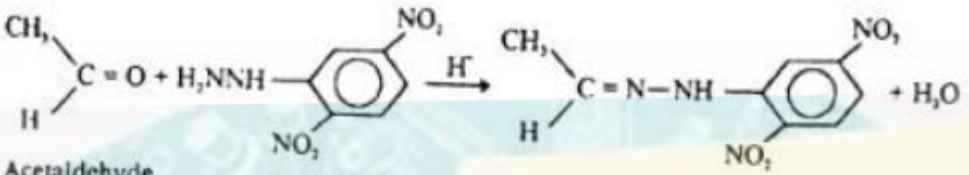
Reacion with hydrazine

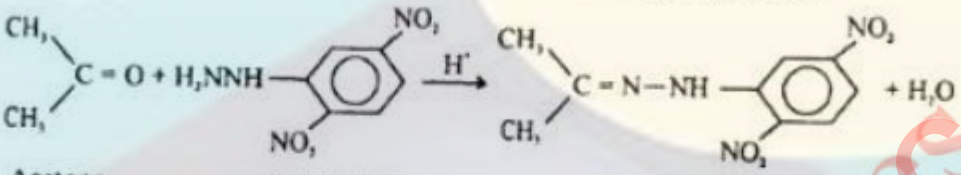
Aldehydes and ketones react with hydrazine to form hyrazones in the presence of an acid.



Reaction with 2,4-dinitrophenylhydrazine

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

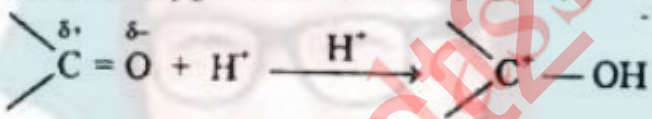




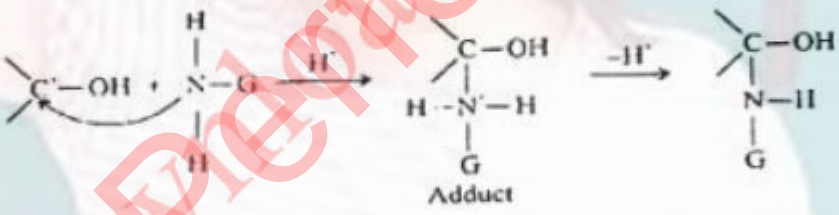
The reaction can be used for the identification of aldehydes and ketones because 2,4-dinitrophenylhydrazones are usually yellow or orange crystalline solids.

Mechanism of the Reaction of ammonia derivatives

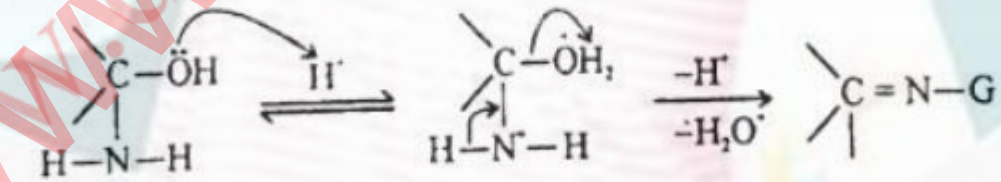
Step (i) Protonation of oxygen of the carbonyl group.



Step (ii) Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.

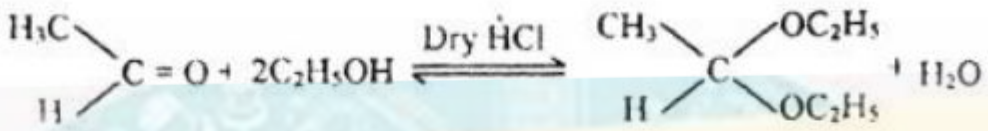


Step (iii) Protonation of oxygen of hydroxyl group followed by the removal of water.



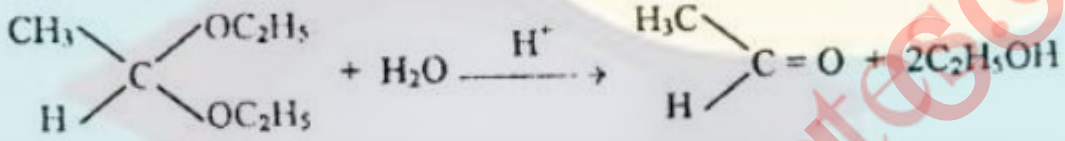
Addition of alcohols

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride acts as a catalyst.



1, 1-Diethoxyethane

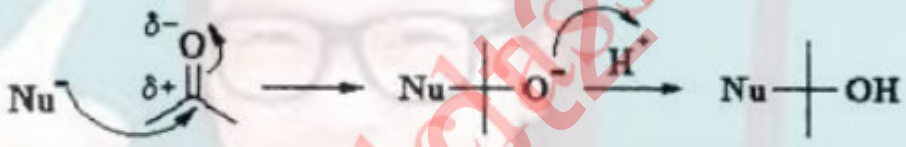
The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrozlysed in the presence of an acid.



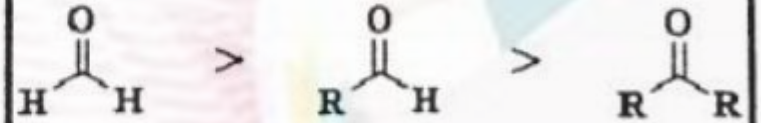
Note: Ketones do not react under these conditions.

19.6.2 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** (see below) The substituents have two contributing factors on the reactivity at the carbonyl C:	
1. Size of the substituents attached to the **C=O**. Larger groups will tend to sterically hinder the approach of the **Nucleophile**. 2. 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.

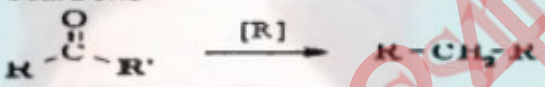
Carbonyl		K / M^{-1}	% Hydrate	
Carbonyl	methanal	41	99.96	Hydrate
	ethanal	1.8×10^{-2}	50	
	2,2-dimethylpropanal	4.1×10^{-3}	19	
	propanone	2.5×10^{-5}	0.14	

(K = [hydrate]/[C=O

Q8. Give Reduction reactions of Aldehydes and Ketones.

Answer

Reduction to Hydrocarbons



1) Clemmensen Reduction (acidic conditions)
Zn(Hg) in HCl reduced the C=O into $-CH_2-$

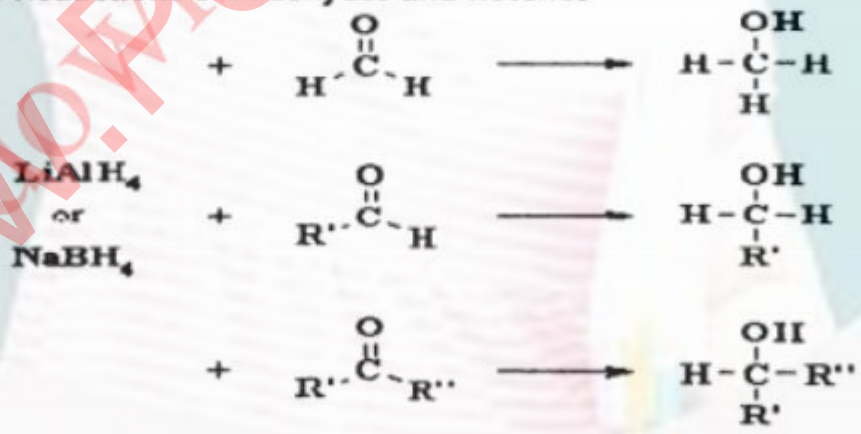
Wolff-Kishner Reduction (basic conditions)

2) 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.

3) Hydride Reductions of Aldehydes and Ketones



- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents $LiAlH_4$ 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.

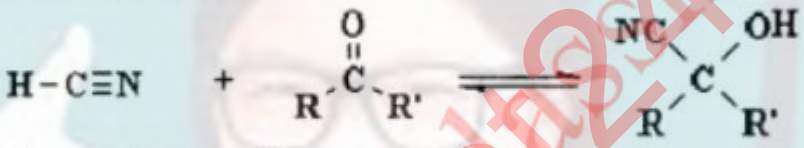
- Hydride reacts with the carbonyl group, **C = O**, in aldehydes or ketones to give alcohols.

- The substituents on the carbonyl tell the nature of the product alcohol.
- Reduction of methanal (formaldehyde) gives methanol.
- Reduction of other aldehydes gives **primary** alcohols.
- Reduction of ketones gives **secondary** alcohols.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction.

Q9. Reactions of aldehydes of ketones using carbon nucleophiles.

