

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

In aldehydes, the carbonyl group is composed of carbon and hydrogen, while in ketones, it is composed of two carbon atoms.

The nature of Carbonyl groups

A carbonyl group is a chemically organic functional group composed of a carbon atom double-bonded to an oxygen atom --> [C=O]. The simplest carbonyl groups are aldehydes and ketones usually attached to another carbon compound. These structures can be found in many aromatic compounds contributing to smell and taste.

Nomenclature of carbonyl compound Important common name:



IUPAC naming of aldehydes

- According to the IUPAC system of nomenclature -al is attached as a suffix to parent alkane for the naming of aldehydes.
- For example, H₂C=O is named as per the IUPAC system as methanal, commonly known as formaldehyde.
- The aldehyde group is always attached at the end of the main carbon chain, and hence the 1st position in the numbering is always assigned to it. It is not always necessary to include numbering in the naming.
- Instead of IUPAC names, aldehydes and ketones are also called by their common names.
- For aldehydes and ketones, the names are reflected in Greek and Latin terms. Greek letters such as α , β etc. are used for the location of the substituents in the carbon chain.
- The α-carbon is directly attached to the aldehyde group, β-carbon is attached to the carbon adjacent to the aldehyde group and so on.

IUPAC naming of Ketones

- Now let's discuss the naming of ketones, according to IUPAC guidelines, the suffix –one is assigned for the ketones.
- The carbonyl group can be located anywhere within the main chain and the position is decided by the location number.
- The numbering of the chain usually starts from the end such that the carbonyl carbon gets the lowest number.
- But there are some ketones such as propanone and phenyl ethanoid which do not require any number locator as there is only one possible site for ketone carbon.

If there are more than one functional groups in a molecule then the functional group with the higher priority is named first and the other ones are considered as a substituent. If there is both a ketone and aldehyde group in a molecule then the aldehyde group is given priority over ketone while naming.

Examples:

	Trivial Name	IUPAC Name
C ₂ H ₅ CHO	Propionaldehyde	Propanal
CH3 — CH — CHO CH3	lsobutyraldehyde	2-Methylpropanal
$CH_3 - CH_3 - CH_2 - $	β-bromo-α-methyl butryaldehyde	3-Bromo-2- methylbutanal
$\begin{array}{c} CH_3 - CH_2 - \overset{\beta}{\overset{CH}}{\overset{CH}{\overset{CH}}{\overset{CH}{\overset{CH}}{\overset{CH}{\overset{CH}{\overset{CH}}{\overset{CH}{\overset{CH}{\overset{CH}{\overset{CH}{\overset{CH}}{\overset{CH}}{\overset{CH}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}{\overset{CH}}}{\overset{CH}}{\overset{CH}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	β-Chloro-α-ethyl valeraldehyde	3-Chloro-2- ethyl pentanal

Examples:

IUPAC Name 1,4 Dichloropentan-3-one

Trivial Name α,β' - Dichloro diethyl ketone

 α , α ', α ' - Trichlorodiethyl ketone IUPAC 2,2,4-Trichloro pentan-3-one

Note

The compound in which carbonyl group is not bonded directly to the benzene ring are considered as arly substituted aliphatic aldehydes

Methods for preparation of aldehydes and ketones

By oxidation of alcohols: Aldehydes and ketones are usually prepared by oxidation of primary and secondary alcohols, respectively.



By dehydrohalogenation of alcohols: In this way alcohol is transferred to heavy metal catalysts (Ag or Cu). The primary and secondary alcohols provide aldehydes and ketones.

$$\begin{array}{ccc} R & -CH_2 & -OH & \frac{Cu}{573 \text{ K}} & RCHO \\ R & -CH & -R' & \frac{Cu}{573 \text{ K}} & R & -C & -R \\ & & & & & \\ OH & & & O \end{array}$$

III By ozonolysis of alkenes



IV By hydration of Alkynes: Acetylene in water extraction gives acetaldehyde and other alkynes in hydration gives ketones.



V With decarboxylation and dehydration of aromatic acids

$$C_{\theta}H_{5}COOH + HCOOH \xrightarrow{MnO} C_{\theta}H_{5}CHO + H_{2}O + CO_{2}$$

$$C_{\theta}H_{5}COOH + HOOCH_{3} \xrightarrow{MnO} C_{\theta}H_{5}COCH_{3} + H_{2}O + CO_{2}$$

Aldehydes Preparation

I Rosenmund reduction: Rosenmund reduction is the hydrogenation of an acyl chloride to an aldehyde, in presence of catalyst (Pd supported on barium sulphate). Barium sulphate partially poisons Pd metal and prevents over-reduction. Untreated Pd catalyst is too reactive.



II from nitriles:

Nitriles are reduced to amine associated with stannous chloride in the presence of hydrochloric acid, which by hydrolysis releases the corresponding aldehyde. This reaction is called Stephen's reduction.



III Etard reaction: Chromyl chloride (CrO₂ClO₂) oxidise methyl group toluene to a chromium complex, which when hydrolysis releases the corresponding benzaldehyde. This reaction is called the Etard reaction.



Toluene

Benzaldehyde

IV Gattermann Koch synthesis: When benzene or its derivatives are treated with CO and HCl in the presence of liquid AlCl₃ or CuCl, it releases benzaldehyde or convertible benzaldehyde. This reaction is called the Gatterman-Koch reaction.



V Side chain halogenation followed by hydrolysis of toluene



Preparation of Ketones

(a) From acyl chloride

$$2 \text{ R} - \text{MgX} + \text{CdCl}_2 \xrightarrow{\text{dry ether}} \text{R}_2\text{Cd} + 2 \text{ Mg(X)Cl}$$

$$2 \text{ R'} \xrightarrow{\text{O}}_{\text{II}} \text{C} \text{CI} + \text{R}_2 \text{Cd} \xrightarrow{\text{dry ether}} 2 \text{ R'} \xrightarrow{\text{O}}_{\text{Ketone}} \text{R} + \text{CdCl}_2$$

(b)From nitriles:

$$CH_{3}CH_{2}C \equiv N + C_{6}H_{5}MgBr \xrightarrow{Ether}$$

$$CH_{3}CH_{2} \xrightarrow{C} C_{6}H_{5}$$

$$\xrightarrow{H_{3}O^{+}} CH_{2}CH_{5} \xrightarrow{O} C_{6}H_{5}$$

(c) Friedel-Crafts acylation

When benzene is treated with acid chloride in the presence of anhydrous AlCl₃, a corresponding ketone is formed. This reaction is known as the Friedel-craft acylation reaction.



aromatic

ketone

Physical properties of Aldehydes and ketones

Lower members have unpleasant smell and up to 11 members they are liquids.

Solubility: Aldehydes are more polar in nature. As we know, in ketones two alkyl groups are present. So, if electron density on carbon increases, the polarity of bond decreases, due to +I effect.

Therefore, solubility of aldehyde is more as they have more tendency to form hydrogen bonds. As number of carbon atoms increase, the solubility decrease because of non-polar nature.

Boiling points: Boiling point is always more for polar compounds.

Ketones have higher boiling points than aldehyde because of more polarity.

Their boiling point is always lower than alcohols and carboxylic acids because they are less polar then them.

In aldehydes and ketones, dipole-dipole interactions are comparitively less.

Chemical reactions of Aldehydes and Ketones

Nucleophilic addition reactions - A nucleophilic addition reaction is a chemical addition reaction in which a nucleophile forms a sigma bond with an electron-deficient species. These reactions are considered very important in organic chemistry since they enable the conversion of carbonvl groups into a variety of functional

groups. Generally, nucleophilic addition reactions of carbonyl compounds can be broken down into the following three steps.

The electrophilic carbonyl carbon forms a sigma bond with the nucleophile.

The carbon-oxygen pi bond is now broken, forming an alkoxide intermediate (the bond pair of electrons are transferred to the oxygen atom).

The subsequent protonation of the alkoxide yields the alcohol derivative.



