Aldehydes, Ketones, Carboxylic Acids & Derivatives

Aldehydes and Ketones

1. Introduction

Aldehydes & ketones have general formula $C_nH_{2n}O$ and contains >C = O group. Thus aldehydes (R–CHO) and ketones (R–CO–R) are collectively called as carbonyl compounds. Aldehyde is always at terminal position while ketone is never at terminal position.

2. Strucutre and bonding in aldehydes and ketones

The carbonyl carbon atom is sp² hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized. Orbital diagram for the formation of carbonyl group is as follows:





ajor

This polarity confirms that there is nucleophilic addition reaction takes place in carbonyl compound. The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.

Carbonyl carbon act as an electrophile (Lewis acid) Carbonyl oxygen act as a nucleophile (Lewis base)

Section (A) : Preparation of Carbonyl Compounds

3. Preparation Carbonyl Compounds :

3.1 By oxidation of alcohols :

Primary alcohols $\xrightarrow{[0]}$ Aldehydes

Secondary alcohols $\xrightarrow{[0]}$ Ketones

3.2 By dehydrogenation of alcohols :

Dehydrogenation means removal of hydrogen and reagent used is heated copper.

1° alcohol (RCH₂OH) $\xrightarrow{-H_2}$ Aldehyde (R–CH = O) 2° alcohol (R₂CHOH) $\xrightarrow{-H_2}$ Ketone (R₂C = O) 3° alcohol $\xrightarrow{-H_2O}$ Alkene

3.3 Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



Note : (i) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.

(ii) By this method we can locate double bond in olefin or exact structrue of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen atoms of two carbonyl compounds.

(iii) Among the three molecules of carbonyl compounds.

(a) If one molecule contains two carbonyl groups, then hydrocarbon will be alkadiene.

(b) If all the three molecules contain two carbonyl group then hydrocarbon will be cycloalkatriene.

3.4 Wacker process :

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in presence of air or O_2 . Except ethene any higher alkene will give ketone.

 $CH_{2}=CH_{2} + H_{2}O + PdCI_{2} \xrightarrow[air or O_{2}]{} CH_{3}-CH=O + Pd + 2HCI$ $R-CH=CH_{2} + H_{2}O + PdCI_{2} \xrightarrow[air or O_{2}]{} R - C - CH_{3} + Pd + 2HCI$

Note : During the reaction PdCl₂ is reduced to Pd and CuCl₂ is reduced to Cu(I)

3.5 Hydration of alkynes :

 $CH \equiv CH \xrightarrow{H_2O} CH_3CHO$

Other alkynes give ketones in this reaction.

$$\begin{array}{c} Hg^{++}/H_2SO_4 \\ \hline H_2O \\ R-C \equiv C-H \\ \end{array} \xrightarrow{} H_2O \\ O \\ H_2O \\ O \\ H \\ O \\ O \\ \end{array}$$

3.6 Hydroboration of alkyne :

It is used to get aldehyde from terminal alkyne. Here reagent is (i) diborane (B₂H₆) (ii) H₂O₂,OH⁻

$$\mathbf{R} - \mathbf{C} \equiv \mathbf{C} - \mathbf{H} \xrightarrow{(i) \mathbf{B}_2 \mathbf{H}_6} \mathbf{R} - \mathbf{C} \mathbf{H}_2 - \mathbf{C} \mathbf{H} = \mathbf{O}$$

In this reaction Borane (BH₃) is act as electrophile.

3.7 Dry distillation of calcium salt of acid :

$$(\mathsf{RCOO})_2\mathsf{Ca} \xrightarrow{\Delta} \mathsf{Ketone} + \mathsf{CaCO}_3$$

Ex. $(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3 - C - CH_3 + CaCO_3$

calcium acetate On dry distillation of calcium salt of acetic acid with calcium salt of formic acid we get a mixture of aldehyde, ketone and formaldehyde.

3.8 On passing vapours of fatty acids over Mangnous oxide at 300°C :

2 RCOOH
$$\xrightarrow{MnO / 300^{\circ}C}$$
 $R - C - R + CO_2 + H_2O$
(Vap) Ketone

On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

3.9 On aqueous alkali hydrolysis of gem-dihalides :

Terminal gemdihalides will give aldehyde while non-terminal will give ketone as follows



Toluene $\xrightarrow{Cl_2/hv}$ Benzal chloride $\xrightarrow{H_2O}$ Benzaldehyde

4. Methods used for the preparation of Aldehydes only.

4.1 Rosenmund's reduction :

Here acid chlorides are reduced to aldehyde with H_2 in boiling xylene using palladium as a catalyst supported on barium sulphate.

$$\begin{array}{c} O \\ \parallel \\ R - C - CI + H_2 \xrightarrow{Pd-BaSO_4} \\ Boiling Xylene \end{array} R - C \xrightarrow{O} \\ H + HCI \end{array}$$

Note : (a) Pd Catalyst is poisoned by BaSO₄ to check further reduction of aldehyde to alcohol.