Answer

I) Cyanohydrin Formation

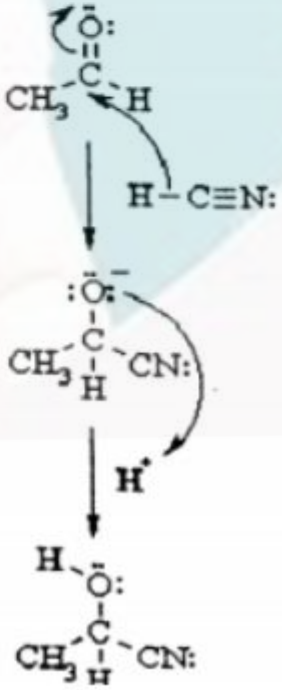


- Cyanide adds to aldehydes and ketones to give a cyanohydrin.
- The reaction is usually carried out using NaCN or KCN with HCl.
- HCN is a fairly weak acid, but *very toxic*.
- The reaction is useful since the cyano group can be converted into other useful functional groups ($-CO_2H$ or $-CH_2NH_2$)

II) 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.



III) Using Nitrogen Nucleophiles

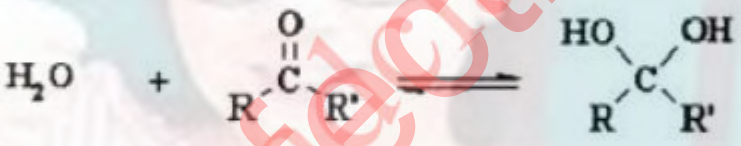
Reactions of Primary Amine derivatives

imine

- Primary amines, **R-NH$_2$** or **ArNH$_2$**, 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-NH$_2$** undergo this type of reaction and can be used

IV) 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:

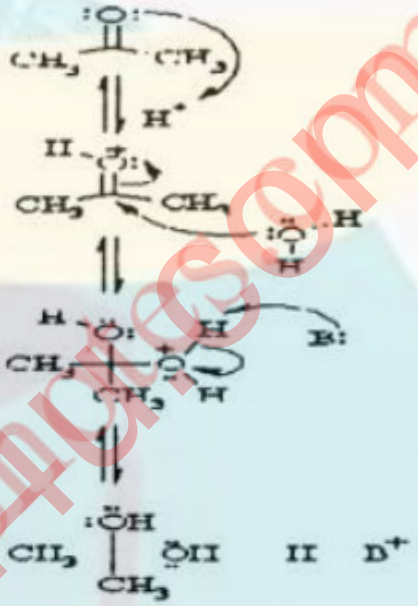
An acid/base reaction. Since there is only a weak nucleophile we need to activate the carbonyl by protonating on O.

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.



V) Oxidation Reactions

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 oxidized to OH group in these reactions.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow{K_2Cr_2O_7 / H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

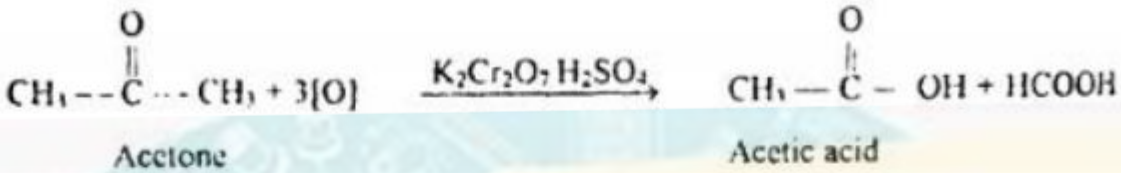
Acetaldehyde → Acetic acid

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow{K_2Cr_2O_7 / H_2SO_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Propionaldehyde → Propionic acid

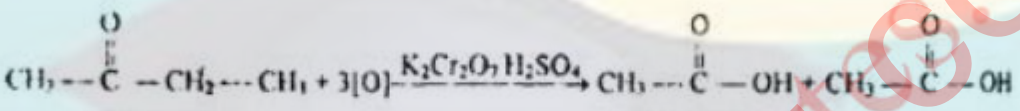
Oxidation of Ketones:

Ketones are only oxidizes by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and conc. HNO_3. The carbon atom joined to the smaller number of hydrogen atoms is oxidized. In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and mixture of two carboxylic acids is always obtained.



Acetone — Acetic acid

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



Butanone — Acetic acid

IMPORTANT INFORMATIONS

Sugars Glucose and Fructose – Naturally occurring carbonyl compounds

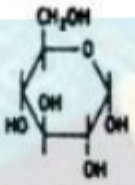
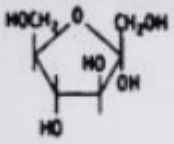
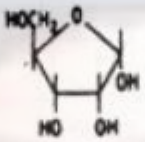
Sugars are sweet tasting soluble carbohydrates. Carbohydrates derive their name for the fact that they are composed of carbon, hydrogen and oxygen with H and O in the ratio of 2:1 as in water. Monosaccharides such as glucose are usually pentoses or hexoses, i.e. they contain 5 or 6 carbon atoms in their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

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 in 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.

The most obvious feature of the structure of the Monosaccharides and disaccharides is the p0resene of large number of –OH groups. These give them a large capacity for hydrogen bonding, so they are involatile 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.

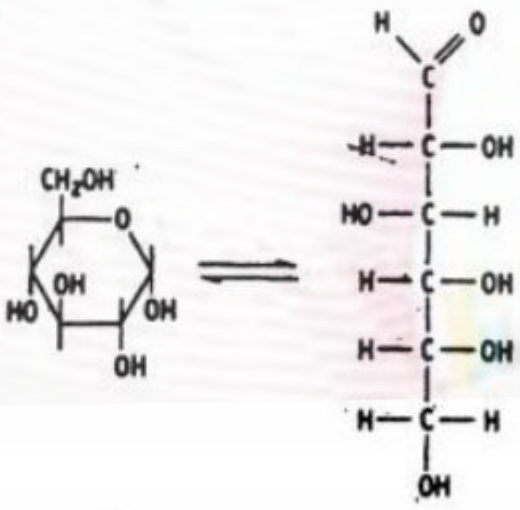
As well as showing the properties of polyhydroxy compounds, sugars show many properties in solution that are typical of carbonyl compounds. For example, glucose gives a crystalline condensation compound with 2,4-dinitrophenylhydrazine. This is surprising since the structure of glucose contains no carbonyl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

Some common carbohydrates. In the ring structures, the C atoms in the ring and the H atoms attached to them have been omitted, for clarity

Name	Type	Structure	Occurrence
glucose	monosaccharide, aldose, hexose	 (this is α-glucose: see section 9.8 for details of α- and β-glucose)	occurs abundantly in plants and animals
fructose	monosaccharide, ketose, hexose		in fruit and honey
ribose	monosaccharide, aldose, pentose		component of the molecules of ribonucleic acid (RNA) and vitamin B12
sucrose	disaccharide	glucose — fructose	sugar cane, sugar beet (commonly simply called 'sugar')
maltose	disaccharide	glucose — glucose	malt
lactose	disaccharide	glucose — galactose	milk
starch	polysaccharide	chains of glucose units	plant storage organs, e.g. potato, wheat grain
cellulose	polysaccharide	chains of 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



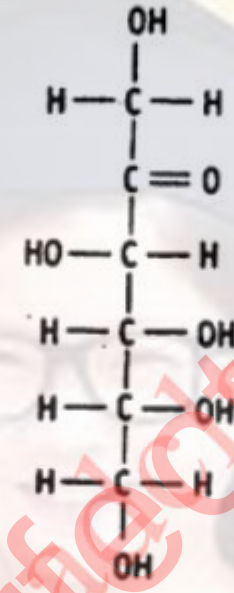
ring form open-chain form

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 sometimes 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 is therefore a ketose.

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

EXERCISE

Q1: Select the right answer from the choices given with each question.

