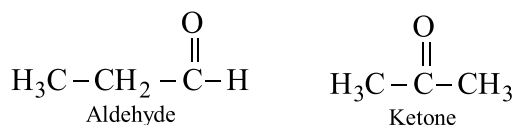# 12

Organic Compounds with Functional Group Containing Oxygen (Part-2)

12.1 Aldehyde and Ketone

Aldehydes and Ketones are hydrocarbon derivatives, which contain carbonyl group $\diagup C = O$. In aldehydehyds, oxygen atom is attached to primary carbon atom whereas in ketones oxygen atom is attached to secondary carbon atom.

$$\underset{\text{Aldehyde}}{H_3C - CH_2 - \overset{O}{\overset{||}{C}} - H} \qquad \underset{\text{Ketone}}{H_3C - \overset{O}{\overset{||}{C}} - CH_3}$$
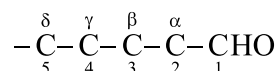
In aldehydes, carbonyl carbon is attached to alkyl or aryl group on one side and on the other side to hydrogen. In ketones carbonyl carbon is attached to alkyl/aryl groups on both side. In aldehyde, functional group present is , it is called aldehyde group. It is always present at the end of carbon chain. Ketonic groups is always present in the middle of the chain. In ketone if both the groups attached to carbonyl group are same, then it is known as simple ketones and if both the groups are different then it is called mixed ketone. The general formula for both aldehyde and ketones is $C_nH_{2n}O$.

12.1.1 Nomenclature

(I) Aldehydes– In the common system of nomenclature of aldehyde the name of aldeydes are derived from the name of corresponding alcohols (obtained by their oxidation) by replacing the ending 'ic acid' with 'aldehyde'. In substituted aldehydes, position of substituents is indicated by Greek letters α, β, γ, δ, ... etc. The carbon atom attached directly with aldehyde group –CHO, is indicated 'α', the next is 'β' and so on.

$$-\underset{5}{\overset{\delta}{C}} - \underset{4}{\overset{\gamma}{C}} - \underset{3}{\overset{\beta}{C}} - \underset{2}{\overset{\alpha}{C}} - \underset{1}{CHO}$$

In IUPAC system of nomenclature, aliphatic aldehyes are called 'alkanal'. It is derivd from the name of corresponding alkanes by replacing the ending 'e' with 'al'. For writing alkane IUPAC name, the longest carbon chain containing carbon atom of aldehyde group is selected. If substituent is present in carbon chain then its position is indicated by number (1, 2, ...). If more than one substituents are present then the name of substitutents are indicated in alphabetical order along with numericals.
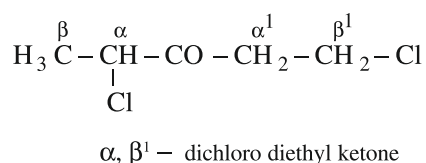
The numbering of the parent chain is done in such a way that the carbon atom of aldehyde group gets minimum number (1). The common and IUPAC name of some aldehydes are given below in table 12.1.

Table 12.1

Formula	Corresponding acid	General Name	IUPAC Name
$HCHO \xrightarrow{\text{O}}$	$\underset{\text{formic acid}}{HCOOH}$	formaldehyde	methanal
$CH_3CHO \xrightarrow{\text{O}}$	$\underset{\text{acetic acid}}{CH_3COOH}$	acetaldehyde	ethanal

|			
$CH_3CH_2CHO \xrightarrow{O}$	CH_3CH_2COOH propionic acid	propionaldehyde	propanal
$CH_3CH_2CH_2CHO \xrightarrow{O}$	$CH_3CH_2CH_2COOH$ butyric acid	butyraldehyde	butanal
$(CH_3)_2CHCHO \xrightarrow{O}$	$(CH_3)_2CH-COOH$ Iso butyric acid	isobutyraldehyde	2-methyl propanal
$CH_3-CH_2-\overset{\alpha}{C}H-CHO \xrightarrow{O}$ $\qquad\qquad\quad CH_3$	$CH_3-CH_2-\overset{\alpha}{C}H-COOH$ $\qquad\qquad\quad CH_3$ α–methyl butyric acid	α–methyl butyraldehyde	2-methyl butanal
$CH_3-\overset{\beta}{C}H-\overset{\alpha}{C}H_2-CHO \xrightarrow{O}$ $\qquad\quad CH_3$	$H_3C-CH_2-\overset{\beta}{C}H-\overset{\alpha}{C}H_2-COOH$ $\qquad\qquad\qquad CH_3$ β–methyl butyric acid	β–methyl butyraldehyde	3-methyl butanal

(II) Ketones : In the common system of nomenclature simple ketones are named as dialkyl ketones. Mixed ketones are named as alkyl alkyl ketones. The names of groups are written alphabetically. In substituted ketones the position of substituents are indicated by Greek letters α, β, γ, δ,....etc. The carbon atom next to ketonic carbonyl group is indicated as α and so on. For example–

$$H_3\overset{\beta}{C}-\overset{\alpha}{C}H-CO-\overset{\alpha^1}{C}H_2-\overset{\beta^1}{C}H_2-Cl$$
$$\qquad\; Cl$$

$$\alpha, \beta^1 - \text{ dichloro diethyl ketone}$$

In IUPAC nomenclature, ketones are known as alkanones. First of all, longest carbon chain of ketone is selected, containing ketonic group. The numbering of the chain being done in such a way that the corbony carbon atom gets the lowest number. The name of ketone is given by replacing 'e' of the name of corresponding alkane by 'one'. In substituted ketones, the parent chain containing the keto group is selected. The numbering of the chain being done in such a way that the carbon atom of the keto group gets the lowest number. Other substituents, present on the chain are named alphabetically. The common and IUPAC name of ketones containing three, four and five carbon atoms are given below.

Formula	General Name	IUPAC Name
$CH_3\,CO\,CH_3$	dimethyl ketone/acetone	Propanone
$CH_3-CH_2-\underset{O}{\overset{\|\|}{C}}-CH_3$	ethyl methyl ketone	butanone
$CH_3-CH_2-CH_2-\underset{O}{\overset{\|\|}{\overset{2}{C}}}-\overset{1}{C}H_3$	methyl propyl ketone	pent-2-one
$CH_3-CH_2-\underset{O}{\overset{\|\|}{\overset{3}{C}}}-\overset{2}{C}H_2-\overset{1}{C}H_3$	diethyl ketone	pent-3-one
$CH_3-\overset{3}{C}H-\underset{O}{\overset{\|\|}{\overset{2}{C}}}-\overset{1}{C}H_3$ $\qquad\; CH_3$	isopropyl methyl ketone	3-methyl but-2-one

Nature of carbonyl group– In carbony group

 the electronegativity of oxygen atom is much higher than hydrogen atom so the electron cloud of π electrons is shifted towards oxygen atom. Therfore, carbon oxygen bond becomes polar in nature. There is partial positive charge on carbon atom and partial negative charge on oxygen atom.
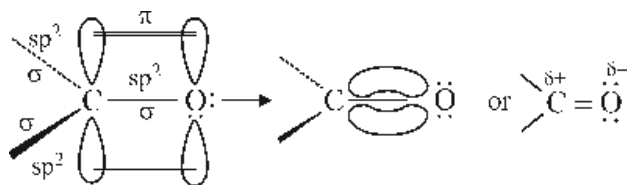
Thus the carbonyl group is the resonance hybrid of two structures.
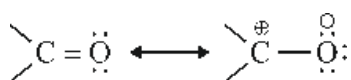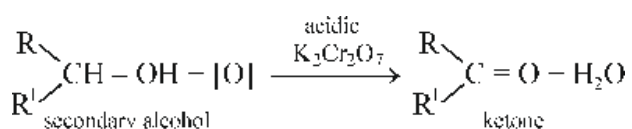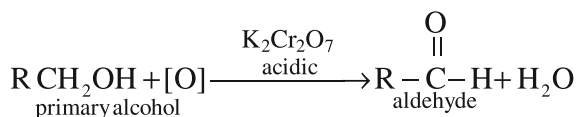

The polarity of carbonyl group is reflected from their dipole moments also. Carbonyl compounds (aldehydes and ketones) have substantial dipole moments (ie. 2.3-2.8D)

Thus, due to polarity, carbonyl carbon behaves as electrophilic centre and carbonyl oxygen as nucleophilic center.