(b) Formaldehyde cannot be obtained by this method because HCOCI is unstable at common temperature.

(c) Reaction with acid chloride and dialkyl cadmium we can obtain ketone.

4.2 Stephen's reduction :

$$R - CH = NHHCI$$

$$R - C \equiv N \xrightarrow{\text{SnCl}_2/HCI} \text{Aldimine hydrochloride} \xrightarrow{H_2O} R - CH = O + NH_4CI$$

4.3 Oxo-process :

It is also called as carbonylation here alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

$$R-CH=CH_{2} \xrightarrow[[Co(CO)_{4}]_{2} \xrightarrow{CO + H_{2}/\Delta, \text{ Pressure}} [Co(CO)_{4}]_{2}} \xrightarrow{R - CH - CH_{3}} R - CH_{2} - CH_{2} - CH_{2} - CH = O$$

4.4 Reimer-Teimann Reaction :

By this method phenolic aldehyde is prepared



Phenol

Salicylic aldehyde

4.5 From esters or nitrile :

$$\begin{array}{c} O \\ \square \\ CH_{3}(CH_{2})_{9}-C-OC_{2}H_{5} \text{ (Esters)} \xrightarrow{1. \text{ DIBAL-H}} CH_{3}(CH_{2})_{9}-C-H \text{ (Aldehydes)} \\ R-CN \xrightarrow{1. \text{ DIBAL-H}} R-CH=O \end{array}$$

DIBAL-H : Diisobutyl aluminium hydride [AlH(i-Bu)₂] is a reducing agent.

4.6 From hydrocarbons :

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO₂Cl₂)



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Propiophenone

(1-Phenylpropanone)





6. Physical properties of Aldehydes and Ketones :

- Methanal Gas at room temperature
- Ethanal Volatile liquid
- Other aldehydes and ketones Liquid or solid at room temperature
- Boilng points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.

Reason : Weak molecular association in aldehydes and ketones, arising out of the dipole-dipole interactions

- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
 Reason : Absence of intermolecular hydrogen bonding
- Lower members of aldehydes and ketones are miscible with water in all proportions.
 Reason : They form hydrogen bonds with water.

$$\begin{array}{c} \mathsf{R} & \overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{+}}{\overset{\delta_{-}}}{\overset{\delta_{-}}{\overset{\delta_{-}}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{-}}}{\overset{\delta_{-}}{\overset{\delta_{-}}{\overset{\delta_{-}}}{\overset{\delta_{-}}}{\overset{\delta_{-}}}{\overset{\delta_{-}}}{\overset{\delta_{-}}{\overset{\delta_{-}}}{\overset{\delta_{-}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

- Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc.
- Lower aldehydes have sharp pungent odours.
- As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

Section (B) : Aldol condensation

7.1 Reactions due to α-Hydrogen

 α -Hydrogen of aldehydes and ketones are acidic: They undergo a number of reactions due to the acidic nature of α -hydrogen.

Reason for the acidity of α **-hydrogen:** Strong electron-withdrawing effect of the carbonyl group, and resonance stabilisation of the conjugate base



Resonating structure of conjugate base

(I) Aldol condensation reaction

Aldehydes and ketones with at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst.



Ex.

(II) Cross-Aldol condensation :

On using two types of carbonyl compounds both having α -hydrogen atoms we get a mixture of four condensed product because two types of carbonyl compounds will give two type of carbanions which will be nucleophile for itself and other molecule.

$$CH_{3}-CH=CH-CHO \quad (Simple or self aldol products) + CH_{3}-CH_{2}-CH_{2}-CHO (Simple or self aldol products) + CH_{3}-CH_{2}-CHO (Simple or self aldol products) + CH_{3}-CH = C - CHO (Cross aldol products) + CH_{3}-CH = C - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH = CH - CHO (Cross aldol products) + CH_{3}-CH_{2}-CH + CH_{3}-CH_{2}-CH + CH_{3}-CH_$$

Ketones can also be used as one component in cross-aldol reactions.