1) **Which compound shows hydrogen bonding?**
   a) C_2H_6 b) C_2H_5Cl
   c) $CH_3 - O - CH_3$ d) C_2H_5OH

2) **Which compound is called a universal solvent?**
   a) H_2O b) CH_3OH
   c) C_2H_5OH d) $CH_3 - O - CH_3$

3) **According to Levis concept ethers behave as:**
   a) Acid b) Base
   c) Acid as well as base d) None of them

4) **Ethanol can be converted into ethanoic acid by:**
   a) Hydrogenation b) Hydration
   c). Oxidation d) Fermentation

==========

5) **Ethanol is denatured by adding:**
   a) Methanol
   b) Carbolic acid
   c) Acetone
   d) Propanol

6) **When phenol reacts with CH_3COCl the product formed is?**
   a) Ether
   b) Alcohol
   c) Aldehyde
   d) Ester

7) **Williamsone synthesis of ethers is superior to alcohols because it makes:**
   a) Symmetrical ethers
   b) Asymmetircal ethers
   c) Ether at room temperature
   d) Both symmetrical and asymmetrical ethers

8) **A methy phenol is also called:**
   a) A Cresol
   b) Benzyl alcohol
   c) Alcohol
   d) Formaldehyde

9) **Which one of the following compounds does not contain carboxylic group?**
   a) Acetic acid
   b) Formic acid
   c) Benzoic acid
   d) Picric acid

10) **Hydrogen boding is maximum in:**
   a) Diethyl ether
   b) Methanol
   c) Ethyl alcohol
   d) Triethyl amine

11) **Which of the following compound has no attraction at all with water?**
   a) C_6H_6
   b) C_2H_5OH
   c) $CH_3CH_2CH_2OH$
   d) $CH_3 - O - CH_3$

12) **Phenols are more acidic than alcohols which statement is correct?**
   a) Phenol turns blue litmus paper red
   b) Alcohol liberates CO2 with carbonate solution
   c) Phenoxide ion is stabilized due to resonance
   d) Alxoxide ion is stabilized due to resonance

13) **Carbolic acid is treated with dilute nitric and at 25°C, the product is:**
   a) O – nitrophenol
   b) P –nitrophenol
   c) m- nitrophenol
   d) Both a and b

14) **Oxonium ion is formed when:**
   a) Ethanol reacts with Na metal
   b) Phenol reacts NaOH solution
   c) Ether is treated with HI
   d) Ethanol is treated with aq NaOH and iodine

15) **2,4,6 – Trinitrophenol is commercially called as:**
   a) TNT
   b) Picric acid
   c) Carbolic acid
   d) Fumeric acid

==========

Answers

1)	d)	2)	a)	3)	b)	4)	d)	5)	a)
6)	d)	7)	c)	8)	a)	9)	d)	10)	d)
11)	a)	12)	c)	13)	d)	14)	c)	15)	b)

Q2. Give short answers of the following questions.

Q1. What are alcohols? How are they classified?

Answer

Aliphatic organic compounds having –OH groups are called as alcohols.

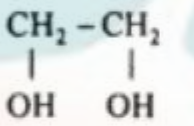
There are two gypes.

1) Monhydric alcohols
2) Polyhydric alcohols

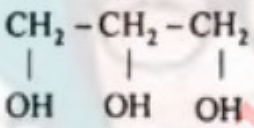
Examples of Monoyhdric alcohols:

$CH_3 - CH_2 - OH$ (methy Alcohol)

$CH_3-CH_2-CH_2-OH$ (ethyl alcohol)



Glycol (A Dihydric alchol)



Glycerol (A trihydric alchol)

Q2. How are monhydric alcohols classified?

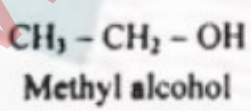
Answer

Classification of Monohydric alcohols

Monohydric alcohols are of three types.

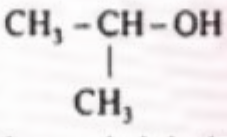
1) Primary alcohols
2) Secondary Alcohols
3) Terittory Alcohols

Examples



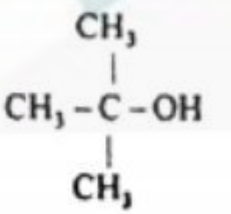
Methyl alcohol

(Prim alcohol)



isoprophylalcohol

(Sec alcohol)



nesbutylalcohol

(tetritory alcohol)

Q3. Compare the acidity of primary secondary and tertiory alcohols.

Answer

Acidity of Alcohols

1) Due to high electronegitivity of the O – atoms, alcohols are slightly acidic.
2) The anion derived by the deprotonation of an alcohol is the alkoxide.
3) Alkoxides are important bases in a organic chemistry.
4) Alcohols reat with Na (or K) like water to give the alkoxide.

$$2R - O - H + 2Na \longrightarrow 2\,NaOR + H_2$$

$$2R - O - H + 2Na \longrightarrow 2\,NaOR + H_2$$

Q4. 2 – butane is the major product when n–butyl alcohol is heated with conc. H_2SO_4. Explain.

Answer

n – butyl alcohol on reaction with H ion of H_2SO_4 produce primary carbonium ion. This primary carbonium ion is converted into secondary carbonium ion by shifting β – hydrogen atom, as secondary carbonium ion is more stable than the primary carbonium ion that is why 2 – butane is the major product.

$$H_2SO_4 \longrightarrow \overset{\oplus}{H} + \overset{\ominus}{HSO_4}$$

$$CH_3 - CH_2 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 + \overset{\oplus}{H} \longrightarrow CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2 + H_2O$$

$$CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2 \longrightarrow CH_3 - CH_2 - \overset{\oplus}{C}H - CH_3$$

(prim carbonium ion) (sec carbonium ion)

$$H_2\overset{\delta}{S}O_4 + CH_3 - \underset{\displaystyle H}{\underset{|}{\overset{\delta+}{C}}}H - \overset{\oplus}{C}H - CH_3 \longrightarrow CH_3 - CH = CH - CH_3 + H_2SO_4$$

(regenerated)

Q5. Give the mechanism of dehydration of alcohols.

Answer

Alcohols on heating at 180°C in presence of H_2SO_4 produce alkenes the reaction takes place as per following mechanism:

i) $H_2SO_4 \longrightarrow \overset{\oplus}{H} + \overset{\ominus}{HSO_4}$

ii) $$CH_3 - CH_2 - \underset{\displaystyle H}{\underset{|}{\overset{\delta-}{O}}} + \overset{\delta+}{H} \xrightarrow{180°C} CH_3 - CH_2 - \overset{\oplus}{O} - H$$

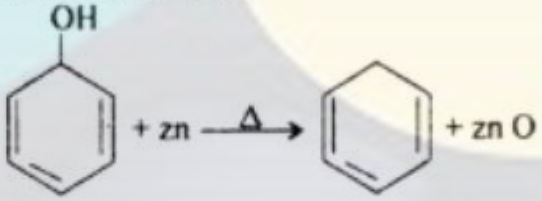
iii) $$H_2\overset{\delta}{S}O_4 + \overset{\delta+}{H} + CH_2 = CH_2 \rightarrow CH_2 - \overset{\oplus}{O} - H \xrightarrow{180°C}$$

$$CH_2 = CH_2 + H_2O + H_2SO_4$$
(regenerated)

Q6. How will you obtain benzene from alcohol?

Answer

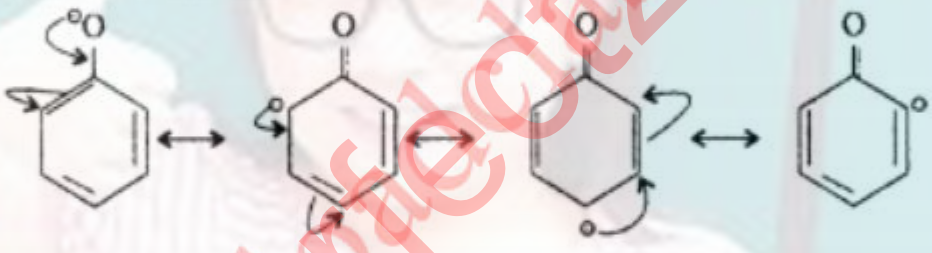
Conversion of phenol into Benzene



Q7. Alcohols phenols both have OH group but phenols are more acidic than alcohols.

Answer

Phenol after release of $H^{\oplus}$ – ion produce phenoxide $\left(\begin{smallmatrix}\ominus\\O\end{smallmatrix}\right)$ as conjugated base which is very stable due to resonance.



Whereas alcohols don't give very stable conjugated base.

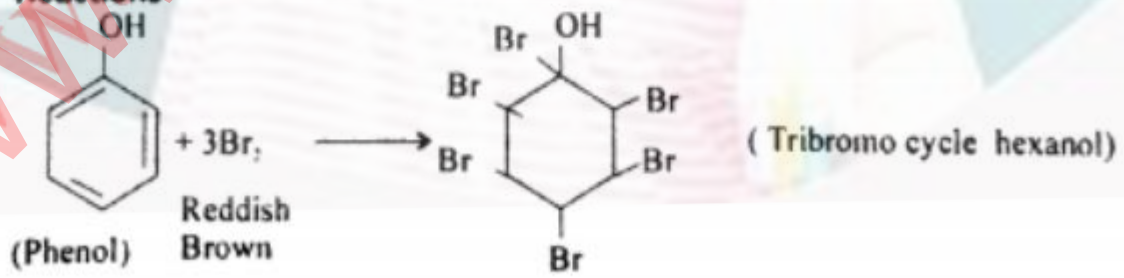
Q8. How will you differentiate between an alcohol and phenol?