12.1.2 Methods of synthesis

(I) The methods of synthesis of both aldehydes and ketones are as follows–

1. **By oxidation of alcohols:** Aldehydes are obtained by oxidation of primary alcohols and ketones are obtained by oxidation of secondary alcohols. The common oxidising agents used for oxidation are acidified $K_2Cr_2O_7$, aqueous or alkaline $KMnO_4$.

$$R\,CH_2OH + [O] \xrightarrow[\substack{acidic}]{K_2Cr_2O_7} \underset{aldehyde}{R-\overset{\overset{O}{\|}}{C}-H} + H_2O$$

$$\underset{secondary\ alcohol}{\overset{R}{\underset{R^I}{>}}CH-OH - |O|} \xrightarrow[\substack{K_2Cr_2O_7}]{acidic} \underset{ketone}{\overset{R}{\underset{R^I}{>}}C=O - H_2O}$$

The aldehydes formed in the reaction gives carboxylic acid on further oxidation. Therefore, to obtain high yield of aldehyes by oxidation of primary alcohols, another catalyst PCC (Pyridinium Chloro chromate $CrO_3.C_5H_5N.HCl$) is used. This catalyst prevents further oxidation of aldehydes to carboxylic acid.

$$R-CH_2-OH \xrightarrow[\substack{K_2Cr_2O_7\\acidic}]{PCC} R-CHO$$
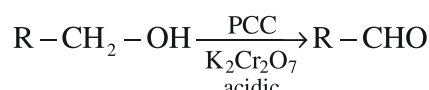
Oppenauer Oxidation: By this method secondary alcohols are oxidised to ketones. (so that ketones not give carboxylic acid on further oxidation). Secondary alcohols are treated with aluminium-t-butoxide in presence of excess of acetone. 2° alcohols are oxidized to ketone and acetone reduce to isopropyl alcohol.
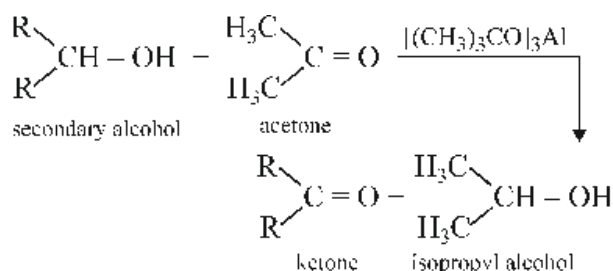
2. **By catalytic dehydrogenation of alcohols:** The dehydrogenation of alcohols is carried out by passing the vapour of primary and secondary alcohols over heated copper at 573K temperature. Primary alcohols give aldehydes and secondary alcohols give ketones.

$$\underset{\substack{ethanol\\(primary\ alcohol)}}{H_3C-CH_2-OH} \xrightarrow{Cu/573K} \underset{ethanal}{CH_3-CHO} + H_2$$
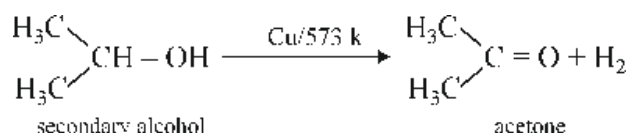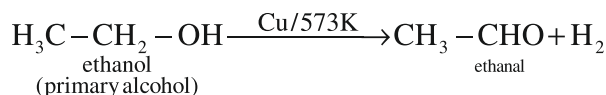
3. **By dry distillation of Calcium salts of alkanoic acids:**

(i) Dry distillation of calcium formate gives for maldehyde.

252
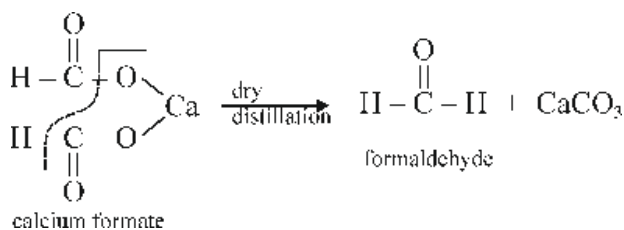
(ii) Dry distillation of mixture of calcium formate and calcium alkanoate gives mainly aldehydes. (other than formaldehyde)
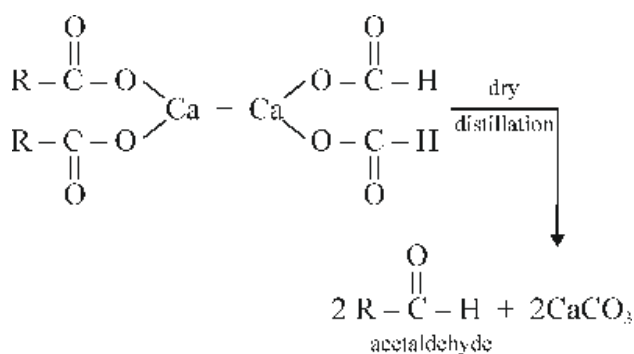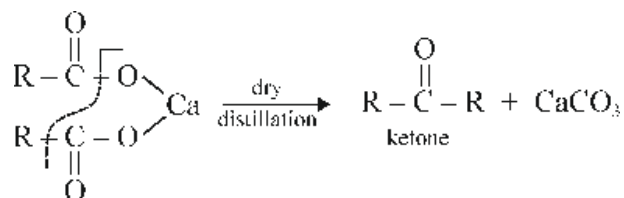

(iii) Dry distillation of calcium alkanoate, other than calcium formate, give ketones.

4. **By ozonolysis of alkenes:** Alkenes react with ozone to form ozonide. Hydrolysis of ozonide in the presence of Zn dust gives aldehydes and ketones. Etheylene gives formaldehyde, symmetrically disubstituted alkenes give other aldehydes and tetrasubstituted alkenes give ketones.

$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$
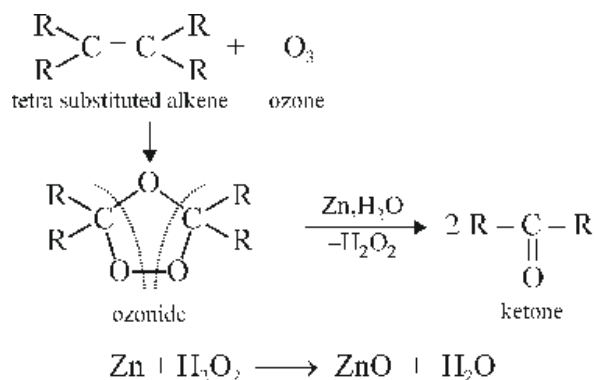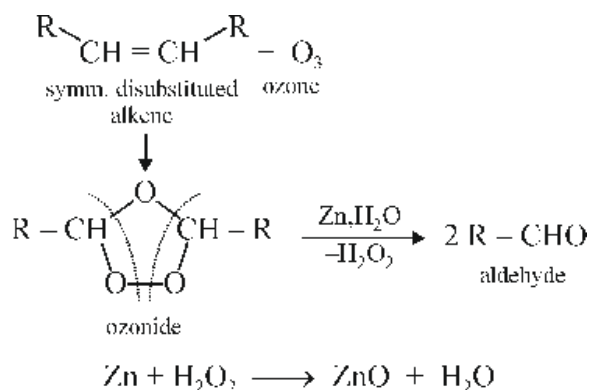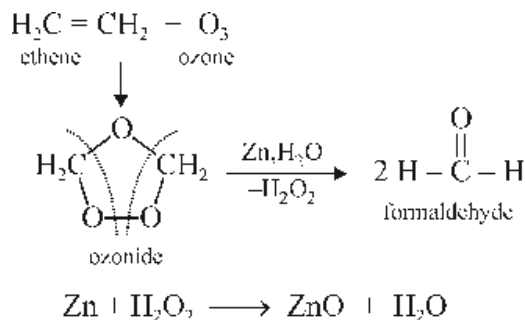
5. **By hydration of alkynes:** In the presence of dil and hot H_2SO_4 and mercurous sulphate $HgSO_4$, alkynes add on a water molecule to give aldehydes and ketones.
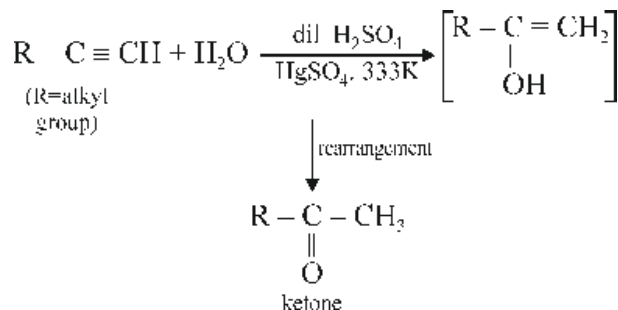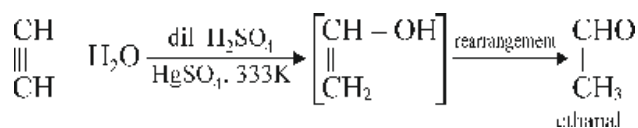
(5) **By Grignard reagents:** Aldehydes and ketones can be prepared with the help of Grignard reagents.

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(I) Synthesis of aldehydes:

(i) By reaction of ethyl formate: One molecule of ethyl formate reacts with one molecule of Grignard reagent and form aldehyde.
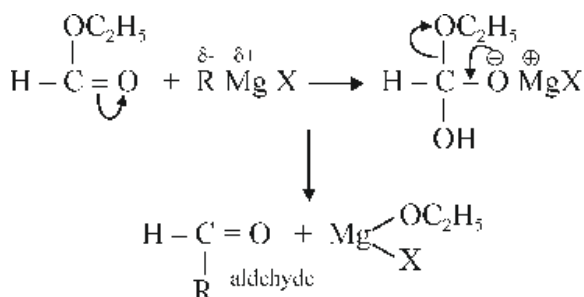
(ii) By reaction with hydrogen cyanide: HCN reacts with Grignard reagent to form an addition product, which on hydrolysis gives aldehyde.
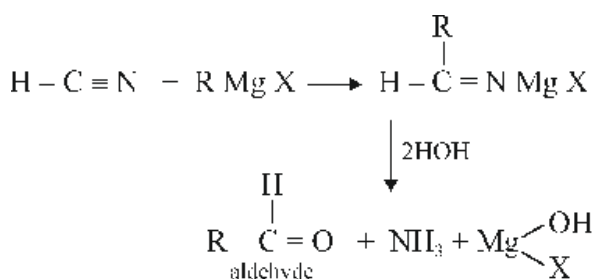
(II) Synthesis of Ketones:

(i) By reaction of Ethyl ester: One molecule of esters of an acid other than formic acid and one molecule of Grignard reagent react with each other and gives ketones.
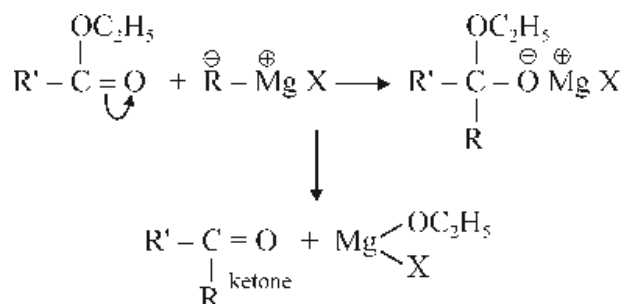
(ii) Reaction with alkyl cyanide: $R - C \equiv N$ reacts with Grignard reagent to form an addition product, which on hydrolysis gives ketone.
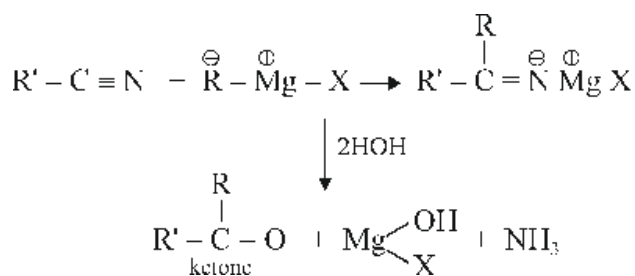
(iii) Reaction with alkanoyl chloride:
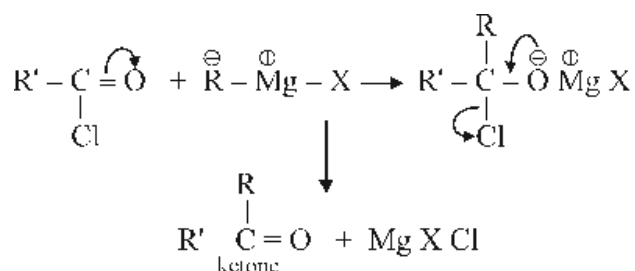
(iv) Reaction with alkanamide:
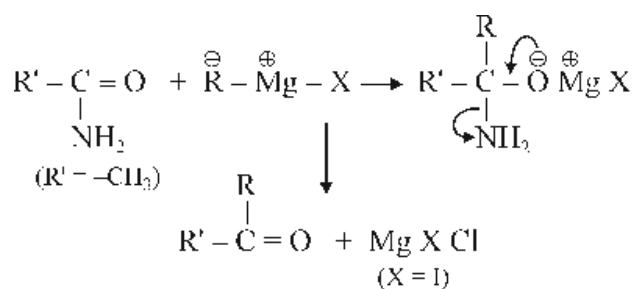
6. By Nitroalkanes (Nef reaction)

Nitroalkanes react with base to form salts, which on hydrolysis by strong acids (H_2SO_4, HCl or HNO_3) give carbonyl compounds. Primary nitroalkanes give alkdehyde and secondary nitroalkanes give ketones.

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$$\underset{\substack{\text{2-nitromethane}\\ \text{(secondary nitroalkane)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-NO_2}-NaOH \xrightarrow{-H_2O} \underset{\substack{\text{sodium salt of}\\ \text{2-nitro propane}}}{Na-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-NO_2}$$

$$\Big\downarrow [O]/H_2SO_4$$

$$\underset{\text{acetone (ketone)}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

7. By hydrolysis of gem dihalides:

On hydrolysis with aqueous KOH, gem dihalides give aldehydes or ketones.

$$\underset{\substack{\text{ethylidene}\\ \text{chloride}}}{CH_3-CH\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{<}}} + 2KOH \xrightarrow[\text{(aq.)}]{-2KCl} \underset{\text{unstable}}{\left[CH_3-CH\overset{\displaystyle OH}{\underset{\displaystyle OH}{<}}\right]}$$

$$\Big\downarrow H_2O$$

$$\underset{\text{acetaldehyde}}{CH_3-CHO}$$

$$\underset{\substack{\text{isopropylidene}\\ \text{chloride}}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{<}}} + 2KOH \xrightarrow[\text{(aq.)}]{-2KCl} \underset{\text{unstable}}{\left[\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C\overset{\displaystyle OH}{\underset{\displaystyle OH}{<}}\right]}$$

$$\Big\downarrow -H_2O$$

$$\underset{\text{acetone}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C=O}$$

8. By oxidation of Glycol:

When oxidation of glycol is carried out in the presence of periodic acid (HIO_4) or lead tetraacetate, it give aldehydes or ketones.

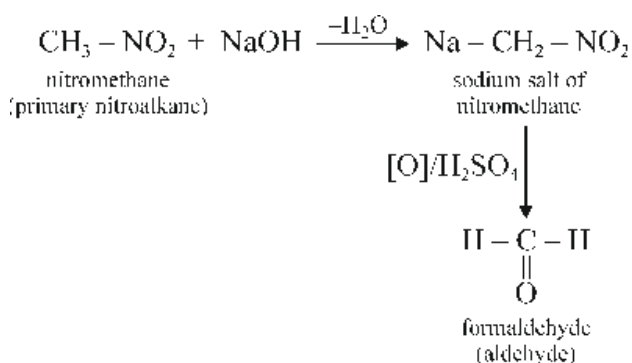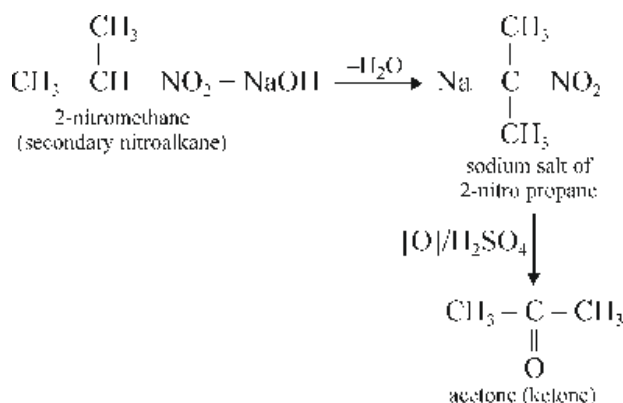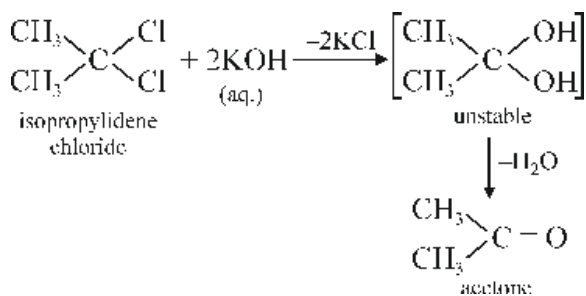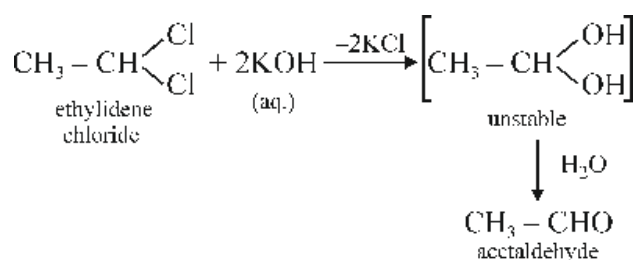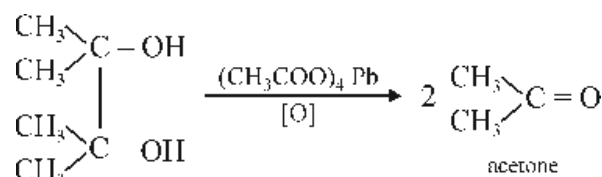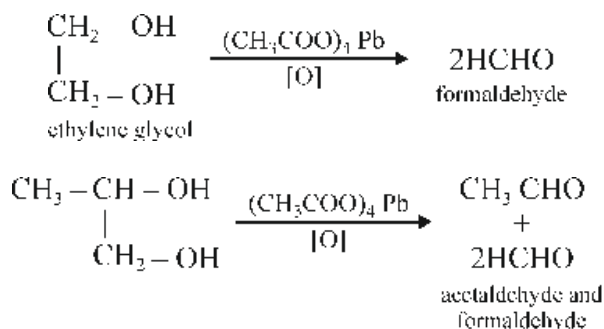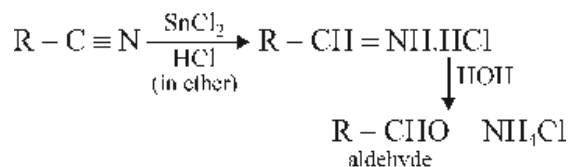$$\underset{\text{ethylene glycol}}{\overset{\displaystyle CH_2-OH}{\underset{\displaystyle CH_2-OH}{|}}} \xrightarrow[{[O]}]{(CH_3COO)_4Pb} \underset{\text{formaldehyde}}{2HCHO}$$

$$\underset{\substack{}}{CH_3-\overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle CH_2-OH}{|}}{CH}}-OH} \xrightarrow[{[O]}]{(CH_3COO)_4Pb} \underset{\substack{\text{acetaldehyde and}\\ \text{formaldehyde}}}{\begin{array}{c}CH_3 CHO\\ +\\ 2HCHO\end{array}}$$

$$\underset{\substack{}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}\overset{\displaystyle }{\underset{\underset{\displaystyle \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C-OH}{|}}{C-OH}}} \xrightarrow[{[O]}]{(CH_3COO)_4Pb} \underset{\text{acetone}}{2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C=O}$$