Reactivity: Aldehyde > ketone

R-CHO > RCOR \rightarrow (as the size of alkyl group increases, approach of nucleophile to carbonyl carbon decreases)

Reactivity order: HCHO > CH₃CHO > acetone

: Acetaldehyde > Acetone > Methyl t-butyl ketone > Ditert-butyl ketone



Addition of HCN:

The nucleophilic addition reaction between hydrogen cyanide (HCN) and carbonyl compounds (generally aldehydes and ketones) results in the formation of cyanohydrins. Base catalysts are often used to increase the rate of the reaction.



Addition of Grignard reagent:



Addition of alcohols:

Alcohols are added to aldehydes and ketones in the presence of dry hydrogen chloride to form hemiacetals. This reaction can continue by adding another alcohol to form an acetal.



Addition of amino and its derivatives





II Reduction of Aldehydes and ketones are reduced to primary and secondary alcohol respectively sodium borohydride (NaBH4) or lithium aluminum hydride [LiAlH4].

 $\begin{array}{ccc} R-CHO + H_2 & \xrightarrow{Pt, Pd \text{ or Ni}} & R-CH_2-OH \\ & & & & & \\ \text{Aldehyde} & & & 1^{\circ} \text{ alcohol} \end{array}$



Reductions to hydrocarbons:

Clemmensen reduction

Wolff-Kishner reduction

$$\begin{array}{c} \searrow C = O \xrightarrow{H_2 N \ NH_2} & C = N - NH_2 \xrightarrow{KOH/ethylene glycol} CH_2 + N_2 \end{array}$$

Oxidation: Aldehyde ______ RCOOH Oxidising agent: HNO₃/KMnO₄/K₂Cr₂O₇

- ➔ Tollen's reagent
- ➔ Fehling reagent

Test for aldehydes and ketones

For aldehydes

Tollen's reagent – Tollens Reagent refers to the chemical reagent which is used in the detection of an aldehyde functional group, an aromatic aldehyde functional group, or an alpha hydroxy ketone functional group in a given test substance.

The Tollens Reagent is named after Bernhard Tollens, A German chemist who discovered this reagent and its uses. Tollens reagent is a solution of silver nitrate (AgNO₃) and Ammonia (NH₃).



Above reaction is not possible with ketone.

Fehling's test: Fehling's solution is used to distinguish between aldehyde and ketone functional groups. Aldehydes oxidize to give a positive result but ketones won't react to the test (except for α -hydroxy ketones). Fehling's test is used as a general test for determining monosaccharides and other reducing sugars



Aldehyde

Carboxylate ion

Any other group (alcohols, ketones) + 2Cu(OH)₂ + NaOH - NR - No reaction

Halofrom reaction:

$$R^{O} \xrightarrow{X_{2}} R^{O} + CHX_{3}$$

III Aldol condensation - Aldol condensation is an organic reaction in which an enolate ion reacts with carboxyl compound in order to form a β - hydroxy aldehyde or β -hydroxy ketone.

- ➔ Hydroxide functions as a base and therefore moves the acidic a-hydrogen producing the reactive enolate ion. This reaction can be seen as an acid-base reaction.
- → The aldehyde is attacked at the electrophilic carbonyl carbon by the nucleophilic enolate ion. This attack is a nucleophilic addition reaction and gives alkoxide intermediate.
- → The alkoxide deprotonates water molecule, thereby producing hydroxide and the β -hydroxy aldehyde.



This reaction is indicated by those aldehyde or ketones containing at least one hydrogen.

Mechanism: Step-I :

In this step, hydroxide ion from alkali removes a proton from the α – carbon of one molecule of ethanal to give a carbanion (i.e. enolate ion).



Step-II :

In this step, there is nucleophilic addition of enolate ion to the carbonyl carbon of second molecule of ethanal to produce an alkoxide ion.

Step-III :

In this step, the alkoxide ion takes up a proton from water to form β -hydroxy aldehyde (aldol).

IV Cross Aldol Condensation - Aldol condensation between two different carbonyl compounds is called a crossed aldol condensation.



Mechanism:

Step-I :

In this step, hydroxide ion from alkali removes a proton from the α – carbon of ethanal to give a carbanion (i.e. enolate ion).



Step-II:

In this step, there is nucleophilic addition of enolate ion to the carbonyl carbon of benzaldehyde to produce an alkoxide ion.



Step-III:

In this step, the alkoxide ion takes up a proton from water to form β -hydroxy aldehyde (aldol).



V Cannizaro reaction - Cannizzaro reaction is an organic reaction of an aldehyde without active hydrogen that undergoes a redox reaction under the action of a strong base. Examples of aldehydes without active hydrogen include vanillin, benzaldehyde, syringaldehyde, and formaldehyde. They undergo intramolecular and intermolecular oxidation-reduction reactions under the action of a strong base (NaOH) to form a molecule of carboxylic acid and a molecule of alcohol [1-5].



Mechanism:

Step 1: Nucleophilic attack on the carbonyl group to give a dianion.



Step 2: Conversion of the dianion to a carboxylate and another aldehyde molecule to an alkoxide ion.



Step 3: Protonation of the alkoxide to an alcohol and the carboxylate to a carboxylic acid.





Carboxylic acids

Carboxylic acids: carboxylic acid, any class of organic compounds in which a carbon atom (C) is combined with an oxygen atom (O) in a double bond and a hydroxyl group (–OH) in a single bond. The main chemical element of carboxylic acid is its acidity.

Nomenclature:

- The suffix "e" in the name of the corresponding alkane is replaced with "oic acid".
- When the aliphatic chain contains only one carboxyl group, the carboxylic carbon is always numbered one. For example, CH3COOH is named as ethanoic acid.
- When the aliphatic chain contains more than one carboxyl group, the total number of carbon atoms is counted and the number of carboxyl groups is represented by Greek numeral prefixes such as "di-", "tri-", etc.
- A carboxylic acid is named by adding these prefixes and suffixes to the parent alkyl chain. Arabic numerals are used for indicating the positions of the carboxyl group.
- The name "carboxylic acid" or "carboxy" can also be assigned for a carboxyl substituent on a carbon chain. An

example of such nomenclature is the name 2-carboxyfuran for the compound 2-Furoic acid.

Trivial Name and Formula	IUPAC Name of the Carboxylic Acid
Formic acid, H-COOH	Methanoic acid
Crotonic acid, CH ₃ CH=CH-COOH	But-2-enoic acid
Carbonic acid, OH-COOH	Carbonic acid
Butyric acid, CH ₃ (CH ₂) ₂ COOH	Butanoic acid







Ethanoic acid



Ethanoic acid

Butanoic acid

3-hydroxybutanoic acid.

$$H_{3}C - C - C - C - OH$$

$$H_{3}C - C - C - OH$$

$$H_{3}C - C - C - OH$$

2,3-dichlorobutanoic acid.

$$\begin{array}{c|c} Cl & Cl & O \\ H_{3}C - C^{2} - C_{1} - C_{2} - C_{1} - C_{1} - C_{2} - OH \\ H_{3} - C_{1} - C_{2} - C_{2} - C_{1} - C_{2} - OH \end{array}$$

Ways to prepare carboxylic acid:

1 From the oxidation of primary alcohols and aldehydes.

$$\begin{array}{c} \text{RCH}_{2}\text{OH} \xrightarrow{1. \text{ alkaline KMnO}_{4}} \text{RCOOH} \\ \hline 2. \text{ H}_{3}^{+} & & \\ \text{CH}_{3}(\text{CH}_{2})_{8}\text{CH}_{2}\text{OH} \xrightarrow{\text{CrO}_{3}\text{-H}_{2}\text{SO}_{4}} \text{CH}_{3}(\text{CH}_{2})_{8}\text{COOH} \\ \hline 1\text{-Decanol} & & \\ \text{Decanoic acid} \end{array}$$

2 Aromatic carboxylic acids can be obtained by side chain oxidation of alkyl benzenes.

Aromatic carboxylic acids can be obtained after vigorous oxidation of alkylbenzenes with chromic acid.