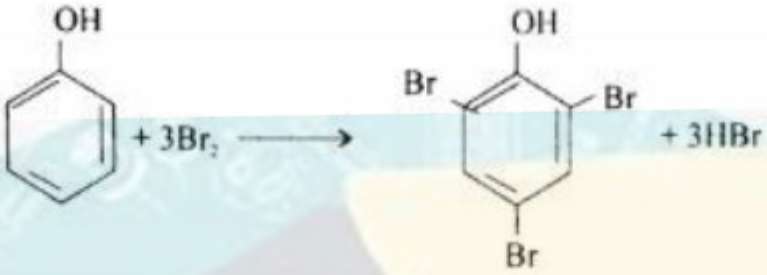
Answer

A test to distinguish alcohols and phenol

Acid bromine water gradually to concentrated solution of phenol in a test tube Bronine water first decolurizes and then on adding excess of it, a white or yellowish white ppt. Of polybromo derivative is produced which indicates the presence of phenolic group.

Reactions





White ppt
of Tribromo phenol

Q9. Write the nomenclature of ether by IUPAC system.

Answer

IUPAC system of Nomenclature of Ethers

IUPAC system of naming simple ethers are named by naming he two groups linked to oxygen atom followed by the word ether e.g.

$CH_3 - O - CH_3$ (Dimethyl ether)

$C_2H_5 - O - C_2H_5$ (Dimethyl ether)

Mixed ether are named as alkyl derivaties of hydrocarbons e.g.

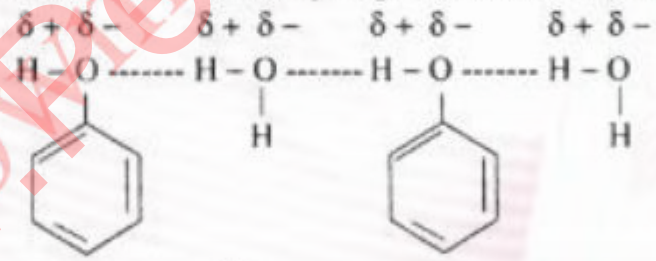
$CH_3 - O - CH_3$
Methoxy ethane

$CH_3 - CH_2 - CH(O - CH_3) - CH_3$
butane

Q10. Why is phenol more soluble in water than toluene?

Answer

Phenol is a polar molecule and forms hydrogen bonds with water molecules as follows:



Whereas toluene is non-polar  and is insoluble in water.

Q3: Give detailed answers for the following questions.

Q1. How will you prepare alcohols on industrial scale?

Answer

Industrially ethanol is prepared by fermentation of molasses, starch grains or fruit juices like sugarcane juice (called molasses by fermentation in presence of enzymes present in yeast.

From Molasses

1) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[(yeast)]{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$

2) $C_6H_{12}O_6 \xrightarrow[(yeast)]{Zymase} 2C_2H_5OH + CO_2$

From Starch

1) $2(C_6H_{10}O_5) + nH_2O \xrightarrow[(yeast)]{Diastase} C_{12}H_{22}O_{11}$

2) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[(yeast)]{Maltase} 2C_6H_{12}O_6$

3) $C_6H_{12}O_6 \xrightarrow[(yeast)]{Zymase} 2C_2H_5OH + 2CO_2$

Q2. Distinction between ethanol and methanol and ethanol from phenol.

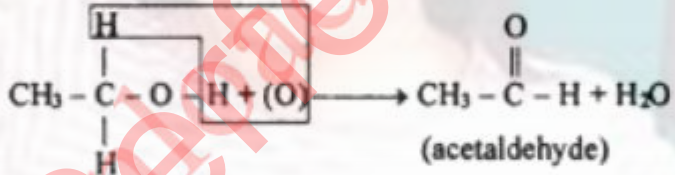
Answer

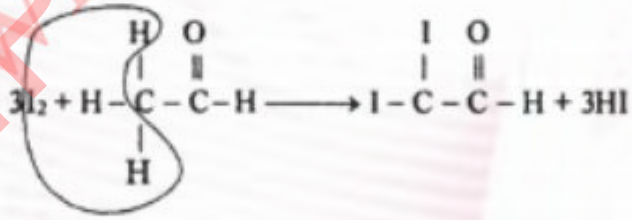
a) Distinction between ethanol and methanol

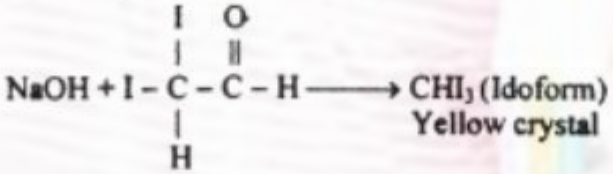
Ethanol on heating with I_2 and NaOH give yellow precipitates of Iodoform whereas methanol does not give this test.

Reactions

$$I_2 + H_2O \longrightarrow 2HI + (O)$$







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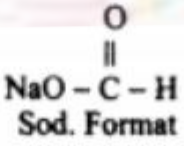


b) Distinction between ethanol and phenol

Ethanol gives idoform test positive but phenol does not.

Idoform Test

Ethanol + Solid Iodine + NaoH ⟶ Yellow crystals of Idoform

(reactions given in part a)

But phenol does not give yellow crystal.

Q3. How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.

Answer

Please see Answer of Q7. of chapter notes.

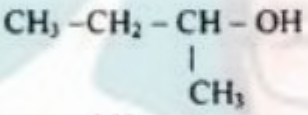
Q4. Give IUPAC names and structures of the following compounds.

i) Sec. butyl alcohol **ii) Lactic acid**

iii) Ter. butyl alcohol **iv) Tartaric acid**

Answer

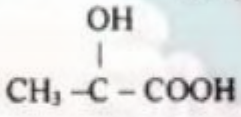
i)



Sec. butyle alcohol

2 – methyl –2 butanol

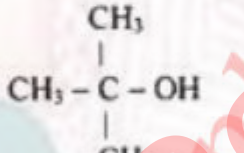
ii)



Lactic acid

2 – hydroxyl propanoic acid

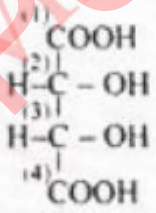
iii)



Ter butyl alcohol

2 – methyl – 2 – propanol

iv)



Tartaric acid

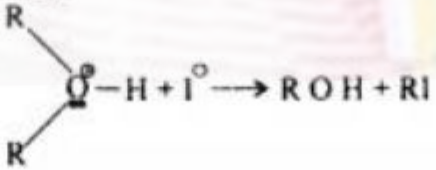
2,3 - dihydroxy

butandioci acid

Q5. Give the reactivity of Ethers.

Answer

Reaction with Haloacids



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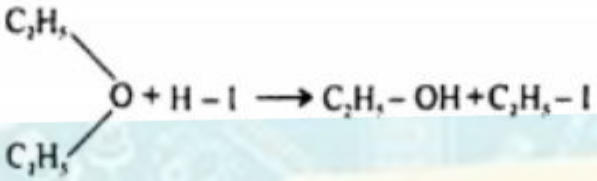
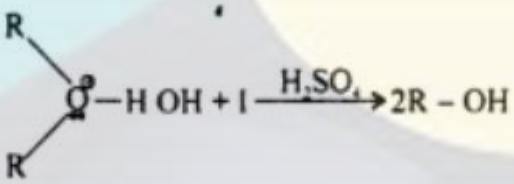


Reaction with water



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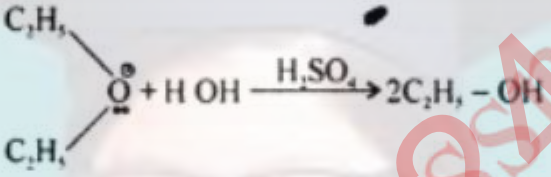
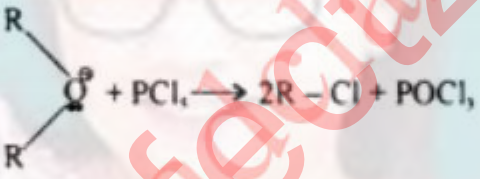


Reaction with PCl_5



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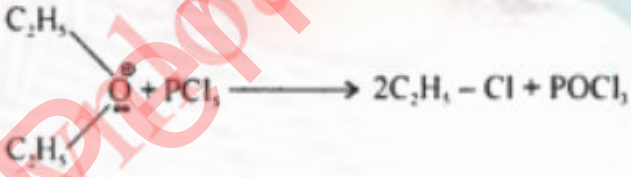


Q6. Give at least two methods for the preparation of phenol.

