

UNIT 19

**Carbonyl Compounds I:
Aldehydes and Ketones****Learning Outcomes:**

After Studying this unit Students will be able to:

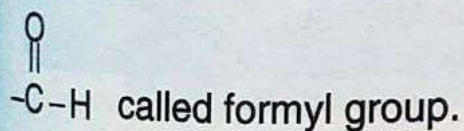
- Explain nomenclature and structure of Aldehydes and ketones.
- Discuss the preparation of aldehydes and ketones.
- Describe the reactivity of aldehydes and ketones and their comparison.
- Describe acid and base catalysed nucleophilic addition reactions of aldehydes and ketones.
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrocarbons. Alcohols by using carbon nucleophiles, nitrogen nucleophiles and oxygen nucleophiles.
- Describe oxidation reactions of aldehydes and ketones.
- Identify aldehydes and ketones in the laboratory tests.

Introduction:

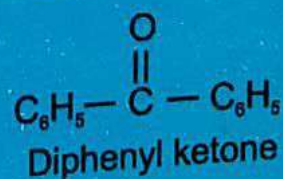
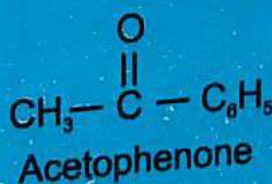
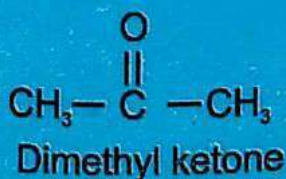
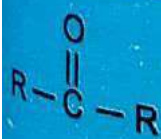
Some important classes of organic compounds like aldehydes, ketones, carboxylic acid, esters, amides, acid halides, acid anhydrides etc contain a functional group called carbonyl group are called carbonyl compounds. Many of these compounds are important commercially and in biological processes. A carbonyl group is a functional group composed of a carbon atom doubly bonded to an oxygen atom.



Aldehydes and ketones are two different classes of organic compounds containing a carbonyl group. Aldehydes have at least one hydrogen atom attached to the carbonyl carbon. The other group may be an alkyl group (or H atom in case of formaldehyde). Thus the functional group of aldehyde is



In ketones the carbonyl carbon atom is connected to two other carbon atoms. The ketone functional group is called keto group and is represented as $-\text{CO}-$. The two groups attached to it may be both alkyl groups (same or different) an alkyl and aryl group or both aryl groups.

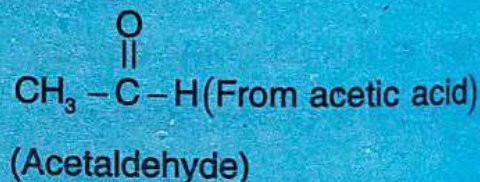
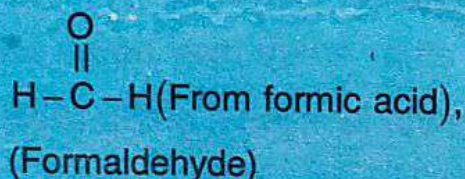


19.1**Nomenclature:**

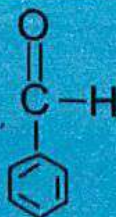
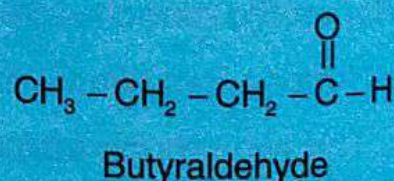
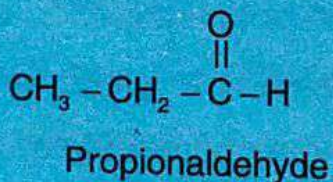
Two types of naming systems are used for naming aldehydes and ketones. Common naming system and IUPAC system.

19.1.1**Nomenclature of Aldehydes:****1. Common Naming System:**

Common names of Aldehydes are derived from the common names of carboxylic acids containing the same number of carbon atoms. While naming aldehydes in this system, the ending "ic acid" in the common name of corresponding carboxylic acid is replaced by the word "aldehyde".

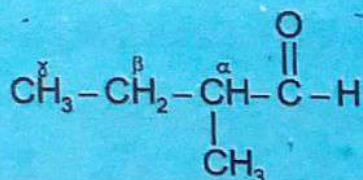


Similarly



Benzaldehyde

The positions of other groups on the chain are indicated by Greek letters ($\alpha, \beta, \gamma, \delta$ etc). Lettering starts from the carbon atom adjacent to formyl group.



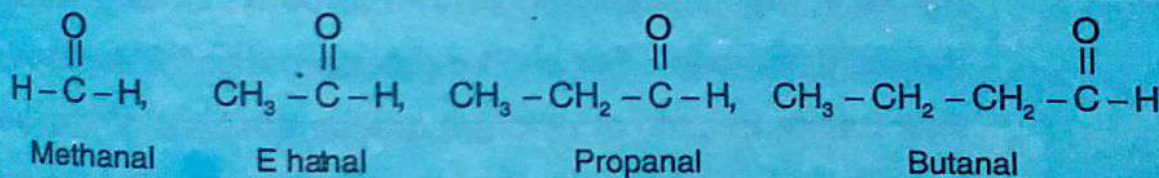
α - Methyl butyraldehyde

2. IUPAC Naming System:

In this system, following rules are used for naming aldehydes.

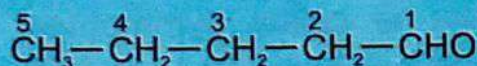
a. Chain Selection:

Locate the longest chain of carbon atoms containing formyl group to get the stem name. In IUPAC system, the ending "-e" of the corresponding alkane is replaced by "al".



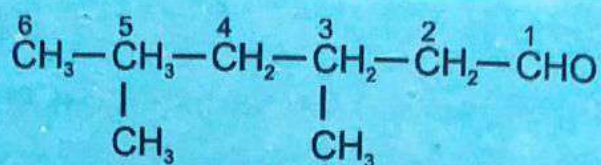
b. Numbering of the Selected Chain:

Carbon atoms of the selected chain are numbered from the carbon of formyl group ($-\text{CHO}$) because it is always at the terminal position. It is not necessary to mention the position of aldehydic group during naming as it is always one.

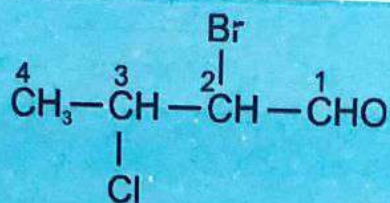


c. Branch Rules:

The rules for naming branches are same as in case of alkanes.