3 From hydrolysis of nitriles and amides.

Amides are prepared by the hydrolysis of nitriles and then converted to acids in the presence of catalysts (H^+ or OH-1). In order to stop the reaction at the amide stage, mild reaction conditions are used.

$$R-CN \xrightarrow{H} or \bar{O}H \xrightarrow{H_2O} R \xrightarrow{-C} -NH_2 \xrightarrow{H} or \bar{O}H \xrightarrow{} RCOOH$$

$$CH_3CONH_2 \xrightarrow{H_3O} CH_3COOH + NH_3$$
Ethanamide
$$(V \xrightarrow{-CONH_2} \xrightarrow{H_3O} (V \xrightarrow{-COOH} + NH_3)$$

Benzamide Benzoic acid From the reaction of the Grignard reagent with carbon dioxide.

When Grignard reagent reacts with carbon dioxide, it forms salts of carboxylic acids which after some times give corresponding carboxylic acid after the acidification with any mineral acid

R-Mg-X + O=C=O
$$\xrightarrow{\text{Dry ether}}$$
 R - C $\xrightarrow{O^{-}MgX^{+}}$ RCOOH

Aliphatic carboxylic acids with four carbon atoms combine in water due to the formation of hydrogen bonds in water.

From acyl halides and anhydrides

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When acid chloride is hydrolysed with water then carboxylic acid is produced and it is more readily hydrolysed with an aqueous base and gives corresponding carboxylic ions which on further acidification gives the carboxylic acid.



Properties of carboxylic acids

Odour of carboxylic acids

1. Aliphatic carboxylic acids upto nine carbon atoms have unpleasant odours.

2. The higher acids are odourless.

Solubility

- 1. Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
- 2. The solubility decreases with increasing number of carbon atoms due to the increased hydrophobic interaction of hydrocarbon part.
- 3. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Boiling point

- 1. Carboxylic acids have much higher boiling points than hydrocarbons, alcohols, ethers, aldehydes, or ketones of similar molecular weight.
- 2. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.
- 3. As the molecular mass increases, boiling point of carboxylic acid also increases.

Acidity of carboxylic acids

The acidity of a carboxylic acid is due to the resonance stabilization of its anion.



Because of the resonance, both the carbon oxygen bond in the carboxylate anion have identical bond length. In the carboxylic acid, these bond lengths are no longer identical.

The acidity of carboxylic acid depends very much on the substituent attached to – COOH group. Since acidity is due to the resonance stabilization of anion, substituent causing stabilization of anion increases acidity whereas substituent causing destabilization of anion decrease acidity. For example, electron withdrawing group disperses the negative charge of the anion and hence makes it more stable causing increase in the acidity of the corresponding acid, on the other hand, electron-releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in the acidity.

Few trends for the order of acidity of carboxylic acids

- (a) Increase in the number of Halogen atoms on a-position increases the acidity, eg.
 Cl₃CCOOH > Cl₂CHCOOH > ClCH₂COOH > CH₃COOH
- (b) Increase in the distance of Halogen from COOH decreases the acidity e.g.



This is due to the fact that inductive effect decreases with increasing distance.

(c) Increase in the electronegativity of halogen increases the acidity.

FCH₂COOH > BrCH₂COOH > ICH₂COOH

Arrange the following illustration in order of increasing acidity **Q**. (i) HCOOH, ClCH₂COOH, CH₃COOH

- (ii) CH-₃COOH, (CH₃)₂CHCOOH, (CH₃)₃CCOOH
- (iii) ClCH₂COOH, Cl₂CHCOOH, Cl₃CCOOH
- (iv) ClCH₂COOH, CH₃CH₂COOH, ClCH₂CH₂COOH, (CH₃)₂CHCOOH, CH₃COOH
- (v) CH₃COOH, Cl₂CHCOOH, CH₃CH₂COOH, Cl₃CCOOH, ClCH-₂COOH
- Sol. (i) CH₃COOH < HCOOH < ClCH₂COOH

(ii)
$$(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3COOH$$

- (iii) ClCH₂COOH < Cl₂CHCOOH < Cl₃CCOOH
- (iv) (CH₃)₂CHCOOH<CH₃CH₂COOH<CH₃COOH<ClCH₂CH₂COOH<ClCH₂COOH
- (v) CH₃CH₂COOH < CH₃COOH < ClCH₂COOH < Cl₂CHCOOH < Cl₃CCOOH

Effect of substituents on the acid strength of aliphatic acids

- 1. Substituents affect the stability of the conjugate base and affecting the acidity of the carboxylic acids.
- 2. Electron withdrawing group increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects.
- 3. Electron donating groups decrease the acidity of carboxylic acids by destabilising the conjugate base by inductive and/or resonance effects.

The acidic strength also depends upon other factors such as:

Type of halogen attached :

F>Cl>Br

Fluroine is much more electronegative

Acidic Strength CH₃COOF more stronger acid > CH₃COCl BrCH₃COOH > CH₃COOI

Reactions involving the cleavage of C-OH bond

Preparation of anhydrides from carboxylic acids

$$\begin{array}{ccc} & & O & O \\ & \parallel & & \parallel \\ 2 \text{ RCOOH} & \xrightarrow{P_2 O_5} & \text{R} \overset{O}{\text{C}} - O - \overset{O}{\text{C}} - \text{R} \\ \textbf{a Carboxylic acid} & \textbf{an Acid Anhydrid} \end{array}$$

Carboxylic acid on heating with mineral acids such as H₂SO₄ or with P₂O₅ forms corresponding anhydride.

Preparation of esters from carboxylic acids

Carboxylic acids react with alcohols in presence of an acid catalyst to give esters and water.



Carboxylic acids react with alcohols in presence of an acid catalyst to give esters and water.

Mechanism of esterification

The esterification reaction of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into

⁺OH2 group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



Carboxylic Thionyl an acid chloride acid chloride

$$\begin{array}{cccc} O & O & O \\ \parallel & & & & \parallel \\ R-C-OH & + & PCl_3 & \longrightarrow 3R & C & Cl & + & H_3PO_3 \\ \hline Phosphorus & & & \\ Phosphorus & & & \\ trichloride & & & \\ 0 & & & & \\ R-C-OH & + & PCl_5 & \longrightarrow R-C-Cl & + & POCl_3 & + & HCl \end{array}$$

Phosphorus

pentachloride

Acid chlorides can be prepared by action of SOCl₂, PCl₃ and PCl₅ on carboxylic acids.

Preparation of amines from carboxylic acids

Carboxylic acids can be converted to amines through schmidt reaction. The acid-catalysed reaction of hydrogen azide with carboxylic acids gives corresponding amines with one less carbon atom.



Reactions involving -COOH group

Reduction:



Decarboxylation: Carboxylic acid loses carbon dioxide to form hydrocarbons when its sodium salt is burned with sodalime NaOH and CaO in a ratio of 3: 1



Kolbe's electrolysis: Carboxylic acids react with alcohol or phenol in the presence of such mineral acids conc. H₂SO₄ as a catalyst for building esters.



Reaction on hydrocarbon part: Hell-Volhard Zelinsky Reaction (HVZ)

Hell-Volhard-Zelinsky halogenation reaction halogenates carboxylic acids to α carbon. In its first step, a mixture of bromine and phosphorus tribromide (catalyst) is used to prepare 2-bromopropanoic acid, which is converted into a racemic mixture of amino acid products by ammonolysis.

$$R - CH_2 - COOH \xrightarrow{(i) X_2/ \text{ Red Phosphorus}} R - CH_2 - COOH \xrightarrow{(ii) H_2O} R - CH_2 - COOH \xrightarrow{(iii) H_2O} R - CH_2 - COOH$$

Alpha halo carboxylic acid

Hydrogen-containing carboxylic acids are incorporated into chlorine or bromine treatment where there is a small amount of red phosphorus to provide halocarboxylic acid.

Ring subsitution reactions:



Benzoic acid bromine

Sulphonation



Nitration



Solubility decreases as the number of carbon atoms increases.

- The electron withdrawal group (Cl, NO₂, CN, etc.) (i) stabilizes the carboxylate anion by dissolving the negative charge of carboxylate anion, RCOO-, and thereby increasing the acidic potential.
- (ii) The presence of an electron donor as an alkyl group strengthens the negative charge in the RCOO⁻ anion and lowers carboxylic acid.