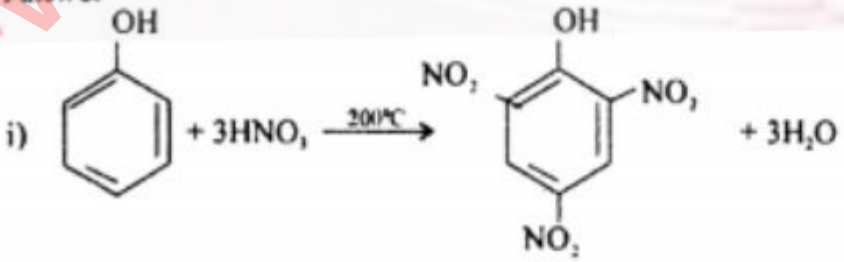
Answer

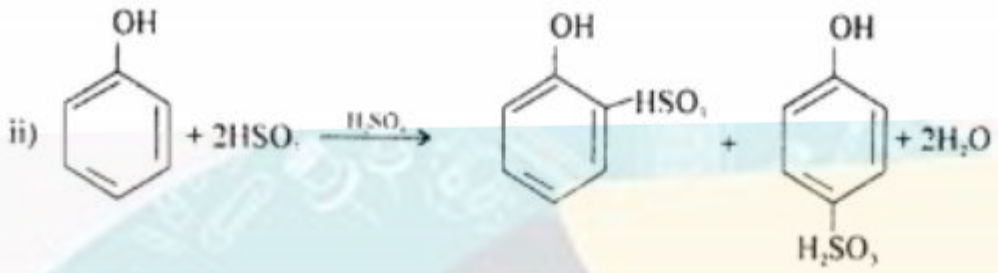
Please Answers of Q15 and Q16.

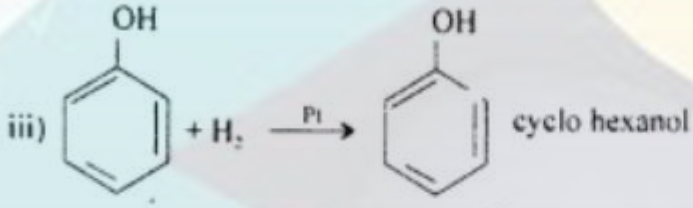
Q7. How does phenol reacts with

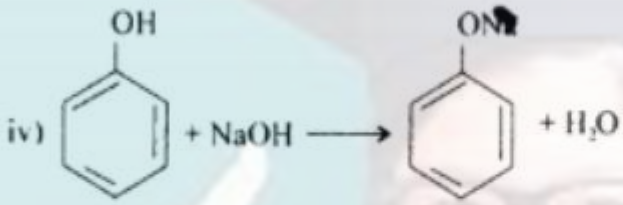
i) HNO_3 **ii) H_2SO_4**
iii) H2/Pt **iv) NaOH**
v) Ag_2O

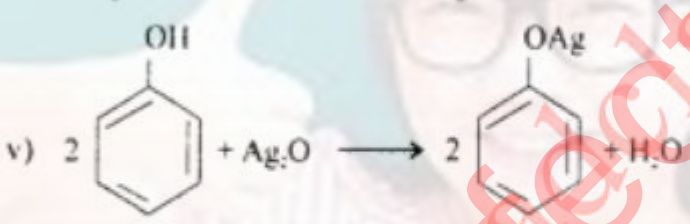
Answer









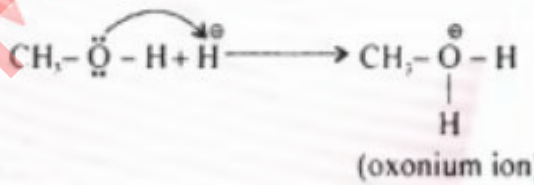


Q8. What is oxonium ion? Describe the chemical reactivity of ether.

Answer

An oxygen having positive charge is called as oxonium ion.

e.g.



Reactivity of Ethers

Please see Answer of reactivity of ether Q5 of exercise.

Q9. Explain following terms using ethyl alcohol as on example;

Answer

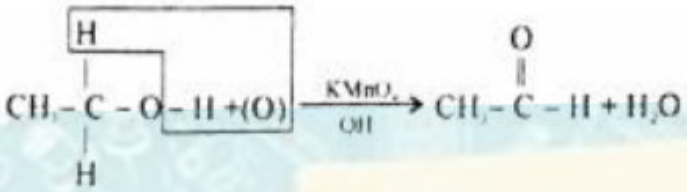
i) Oxidation **ii) Dehydration**

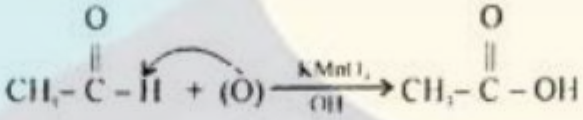
iii) Esterificatin **iv) Ether formation**

Answer

I) Oxidation

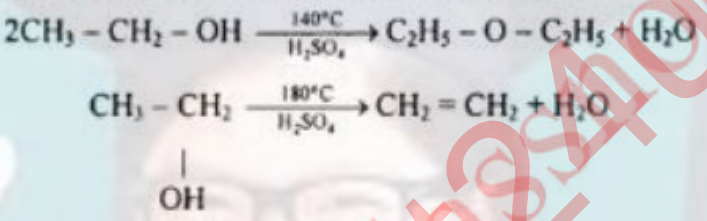
Oxidation of ethyl alcohol procedure octadehyle which on oxidation is converted into acetic acid.





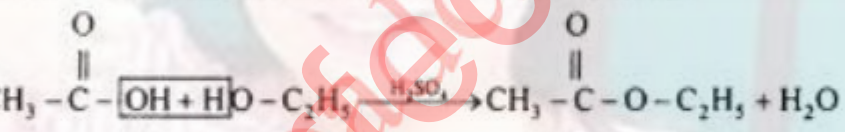
ii) Dehydration

Removal of hydrogen from a substance is called dehydration Dehydration of ethyl alcohol at different temperature produce different products.



iii) Esterification

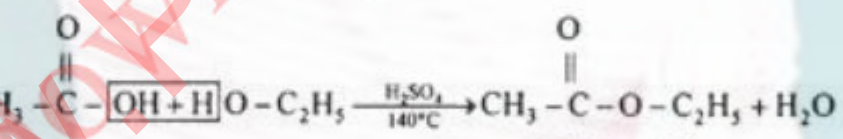
Formation of an ester from an alcohol is called estrification.



Ethylmethylester

iv) Ether Formation

Ethyl alcohol on heating with H_2SO_4 at 140°C.



Ethylmethylester

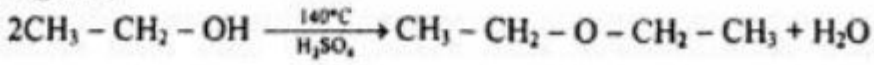
Q10. How does ethyl alcohols react with the following reagents?

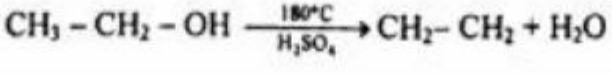
Answer

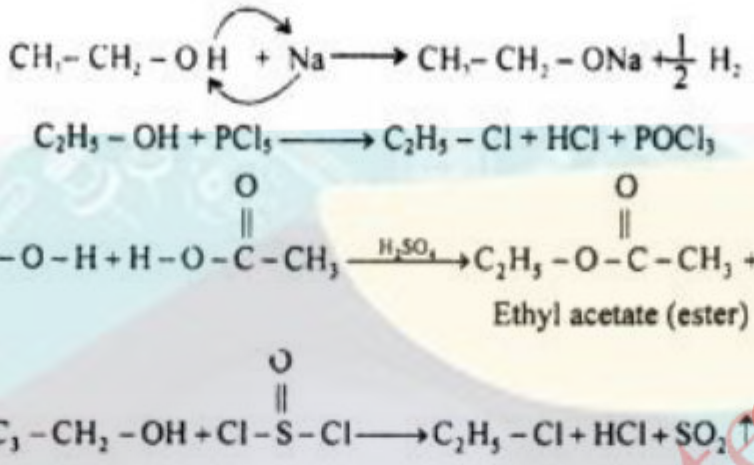
i) Conc. H_2SO^4
ii) Na
iii) PCl_5
iv) CH_3COOH
v) $SOCl_2$

Answer

i) Conc. H_2SO_4







Ethyl acetate (ester)

Q11. How will you distinguish between

i) **an alcohol and a phenol**
ii) **an alcohol and an ether**
iii) **Methanol and ethanol**
iv) **A tertiory alcohol and a primary alcohol**
v) **1 – propanol and 2 – propanol**

Answer

An alcohol and a phenol

Please see Answer of Q2,8 of exercise.

ii) Distinction between alcohol on reaction with Na – metal generate H_2 gas which burn luminous flame.
But ethers don't react with Na-metal.

iii) Distinction between ehanol and methanols
Please see Answer of Q3. 2 of exercise.

iv. A tertiary alcohol and a primary alcohol.
Please see Answer of Q7. of chapter notes.

v) 1 – propanol and 2 – propanol
Please see Answer of Q7. of chapter notes.