3,5 - Dimethylhexanal



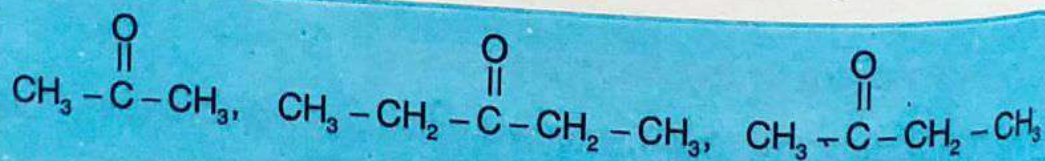
2-Bromo-3-chlorobutanal

19.1.2

Nomenclature of Ketones:

a. Common System

In this system ketones are named by writing first the name for the alkyl groups attached to the carbonyl carbon followed by the word "Ketone". For similar groups prefix "di" is used before their name. In case of different groups attached to the carbonyl carbon, alphabetical order is followed for writing their names.



Dimethyl ketone

Diethyl ketone

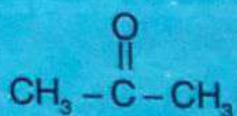
Ethyl methyl ketone

If the two alkyl groups attached to carbonyl carbon are the same the ketone is called symmetrical and if different, it is called unsymmetrical ketone.

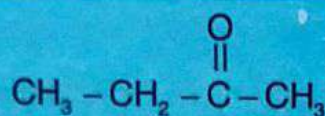
b. IUPAC System:

While naming ketones in IUPAC system following steps are taken

- i. **Chain Selection:** Select the longest chain as stem name for ketone, which is then named by replacing the ending "-e" of corresponding alkane by "-one". No numbering is necessary for propanone and butanone.

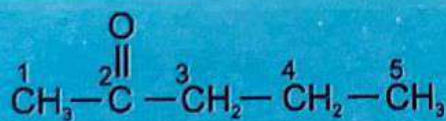


propanone



butanone

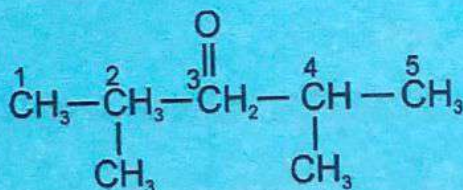
- ii. **Numbering the Chain:** The carbons of the selected chain are numbered to mention the position of the carbonyl carbon before stem name because in ketones carbonyl group may occur at various positions on the carbon chain. Numbering is done from that end at which the carbonyl carbon has the lowest possible number.



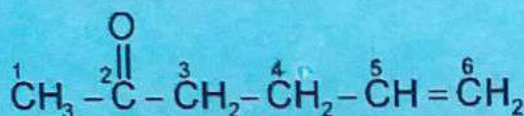
2-Pentanone

c. Branch Rules:

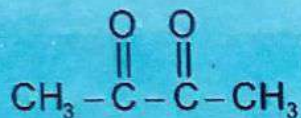
If one or more branches are attached to the selected chain then the same rules are obeyed as mentioned for IUPAC names of alkanes.



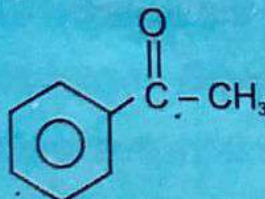
2,4-Dimethylpentan-3-one
(2,4-Dimethyl-3-pentanone)



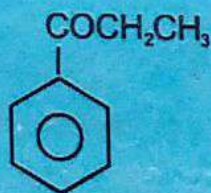
5-Hexen - 2-one



Butan-2, 3-dione



Phenylethanone
(Acetophenone)



Phenyl propanone
(Propiophenone)

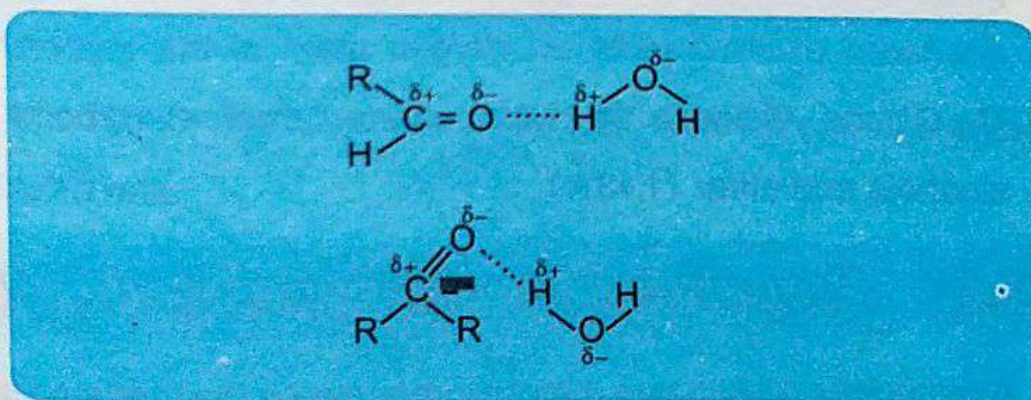
19.2

Physical Properties:

- Lower aldehydes like formaldehyde and acetaldehyde have very sharp pungent odour whereas higher members of aldehydes,

aromatic aldehydes as well as most of the ketones have pleasant smell.

- 2 Formaldehyde is a gas at room temperature while aldehydes are colourless liquids. Acetone, the simplest ketone, is a liquids at room temperature with pleasant odour. All the other members of ketone series are also colourless liquids with characteristic odour.
- 3 Low molecular weight aldehydes and ketones (up to C_4) are water soluble. Water solubility decreases as the size of the molecules increases. Higher members of aldehydes and ketones (C_5 onward) are usually insoluble in water, while formaldehyde is highly soluble in water. Carbonyl compounds cannot form hydrogen bonds with themselves as there is no hydrogen on the carbonyl oxygen. However, their solubility in water is due to hydrogen bond formation of carbonyl oxygen with water molecules



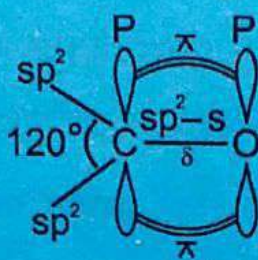
- 4 Aldehydes and ketones are polar compounds due to high dipole moment of their $C = O$ bond. As a result they have high boiling points than the corresponding alkanes and non-polar compounds like ethers but lower than alcohols. The boiling point of methanal is -21°C whereas ethanal boils at 21°C , close to room temperature.