Note : On using formaldehyde and acetaldehyde during crossed aldol all the α-hydrogen atom of acetaldehyde are replaced one by one by hydroxymethyl group because of smaller size of formaldehyde to give trihydroxymethylacetaldehyde which undergoes crossed cannizaro's reaction with formaldehyde to give tetrahydroxymethyl methane and formate ion as a final product.



Ex. Show how cinnamaldehyde is prepared by crossed aldol condensation ?

) + CH₃CHO
$$\xrightarrow{OH^{\Theta}}$$
 C₆H₅CH=CH-

 $C_6H_5CHO + CH_3CHO$ (-H₂O) $C_6H_5CH=CH-CHO + H_2O$

(III) Intramolecular aldol condensation :

If two carbonyl groups with α -hydrogen atoms are present within the same molecule, then we get cyclic α , β -unsaturated aldehyde / ketones via the formation of cyclic- β -hydroxy aldehyde / ketone in presence of basic medium.



By knowing product we can get reactant as in case of intermolecular aldol condensation :

Section (C) : Cannizaro reaction

7.2 Cannizzaro reaction :

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with a concentrated alkali.



Ex.

Sol.

Mechanism :

$$H = C = O + CH_{3}O^{-} \rightarrow H - C = O + CH_{3}OH$$

$$H = C = O + CH_{3}O^{-} \rightarrow H - C = O + CH_{3}O^{-} \rightarrow H - C = O + CH_{3}OH$$

$$H = C = O + CH_{3}O^{-} \rightarrow H - C = O + CH_{3}O^{-} \rightarrow H - C = O + CH_{3}OH$$

By this mechanism it is clear that acid corresponds to that carbonyl compound over which can attack easily as nucleophile.

Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Crossed Cannizzaro reaction :

On using two types of carbonyl compounds not having α -hydrogen atom, acid salt will be corresponding to that aldehyde over which OH will approach without any hindrence.

(i)

$$\begin{array}{c}
H - C = O + C_{6}H_{5}-CH=O & \stackrel{\Theta}{\longrightarrow} H - C & \stackrel{\Theta}{\longrightarrow} + C_{6}H_{5}CH_{2}OH \\
(i) & (CH_{2}OH)_{3}C-CH=O + H - C & \stackrel{H}{\longrightarrow} O & \stackrel{\Theta}{\longrightarrow} (CH_{2}OH)_{3}C-CH_{2}OH + H - C & \stackrel{\Theta}{\longrightarrow} O^{-1} \\
(ii) & (A) & (B) & \stackrel{\Theta}{\longrightarrow} O^{-1} & (CH_{2}OH)_{3}C-CH_{2}OH + H - C & \stackrel{\Theta}{\longrightarrow} O^{-1} & \stackrel{\Theta}{\longrightarrow} O$$

(11)

In case (i) OH will easily go to (A) and in case (ii) it will go to (B) hence acid salt will be formate ion in both the cases.

Intramolecular Cannizzaro reaction :

Here two carbonyl groups (without α -hydrogen atom) are present within the same molecule.

$$\begin{array}{ccc} CH=O & \bigoplus & CH_2OH \\ | & \bigoplus & | \\ CH=O & & COO^- \\ & & & Glycolate ion \end{array}$$

Mechanism :

$$\begin{array}{c} H - C = O \\ OH \end{array} \xrightarrow{\Theta}_{OH} \begin{array}{c} H + C = O \\ H + C = O \\ H - C = O \\ OH \end{array} \xrightarrow{\Theta}_{OH} \begin{array}{c} H + C - O \\ H + C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array} \xrightarrow{O}_{OH} \begin{array}{c} C + O \\ C = O \\ OH \end{array}$$

 $H - C = O \xrightarrow{OH} COO^{-1}$ (mendalic acid ion) Ex.

Section (D) : Perkin, Haloform and other name reactions 7.3 **Perkin reaction :**

When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get α , β -unsaturated acid.



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Note : By knowing α , β -unsaturated acid we can get idea about the anhydride used in Perkin reaction. This can be done by keeping 'H' at α and –OH at β -carbon atom followed by breaking α , β carbon. By this we can know about acid and it will be anhydride of this acid only.

7.4 Wittig reaction :

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



Note : Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as :



(II) Clemmensen reduction : Used to get alkane from carbonyl compounds.

$$C = 0$$

$$\int_{sp^2} Zn - Hg / HCl$$

Mechanism :

Ex.