Uses of carboxylic acid

- Methanoic acid is used as coagulating agent in rubber industry.
- Benzoic acid is used as antiseptic and also in perfumery.

Ethanoic acid is used as solvent and also in cooking as vinegar and much more

SUMMARY

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses. The lower members are more soluble in water because they form hydrogen bonds with water. The higher members, because of large size of hydrophobic chain of carbon atoms, are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Aromatic aldehydes may also be prepared by oxidation of (i) methylbenzene with chromyl chloride or CrO3 in the presence of acetic anhydride, (ii) formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride, and (iii) cuprous chloride or by hydrolysis of benzal chloride. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Ketones are also prepared by reaction of acyl chloride with dialkylcadmium. A good method for the preparation of aromatic ketones is the Friedel-Crafts acylation of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN, NaHSO3, alcohols (or diols), ammonia derivatives, and Grignard

reagents. The α -hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one α -hydrogen, undergo Aldol condensation in the presence of a base to give α hydroxyaldehydes (aldol) and α -hydroxyketones(ketol), respectively. Aldehydes having no α-hydrogen undergo Cannizzaro reaction in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with NaBH4. LiAlH4. or by catalytic hydrogenation. The carbonyl group of aldehydes and ketones can be reduced to a methylene group by Clemmensen reduction or Wolff-Kishner reduction. Aldehydes are easily oxidised to carboxylic acids by mild oxidising reagents such as Tollens' reagent and Fehling's reagent. These oxidation reactions are used to distinguish aldehydes from ketones. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and alkenes by hydrolysis of nitriles, and by treatment of Grignard reagents with carbon dioxide. Aromatic carboxylic acids are also prepared by side-chain oxidation of alkylbenzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols. Carboxylic acids are reduced to primary alcohols with LiAlH4, or better with diborane in ether solution and also undergo α -halogenation with Cl2 and Br2 in the presence of red phosphorus (Hell-Volhard Zelinsky reaction). Methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid and benzoic acid are highly useful compounds in industry.





QUESTIONS FOR PRACTICE

- **Q1.** Compound which is used for separation of acetone and acetophenone :-
 - (a) sodium bisulphate
 - (b) Grignard reagent
 - (c) sodium sulphate
 - (d) ammonium chloride
- **Q2.** The polar nature of carbonyl group in aldehydes and ketones is due to
 - (a) very less electronegative difference
 - (b) very large electronagative difference
 - (c) presence ot hydrogen bonding
 - (d) presence of sp hybridised characters in carbonyl compound
- Q3. Phenones are
 - (a) aldehyde in which carbonyl group is attached with benzene ring
 - (b) ketone in which carbonyl group is attached with benzene ring
 - (c) phenols in which carbonyl group is attached with alkyl group
 - (d) phenols in which carbonyl group is attached with group

(d) none of the above

- **Q4.** Which of the following is a geminal dihalide?
 - (a) Ethylene dibromide (b) propylidenechloride
 - (C) Isopropyl bromide
- **Q5.** In IUPAC system



is named as_

- (a) naphthalene aldehyde
- (b) naphthalene carbaldehyde
- (C) dibenzene aldehyde
- (d) naphanal
- **Q6.** Which of the reactions below can result in ketones? (a) Oxidation of primary alcohols
 - (b) Oxidation of secondary alcohols
 - (c) Dehydrogenation of tertiary alcohols
 - (d) Dehydrogenation of primary alcohols
- **Q7.** The Rosenmund reaction can produce which of the following carbonyl compounds?
 - (a) Methanal (b) Benzaldehyde
 - (c) Butanone (d) Acetone
- **Q8.** Reactions occur between aldehydes and ketones. (a) nucleophilic addition
 - (b) electrophilic substitution
 - (c) electrophilic addition
 - (d) nucleophilic substitution

- **Q9.** Which of the following reactions to a nucleophilic assault is the least reactive?
 - (a) Acetaldehyde
 - (b) Di Tert-Butyl ketone
 - (c) Diisopropyl ketone
 - (d) Butanone
- Q10. Acetone combines with ethylene glycol in dry HCl gas to generate(a) hemiacetals(b) cyclic ketals
 - (c) cyclic acetals (d) acetals
- Q11. Which of the following is not a formaldehyde application?(a) Preservation of biological specimens(b) Preparation of acetic acid
 - (c) Silvering of mirrors
 - (d) Manufacturing of bakelite
- Q12. Which of the following compounds is formed when benzyl alcohol is oxidised with KMnO₄?
 (a) CO₂ and H₂O
 (b) Benzoic acid
 - (c) Benzaldehyde (d) Benzophenone
- Q13. At 287K, which of the following is a gas? (a) Propanal (b) Acetaldehyde (c) Formaldehyde (d) Acetone
- **Q14.** Which of the following substances is the least water-soluble?
 - (a) Methanal(b) Pentanal(c) Propanone(d) Ethanal
- Q15. Which of these has the least unpleasant odour? (a) Methanal (b) Butanal
 - (c) Propanal (d) Ethanal
- **Q16.** Ester is formed by a reaction between (a) An acid and an alcohol
 - (b) An acid and a base
 - (c) An alkane and an alcohol
 - (d) A ketone and an alcohol
- Q17. Vinegar is primarily composed of (a) Tartaric acid (b) Citric acid
 - (c) Acetic acid (d) Nitric Acid
- **Q18.** Formic acid can reduce
 - (a) Tollen's reagent
 - (b) Potassium permanganate
 - (c) Mercuric chloride
 - (d) All of the above
- **Q19.** Soap has a similar cleaning mechanism to:
 - (a) Shaping soaps
 - (b) Liquid dishwashing detergents
 - (c) Toothpaste
 - (d) Hair conditioner

Q20. Q21.	What is a characteristic of (a) Hydrophobic (c) Both An aqueous NaOH solution benzaldehyde and formald (a) benzyl alcohol + sodium (b) sodium benzoate + me	f detergent? (b) Hydrophilic (d) None on is added to a mixture of lehyde to produce m formate thanol	Q31.	The oxidation of toluene t chloride is called (a) Etard reaction (b) Riemer-Tiemann react (c) Wurtz reaction (d) Cannizzaro's reaction The addition of HCN to	o benzaldehyde by chromyl, ion carbonyl compounds is an
Q22.	 (c) benzyl alcohol + metha (d) sodium benzoate + sod As a result of Wolff-Kishn 	nol lium formate ner reduction, the following	033	example of (a) nucleophilic addition (c) free radical addition	(b) electrophilic addition (d) electromeric addition formaldehyde react with
	 (a) Benzaldehyde into Ben (b) Cyclohexanol into Cycl (c) Cyclohexanone into Cy (d) Benzophenone into Dij 	izyl alcohol ohexane clohexanol phenylmethane.	QUUI	Grignard's reagent to give hydrolysis give (a) tertiary alcohols (c) primary alcohols	(b) secondary alcohols(d) carboxylic acids
Q23.	The formation of cyanob example of: (a) electrophilic addition (b) nucleophilic addition	nydrin from a ketone is an	Q34.	Which of the followi condensation? (a) Phenyl acetaldehyde (c) Benzaldehyde	ng will not give aldol (b) 2-Methylpentanal (d) 1-Phenylpropanone
Q24.	(d) electrophilic substitution (d) electrophilic substitution The process of heating	on on an inorganic compound to	Q35.	Benzoyl Chloride on red produces (a) benzoic acid (c) benzoyl sulphate	(b) benzyl alochol (d) benzyl dochol
	produce an organic compo (a) ammonium cyanate (c) sodamide	ound is: (b) soda-lime (d) potassium cyanide	Q36.	What is the test to differe and pentan-3-one?	ntiate between penta-2-one
Q25.	Formic acid and acetic aci (a) NaHCO ₃	d are distinguished by (b) FeCl ₃ (d) Tollen's reagent	037.	(c) Fehling's test Which of the following doe	(d) Aldol condensation test
Q26.	By reacting with Grignard than formaldehyde produ include: (a) tertiary alcohols (c) primary alcohols	 (d) Fonce a reagent d's reagent, other aldehydes ice additional products that (b) secondary alcohols (d) carboxylic acids 		reaction? (a) Benzaldehyde (b) 2-Methylpropanal (c) p-Methoxybenzaldehyd (d) 2, 2-Dimethylpropanal	le
Q27.	Which of the following co NaHSO ₃ ? (a) HCHO (c) CH ₂ COCH ₂	(d) Ch ₅ COCH ₃ (d) Ch ₅ COCH ₃	Q38.	Which among the followinucleophilic addition? (a) FCH ₂ CHO (c) BrCH ₂ CHO	ng is most reactive to give (b) ClCH2CHO (d) ICH2CHO
Q28.	How can Penta-2-one differentiated? (a) Iodoform test (c) Febling's test	(d) Ensento e and Pentan-3-one be (b) Benedict's test (d) Aldol condensation test	Q39.	Which compound is obtain treated with dilute solution (a) Sodium acetate (c) Aldol	ned when acetaldehydes are n of caustic soda? (b) Resinous mass (d) Ethyl acetate
Q29.	Toluene is oxidized to chloride is called: (a) Etard reaction (b) Riemer-Tiemann react (c) Wurtz reaction	benzaldehyde by chromyl	Q40.	Which of the following for of aldehydes and ketones? (a) Hydrogen bonding (b) van der Waal's forces (c) Dipole-dipole attraction (d) None of these	ces explain the boiling point
Q30.	(d) Cannizzaro's reactionWhich compound is obtaitreated with a dilute soluti(a) Sodium acetate(c) Aldol	ned when acetaldehydes are ion of caustic soda? (b) Resinous mass (d) Ethyl acetate	Q41.	Acetaldehyde reacts with (a) Electrophiles only (b) Nucleophiles only (c) Free radicals only (d) Both electrophiles and	nucleophiles