Acetone has boiling point of 56°C . The boiling point of aldehydes and ketones increase with the increase in the molecular weights.

19.3

Structure:

The carbon and oxygen in the carbonyl group, present in aldehydes and ketones, consists of a sigma bond and a pi bond. Both carbon as well as oxygen of the carbonyl group are sp^2 – hybridized.



The three atoms attached to carbonyl carbon lie in a plane with bond angles of approximately 120° . The pi bond is formed by the overlap of a p-orbital of carbon with p-orbital of oxygen atom. There are two unshared electron pairs on oxygen atom of the carbonyl group. The $\text{C}=\text{O}$ bond distance is 1.23\AA , shorter than $\text{C}-\text{O}$ bond distance in alcohols and ether (1.43\AA).

19.4

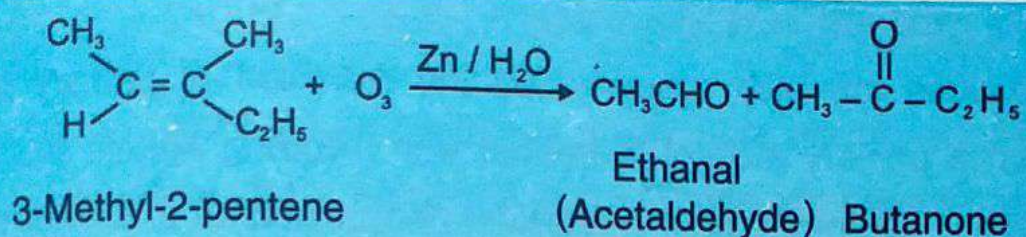
Preparation of aldehydes and Ketones:

Aldehydes and ketones may be prepared by the following methods.

19.4.1

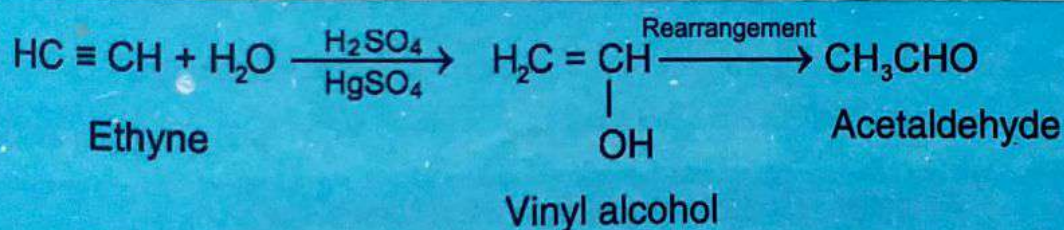
Ozonolysis of Alkenes:

Ozone, an allotropic form of oxygen, reacts vigorously with alkenes to form an unstable intermediate compound called ozonide. The ozonide is reduced directly to aldehydes and ketones by zinc and water. This reaction is called ozonolysis.

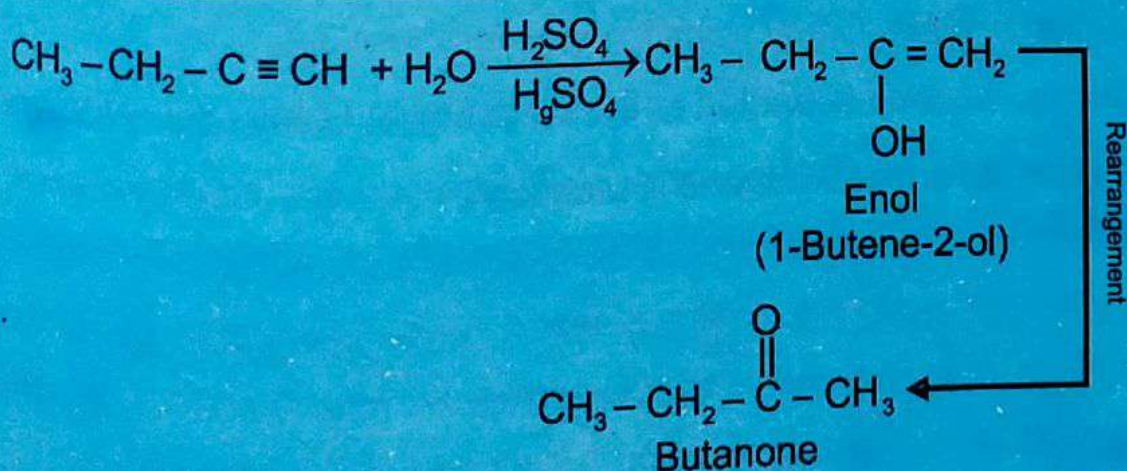


19.4.2 Hydration of Alkynes:

Water adds to alkynes in the presence of mercuric sulphate and sulphuric acid to form an unstable intermediate, unsaturated alcohol (enol). The enol intermediate then undergoes rearrangement to form aldehyde or ketone depending on the starting alkyne used.

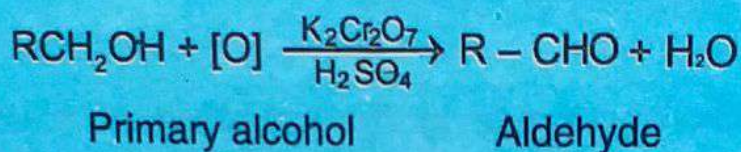


In case of unsymmetric alkynes H_2O addition takes place according to Markovinkoff's rule.

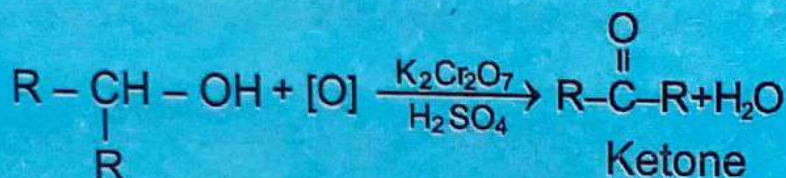


19.4.3 Oxidation of Alcohols:

Aldehydes are also prepared by the oxidation of primary alcohols. When a primary alcohol is treated with oxidizing agents like acidified potassium dichromate or potassium permanganate it is oxidized to an aldehyde.