Methods of preparation of only aldehydes:

1. By reduction of alkane nitrile (Stephen's reaction):
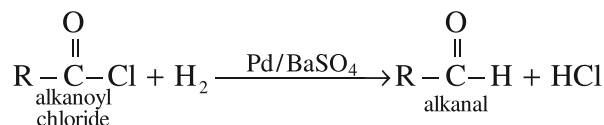
Alkane nitriles are reduced with stannous chlorides and hydrochloric acid ($SnCl_2 + HCl$) in the presence of ether to form corresponding aldimines. Aldimines give aldehydes on hydrolysis. This reaction is known as **Stephen's reaction**.

$$R-C\equiv N \xrightarrow[\substack{HCl\\ \text{(in ether)}}]{SnCl_2} R-CH=NH.HCl$$

$$\Big\downarrow HOH$$

$$\underset{\text{aldehyde}}{R-CHO} \quad NH_4Cl$$

2. By the reduction of alkanoyl chloride (Rosenmund's Reduction):

When hydrogen is bubbled through a heated suspension of the catalyst ($Pd/BaSO_4$) in a xylene solution of alkanoyl chloride ($R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$), it is reduced to give aldehydes. This catalytic hydrogenation of acid chlorides is knwon as **Rosenmund reduction**.

$$\underset{\substack{\text{alkanoyl}\\ \text{chloride}}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{alkanal}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$
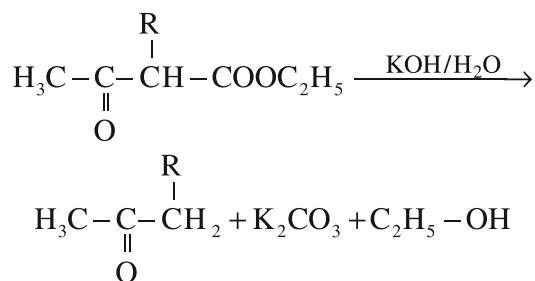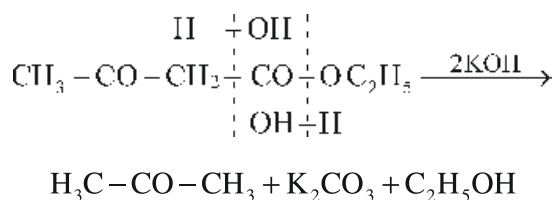
Formaldehyde cannot be prepared by this method because HCOCl is unstable at room temperature.

Generally, aldehydes on further reduction give primary alcohols, but here $BaSO_4$ acts as a poison for Pd and prevent further reduction of aldehydes to alcohols.
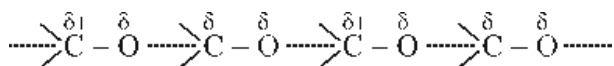
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Method of preparation of only Ketones:

1. **By ketonic hydrolysis of acetoacetic ester or its alkyl derivatives:** Acetoacetic ester or its alkyl derivatives are heated with dilute bases to give ketones on ketonic hydrolysis.

$$CH_3-CO-CH_2 \overset{\overset{\text{H}}{|} \; \overset{\text{OH}}{|}}{\vdots} \; CO \overset{\text{}}{\vdots} O \; C_2H_5 \; \overset{\overset{\text{}}{|} \; \overset{\text{H}}{|}}{\xrightarrow{2KOH}}$$

$$H_3C-CO-CH_3 + K_2CO_3 + C_2H_5OH$$

$$\underset{\overset{\|}{O}}{H_3C-\overset{\overset{\text{R}}{|}}{C}-CH-COOC_2H_5} \xrightarrow{KOH/H_2O}$$

$$\underset{\overset{\|}{O}}{H_3C-\overset{\overset{\text{R}}{|}}{C}-CH_2} + K_2CO_3 + C_2H_5-OH$$

12.1.3 Physical properties of aldehyde and ketone:

1. **Physical state:** Formaldehyde is a gas. Lower members of aldehydes and ketones are colourless volatile liquid. Higher members of aldehydes and ketones (above C_{11}) are solids.

2. **Odour:** The lower members of aldehydes have unpleasant smell but higher aldehydes smell like fruits. Ketones are liquid with pleasant odour. These are used in perfumes.

3. **Boiling point:** In aldehydes and ketones polar carbonyl group is present. Thus, strong dipole-dipole interaction is present between $>C=O$ dipoles of its molecules.

$$----\overset{\delta+}{\underset{}{>}}\overset{}{C}-\overset{\delta-}{O}----\overset{\delta+}{>}\overset{}{C}-\overset{\delta-}{O}----\overset{\delta+}{>}\overset{}{C}-\overset{\delta-}{O}----\overset{\delta+}{>}\overset{}{C}-\overset{\delta-}{O}-------$$
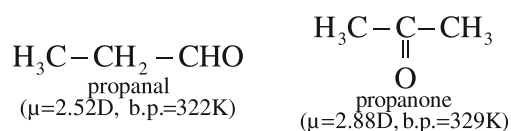
Due to this type of intermolecular association, the boiling point of aldehydes and ketones are higher than hydrocarbons of comparable molecular mass.

Compound : n-butane butanal butanol
b.b.(K) : 309 349 391

Intermolecular attraction force between molecules of carbonyl compounds is less than hydrogen bonding between molecules in alcohols. Therefore carbonyl compounds have lower boiling point than alcohols. Among isomeric aldehydes and ketones, ketones have higher boiling point as compare to aldehydes.

$$\underset{\substack{\text{propanal} \\ (\mu=2.52D, \; b.p.=322K)}}{H_3C-CH_2-CHO} \qquad \underset{\substack{\text{propanone} \\ (\mu=2.88D, b.p.=329K)}}{\underset{\overset{\|}{O}}{H_3C-C-CH_3}}$$

In general, as molecular masses of aldehydes and ketones increases, boiling point also increases.

4. **Solubility:** The lower members of carbonyl compounds (up to four carbon atoms) are miscible in water. There solubility in water is due to the formation of hydrogen bond between polar carbonyl group and water molecules.
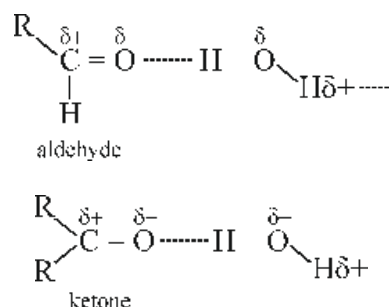
As the molecular mass increases the size/number of alkyl groups attached to carbonyl group increases and its solubility in water decreases. Carbonyl compounds having C_5 and above carbon atoms are less soluble or insoluble in water. These are completely soluble in organic solvents like alcohols, ethers, etc.

12.1.4 Chemical properties of aldehyde and ketone

The chemical reactions of carbonyl compounds can be classfied in following groups:

[A] Nucleophilic addition reactions

[B] Nucleophilic addition elimination reactions

[C] Oxidation, Reduction and Halogenation

[D] Reactions shown by aldehydes only

[E] Reactions shown by ketones only

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[A] Nucleophilic addition Reactions

Nuclophilic addition reactions are the important reactions given by aldehydes and ketones. We know that carbonyl group is a polar group. Electronegativity of oxygen atom is more than carbon atom. Hence in carbonyl group, oxygen atom is partially negatively charged and carbon atom is partialy positively charged. when reaction of polar reagents is carried out with carbonyl compounds, in the first step, nucleophilic part (Nu⁻) of polar reagents attack on carbon atom of carbonyl group and form anion (intermediate).

The intermediate thus formed is stable due to presence of negative charge on more electronegative oxygen atom.

In second step electrophilic part (E⁺) of regent adds on oxygen atom and thus the reaction is completed.

(stable)
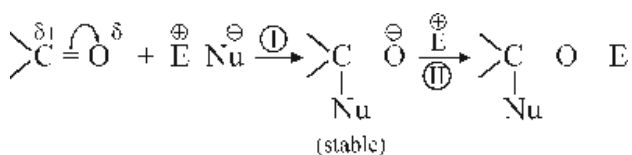
The reaction with strong nucleophile is irreversible and proceed in the direction of products. The reaction with weak nucleophiles is carried out in acidic medium. In the presence of acid, the oxygen atom of carbonyl group gets protonised and this increases the positive charge on carbon atom. As a result, weak electrophiles easily attack on carbon atom of carbonyl group.
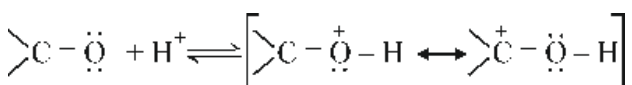

Relative reactivity of aldehydes and ketones:

Aldehydes are more reactive than ketones towards nucleophilic addition reactions. The more reactivity of aldehydes than ketones can be explained on the basis of following–

1. **Inductive effect:** The attack of nucleophile on carbonyl group is easy when positive charge on carbonyl carbon is more i.e. carbon is electron dificient in carbonyl group.