Q42.	If formaldehyde and KOH are heated, then we ge		
	(a) methane	(b) methyl alcohol	
	(c) ethyl formate	(d) acetylene	

Q43.	Schiff's reagent gives pink colour with		
	(a) acetaldehyde	(b) acetone	
	(c) acetic acid	(d) methyl acetate	

- **Q44.** The IUPAC name of CH₃COCH(CH₃)₂ is (a) 2-methyl-3-butanone
 - (b) 4-methylisopropyl ketone
 - (c) 3-methyl-2-butanone
 - (d) Isopropylmethyl ketone
- Q45. IUPAC name of ethyl isopropyl ketone is(a) 4-methyl pent-3-one(b) 2-methyl pent-3-one(c) 4-methyl pent-2-one(d) 2-methyl pent-2-one
- Q46. The π-bond in carbonyl group is formed by
(a) s-s-overlapping
(c) s-p-overlapping(b) p-p-overlapping
(d) p-d-overlapping
- Q47. Which of the following have pleasant smell? (a) Methanal (b) Propanal (c) Ethanal (d) Hexanal
- **Q48.** Which one of the following can be oxidised to the corresponding carbonyl compound?
 - (a) 2-hydroxy-propane
 - (b) Ortho-nitrophenol
 - (c) Phenol
 - (d) 2-methyl-2 hydroxy-propane
- Q49. The catalyst used in Rosenmund's reduction is (a) HgSO₄ (b) Pd/BaSO₄ (c) anhydrous AlCl₃ (d) anhydrous ZnCl₂
- **Q50.** Vinegar is a solution of acetic acid which is: (a) 15-20% (b) 20 -25% (c) 6 - 8% (d) 2 - 4%

ASSERTION AND REASONING

Q1. Assertion: The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

Reason: There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- **Q2. Assertion:** Formaldehyde is a planar molecule. **Reason:** It contains sp2 hybridised carbon atom.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- Q3. Assertion: Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.
 Reason: Carboxylic acids can be reduced to alcohols by treatment with LiAlH4
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- **Q4.** Assertion: Acetic acid does not undergo a haloform reaction.

Reason: Acetic acid has no alpha hydrogens.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

TRUE/FALSE

- Q1. Highly branched carboxylic acids are more acidic than unbranched acids.(a) True(b) False
- **Q2.** Aldol condensation is given by all aldehydes and ketones.

(b) False

Q3. Aldehydes and ketones form functional pairs.(a) True(b) False

HOMEWORK

(a) True

- **Q1.** Which of the following is used to shift the esterification reaction of carboxylic acids towards the right?
 - (a) Removal of ester by distillation
 - (b) Using excess of carboxylic acid
 - (c) Using excess of acid catalyst
 - (d) Removal of water by distillation

- **Q2.** Which is the most preferred reagent in the product of acetyl chloride from acetic acid?
 - (a) SOCl₂ (b) Cl₂ (c) PCl₃ (d) PCl₅

Q3.	Benzoic acid reacts with p	hosphorus pentachloride to	Q14
	give (a) chlorobenzoic acid (b) chlorobenzene (c) benzyl chloride (d) benzoyl chloride		
Q4.	Benzoic acid reacts with benzoate salt, which on benzamide. (a) N ₂ (c) NH4OH	 to give ammonium further dehydration gives (b) NH₃ (d) HNO₃ 	Q15
Q5.	The conversion of phth brought about by the loss of (a) two NH ₃ (c) two H ₂ O	alamide to phthalimide is of molecule. (b) one H2O (d) one NH3	Q16
Q6.	Soda lime consists of NaC the ratio of (a) 3:1 (c) 2:1	0H and CaO respectively, in (b) 1:2 (d) 1:3	Q17
Q7.	Sodium acetate on heatin mixture) gives (a) ethanal (c) ethane	g with NaOH and CaO (3:1 (b) methane (d) methanol	
Q8.	What is formed when nitration in the presence H ₂ SO ₄ ? (a) 3,5-Dinitrobenzoic acid (c) m-Nitrobenzoic acid	benzoic acid undergoes e of conc. HNO ₃ and conc. l (b) o-Nitrobenzoic acid (d) p-Nitrobenzoic acid	Q18
Q9.	Benzoic acid reacts Bromobenzoic acid. (a) PBr ₃ /heat (c) Br ₂ -FeBr ₃	with to give m- (b) Br2/light (d) NaBr	Q19
Q10.	Which of the following al solid at room temperature (a) Decanoic acid (c) Octanoic acid	iphatic carboxylic acids is a ? (b) Heptanoic acid (d) Nonanoic acid	Q20
Q11.	Which among the followi odour? (a) Palmitic acid (c) Lauric acid	ng has the most unpleasant (b) Caproic acid (d) Myristic acid	Q21
Q12.	Benzoic acid is almost following solvents? (a) Alcohol (c) Benzene	insoluble in which of the (b) Cold water (d) Ether	Q22
Q13.	As a result of intermo	ecular hydrogen bonding,	Q23

- (a) dimers
 (b) acetals
 (c) aldols
 (d) hemiacetals
- 4. Which of the following is not a reason for carboxylic acids having higher boiling point than alcohols of comparable molecular masses? (a) Presence of more alkyl groups in carboxylic acids (b) Presence of electron withdrawing carbonyl group (c) Higher polarity of OH bond than in alcohols (d) Formation of two hydrogen bonds to form cyclic dimers 5. What is the correct order of boiling points of the following? (a) $CH_3COOH > HCOOH > C_2H_5COOH$ (b) $HCOOH > CH_3COOH > C_2H_5COOH$ (c) $C_2H_5COOH > CH_3COOH > HCOOH$ (d) $HCOOH > C_2H_5COOH > CH_3COOH$ 5. If the boiling point of propanol is 370 K, predict the boiling point of acetic acid. (a) 390 K (b) 322 K (d) 370 K (c) 329 K 7. Which of the following methods cannot produce aldehydes? (a) Oxidation of primary alcohols (b) Dehydrogenation of secondary alcohols (c) Ozonolysis of alkenes (d) Hydration of ethyne with acid B. Which of the following reactions can produce ketones? (a) Oxidation of secondary alcohols (b) Oxidation of primary alcohols (c) Dehydrogenation of primary alcohols (d) Dehydrogenation of tertiary alcohols **9.** Conversion of propyne to acetone requires three important reagents. Identify which of the following is not one of the three? (a) HgSO₄ (b) Water (d) H_2SO_4 (c) Zinc dust **).** Which of the following carbonyl compounds can be prepared from Rosenmund reaction? (a) Benzaldehyde (b) Methanal (c) Acetone (d) Butanone . Which of the following is required in Stephen reaction? (a) TiCl₄ (b) LiCl (c) NiCl₂ (d) SnCl₂ . Which of the following compounds helps in reducing esters to aldehydes? (a) TBAF (b) BINAL-H (d) DIPT (c) DIBAL-H **B.** Acetyl chloride reacts with _____ to give butan-2-one. (a) diethyl cadmium (b) cadmium chloride
 - (c) methyl magnesium chloride
 - (d) dimethyl cadmium