Q12. Give reason for the followings:

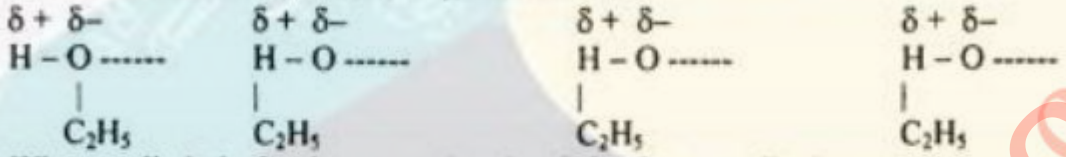
i) **Ethyl alcohol is a liquid while ethyl chloride is a gas.**
ii) **Ethanol has higher boiling point than diethyl ether.**
iii) **Absolute alcohol cannot be prepared by fermentation process.**
iv) **Ethanol gives different products with Conc. H_2SO_4 under different conditicns.**
v) **Water has higher boiling point than ethanol.**

Answer

i) Ethyl alcohol is liquid due to strong hydrogen bonds which are not present in ethyl chloride i.e.

$\delta+\ \delta-$ $\delta+\ \delta-$ $\delta+\ \delta-$ $\delta+\ \delta-$

ii) In ethanol there are strong hydrogen bonds like.



Whereas diethyl ether is a neutral molecule having zero dipole moment

iii) During fermentation there are obtained mixture of compounds whereas absolute alcohol is 100% pure alcohol. The fractional separation of alcohols by distillation of alcohols is not easy due to strong hydrogen bonds among alcohols.

iv) Ethanol on heating with concentrated H_2SO_4 at 140°C produce an ether. Whereas ethanol on heating with H_2SO_4 at 180°C produce on alkene.

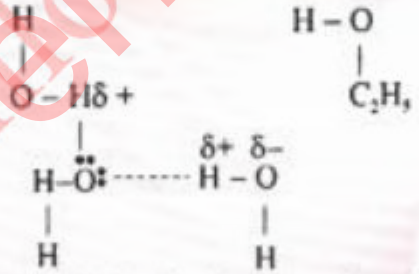
$$2CH_3 - CH_2 - OH \xrightarrow[H_2SO_4]{140^\circ C} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

Diethyl ether

$$CH_3 - CH_2 - OH \xrightarrow[H_2SO_4]{180^\circ C} CH_2 = CH_2 + H_2O$$

alkene

v) I one water molecule may forms two hydrogen bonds whereas one ethanol molecule may form one hydrogen bond that is why boiling point of water is 100°C and that of ethanol is 78.5°C.



Two H - bonds of water molecule

Short Answers Questions

Q1: What is difference between Aldehydes and Ketones?

Answer

Functional group	
In aldehydes, the cation of carboxyl group is directly attached to at least one H atom.	In Ketons, the C atom of carboxyl group is bonded to two carbon atoms called Ketone group.

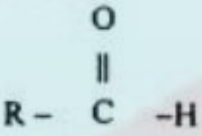
General formula

The homogenous series of aldehydes have general formula $C_nH_{2n}O$.

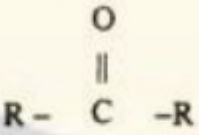
The homologous series of Ketones have general formula $C_nH_{2n}O$.

Functional formula structure

An aldehyde may be represented by the general formula structure



A ketones may be represented by the general formula structure.



Occurrence

Aldehydes groups are present in most sugars. They are the principal constituents oils used as fragrances and flowers.

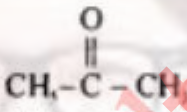
Ketonic group is present in camphor and fructose.

Examples

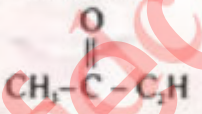
i) H – CHO
(Famaldehyde)

ii) CH_3 – CHO
orectaldehyde

i)



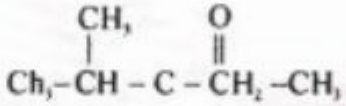
ii) Acetone



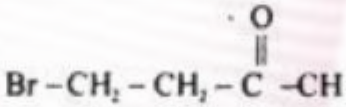
Q2: Write down the structure of following.

Answer

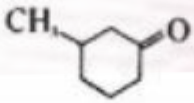
a) 2 – methyl – 3 hexanone



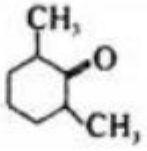
b) 4 bromo – 2 – butanone



c) 3 – Methyl cycle hexanone



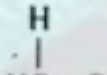
d) 2,6 dimethyl cycle hexanone



Q3: Write down the momendature of Aldehydes?

Answer

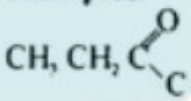
An aldehydes is named after the name of carboxlyic acid obtained on its oxidation the ending – ic acid is replaced by aldehyde.



formaldehyde

1) The longest carbon chain containing the aldehyic group is taken as the parent hydrocarbon.
2) The position of the substituent is indicated by numbers which is written before their number.

Examples



Propanal

Q4: Write down the reaction of ozonlysis of Alkenes for the preparations of aldehydes and ketones?

Answer

Reaction type: Electrophetic Additon overall transformation C = to 2c = O

Mechanism for Reaction of Alkenes with O_3.

Step1

The π electrons act as the nucleophilc 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 rearrange to the ozonide.

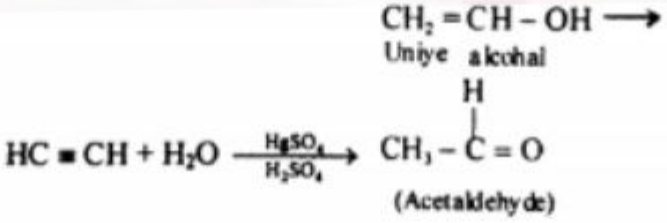
Step 3

The malozonide decomposes to give two carboxyl compounds.

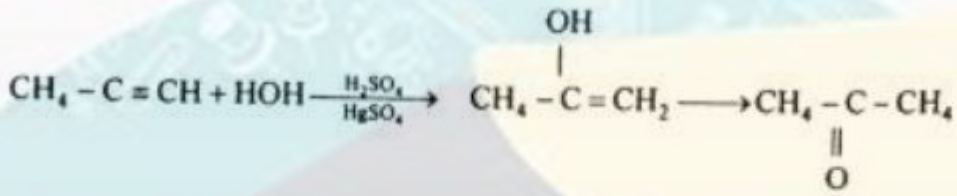
Q5: Write down the reaction of hydration of Alkynes?

Answer

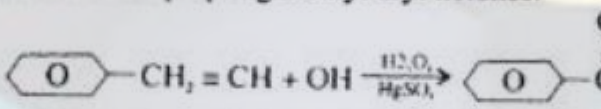
Water adds on to alkynes in the pusena of dil H_2SO_4 and $HgSO_4$ to produce an aldehyde or Ketone. Enol forms as intermediate which isomerizes into aldehydes or Ketones.



Propyne gives aitone.



This reaction is useful for prepling methyl aryl ketones.

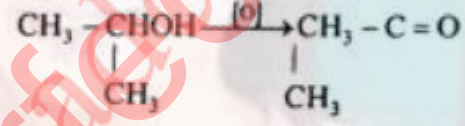


Q6: Write down the Reaction of oxidation of primary and secondary alcohols?

Answer

Primary alcohols are oxidized to aldehydes by (i) warming with acidic dichtomate solutions (ii) Jone reagent (CrO_3 + dil H_2SO_4 + acetone) (iii) sorett reagent (CrO_3 in pyridine)

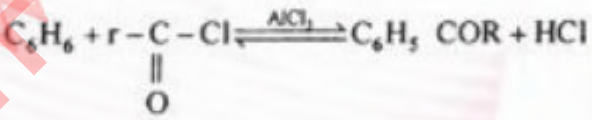
Now aquous solvents are employed to avoid further oxidation, secondary alcohols are oxidezed to ketones.



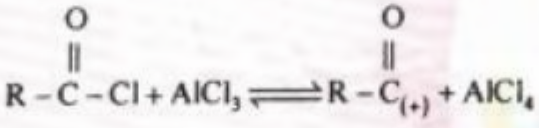
Q7: Write down the reaction of friedel crafts Acylation of Benzene?

Answer

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



$AlCl_3$ generates acylenium ion (electophite) which is substituted in the aromatic rings.