   The alkyl group has electron donating inductive effect (+I effect) therefore as a number of alkyl groups on the carbonyl group increases, density of electrons on carbon atom of carbonyl group increases, which decreases the reactivity towards nucleophilic addition reactions. The number of alkyl groups on carbonyl group in ketones are more as compared to aldehydes, hence aldehydes are more reactive towards nucleophilic addition reactions.
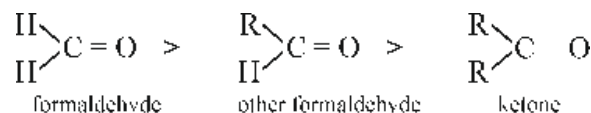

2. **Steric effect:** There is no alkyl group is attached to carbonyl carbon of formaldehyde and in other aldehydes only one and in ketones two alkyl groups are present on carbonyl carbon. As the number and size of alkyl group increases, attack of nucleophile on carbon atom of carbonyl group become difficult due to steric hinderance. In other words, we can say that as the steric hinderance increases, reactivity decreases.
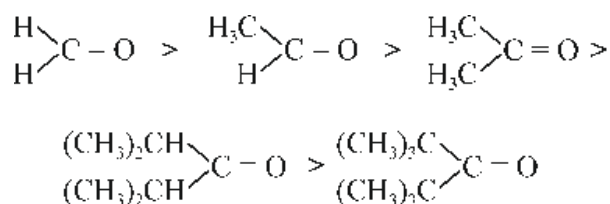
Some of the important nucleophilic addition reactions of aldehydes and ketones are-

(i) **Addition of sodium bisulphite:** Aldehydes and ketones when treated with sodium bisulphite form crystalline bisulphite addition products.

carbonyl compound   sodium bisulphite   sodium bisulphite addition product
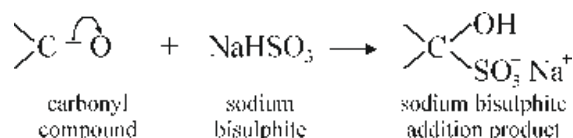
When addition product is heated with dil acid or sodium carbonate, it can be converted back to the original aldehydes and ketones so these reactions are useful for separation of aldehydes and ketones from other organic compounds.

(ii) **Addition of hydrogen cyanide:** When reaction of aldehydes and ketones is carried out with sodium cyanide and dilute suphuric acid, one

molecule of hydrogen cyanide adds to carbonyl group to yield cyanohydrin.

$$>C = O \;+\; H—CN \longrightarrow\; >C\!\!<^{OH}_{CN}$$

cyanohydrin

$$CH_3—\overset{\overset{O}{\|}}{C}—H \;+\; H—CN \longrightarrow\; H_3C—\overset{\overset{OH}{|}}{\underset{\underset{CN}{|}}{C}}—H$$

acetaldehyde cyanohydrin

$$\overset{H_3C}{\underset{H_3C}{>}}C = O \;+\; HCN \longrightarrow\; \overset{H_3C}{\underset{H_3C}{>}}C\!\!<^{OH}_{CN}$$

acetone cyanohydrin
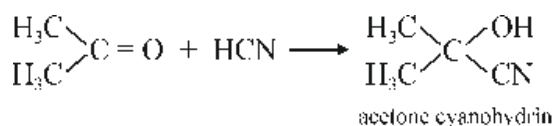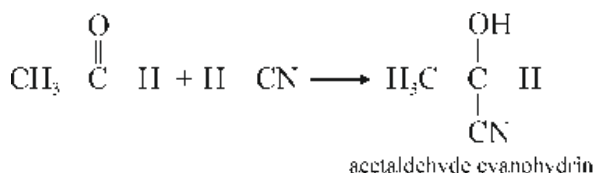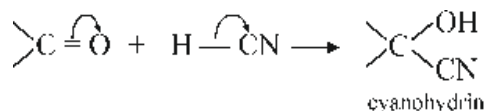
Cyanohydrins are important compounds. These can be easily hydrolysed to give α- hydroxy acids.

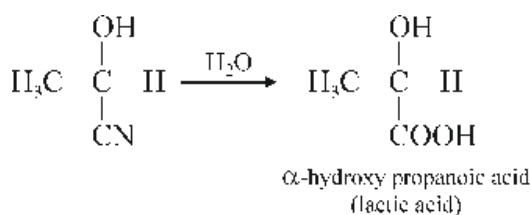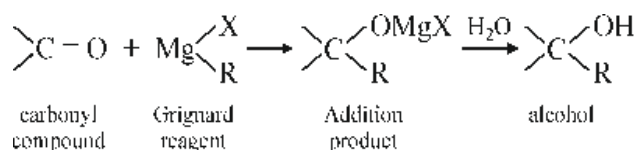$$H_3C—\overset{\overset{OH}{|}}{\underset{\underset{CN}{|}}{C}}—H \;\xrightarrow{H_2O}\; H_3C—\overset{\overset{OH}{|}}{\underset{\underset{COOH}{|}}{C}}—H$$

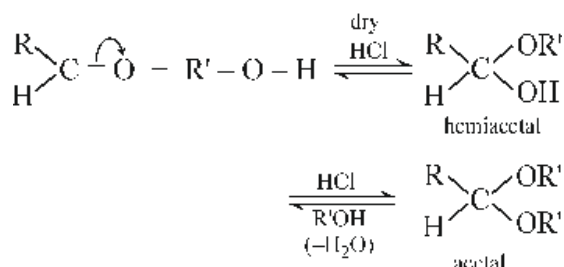α-hydroxy propanoic acid (lactic acid)

(iii) **Addition of Grignard reagent:** The reaction of Grignard reagents with carbonyl group gives an addition product which on hydrolysis gives alcohols.

$$>C - O \;+\; Mg\!\!<^{X}_{R} \longrightarrow\; >C\!\!<^{OMgX}_{R} \;\xrightarrow{H_2O}\; >C\!\!<^{OH}_{R}$$

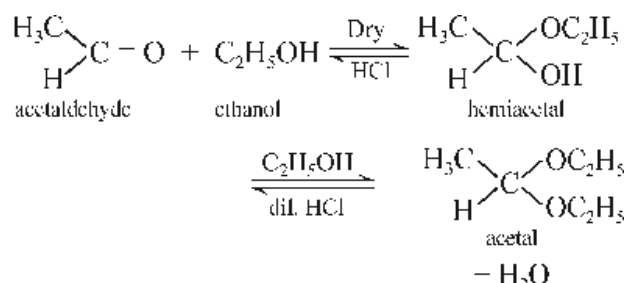carbonyl compound   Grignard reagent   Addition product   alcohol

These reactions are discussed earlier in the preparation methods of alcohols.
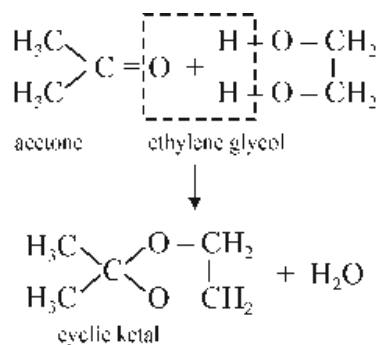
(iv) **Addition of Alcohols : formation of acetal and Ketal:** Aldehydes react with one molecule of alcohols in the presence of dry HCl gas to first form hemiacetal. It is being unstable, immediately reacts with another molecule of alcohol and form acetal.

$$\overset{R}{\underset{H}{>}}C\!-\!O \;-\; R'—O—H \;\xrightleftharpoons{dry\;HCl}\; \overset{R}{\underset{H}{>}}C\!\!<^{OR'}_{OH}$$

hemiacetal

$$\xrightleftharpoons[R'OH\;(-H_2O)]{HCl}\; \overset{R}{\underset{H}{>}}C\!\!<^{OR'}_{OR'}$$

acetal

It is reversible reaction. In the presence of dilute acid, acetal decomposes to yield aldehyde again.

$$\overset{H_3C}{\underset{H}{>}}C\!-\!O \;+\; C_2H_5OH \;\xrightleftharpoons{Dry\;HCl}\; \overset{H_3C}{\underset{H}{>}}C\!\!<^{OC_2H_5}_{OH}$$

acetaldehyde   ethanol   hemiacetal

$$\xrightleftharpoons[dil.\;HCl]{C_2H_5OH}\; \overset{H_3C}{\underset{H}{>}}C\!\!<^{OC_2H_5}_{OC_2H_5}$$

acetal
$$- H_2O$$

Ketones do not react with monohydric alcohols but react with dihydric alcohols to give cyclic ketals.

$$\overset{H_3C}{\underset{H_3C}{>}}C = O \;+\; \begin{array}{c} H—O—CH_2 \\ | \\ H—O—CH_2 \end{array}$$

acetone   ethylene glycol

$$\downarrow$$

$$\overset{H_3C}{\underset{H_3C}{>}}C\!\!<^{O—CH_2}_{O—CH_2} \;+\; H_2O$$

cyclic ketal

**[B] Nucleophilic addition elimination reactions–**
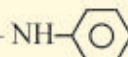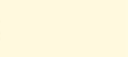
Carbonyl compounds react with a number of ammonia derivatives (H_2N-G) in the presence of catalyst to form addition products, from which one molecule of water is removed and final product is obtained. Overall reaction is as follows:

$$>C - O \;\xrightarrow{H_2N-G}\; >C - N - G \quad H_2O$$
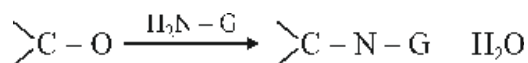
Actually, first the reagents add to the carbonyl group.