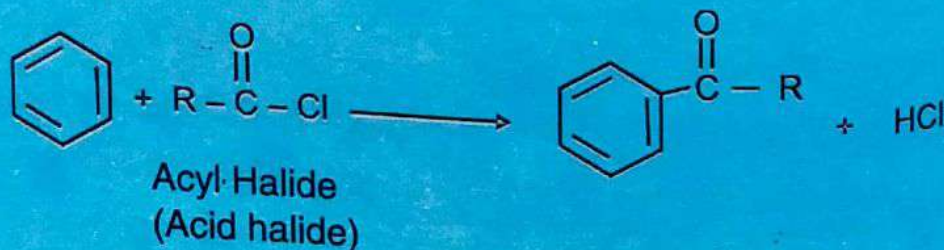


While oxidation of secondary alcohols gives ketones

**19.4.4 Friedel -Crafts Acylation of Aromatics:**

The introduction of acyl group ($\text{R}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$) into the aromatic ring (benzene ring) in the presence of acyl halide and anhydrous AlCl_3 catalyst is called Friedel -Crafts acylation or simply acylation.

When benzene is treated in the presence of Lewis acid, AlCl_3 , with acid halide, an aromatic ketone is produced.

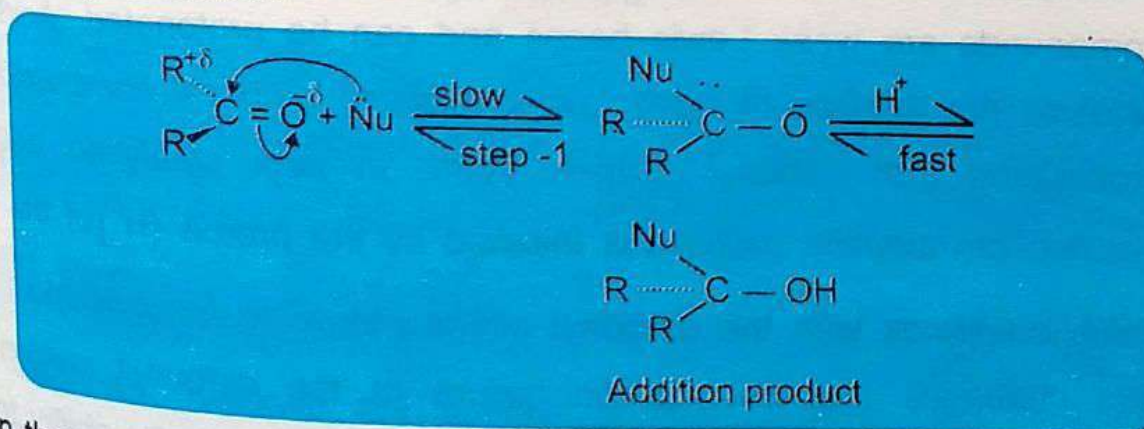


19.5

Reactivity of Carbonyl Group:

In carbonyl group (>C=O) oxygen is much more electronegative than carbon. Therefore, the π -electrons in C=O bond are strongly attracted by the oxygen atom. As a result, the carbonyl group becomes highly polar with a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom.

As a result of this polarization, most carbonyl reactions involve nucleophilic attacks at the carbonyl carbon often accompanied by addition of a proton to the oxygen. The aldehydes and ketones usually undergo nucleophilic addition reactions as compared to alkenes where C=C are not polarized and hence they usually involve electrophilic addition. The nucleophilic addition in aldehydes and ketones is generally shown as:



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

19.6

Reactions of Aldehydes and ketones:

Aldehydes and ketones are very reactive substances mostly undergoing addition reaction across C=O bond. These can also be oxidized as well as reduced. Thus they undergo a very large variety of reactions. Some of their reactions are.

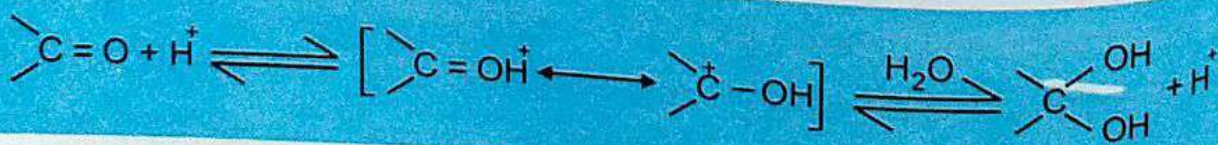
19.6.1

Nucleophilic Addition reactions: (Acid and Base catalyzed)

Aldehydes and ketones mainly undergo nucleophilic additions reactions. These reactions may be either acid catalyzed or base catalyzed.

a. Acid –Catalyzed Addition Reactions:

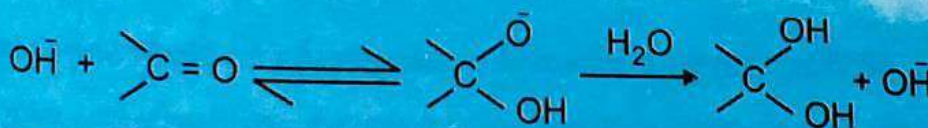
Because of the unshared electron pair on oxygen atom, carbonyl compounds are weak Lewis bases and can be protonated. Acid can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom. In acid catalyzed addition reaction the addition process is initiated by the proton (H^+) of the acid which combines with the carbonyl oxygen atom to form oxonium ion. This increases the electrophilic nature of the carbonyl carbon by inducing more positive charge on it and thus enhances its ability to be attacked by weak nucleophiles.



The carbonyl carbon, which is trigonal and sp^2 -hybridized in the starting aldehyde and ketones becomes tetrahedral and sp^3 -hybridized in the reaction product.

b. Base-Catalysed Addition Reactions:

A base catalyzed nucleophilic addition will take place with a strong nucleophile. The base reacts with the reagent and generates the nucleophile. This nucleophile attacks at the carbon atom of the carbon-oxygen double bond because that carbon has a partial positive charge and π electrons of $C=O$ bond move to the oxygen atom, which, because of its electronegativity, can easily accommodate the negative charge. The reaction is completed by addition of proton to the negative oxygen.



19.6.2

Relative Reactivity:

Generally, Ketones are somewhat less reactive than aldehydes towards nucleophiles. There are two main reasons for this reactivity difference.

i. Steric Hindrance:

The carbonyl carbon is more crowded in ketones as compared to aldehydes. In nucleophilic addition, the attached groups come even closer because in the product the hybridization

changes from sp^2 to sp^3 and the bond angles decrease from 120° to 109.5° .

ii. Electronic Effect: As alkyl groups are usually electron donating compared to hydrogen. They, therefore, tend to neutralize the partial positive charge on the carbonyl carbon decreasing its reactivity towards nucleophiles. Ketones have two such alkyl groups; aldehydes have only one.