7.5

(I)

$$C = O \qquad 2H^{\oplus}$$

$$Sp^{2} \qquad H^{\oplus} \qquad C = O \qquad 2H^{\oplus} \qquad 2H^{\oplus} \qquad C = O \qquad 2H^{\oplus} \qquad 2H^{\oplus$$

Note : Generally this reaction is avoid if **acid sensitive** groups are present in the carbonyl compounds. e.g. (OH, C=C, C=C, OR) –OHm >C = C <, –C = C –, –OR

(III) Wolf-Kishner reduction :

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$$\begin{array}{c} \searrow CH_2 & \xrightarrow{BH} \\ \downarrow \\ sp^3 & \xrightarrow{BH} \\ -\overrightarrow{B} \end{array} \xrightarrow{\Theta} CH \xrightarrow{O} - N_2 \xrightarrow{O} CH \xrightarrow{O} N \xrightarrow{O} CH - N = NH \xrightarrow{O} CH - N = NH \xrightarrow{O} CH \xrightarrow{BH}$$

- Note : Generally this reaction is avoid if **base sensitive** groups are present in the carbonyl compounds (e.g. X, COX, COOR, COOCOR) (-X, -COX, -COOR, -COOCOR)
- (IV) Reaction with PCI₅ : Carbonyl compounds give gemdihalides

$$>C = O + PCI_5 \rightarrow C \subset CI + POCI_3$$

i)
$$CH_3CH = O + PCI_5 \rightarrow CH_3 - CHCI_2 + POCI_3$$

$$\begin{array}{c} \mathsf{CH}_3\\\mathsf{I}\\\mathsf{CH}_3-\mathsf{C=O}+\mathsf{PCI}_5\xrightarrow{}\mathsf{CI}\\\mathsf{CH}_3-\mathsf{C=O}+\mathsf{PCI}_5\xrightarrow{}\mathsf{CI}\\\mathsf{CI}\\\mathsf{CH}_3-\mathsf{C=O}+\mathsf{PCI}_5\xrightarrow{}\mathsf{CI}\\\mathsf{CI$$

(V) Pinacol-Pinacolon rearrangement :

Pinacol is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.

(ii)

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{$$

Pinacol undergoes rearrangement in acidic media to give pinacolon.

$$(CH_{3})_{2}C \longrightarrow C(CH_{3})_{2} \qquad CH_{3} O \qquad I \qquad II \\ (CH_{3})_{2}C \longrightarrow C(CH_{3})_{2} \qquad CH_{3} - C \longrightarrow C - CH_{3} \qquad I \qquad I \\ OH \quad OH \qquad H^{\oplus} \qquad CH_{3} \qquad CH_{3} \qquad Pinacolone$$

7.6 Oxidation reactions

(I) Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl₂, Br₂ or I₂) in the presence of alkali to give haloform and acid salt.



In this reaction – CH_3 of $CH_3 - C -$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone. Preparation of haloform from methylketone involves two steps.



0

Note : This reaction is used to distinguish the presence of $CH_3 - C^{-}$ group.

(II) Oxidation of Aldehydes :

Aldehydes are oxidised to carboxylic acids by common oxidising agents such as KMnO₄, HNO₃, K₂Cr₂O₇, etc.

 $\mathsf{R-CHO} \xrightarrow{[\mathsf{O}]} \mathsf{RCOOH}$

- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On the other hand, ketones are not oxidised by mild oxidising agents.
- Ketones are oxidised under vigorous conditions, i.e., by strong oxidising agents and at elevated temperatures.

It involves carbon-carbon bond cleavage.

 $\begin{array}{c} \begin{array}{c} 1 \\ R-CH_2-C_2-C_1-CH_2-R' \\ 0 \end{array} \xrightarrow{[0]} \end{array} \begin{array}{c} R-COOH+R'-CH_2COOH \\ (By \ cleavage \ of \ C_1-C_2 \ bond) \end{array} \begin{array}{c} R-CH_2COOH+R'-COOH \\ (By \ cleavage \ of \ C_2-C_3 \ bond) \end{array} \end{array}$

(a) Tollen's reagent :

It is ammonical silver nitrate solution, prepared by adding ammonium hydroxide to AgNO₃ solution. During reaction, first Ag₂O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.