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$$>C - O + H_2N - G \rightleftharpoons \left[>C < {}^{OH}_{NHG} \right]$$

$$\downarrow H^+$$

$$>C - NG \quad H_2O$$
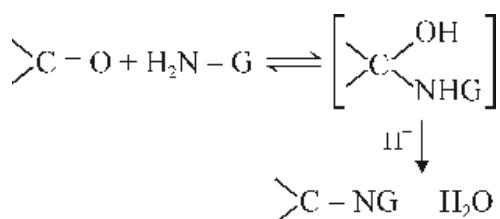
Some important structure and name of ammonia derivatives and their products are given below:

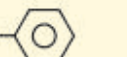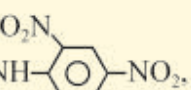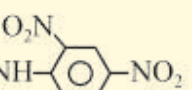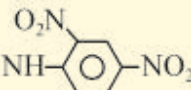| Ammonia derivatives		Product	
Formula (H$_2$N–G)	name	Formula	name*
NH$_2$OH, G = – OH	hydroxyl amine	$>C = N – OH$	oxime
NH$_2$– NH$_2$, G = – NH$_2$	hydrazine	$>C = N – NH_2$	hydrazone
NH$_2$– NH–⬡, G = – NH–⬡	phenyl hydrazine	$>C = N – NH$–⬡	phenyl hydrazone
NH$_2$– NH–⬡–NO$_2$, G = –NH–⬡–NO$_2$ (with O$_2$N)	2,4-dinitro phenyl hydrazine	$>C = N – NH$–⬡–NO$_2$ (with O$_2$N)	2,4-dinitro phenyl hydrazone
NH$_2$– CO – NHNH$_2$, G = –NH–CO–NH$_2$	semicarbazide	$>C = N – NHCONH_2$	semi carbazone

[* in writing the name of product, first write the name of aldehyde or ketone and then write the name written in column (iv)]

The products obtained by reaction of aldehydes and ketones with ammonia derivatives are crystalline solids. These are used to identify aldehydes and ketones. These products decompose to original carbonyl compounds when heated with dil mineral acid. Therefore, these are used in purification of aldehydes and ketones.
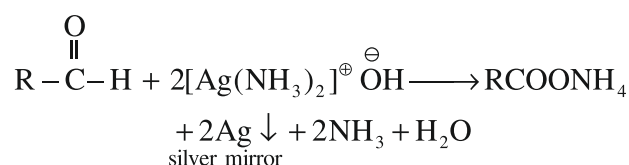
[C] **Oxidation**

(1) **Oxidation of Aldehydes:** Aldehydes are easily oxidised to carboxylic acid containing the same number of carbon atoms. Some common oxidizing agents used for oxidation are- KMnO$_4$, K$_2$Cr$_2$O$_7$ (acidic), bromine water, Ag$^+$, Cu^{2+} etc. In aldehydes, hydrogen atom is attached to carbonyl group, which easily oxidize to -OH group.

$$\overset{O}{\underset{\|}{R – C – H}} + [O] \longrightarrow \overset{O}{\underset{\|}{R – C – O – H}}$$
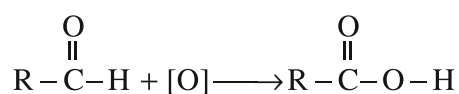
Thus, aldehydes are used as strong reducing agents. They reduce Tollen's reagent and Fehling solution. These reactions are used to identify or test of aldehydes.

(i) **Reduction of Tollen's reagent:** Tollen's reagent is an ammonical solution of silver ntirate. The reagent is prepared by adding sodium hydroxide solution to silver nitrate solution, by this Ag$_2$O is precipitated. This precipitate is dissolved in NH$_4$OH solution. When any alphatic or aromatic aldehyde is warmed with Tollen's reagent, then it is reduced to silver metal. This silver metal deposits on the walls of test tubes and appears as silver mirror so this test is also known as **silver mirror test**. Some times this silver metal do not form silver mirror but precipitated out. Main reaction involved in the test is as follows-
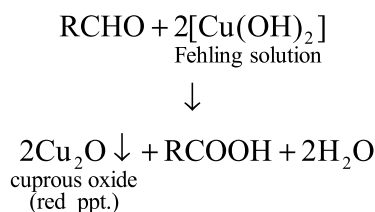
$$\overset{O}{\underset{\|}{R – C – H}} + 2[Ag(NH_3)_2]^{\oplus} \overset{\ominus}{OH} \longrightarrow RCOONH_4$$
$$+ 2Ag \downarrow + 2NH_3 + H_2O$$
$$\underset{\text{silver mirror}}{}$$

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(ii) **Reduction of Fehling solution:** Fehling solution comprises of two solutions, Fehling solution A and Fehling solution B.
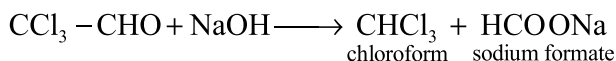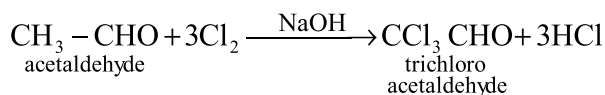
Fehling solution A: It is aqueous solution of copper sulphate.

Fehling solution B: It is colourless aqueous solution of Rochelle salts (sodium potassium tartrate) and sodium hydroxide.
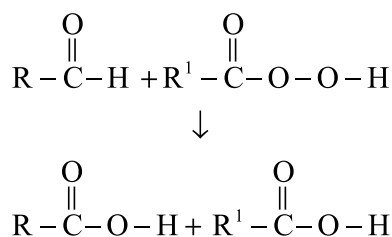
When Fehling solution A and Fehling solution B are mixed in equal amount, precipitate of $Cu(OH)_2$ is formed, which readily dissolved in solution to give dark blue colour solution. When alphatic aldehydes are heated with Fehling solution, then $Cu(OH)_2$ is converted to red colour precipitate of Cu_2O. Chemical reaction involved in the test is as follows-

$$\underset{\text{Fehling solution}}{RCHO + 2[Cu(OH)_2]}$$

$$\downarrow$$

$$\underset{\substack{\text{cuprous oxide} \\ \text{(red ppt.)}}}{2Cu_2O \downarrow} + RCOOH + 2H_2O$$

(iii) **Oxidation by sodium hypohalite (NaOX or X$_2$+NaOH), Haloform reaction:** Acetaldehyde on treatment with excess of halogen in presence of base, give haloform (chloroform, bromoform, iodoform). In this reaction first of all the three hydrogens of methyl group are replaced by halogen atom, to form trihalo aldehyde, which further reacts with base to form haloform and carboxylic acid.

$$\underset{\text{acetaldehyde}}{CH_3 - CHO} + 3Cl_2 \xrightarrow{\text{NaOH}} \underset{\substack{\text{trichloro} \\ \text{acetaldehyde}}}{CCl_3CHO} + 3HCl$$

$$CCl_3 - CHO + NaOH \longrightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{sodium formate}}{HCOONa}$$

(iv) **Baeyer-villiger oxidation:** Aldehydes are oxidised with perbenzoic acid (per acids) to form carboxylic acids.

$$\underset{\substack{O \\ \parallel}}{R - C - H} + \underset{\substack{O \\ \parallel}}{R^1 - C - O - O - H}$$

$$\downarrow$$

$$\underset{\substack{O \\ \parallel}}{R - C - O - H} + \underset{\substack{O \\ \parallel}}{R^1 - C - O - H}$$

(v) **Reaction with Schiff's Reagent:** Aqueous solution of rosaniline hydrochloride is pink in colour, when SO_2 gas is passed through it, it becomes colourless, which is known as Schiff's reagent.

When reaction of aldehydes is carried out with Schiff's reagent, pink colour again appears.

(vi) **Reduction of Benedict's solution:** When aldehydes are heated with Bendict's solution, red brown precipitate of cuprous oxide is obtained. Benedict's solution is a mixture of copper sulphate, sodium citrate and sodium carbonate.

$$R - CHO + 2CuO \xrightarrow{\Delta} RCOOH + \underset{\text{red brown ppt.}}{Cu_2O \downarrow}$$
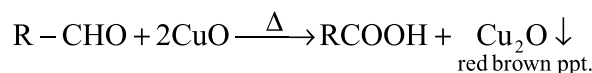
(2) **Oxidation of Ketones:**

Ketones are generally not oxidised easily. When reaction is carried out for long time with strong oxidizing agent like acidic $KMnO_4$, acidic $K_2Cr_2O_7$, concentrated HNO_3, it gives mixture of carboxylic acids which contain lesser number of carbon atom than the parent ketones.

$$\underset{\substack{| \\ O}}{CH_3 - C - CH_3} \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$
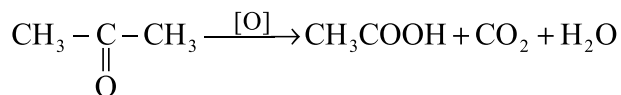
In case of unsymmetrical ketones, the keto group stays preferentially with smaller alkyl group. This rule is known as **Popoff's rule**.