19.6.3

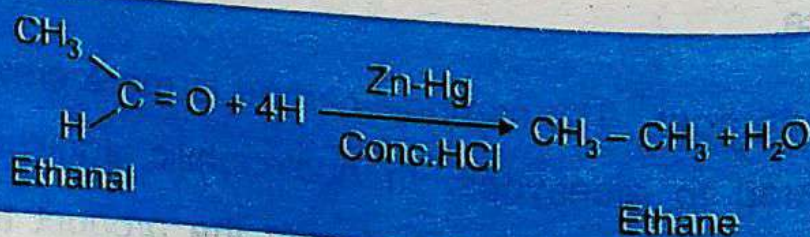
Reduction of Aldehydes and Ketones:

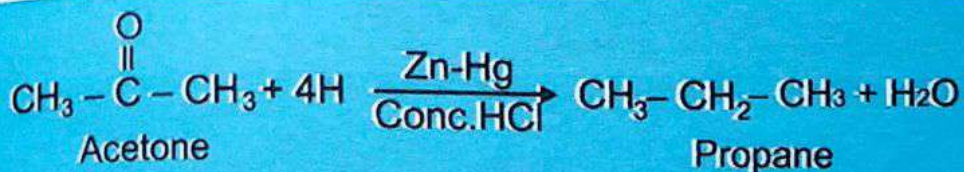
Addition of hydrogen to aldehydes and ketones is called reduction. Following are some important reactions of aldehydes and ketones that involve reduction.

1. Reduction of carbonyl compounds to Hydrocarbons:

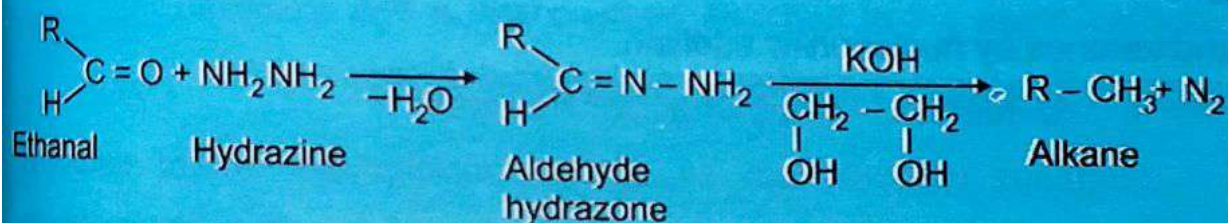
Aldehydes and ketones can be reduced to saturated hydrocarbons either by Clemmensen reduction or by Wolf – Kishner reduction.

a. Clemmenson Reduction: In this reaction aldehydes and ketones are reduced to alkanes in the presence of Zinc amalgam and HCl as reducing agent.

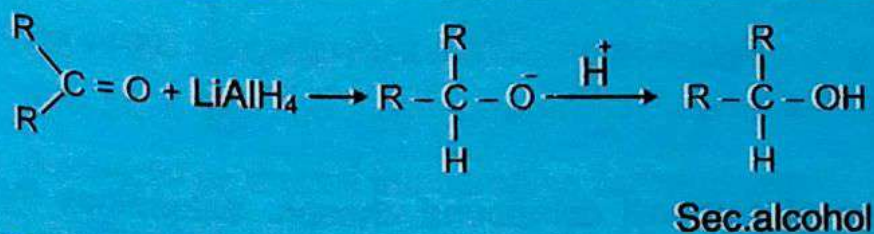


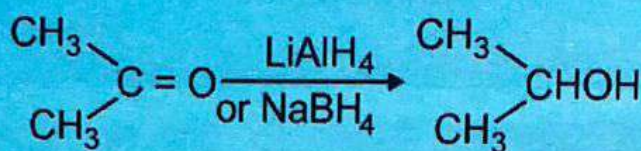
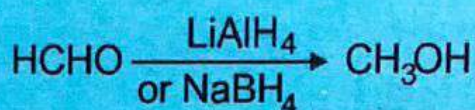
**(b) Wolf-Kishner Reduction:**

When an aldehyde or ketone is treated with hydrazine a corresponding hydrazone is obtained which on heating with KOH in boiling ethylene glycol gives corresponding alkane.

**2. Reduction Using Hydrides to give Alcohols:**

Aldehydes and ketones are easily reduced to primary and secondary alcohols respectively by using metal hydrides as reducing agents. The most common metal hydrides used to reduce carbonyl compounds are lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4).