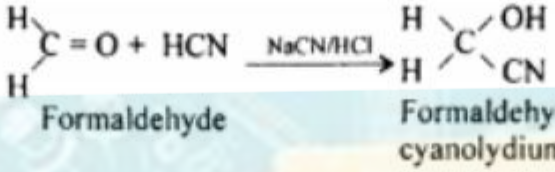


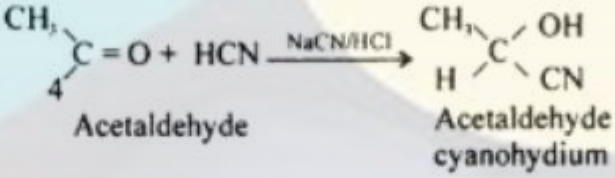
Q8: Write down the base catalysed nuceophitic addition reactions of carboxyl compounds?

Answer

1) Addition of hydrogen cyanide

Hydrogen cyanide adds to aldehydes and ketones to form cyanohyduims. The acid generates HcN form sodium cyanide in HCl.





Mechanism

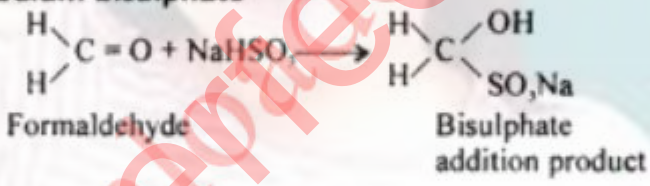
i) $H-\overset{\oplus}{O}+H-CN \rightleftharpoons CN^- + H_2O$

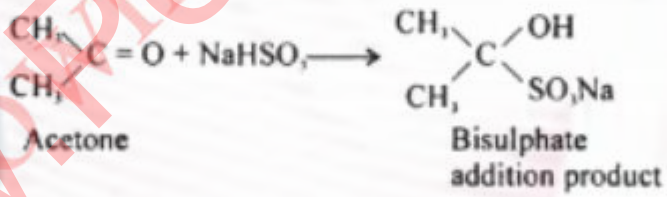
ii) $C^{\delta+}O^{\delta-}CN \rightleftharpoons C(O^-)(CN)$

2) Addition of Grignard's reagent

Grignard's reagents add to aldehydes and ketones to form adduct which on hydrolysis with a dilute mineral acid give alcohols.

3) Addition of sodium bisulphate

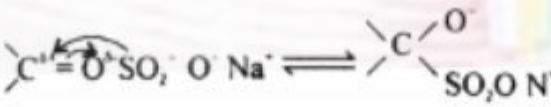




Mechanism

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

He sulphate in act as a nucleophile, since the sulphur atom is more nucleophile than oxygen a c – s bond is formed.



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

Condensation reaction

The reaction in which tow molecules of the same or different compounds combine to

form a new compound with or without the elimination of a small molecules like H_2O or NH_3 are called condensation reactions.

Q9: Define Aldol condensation and write down its types?

Answer

Definition

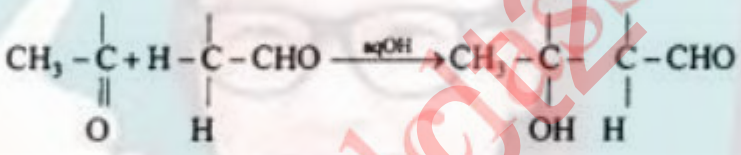
Aldol condensation is a reaction in which two molecules of same or different carboxyl compound containing ∝–hydrogen (hydrogen attached to the carbon atom next ot carboxyl group) combine together to from aldol or Ketol, which usually loses water molecule.

Types

Aldol condensation can occur.

1) Between two aldehydes.
2) Between an aldehyde and a ketone.
3) Between two ketone.

i) Condensation b/w tow aldehydes

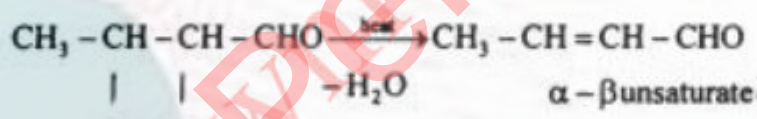


Ethanal ethanal (acetaldol)

βhydroxy butraldehyd

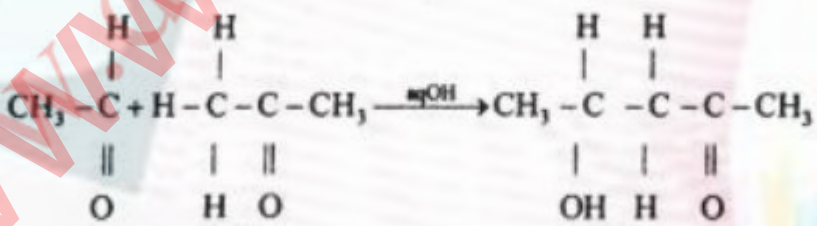
3 – hydroxybu tan al

b)



α – β unsaturate daldehyde

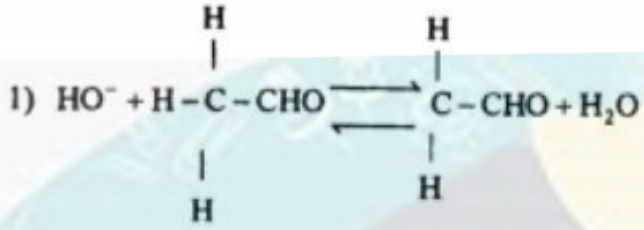
ii) Condesation between aldehyde and Ketone

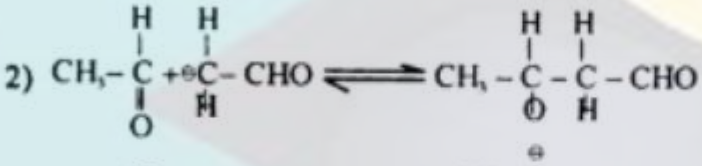


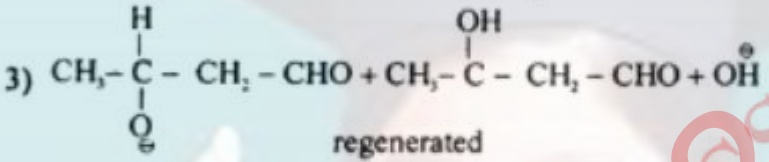
Ethanal Propanone 4 hydroxy – 2 – pen tan one

Mechanisms of Aldol condensation

Following steps are involved in aldol condensation.







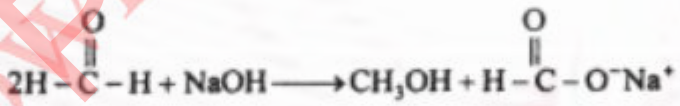
Q10: Write down the reaction and Mechanism of Cannizzaro's reaction.

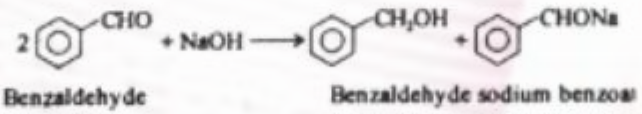
Answer

Aldehydes having no hydrogen atoms undergo Cannizzaro's reactionit a disproportionate reaction.

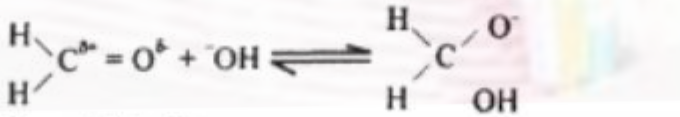
Two molecules of the aldehyde are involved.

One molecule is reduced into corresponding alcohol and the other is oxidized into the acid. The reaction is carried out with 50 prevent aquous solution by hydrodxide at room temperature.

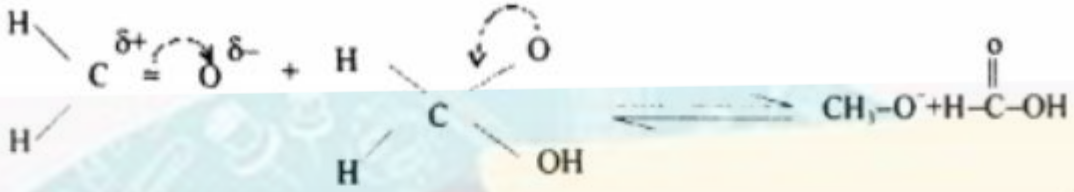




Mechanism

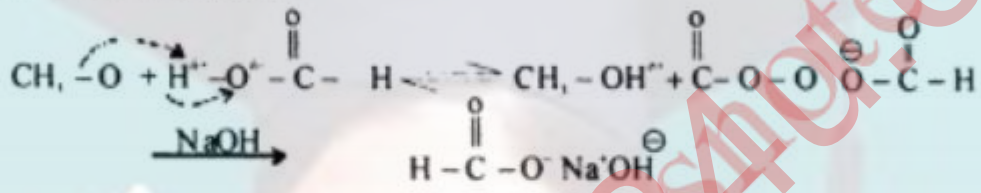


The amino transfer a hydroxide ion to second molecules of formaldehyde.