Popoff's Rule–

$$CH_3 - CH_2 - CH_2 \overset{|}{\underset{\substack{| \\ \parallel \\ O}}{+}} C - CH_3$$

$$\downarrow [O]$$

$$CH_3 - CH_2COOH + CH_3COOH$$
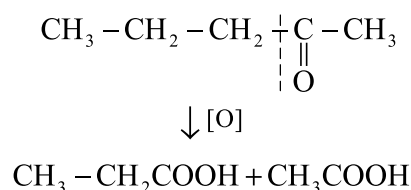
(ii) Baeyer Villiger Oxidation: Ketones are oxidized by per acids to form esters.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R + R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-H$$

$$\downarrow$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R + R^1-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$
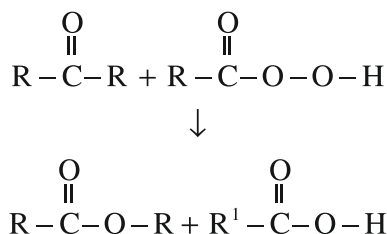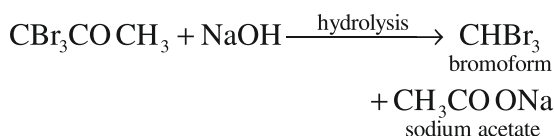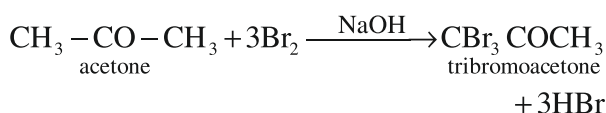
(iii) Oxidation of ketones by sodium hypohalite (NaO X or X_2+NaOH) Haloform reaction: Ketones which contain CH_3-CO- group react with excess of halogen in presence of base to form haloforms (chloroform, bromoform, iodoform)

$$\underset{\text{acetone}}{CH_3-CO-CH_3} + 3Br_2 \xrightarrow{NaOH} \underset{\substack{\text{tribromoacetone} \\ +3HBr}}{CBr_3COCH_3}$$

$$CBr_3CO\,CH_3 + NaOH \xrightarrow{\text{hydrolysis}} \underset{\substack{\text{bromoform} \\ +CH_3CO\,ONa \\ \text{sodium acetate}}}{CHBr_3}$$
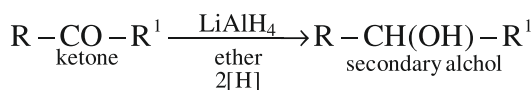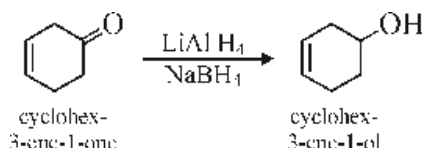
[D] Reduction: Aldehydes and Ketones can be reduced with hydrogen, when react with different reagents and form different products.

(i) Reduction to alcohols: In presence of metallic catalyst like Pt, Pd, Ni, aldehydes and ketones react with molecular hydrogen to form primary alcohols and secondary alcohols, respectively.
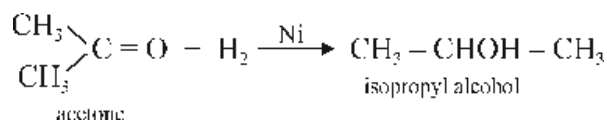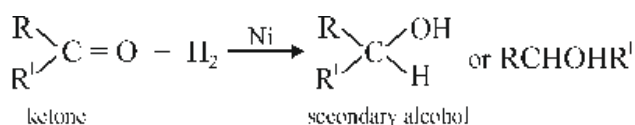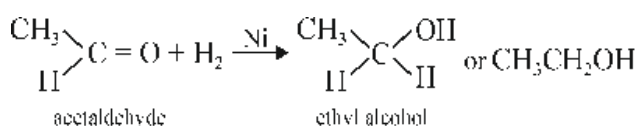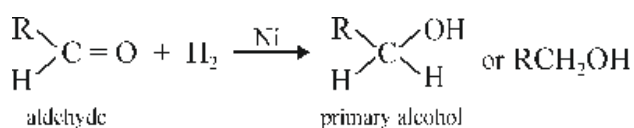
Aldehydes and ketones can also be reduced with $LiAlH_4$ and $NaBH_4$. When $LiAlH_4$ in dry ether and $NaBH_4$ in alcohol is used as reducing agents, unsaturated aldehydes can be reduced to primary alcohols, here double bond remains unaffected.

$$\underset{\text{aldehyde}}{R-CHO} + 2[H] \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{primary alcohol}}{R-CH_2-OH}$$

$$\underset{\text{acroline}}{H_2C=CH-CHO} \xrightarrow[\substack{\text{ether} \\ 2[H]}]{LiAlH_4} \underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH}$$

$$\underset{\text{ketone}}{R-CO-R^1} \xrightarrow[\substack{\text{ether} \\ 2[H]}]{LiAlH_4} \underset{\text{secondary alchol}}{R-CH(OH)-R^1}$$
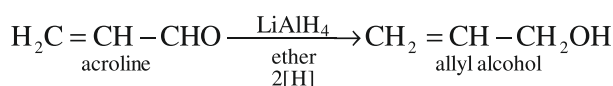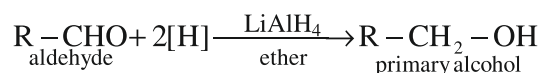
(ii) Meerwein - Ponndorf - verley (MPV) Reduction: Ketones react with aluminium isopropoxide in isopropyl alcohol to give secondary alcohols. This is known as Meerwein-Ponndorf-Verley reduction.
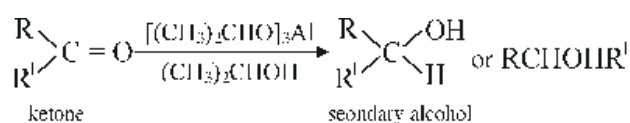
(iii) Reduction to hydrocarbons: The carbonyl group of aldehydes and ketones can be reduced to methylene group.

(a) Clemmenson Reduction: In this reaction reduction of aldehydes and ketones is carried out with zinc amalgam and concentated HCl.

$$\underset{\text{acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + 4H \xrightarrow[\text{conc. HCl}]{Zn-Hg} \underset{\text{ethane}}{CH_3-CH_3} + H_2O$$

$$\underset{\underset{\text{acetone}}{}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 4H \xrightarrow[\text{conc. HCl}]{Zn-Hg} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$
$$+ H_2O$$
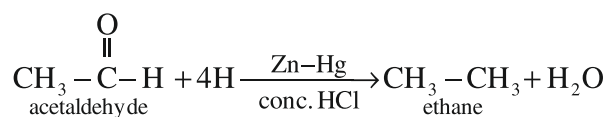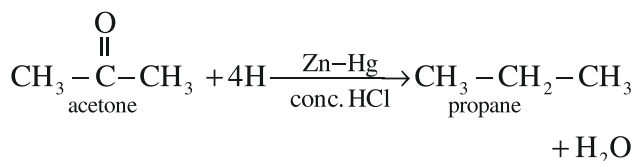
(b) Reduction by red phophorous and HI: Alkanes are obtained when aldehydes and ketones are heated with red phosphorous and HI at 423K.

$$\underset{\underset{\text{acetaldehyde}}{}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + 4HI \xrightarrow[423K]{red\ P} \underset{\text{ethane}}{CH_3-CH_3} + H_2O + 2I_2$$

$$\underset{\underset{\text{acetone}}{}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 4HI \xrightarrow[423K]{red\ P} \underset{\text{ethane}}{CH_3-CH_2-CH_3}$$
$$+ H_2O + 2I_2$$

(c) Wolff-Kishner Reduction or Huang Minlon reaction- When hydrazone of aldehydes and ketones are heated with sodium ethoxide at 453 K temperature, the N_2 gas is eliminated and alkanes are obtained. This reaction is known as Wolff Kishner reduction.

$$\underset{\text{hydrazone}}{{>}C-N.NH_2} + C_2H_5ONa \xrightarrow{453\ K} {>}CH_2 + N_2$$

In this reaction the yield of alkane is more than Clemmenson's reduction but Clemmenson reduction and Wolff–Kishner reduction both are not very useful for sterical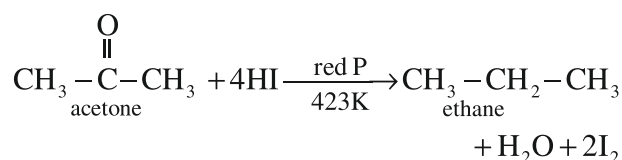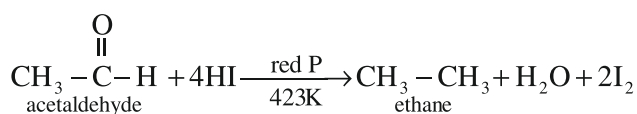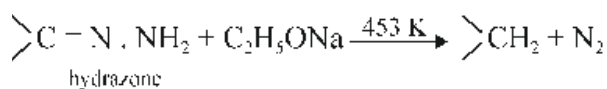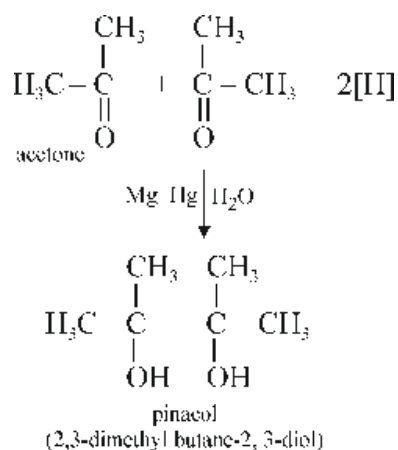ly hindered ketones. Hence, Huang Minlon modified Woff–Kishner reduction. According to him when aldehydes and ketones, react with hydrazine and KOH in presence of diethylene glycol ($HOCH_2CH_2$-CH_2CH_2OH) at 473 K temperature, then alkane is obtained.