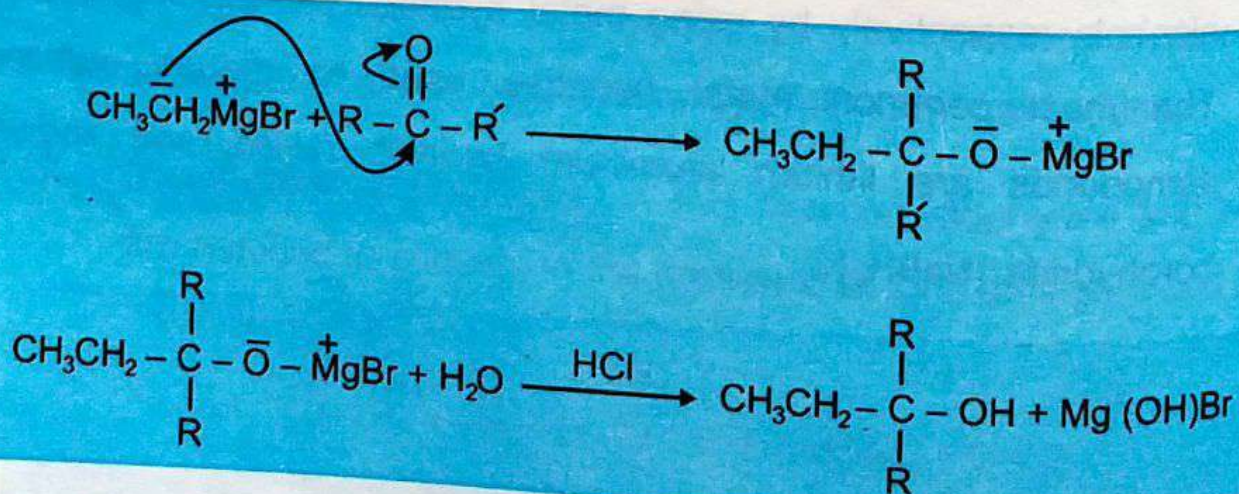


3. Reduction –Using Carbon Nucleophiles:

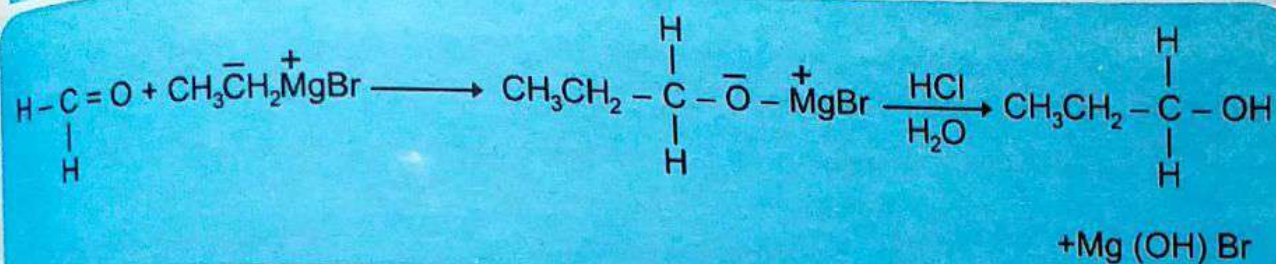
In organometallic compounds (e.g Grignard reagent) and hydrogen cyanide (HCN), the carbon acts as nucleophile and can reduce aldehydes and ketones by nucleophilic addition.

i. Reduction –Using Grignard Reagent:

Grignard reagents act as carbon nucleophiles toward carbonyl compounds. The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon –carbon bond that gives an intermediate alkoxide. The alkoxide can be protonated by dilute HCl to give alcohol.

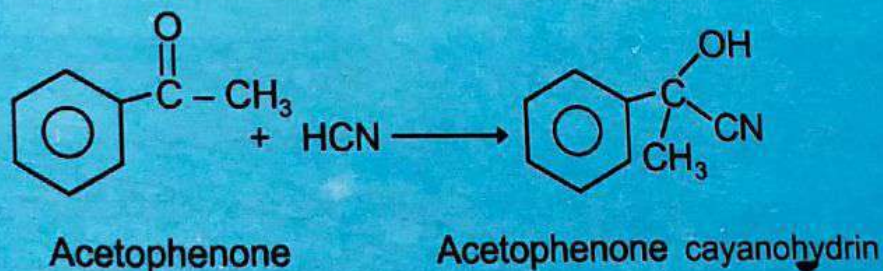
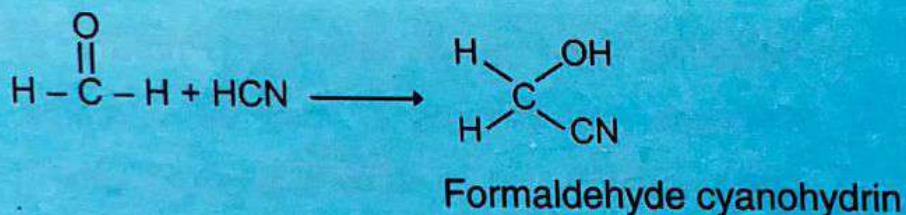


The type of carbonyl compound chosen, determines the class of alcohol produced e.g. formaldehyde gives primary alcohols.



ii. Reduction –Using HCN:

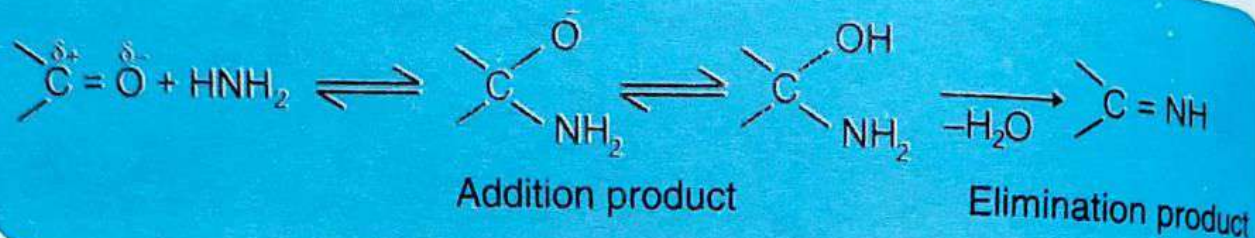
The carbon in hydrocyanic acid also acts as carbon nucleophile and undergoes nucleophilic addition to aldehydes and ketones in the presence of base to yield cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon. The reaction is carried out in basic medium.



4. Reduction –Using Nitrogen Nucleophiles:

Ammonia, amines and some other related compounds have an unshared electron pair on nitrogen atom and therefore act as nucleophiles toward the carbonyl carbon atom.

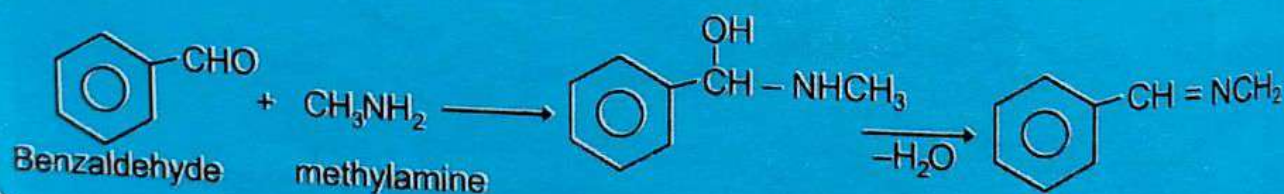
a. Reaction with Ammonia: Aldehydes react with ammonia to form solid aldehyde ammonia.