 $\begin{array}{rcl} 2AgNO_{3}+2NH_{4}OH & \longrightarrow & Ag_{2}O+NH_{4}NO_{3}+H_{2}O\\ Ag_{2}O+4NH_{4}OH & \longrightarrow & 2\left[Ag(NH_{3})_{2}\right]OH+3H_{2}O \end{array}$

tollen's reagent

Tollen's reagent is weak oxidising agent. It gives Ag mirror test with aldehyde.

$$\begin{array}{l} \mathsf{R}-\mathsf{CH}=\mathsf{O}+2\mathsf{Ag} \xrightarrow{(\mathsf{NH}_3)_2^{\ominus}} + 3\mathsf{OH}^{\ominus} \longrightarrow \mathsf{RCOO}^{\ominus} & + 2\mathsf{Ag}+2\mathsf{NH}_3+2\mathsf{H}_2\mathsf{O} \\ \\ \mathsf{R}-\mathsf{CH}=\mathsf{O}+\mathsf{Ag}_2\mathsf{O} \longrightarrow \mathsf{R}-\mathsf{COOH}+2\mathsf{Ag} \text{ (Silver mirror)} \end{array}$$

(b) Fehling's solution :

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate. There are two solutions in Fehling solution

Solution (A) CuSO₄ solution and

Solution (B) Alkaline solution of sodium potassiumtartarate.

When these two solutions are mixed we get deep blue coloured solution.

 $\begin{array}{cccc} CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4 \\ HO - CH - COONa \\ & & \\ HO - CH - COOK \\ Cu(OH)_2 + Roschelle salt \longrightarrow (Blue coloured compound) \end{array}$

Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu₂O) which confirms the presence of aldehyde.

$$\begin{array}{cccc} \text{R-CHO} + & \text{Blue} & \longrightarrow & \text{RCOOH} + \text{Cu}_2\text{O} (\text{Red ppt}) \\ & & 2\text{Cu}^{\oplus} \\ \text{RCHO} + 2\text{Cu}^{2+} + 3\text{OH}^{\ominus} & \longrightarrow & \text{RCOO}^{\ominus} + (\text{Red ppt}) + 2\text{H}_2\text{O} \end{array}$$

(c) Benedict solution :

It also consists of two solutions.

Solution (A) CuSO₄ solution and

Solution (B) Alkaline solution of sodium Citrate.

$$\begin{array}{cccc} CuSO_4 + 2NaOH & \longrightarrow & Cu(OH)_2 + Na_2SO_4 \\ & & CH_2COONa & & | \\ & & | \\ & HO - C - COONa & & | \\ & HO - C - COONa & & | \\ & & CH_2COONa \\ & & CH_2COONa \\ & & CH_2COONa \end{array}$$

Aldehyde gives positive test with Benedict solution.

$$2Cu^{2^{+}} \qquad 2Cu^{\oplus} + 2H_2O$$

$$RCH = O + (blue) + 3OH^{\Theta} \longrightarrow RCOO^{\Theta} + (Red ppt.)$$

(d) Schiff's reagent :

It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO₂. Aldehyde restores pink colour when treated with schiff's reagent (Magenta solution in H₂SO₃).

7.7 Other miscellaneous reactions :





(V)

8. Uses of Aldehydes and Ketones

- Act as solvents.
- Act as starting materials and reagents for the synthesis of other products.
- Formalin (40% solution of formaldehyde)- Used for preserving biological specimens manufacturing of bakelite, urea, formaldehyde glues and other polymers products.
- Acetaldehyde used in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde used in perfumery and in dye industries.
- Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- Acetone and ethyl methyl ketone are common industrial solvents.

Section (E) : Preparation and chemical reaction of carboxylic acid Introduction :

Carboxyl carbon is less electrophilic than carbonyl carbon because of resonance.

$$-\overbrace{\overset{{\scriptstyle \bigcirc}}{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \leftarrow}}}^{\scriptstyle \bigcirc}-H} - \overbrace{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \frown}}}^{\scriptstyle \bigcirc}-H} - \overbrace{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \ominus}}}^{\scriptstyle \bigcirc}-H} - \overbrace{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \bigcirc}{\overset{\scriptstyle \ominus}{\overset{\scriptstyle \frown}{\overset{\scriptstyle \leftarrow}}}}^{\scriptstyle \frown}{\overset{\scriptstyle \frown}{\overset{\scriptstyle \leftarrow}}}} - H$$

Bonds to the carboxyl carbon lie in one plane and are separated by about 120°.