- **Q24.** What is formed after the hydrolysis of the product of the reaction between benzonitrile and methyl magnesium bromide in dry ether?
 - (a) Benzaldehyde (b) Phenyl acetaldehyde
 - (c) Acetophenone (d) 1-Phenylpropanone
- Q25. Friedel-Crafts benzoylation of benzene gives _____ (a) no reaction (b) acetophenone (c) propiophenone (d) benzophenone
- **Q26.** Which of the following reactions does not give benzaldehyde?
 - (a) Friedel-Craft acylation reaction
 - (b) Rosenmund reaction
 - (c) Etard reaction
 - (d) Gatterman-Koch reaction
- Q27. Which of the following exists as a gas at 287K? (a) Acetone (b) Formaldehyde (c) Acetaldehyde (d) Propanal
- **Q28.** If the boiling points of methoxyethane and propanol are 281 K and 370 K respectively, predict the boiling point of propanal. (a) 370 K (b) 273 K

(a) 570 K	(D) 273 K
(c) 281 K	(d) 322 K

- **Q29.** Which of the following is the least soluble in water?
 - (a) Pentanal(b) Methanal(c) Ethanal(d) Propanone
- **Q30.** Two compounds A and B were being tested for their boiling points. It was observed that A started boiling after B, when both were subjected to same conditions. If the compound B is acetone, which of the following can be compound A?
 - (a) Propanol (b) n-Butane
 - (c) Methoxyethane (d) Propanal

ASSERTION AND REASONING

Q1. Assertion: Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.

Reason: Aldehydes and ketones can be distinguished by Tollen's reagent.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

Q2. Assertion: Acetaldehyde on treatment with alkaline gives aldol.

Reason: Acetaldehyde molecules contain a hydrogen atom.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- **Q3.** Assertion: Acetylene on treatment with alkaline KMnO₄ produce acetaldehyde.
 - **Reason:** Alkaline KMnO₄ is a reducing agent.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- Q4. Assertion: Acetophenone and benzophenone can be distinguished by the iodoform test.Reason: Acetophenone and benzophenone both are carbonyl compounds.
 - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.

TRUE/FALSE

- **Q1.** Unsymmetrical ketones can be prepared by distilling a mixture of calcium salts of two different carboxylic acids.
 - (a) True (b) False
- Q2. In Rosenmund's reduction, BaSO₄ and S act as promoters and increase the catalytic activity of Pd which acts as catalyst.
 (a) True
 (b) False
- Q3. Ketones can be obtained by the reductive ozonolysis of alkenes possessing no branching at the carbon atoms involved in double bond formation.(a) True(b) False
- Q4. Aldehydes and ketones possess higher boiling points as compared to those of corresponding alkanes due to intermolecular hydrogen bonding.
 (a) True
 (b) False

SOLUTIONS

Sodium bisulphite is used for separation of acetone and acetophenone. Acetophenone (an aromatic ketone) does not react with sodium bisulphite whereas acetone (an aliphatic ketone) reacts with sodium bisulphite to form a solid adduct which can be filtered. Then, it can be decomposed by acid or base to regenerate acetone.

S2. (b)

- S3. (b)
- **S4.** (b) Geminal refers to the relationship between two atoms or functional groups that are attached to the same atom. Propylidene chloride is the common name of IUPAC compound 1,1–dichloropropane.
- S5. (b)
- **S6.** (b) Ketones are formed when secondary alcohols are oxidised and dehydrogenated. Aldehydes are produced by the same processes with primary alcohols.
- S7. (b) The Rosenmund reaction, which involves replacing chloride with hydrogen, is only utilised to make aldehydes. Methanal cannot be produced from this process because the acyl chloride that corresponds to it, formyl chloride, is unstable at ambient temperature. Benzoyl chloride produces benzaldehyde.
- S8. (a) The polar CO group in aldehydes and ketones consists of double bond. The nucleophile attacks the sp² hybridised carbon, shattering the double bond and converting it to sp³, resulting in the formation of a tetrahedral alkoxide intermediate. This goes through another quick step to create an additional product.
- **S9. (b)** When comparing these substances, the steric effects are taken into account. The tert-butyl groups on either side of the carbonyl atom of the ketone are highly bulky. This reduces reactivity by increasing the hindrance to the approaching nucleophile.
- **S10. (b)** Dihydric alcohols, such as ethylene glycol, react immediately with aldehydes and ketones to generate cyclic acetals and cyclic ketals, respectively. Ethylene glycol ketals are another name for cyclic ketals.
- **S11. (b)** Because formaldehyde has only one carbon atom, it cannot be employed as a starting material for the production of acetic acid. It is, nevertheless, utilised to make bakelite, glues, and polymeric

items. In the silvering of mirrors, it also works as a reducing agent.

- **S12. (b)** When benzyl alcohol is oxidised with KMnO₄, benzoic acid is the result.
- **S13. (c)** At room temperature, methane is a foul-smelling gas. Ethanal is a volatile liquid that boils at 294 degrees Fahrenheit. At room temperature, other aldehydes and ketones exist as liquids or solids.
- S14. (b) As polar carbonyl group may establish hydrogen bonds with water molecules, the lower aldehydes and ketones are miscible in water in all quantities. However, as the length of the alkyl chain grows longer, the solubility drops dramatically. Aldehydes and ketones with more than four carbon atoms are nearly water- insoluble.
- **S15. (b)** The odour gets less strong and more fragrant as the size of the aldehyde molecule grows. Methanal has the strongest odour of all the aldehydes.
- **S16. (a)** Esters are formed when the reaction of an acid and alcohol takes place.

The reaction is known as the esterification reaction. The reaction is

 $CH_3COOH + CH_3CH_2COOH \rightarrow CH_3COOCH_2CH_3$

- The reaction takes place in the presence of Sulphuric acid (H_2SO_4) .
- **S17. (c)** Vinegar contains acetic acid, also known as ethanol.
- Acetic acid is a colourless liquid with a sour and pungent smell
- In its chemical formula, it has carbon atoms so it is considered to be an organic compound.
- **S18. (d)** Due to its carboxyl group and aldehyde, formic acid is unique.
- Due to the carbonyl group, this acid reacts with aldehydes in a way that does.
- Aldehydes and acidified KMNO4 are also reduced by this compound.
- In combination with Tollen's reagent, potassium permanganate, and mercuric chloride, formic acid gives a silver mirror.
- **S19. (b)** Soaps are molecules in which two ends have different properties.
 - Water interacts with the head, while hydrocarbons interact with the tail.
 - Water interacts with the ionic end of soap while oil interacts with the carbon end.
 - Consequently, soap molecules are arranged in micelles with one end facing the droplet of oil and the other facing the outside.

- This forms an emulsion in water.
- The soap micelles thus help in pulling out the dirt in water and we can wash our clothes and utensils clean.
- **S20. (c)** Detergents have characteristics similar to that of soap.

The head of an ant is hydrophilic, since it interacts with water, while the tail is hydrophobic because it interacts with hydrocarbons.

During soaping, the ionic end interacts with the water, while the carbon ends interact with the oil. Soap molecules thus form micelles, structures where the oil droplet is on one end and the outside is on the other.