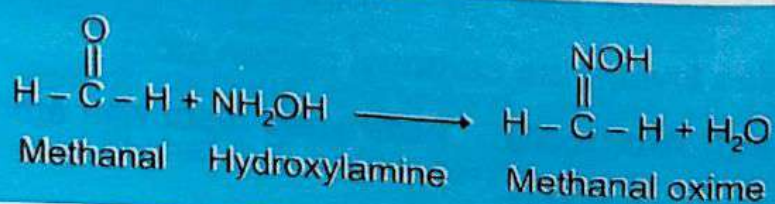
Ketones do not form addition product when treated with ammonia, rather it gives condensation products.

b. Reaction with ammonia derivatives: Some important ammonia derivatives are alkyl amines, hydroxyl amines (NH_2OH), hydrazine (NH_2NH_2), phenyl hydrazine etc. ($\text{C}_6\text{H}_5\text{NHNH}_2$)

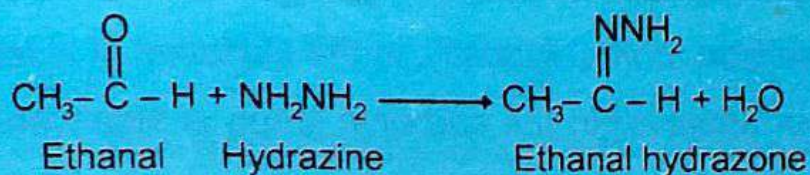
i. Reaction with alkyl Amines: Primary amines react with aldehyde and ketones to form an unstable addition product which loses water to form a product with a carbon nitrogen double bond, called imines.



ii. Reaction with hydroxylamine: Aldehydes and ketones form oximes on reaction with hydroxylamine.

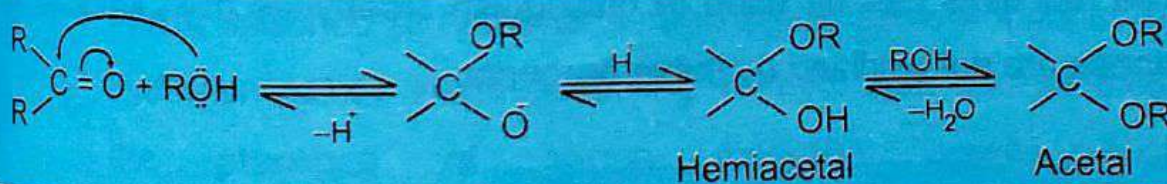


iii. **Reaction with Hydrazine NH_2NH_2 :** Aldehydes and ketones reacts with hydrazine to form hydrazone.



5. Reduction –Using Oxygen Nucleophiles:

Alcohols are oxygen nucleophiles as alcohols are weak acids having O-H bond. The oxygen of the alkoxy group attacks the carbonyl carbon of aldehydes and ketones, resulting in addition to the C=O bond. Since alcohols are weak nucleophiles, an acid catalyst (H_2SO_4) is required.



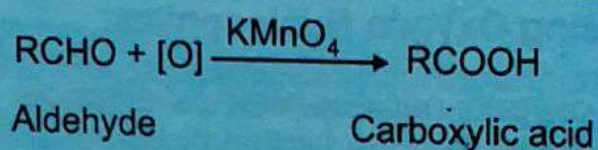
The addition process is reversible and the product obtained is called hemiacetal, which contains both alcohol and ether functional groups on the same carbon. In the presence of excess alcohol, hemiacetal reacts further to form acetal, which has two ether functional groups (a gem-ether) at the same carbon.

19.6.4

Oxidation Reactions of Carbonyl compounds:

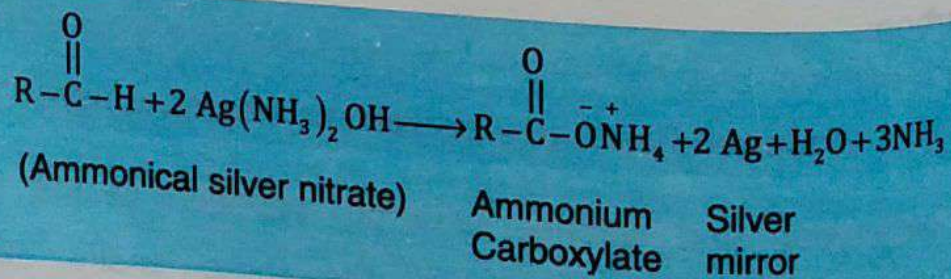
Both aldehydes and ketones undergo oxidation in the presence of oxidizing agents, however, aldehydes are more easily oxidized than ketones.

a. Oxidation of Aldehydes: Oxidation of an aldehyde, in the presence of strong oxidizing agents like acidified KMnO_4 or acidified sodium / potassium dichromate, or Ag_2O gives an acid with the same number of carbon atoms. Actually, in the oxidation of aldehyde, the hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group.

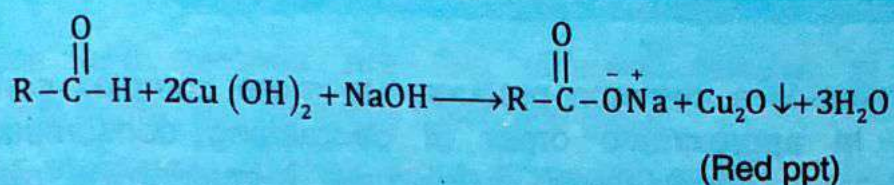


Since aldehydes can be oxidized by much milder oxidizing agents such as Tollen's reagent, Fehling's solution and Benedict's solution. These three reactants can be used to distinguish aldehydes from ketones as ketones are not oxidized by these reagents.

i. Oxidation by Tollen's Reagent: If an aldehyde is treated with Tollen's reagent, the silver ion present in Tollen's reagent is reduced to metallic silver which is deposited on the wall of test tube to form a silver mirror. Therefore, it is also known as silver mirror test.

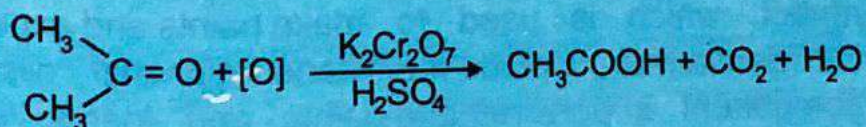


ii. Oxidation by Fehling's Solution: If aldehyde is treated with Fehling's solution, the deep blue colour of cupric ion is reduced to red precipitates of cuprous oxide. Ketones do not given this reaction.



This test is widely used for the estimation of glucose in blood and urine.

b. Oxidations of Ketones: In aldehydes, oxidation involve hydrogen that is attached to carbonyl carbon but in case of ketones no such hydrogen exists. Ketones having α -hydrogen can be oxidized in the presence of strong oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$, $\text{KMnO}_4 / \text{H}_2\text{SO}_4$ or concentrated HNO_3 etc which involves breaking of C-C bond.



In case of unsymmetrical ketones, the carbonyl group remain with smaller alkyl group as oxidation takes place at this site.