9. Preparation of Carboxylic Acid

9.1 From primary alcohols

 $\xrightarrow{1. \text{ Alkaline KMnO}_4} \xrightarrow{2. H_2O^+} \text{RCOOH}$



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CH₂CH₂CH₂COOC₂H₅

Ethyl butanoate

 $CH_{3}CH_{2}CH_{2}COONa + C_{2}H_{5}OH$ $H_{3}O^{\dagger}$

Ex.

10. Physical Properties of Carboxylic acids

- * Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility.
- * Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. 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.

NaOH, CH₃CH₂CH₂COOH

Butanoic acid

- * Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
- * The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
- * Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
- * Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



11. Chemical Reactions of Carboxylic Acids

11.1 Reactions Involving Cleavage of O-H Bond (Acidity of acids)

Reactions with metals and alkalies :

 $\begin{array}{c} 2\text{RCOONa} + \text{H}_2 \\ 2\text{R} -\text{COOH} + 2\text{Na} & \rightarrow \end{array} \\ \text{R-COOH} + \text{NaOH} & \rightarrow \text{R} - \text{COONa} + \text{H}_2\text{O} \\ \text{R-COOH} + \text{NaHCO}_3 & \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \end{array}$

Dissociate in water to give resonance-stabilised carboxylate anions and hydronium ion

$$R - C \stackrel{0}{\longleftarrow} H_{2}O \stackrel{0}{\longleftarrow} H_{3}O^{\oplus} + \left| \begin{array}{c} & & & \\ R - C \stackrel{0}{\longleftarrow} & R - C \stackrel{0}{\longleftarrow} \\ & & \\ OH \end{array} \right| = R - C \stackrel{0}{\bigoplus} \\ = R - C \stackrel{0}{\bigoplus} \\ & \\ OH \\ & \\ O$$

Effects of substituents on the acidity of carboxylic acids



Electron-withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



- The order of the effect of the groups in increasing acidity is Ph < I < Br < CI < F < CN < NO₂ < CF₃
- 11.2 Reactions Involving Cleavage of C–OH Bond (i) Formation of anhydride :



Undergo electrophilic substitution reactions (except Friedel-Craft reaction) COOH COOH



12. Carboxylic Acid Derivatives :

Characteristic reaction of acid deerivatives (Nucleophilic acyl substitution) : Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism. The incoming nucleophile adds to the carbonyl to form a tetrasubstituted intermediate with a tetrahedral carbon.

₿ Nu



The tetrahedral intermediate formed when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative is not stable and cannot be isolated.

A pair of nonbonding electrons on the oxygen reforms the π bond, and either L^{\ominus} or Nu^{\ominus} is eliminated with its bonding electrons. Whether Nu^{\ominus} or Nu^{\ominus} is eliminated depends on their relative basicities. The weaker base is preferentially eliminated because the weaker the base, the better it is a leaving group.

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ R - C - L + Nu \longrightarrow R - C - Nu + L \\ & \uparrow & \uparrow \\ basicity of Nu should & basicity of L should be \\ be more than that of L & less than the basicity of \\ \end{array}$$

Condition for acyl nucleophilic substitution reaction :

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ R - C - L + Nu \longrightarrow R - C - Nu + L \\ \end{array}$$

(i) L must be better leaving group than Nu^{\ominus} , i.e., basicity of Nucleophile must be more than that of $\overset{\Theta}{L}$ (Leaving group).

(ii) Nu must be a strong enough nucleophilic to attack RCOL.

(iii) Carbonyl carbon must be enough electrophilic to react with Nu.

Reactivity:

Example :

(i) CH₃COOH + C₂H₅OH
$$\xrightarrow{H}$$
 CH₃COOC₂H₅ + H₂O
Ethyl acetate
(ii) C₆H₅COOH + CH₃OH $\xrightarrow{H^+}$ C₆H₅COOCH₃ + H₂O
Methyl benzoate
(iii) CH₃-C-NH₂ + Br₂ + NaOH \longrightarrow $\xrightarrow{CH_3-NH_2}$ + Na₂CO₃
It is a Hoffmann Bromide reaction.
(iv) CH₃COCI + C₂H₅OH $\xrightarrow{Pyridine}$ CH₃COOC₂H₅ + HCI
Ethyl acetate
(v) CH₃-C-OC₂H₅ $\xrightarrow{CH_3-NH_2}$ H⁺ CH₃-C-NH-CH₃ + C₂H₅OH
N-Methyl acetamide
 $\xrightarrow{CH_3-C}$ + NH₃ \longrightarrow CH₃-C-NH₂ + CH₃-C-OH
Ethanamide

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