Formaldehyde Complexanion Methoxide ion formic acid

The methoxide ion acts as a base and abstract a proton form formic acid to form methanol and formation.



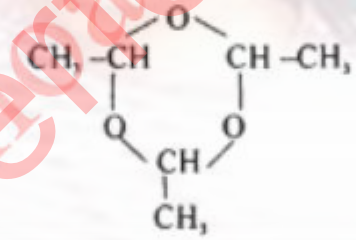
Q11: Write down the types involved in acid catalysed nucleophilic Addition Reactions?

Answer

The three types are:

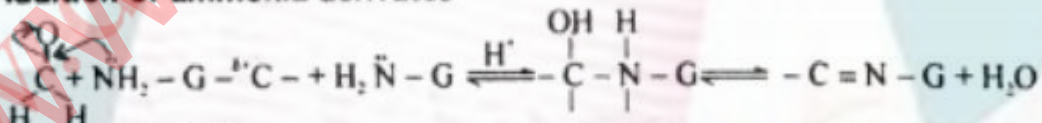
1) Polymerization 2) Addition of ammonia derivates. 3) Additionof alcohol

Polymerization



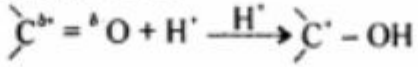
Paraldehyde

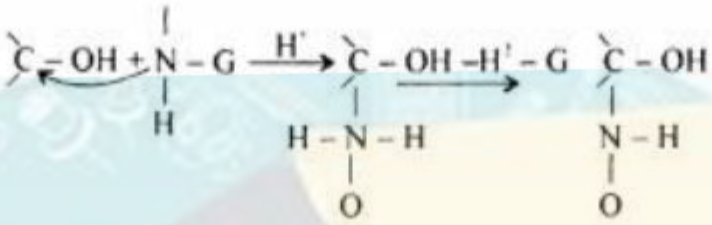
Addition of ammonia derivates



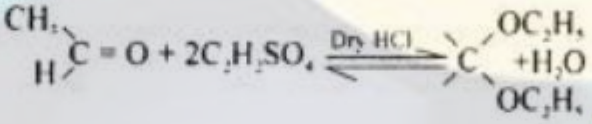
Aldehyde or Keton Ammonia derivate Amminо alchol condensation product

Mechanism of ammonia derivates





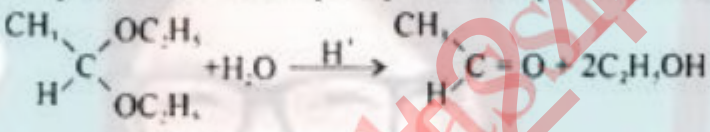
Addition of Alcohol



1.1 Dicthoxyethone

The reaction may be used protect aldehyde group against alkaline oxidizing agents.

To regenate aldehyde, the acetate is hydrolyzed in the presence of an acid.

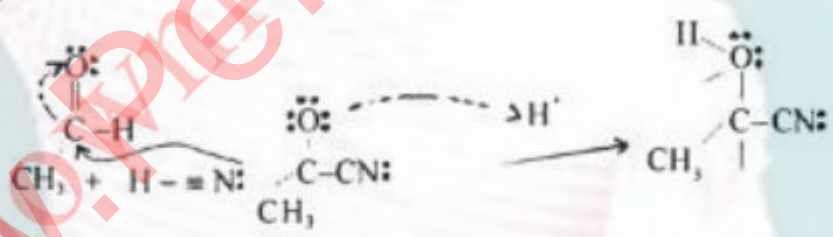


Q12: Write down the step involved the nucleophite addition of cyanide to an aldehyded.

Answer

Step 1

The nucleophilic C in the cyanide adds to the electrophitic c in the polar carboxyl group, electrons from the c = 0 move to the electgronegative o creating an intermediate alkoxide.



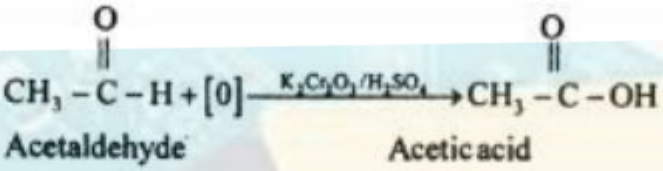
Step 2

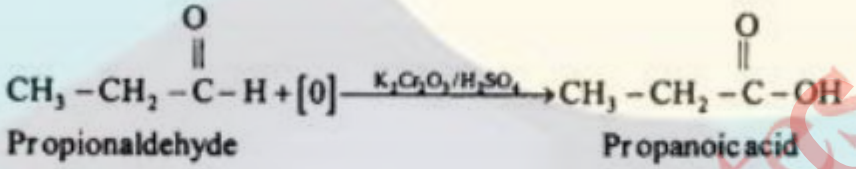
An acid base reaction Protonation of the alkomide oxygen creates the cyanohyd product.

Q13: Write down the oxidation Reaction of aldehydes?

Answer

Mild oxidizing agents like Tollen's reagent Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acid. They are also oxidized by strong oxdizing 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 carboxyl group in aldehydes is oxidized to OH group in these reaction

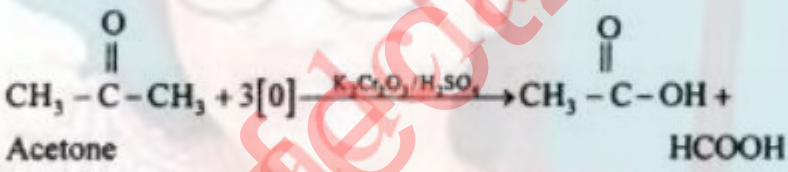




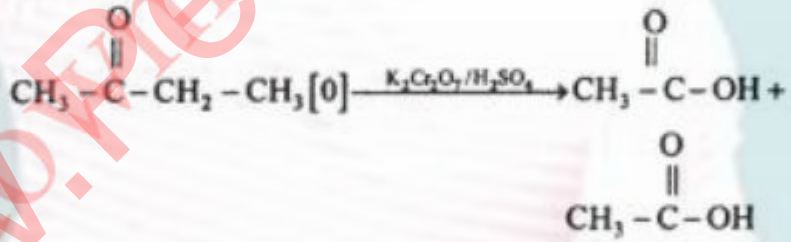
Q14: Write down the reaction involved in the oxidation of ketones.

Answer

Ketones are only oxidizes by strong oxidizing agents such as $K_2Cr_2O_7/ H_2SO_4$ KMO_4/H_2SO_4 and cone HNO_3. The carbon atom joined to the smaller number of hydrogen atoms is oxidized. Ketones only one carbon atom adjacent to the carboxyl group is oxidized and mixture of two carboxylic acid is always obtained.



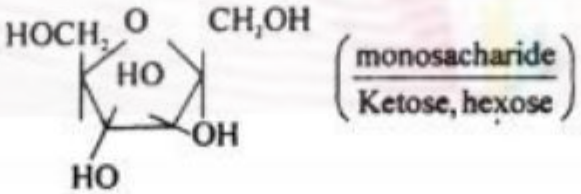
In unsymmetrical Ketones, the carbon atom joined to the smaller number of hydrogen atoms is oxidized and the carboxyl group remain with smaller alkyl group.



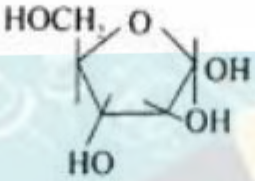
Q15: Write down the Ring form structure of fructose, ribose and maltose.

Answer

Fructose



Ribose



(monosacharide)

Maltose

glucose — glucose (disaccharide)

Q16: Why does the open chain form of glucose and other sugars charges to the ring form?

Answer

It is the result of the tendency of the carboxyl group to undergo nucleophilic addition. The nucleophitic involved in the oxygen atom of one of the OH group the same molecule. An internal nucleophitic addition reaction occur, forming a ring.

Q17: What is haloform reactions?

Answer

Only acetaldehyde and methyl Ketones react with halogens (Cl, Br, I) in the presence of sodium hydroxide to give haloform and sodium salt of the acid.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CH_{X3} + RCOONa + 3NaX + 3H_2O$$

R = alcylalyloe hydrogen — Haloform sod.carboxylate

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

acctaldehyde — lodoform sodium formate

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CHI_3 + CH_2COONa + 3NaI + 3H_2O$$

acetne — lodoform sodium formate (yellow ppt.)

Secondary alcohol containing the methyl group also undergo this reaction.

Ethanol is the only primary alcohol that gives this reaction.

$$K-\overset{\|}{C}H-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NAI + 5H_2O$$

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CH_3 + HCOONa + 5NAI + 5H_2O$$