Society, Technology and Science

Formaldehyde is a common precursor to more complex compounds and materials. In approximate order of decreasing consumption, products generated from formaldehyde include urea formaldehyde resin, melamine resin, phenol formaldehyde resin, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate. The textile industry uses formaldehyde-based resins as finishers to make fabrics crease-resistant. Formaldehyde-based materials are key to the manufacture of automobiles, and used to make components for the transmission, electrical system, engine block, door panels, axles and brake shoes.

When treated with phenol, urea, or melamine, formaldehyde produces, respectively, hard thermoset phenol formaldehyde resin, urea formaldehyde resin, and melamine resin. These polymers are common permanent adhesives used in plywood and carpeting. It is used as the wet-strength resin added to sanitary paper products such as facial tissue, table napkins, and roll towels. They are also foamed to make insulation, or cast into moulded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption.

Formaldehyde is also a precursor to polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, an important component in polyurethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins as well as the explosive RDX. Since 2006, formaldehyde (methylene glycol) is also used in hair smoothing treatments in order to straighten wavy/curly hair and make hair less prone to frizz under high humid weather.

Key Points:

- Aldehydes and ketones are two different classes of organic compounds containing carbonyl functional group.
- Oxidation of primary alcohols gives aldehydes and that of secondary alcohol gives ketones.
- The $C=O$ bond in aldehydes and ketones is highly polar and hence they are very reactive compounds.
- Both aldehydes and ketones undergo nucleophilic addition reactions.
- Generally, ketones are somewhat less reactive than aldehydes towards nucleophiles.
- Aldehydes and ketones undergo condensation reactions with ammonia and its derivatives to form compounds containing $>C=N-$ linkage.
- Aldehydes are oxidized to alcohols in the presence of oxidizing agents like $K_2Cr_2O_7$ in H_2SO_4 , $KMnO_4$ in H_2SO_4 . However, ketones usually resist oxidation.
- Aldehydes form silver mirror with Tollen's reagent and gives red precipitates with Fehling's solution on heating. Whereas ketones do not undergo these reactions.

EXERCISE

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Exercise

Q.1 Choose the correct answer.

- i. The carbon of the carbonyl group is
 - a. sp^3 – hybridized
 - b. trigonal planar
 - c. Pyramidal in geometry
 - d. tetrahedral in geometry
- ii. The reduction of $>C=O$ to $>CH_2$ is carried out with
 - a. Catalytic reduction
 - b. Zn-Hg and conc. HCl
 - c. Wolff Kishner reduction
 - d. $LiAlH_4$
- iii. A compound $C_4H_{10}O$ yields a compound C_4H_8O on oxidation. The compound $C_4H_{10}O$ is.
 - a. An aldehyde
 - b. An alcohol
 - c. A ketone
 - d. An acid
- iv. Formaldehyde gives an additive product with methyl magnesium iodide which on hydrolysis gives,
 - a. n-Propyl alcohol
 - b. Iso propyl alcohol
 - c. Methyl alcohol
 - d. Ethyl alcohol
- v. Which of the following compounds can react with ammonical silver nitrate solution to form silver mirror?
 - a. Acetone
 - b. Ethanol
 - c. Ether
 - d. Ethanal
- vi. Which of the following compounds precipitates Cu_2O from Fehling's reagent but does not react with sodium metal?
 - a. C_2H_5OH
 - b. C_2H_5CHO
 - c. $CH_3CH(OH)CH_3$
 - d. CH_3COCH_3

vii. When propanal is heated with Fehling's solution there is.

- A colour change from green to orange.
- A colour change from blue to red.
- A negative test with Tollen's reagent
- No colour change.

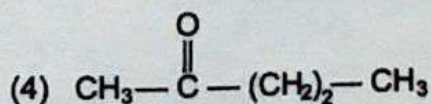
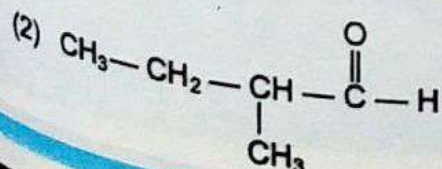
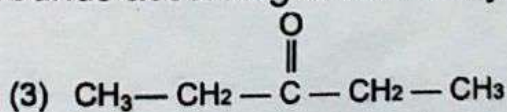
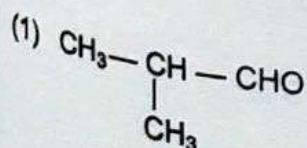
Q.2 Explain briefly.

- Aldehyde contains the carbonyl group. ketones, carboxylic acids and esters also contain carbonyl group. What distinguishes these later compounds from an aldehyde?
- The mechanism of nucleophilic addition to a carbonyl compound.
- Aldehydes and ketones undergo nucleophilic addition while alkenes undergo electrophilic addition.
- Aldehydes are oxidized easily than ketones.
- Ketones are somewhat less reactive than aldehydes towards nucleophile.
- Which test can be used for the identification of aldehydes from ketones in laboratory?

Q.3 Write the structural formulae and give IUPAC names for all aldehyde and ketone isomers of the molecular formula $C_5H_{10}O$.

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

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



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

- | | |
|------------------------|------------------------|
| i. 2-Octanone | ii. Di-n-propyl ketone |
| iii. 4-Methyl pentanal | iv. 2,2-Dibromohexanal |
| v. 3-Ethylpentanal | vi. Hexane-2,4-dione |

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

- | | | |
|----------------|-----------|------------|
| i. Cyanohydrin | ii. Oxime | iii. Imine |
| iv. Hydrazone | v. Acetal | |

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

- | | |
|------------------------|------------------------|
| i. 1-Butanol | ii. Ethyl alcohol |
| iii. 2-Butanol | iv. 2-Methyl-2-butanol |
| v. 3-Methyl-3-pentanol | |

Q.9 (a) Write any three methods for preparation of acetaldehyde.

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

- | | |
|--------------------------------|----------------------------------|
| i. Ethyl magnesium iodide | ii. Zinc-mercury amalgam and HCl |
| iii. Lithium Aluminium hydride | iv. Acidified $K_2Cr_2O_7$ |

Q.10 (a) How aromatic ketones are prepared by Friedel-Craft acylation?

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

- | | | |
|-----------------------|----------------|--------------------------|
| i. Propane | ii. 2-Propanol | iii. Acetone cyanohydrin |
| iv. Acetone hydrazone | v. Hemiketal | vi. Acetic acid |