Water emulsifies the soap molecules.

As a result, soap micelles help to remove dirt from water, so that we can wash our clothes and utensils.

- S21. (a) When a mixture of formaldehyde and another aldehyde without an α -hydrogen atom is treated with concentrated alkali, it oxidizes formaldehyde to carboxylic acid and reduces another aldehyde to alcohol.
- **S22. (d)** Under Wolff Kishner reduction, an aldehyde or ketone is converted into the corresponding alkane.
- **S23. (b)** Since the initial attack is by CN⁻ (nucleophile), it is an example of nucleophilic addition reaction
- **S24. (a)** Upon decomposition, ammonium cyanate transforms into an organic compound called urea through the reaction of ammonia and cyanic acid.
- **S25. (d)** Formic acid has an aldehyde group. It reduces Tollen's reagent to a silver mirror-like other aldehydes. Tollen's test is not given by Carboxylic acids.
- **S26. (b)** Upon reaction with Grignard's reagent followed by hydrolysis, formaldehyde forms primary alcohol, while all other aldehydes from secondary alcohols.
- **S27. (b)** Compared with aliphatic ketones, aromatic ketones are less reactive than aldehydes. The reaction between acetophenone and NaHSO₃ is therefore not initiated.
- S28. (a) Pentan-2-one is a methyl ketone useful for Iodoform testing.Benedict's test will result in both positive results.Both tests will be negative for Fehling.Both can give Aldol.
- **S29. (a)** Oxidation of toluene with chromyl chloride in the Etard reaction gives benzaldehyde. In this reaction, the chromyl chloride first forms a brown complex, which is separated and then decomposed with H₂O to give benzaldehvde.

S30. (c)

- **S31. (a)** oxidation of toluene to benzaldehyde by the use of chromyl chloride is called Etard's reaction.
- **S32. (a)** The reaction of HCN with carbonyl compounds is an example of the nucleophilic addition reaction.
- **S33. (b)** aldehydes other than formaldehyde react with Grignard's reagent to give additional products which on hydrolysis give secondary alcohols.
- **S34. (c)** Benzaldehyde will not give aldol condensation due to absence of α -H atom.
- **S35. (d)** Benzoyl chloride on reduction with hydrogen in the presence of Pd and `BaSO₄ gives acetophenone/ benzaldehyde.
- **S36. (a)** Iodoform test is performed to differentiate between pentan-2-one and pentan-3-one.
- **S37. (b)** The alpha carbon i.e., the carbon atom adjacent to the carbonyl group is connected to three methyl groups and no hydrogen atom is bonded to it. Thus, the compound has no alpha hydrogen and can undergo a Cannizzaro reaction. Hence, the compound which cannot undergo a Cannizzaro reaction is 2-methylpropanal.
- **S38. (a)** FCH₂CHO is most reactive towards nucleophilic addition since presence of most electrophilic addition since presence of most electronegative F withdraws electrons from carbon of carbonyl group making it more polar.
- **S39. (c)** Aldehyde and ketones which have at least one α -hydrogen atom are known to react with dilute aqueous caustic soda. As a result, they produce α -hydroxy aldehydes. These compounds are known as aldols and reaction is known as aldol reaction.
- **S40. (c)** The boiling point of molecules depends on the intermolecular force of attraction, stronger the force, higher is the boiling point. Boiling points of aldehydes and ketone depend on intermolecular dipole-dipole attraction. This is because of electronegative oxygen attached to the carbon atom.
- **S41. (b)** The carbonyl group is highly reactive polar group. It is polarised due to the higher electronegativity of oxygen in comparison to carbon. As a result, the electrons present between carbon and oxygen are more attracted towards oxygen atom. The actual structure may be represented as consequently, the carbonyl carbon is positively charged while the oxygen is negatively charged. The positively charged carbon is easily attacked by a nucleophilic reagent (Nu-).

- **S42. (b)** When α -hydrogen is absent in carbonyl group, those compound gives cannizaro reaction. This reaction show disproportionation. The oxidation product is salt of carboxylic acid and reduced product is alcohol. HCHO + HCHO \rightarrow CH₃OH + HCOO-K⁺
- **S43. (a)** Schiff's reagent is used to detect the presence of aldehydic and ketonic group. It consists of fuchsin dye decolourised by sulphurous acid. Immediate red/pink colour appearance detects the presence of aliphatic aldehyde. Aliphatic ketone and aromatic aldehydes takes time and slowly pink colour blooms.
- **S44. (a)** The IUPAC name of CH₃COCH(CH₃)₂ (c) 3-methyl-2-butanone.
- **S45. (b)** The IUPAC name of ethyl isopropyl ketone is 2-methyl-3-pentanone.
- **S46. (b)** π bonds are formed by the sidewise or lateral overlapping of p orbitals. Where, as σ bonds are formed by axial overlapping of molecular orbitals.
- **S47. (d)** Hexanal, also called hexanaldehyde or caproaldehyde is an alkyl aldehyde used in the flavor industry to produce fruity flavors. Its scent resembles freshly cut grass, like cis-3-hexenal. It is potentially useful as a natural extract that prevents fruit spoilage.
- **S48. (a)** 2-hydroxy propane or secondary alcohol is oxidised into propanone (corresponding because in 2-hydroxy propane, secondary alcoholic group is present and it is oxidised into ketone).
- **S49. (b)** The reaction, a hydrogenolysis, is catalysed by palladium on barium sulfate, which is sometimes called the Rosenmund catalyst. Barium sulfate has a low surface area which reduces the activity of the palladium, preventing over-reduction.
- **S50. (c)** An aqueous of acetic acid is called vinegar which contains 5-8% acetic acid. Vinegar is a solution of 5-8% acetic acid in water, that's why it is aqueous

(containing water) solution of 5%-8% of acetic acid. Other names are Ethanoic acid or Methane carboxylic acid.

ASSERTION AND REASONING

S1. (a)

- S2. (a)
- S3. **(b)** If R-CHO + $H_2O \rightarrow$ R-COOH + 2H⁺ + 2e⁻ For example: Tollen's reagent: RCHO + 2Ag(NH₃)₂ + 3OH⁻ \rightarrow RCOO⁻ + 2Ag + 4NH₃ + 2H₂O That means -CHO group easily oxidised to corresponding COOH.
 - Whereas, RCOOH LIAIH4 H30+ RCH2OH That means carboxylic acids can be reduced to alcohols by treatment with LiAlH4. But it doesn't justified the reason of Assertion.
- **S4.** (c) Haloform test identifies the presence of a CH3 CO group in aldehydes and ketones. $CH_3COR + 3I_2 + 4OH^- \rightarrow CHI_3 + RCOO^- + 3I^- + 3H_2O$ Acetic acid does not undergo haloform reaction because in presence of OH⁻ ions it acts as an acid and does not forms CHX₃ haloform. Therefore assertion is correct. Acetic acid has three α hydrogens, thus the reason

Acetic acid has three α hydrogens, thus the reason is incorrect.

TRUE/FALSE

- **S1.** (b) false- highly branched acids are less acidic
- **S2. (b)** Aldol condensation is given by all aldehydes and ketones.
- S3. (a) Aldehydes have a general formula RCHO while ketones have the general formula RCOR. They can have the same molecular formula of different arrangement and combination of atoms. Thus, they form a functional pair.

HOMEWORK

- **S1. (d)** Since the esterification of carboxylic acids is a reversible reaction, it can be shifted towards the right by using excess of alcohol or by the removal the water formed by distillation.
- S2. (a) Thionyl chloride reacts with acetic acid to form acetyl chloride along with two gaseous compounds (SO₂ and HCl) that escape the reaction mixture, making the purification of the product easier.
- S3. (d) The hydroxyl group (OH) of benzoic acid id easily replaced by chlorine atom on treatment with PCl5. This results in the formation of C₆H₅COCl, or benzoyl chloride.
- S4. (b) Benzoic acid reacts with ammonia in a reversible reaction to form ammonium benzoate by addition reaction. This salt then loses water on heating to form benzamide.

- S5. (d) Phthalic acid on reaction with NH3 forms ammonium phthalate, which on heating loses two H₂O molecules, one from each COONH₄ group, to form phthalamide. This on further strong heating loses one NH₃ molecule to form phthalimide, which is an imide derivative of phthalic anhydride.
- **S6.** (a) Soda lime is the 3:1 mixture of sodium hydroxide and calcium oxide, and is used in the decarboxylation reaction (loss of carbon dioxide) of carboxylic acids.
- S7. (b) Sodium acetate undergoes decarboxylation (loss of CO₂) when heated with soda lime. This is proceeded by the loss of COONa from the sodium salt and NaO from sodium hydroxide. They combine to form CH₄ and Na₂CO₃. The hydrocarbon formed has one less carbon atom than the parent acid.
- **S8.** (c) Benzoic acid undergoes ring substitution in which the COOH group acts as a deactivating group and is meta-directing in nature.
- S9. (c) Benzoic acid undergoes electrophilic substitution with bromine at the meta position in the presence of FeBr₃ to form 3-bromobenzoic acid and hydrogen bromide as side product.
- **S10. (a)** The members butanoic acid to nonanoic acid are colourless oily liquids at room temperature. The compounds with ten or more carbon atoms exists as waxy solids at room temperature.
- **S11. (b)** The first three members of carboxylic acids have pungent smell. The next six members have a faint unpleasant odour. The higher members (lauric acid, myristic acid, palmitic acid) are practically odourless due to their low volatility.
- **S12. (b)** The large hydrophobic benzene ring of benzoic acid prevents the carboxyl group from taking part in hydrogen bonding. However, benzoic acid is soluble in non-polar solvents like benzene, ether, alcohol, chloroform, etc.
- **S13. (a)** The intermolecular hydrogen bonds between carboxylic acids are not broken even in vapour phase. In fact, most carboxylic acids exist as dimer in vapour phase or in aprotic solvents.
- **S14. (a)** The OH bond in carboxylic acids is more strongly polarised due to the presence of adjacent electron withdrawing CO group. This results in stronger hydrogen bonds. Also, the presence of alkyl groups should increase the polarity of OH bond as they are electron releasing in nature. Furthermore, carboxylic acids form two hydrogen bonds between molecules compared to the only one between alcohols.

- **S15. (c)** The boiling points increase with the increase in molecular mass, because as the size of alkyl group increases, the magnitude of van der Waal forces increases, thus making the bonds difficult to break.
- **S16. (a)** Acetic acid and propanol both have same molecular mass. Acetic acid should have a higher boiling point than propanol because of its stronger hydrogen bonds and the fact that it forms cyclic dimers.
- **S17. (b)** The dehydrogenation of secondary alcohols give ketones. Aldehydes are obtained by the dehydrogenation of primary alcohols.
- **S18. (a)** Oxidation and dehydrogenation of secondary alcohols results in ketones. The same reactions with primary alcohols give aldehydes.
- **S19. (c)** Addition of water to propyne in the presence of H₂SO₄ and HgSO₄ gives acetone. Zinc dust is an important reagent in the ozonolysis of alkenes.
- **S20. (a)** Rosenmund reaction is exclusively used for the preparation of aldehydes by the substitution of chloride by hydrogen. Given this, methanal cannot be formed from this reaction because its corresponding acyl chloride, i.e., formyl chloride, is unstable at room temperature. Benzaldehyde is formed from benzoyl chloride.
- **S21. (d)** Nitriles are converted to respective imines with SnCl₂ in the presence of HCl, which on hydrolysis gives corresponding aldehyde.
- **S22. (c)** DIBAL-H or diisobutylaluminium hydride is a reducing agent which are used to reduce nitriles to imines or esters to aldehydes. These are important in the preparation of aldehydes.
- **S23. (a)** For butan-2-one to form from acetyl chloride, the Cl group needs to be replaced by an ethyl group. This ethyl group is obtained from diethyl cadmium which is produced from the reaction between ethyl magnesium bromide and cadmium chloride.
- **S24. (c)** When a nitrile is treated with a Grignard reagent in the presence of dry ether, an addition product is formed which on hydrolysis gives a ketone.
- **S25. (d)** When benzene is treated with benzoyl chloride in the presence of anhydrous aluminium chloride, it forms benzophenone which is an aromatic ketone.
- **S26. (a)** Friedel-Crafts acylation of benzene produces an aromatic ketone and not benzaldehyde. Benzene on Gatterman-Koch reaction gives benzaldehyde, so does toluene on Etard reaction. Rosenmund reaction also gives benzaldehyde but from benzoyl chloride.

- **S27. (b)** Methanal exists as foul-smelling gas at room temperature. Ethanal is a volatile liquid which boils at 294K. Other aldehydes and ketones exist as either liquids or solids at room temperature.
- **S28. (d)** The boiling point of aldehydes are higher than those of non-polar hydrocarbons of comparable molecular masses. However, their boiling points are lower than comparable alcohols, due to the absence of intermolecular hydrogen bonding.
- **S29. (a)** The lower aldehydes and ketones are miscible in water in all proportions due to the ability of the polar carbonyl group to form hydrogen bonds with water molecules. However, the solubility rapidly decreases as the length of the alkyl chain increases. Precisely, aldehydes and ketones with more than 4 carbon atoms are practically insoluble in water.
- **S30. (a)** It can be inferred that B has a higher boiling point than A. Since hydrocarbons, ethers and aldehydes have lower boiling points than ketones of similar molecular masses, none of them can be compound A. Also, alcohols have a higher boiling point than similar ketones hence, the compound A is propanol.

ASSERTION AND REASONING

- S1. (b) Lower aldelnydes and ketones are soluble in water due to polar effect of >C=O which makes liydrogen bonds with water molecules.
 - As the size of the aldehydes and ketones increases the hydrophobic part i.e., alkyl chain increases which weakens the H-bond formations with H₂O molecules and decreases the solubility.
- **S2. (a)** Carbonyl compounds having α-hydrogen condenses to produce aldol in presence of alkali.

$$\begin{array}{c} CH_3 - CH + HCH_2CHO \xrightarrow{\text{dil.NaOH}} & CH_3 - CH - CH_2CHO \\ \downarrow \\ O \\ Acetaldehyde \\ \end{array} \xrightarrow{OH} Aldol$$

S3. (d) Acetylene, on treatment with alkaline KMnO₄ is oxidised to produce oxalic acid.

CH	4[0]	COOH
CH	alk.KMnO4	COOH
Acetylene	2	Oxalic acid

S4. (b) Acetophenone and benzophenone can be distinguish by iodoform test. Both are carbonyl compounds.

TRUE/FALSE

S1. (a) When a mixture of calcium salts of two different carboxylic acids is dry distilled, it results in the formation of unsymmetrical ketones.

$$(CH_{3}CH_{2}COO)_{2}Ca + (CH_{3}COO)_{2}Ca \xrightarrow{Heat} \\ (Calcium propionate) \\ (Calcium propionate) \\ (Calcium acetate) \\ 2 \xrightarrow{CH_{3}CH_{2}} C=0 + 2CaCO_{3}$$

S2. (b) In Rosenmund's reduction, the palladium catalyst is poisoned by barium sulphate and sulphur to check the further reduction of aldehyde to corresponding alcohol.

$$\begin{array}{c} & & \\ || \\ CH_3 - C - Cl + H_2 \xrightarrow{Pd / BaSO_4, S} \\ Ethanoyl chloride \\ (Acetyl chloride) \end{array} \xrightarrow{CH_3CHO} + HCl \\ \hline Boiling xylene \\ (Acetaldehyde) \end{array}$$

It decreases the catalytic activity of palladium.

S3. (b) The formation of ketones from the reductive ozonolysis reaction of alkenes requires alkenes have branching at the carbon atoms involved in double bond formation.



S4. (b) Aldehydes and ketones have a polar carbonyl group.

The polarity of the carbonyl group results in the intermolecular association between the molecules in aldehydes and ketones due to dipole-dipole interactions.

Therefore, the boiling points of aldehydes and ketones are higher than those of alkanes and ethers.