$$\underset{\underset{\text{ethanal}}{}}{\overset{\displaystyle CH_3}{\underset{\displaystyle H}{>}}C=O} + H_2N.NH_2 \quad \text{hydrazine}$$
$$\downarrow \overset{\text{KOH/}}{\underset{\text{glycol}}{\text{diethylene}}} \;\; 473K$$
$$\underset{\text{ethane}}{\overset{\displaystyle CH_3}{\underset{\displaystyle H}{>}}CH_2} + N_2 + H_2O$$

$$\underset{\underset{\text{acetone}}{}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C=O} + H_2N.NH_2$$
$$\downarrow \overset{\text{KOH/}}{\underset{\text{glycol}}{\text{diethylene}}} \;\; 473K$$
$$\underset{\text{propane}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}CH_2} + N_2-H_2O$$
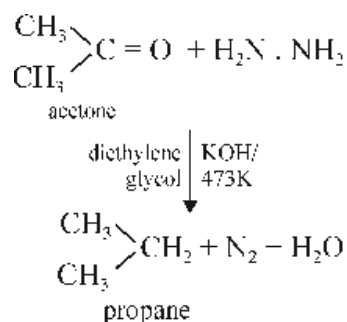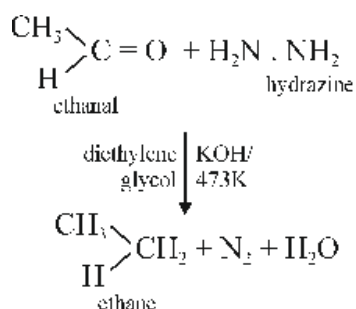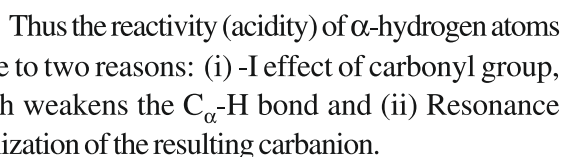
(iv) Reduction to Pinacols: When reduction of ketones is carried out with magnesium amalgam (Mg-Hg) and water, Pinacols are obtained. Aldehydes do not show this reaction.

$$\underset{\text{acetone}}{H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}} \quad \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-CH_3 \quad 2[H]$$
$$\downarrow Mg\ Hg \mid H_2O$$
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} \quad \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} CH_3$$
$$\underset{\text{(2,3-dimethyl butane-2, 3-diol)}}{\text{pinacol}}$$

Reactivity of α-hydrogen of aldehydes:

(I) Acidic nature (acidity) of α-hydrogen– In carbonyl compounds, hydrogen atom present on the carbon atom next to the carbonyl group is called the α-hydrogen atom. Carbonyl group show electron withdrawing inductive effect (-I effect). It withdraws electrons from the adjacent carbon-carbon bond., this makes α-carbon electron deficient. The α-carbon, in turn, withdraws electrons from the C_α-H bonds, in other words, α-hydrogens are held quite weakly (acidic). When carbonyl compounds react with strong base, base easily abstracts hydrogen atom present on α-carbon and carbanions are produced. Carbanions (anion) are stabilized by resonance.

Thus the reactivity (acidity) of α-hydrogen atoms is due to two reasons: (i) -I effect of carbonyl group, which weakens the C_α-H bond and (ii) Resonance stabilization of the resulting carbanion.

The inductive effect decreases with distance thus, -I effect of carbonyl group only affect α-H. The β-, γ-, δ-... etc hydrogens are not acidic.

Aldol Condensation– Aldol condensation is a important reaction based on the acidity of α-H of carbonyl compounds. Aldehydes or ketones having α-hydrogen atom react with dil base (dil NaOH, Na_2CO_3, $Ba(OH)_2$, etc.), its two molecules condense to form a β-hydroxy aldehydes or β-hydroxy ketones. The obtained product is called aldol because it contain both aldehyde and alcohol groups and the reaction is called **aldol condensation**.

Example:

Mechanism: Aldol condensation reaction occurs through the following steps.

Step-I : Formation of enolate ion, which is stabilized by resonance.

Step II : Enolate ion (nucleophilic) attacks on the carbonyl carbon of second molecule of aldehyde and form the anion.

Step III : Anion abstracts proton from water and form aldol and hydroxide ion.

The products of aldol condensation when heated with dilute acids undergo dehydration leading to the formation of α, β- unsaturated aldehydes or ketones.

Cross aldol condensation: When aldol condensation is carried out between two different aldehyde molecules or two different ketone molecules

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or one aldehyde or one ketone molecule, then it is called cross aldol condensation. In principle, if α-hydrogen atom is present on two different molecules, then a mixture of four products is obtained, which are difficult to separate. Therefore cross aldol condensations are of little synthetic value. Example: Aldol condansations of ethanol and propanol. As both molecules contain α-H atoms, four products are possible.

(i)
$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - H - \overset{\overset{\displaystyle H}{|}}{CH_2} - CHO \xrightarrow[\text{NaOH}]{\text{dil}}$$

$$H_3C - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_2 - CHO$$

(ii)
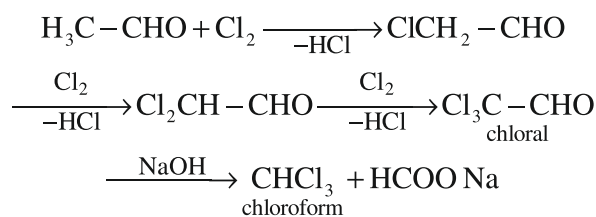$$H_3C - CH_2 - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} + H\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CHO \xrightarrow[\text{alkali}]{\text{dil.}}$$
$$\text{propanal} \qquad \text{propanal}$$

$$H_3C - CH_2 - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - CHO$$
$$\text{aldol product}$$

(iii)
$$H_3C - CH_2 - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} + \overset{\overset{\displaystyle H}{|}}{CH_2} - CHO \xrightarrow[\text{alkali}]{\text{dil.}}$$
$$\text{propanal} \qquad\quad \text{ethanal}$$

$$H_3C - CH_2 - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_2 - CHO$$
$$\text{aldol}$$

(iv)
$$H_3C - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - CHO \xrightarrow[\text{alkali}]{\text{dil.}} H_3C - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - CHO$$
$$\text{ethanal} \qquad \text{propanal} \qquad\qquad\qquad \text{aldol}$$
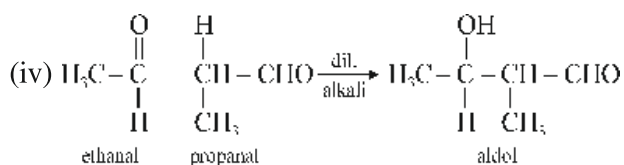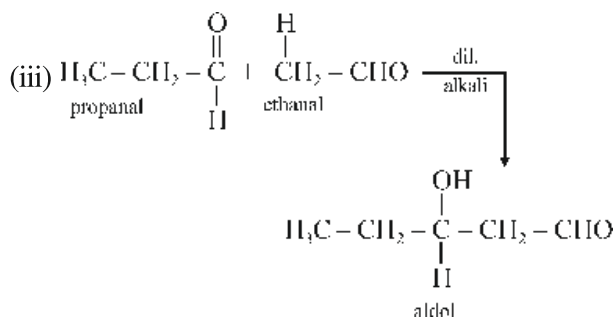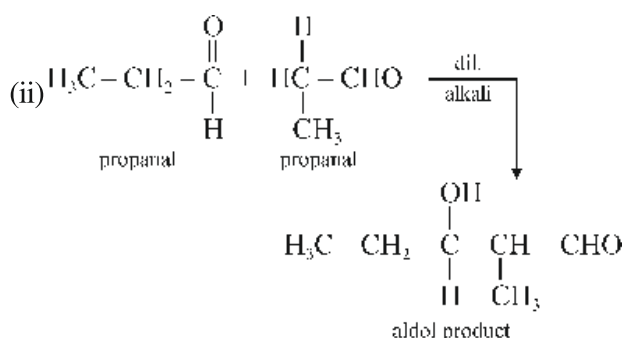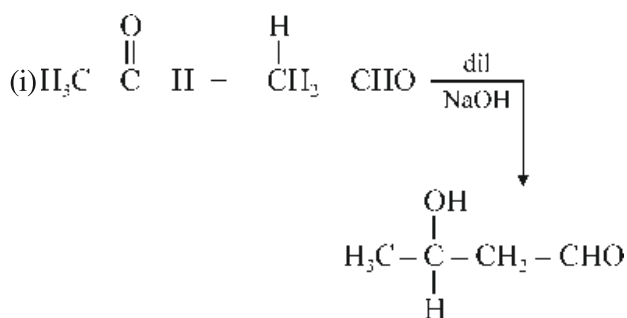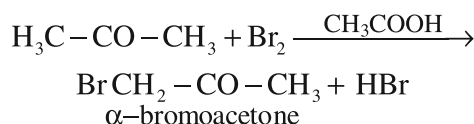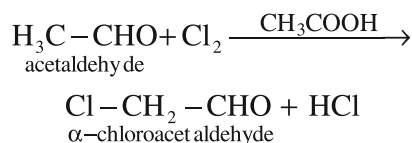
Formaldehyde do not undergoes aldol condensation because it does not contain α-H atom.

2. Halogenation: When aldehydes and ketones having α-hydrogen atom react with halogen in the presence of acid or base, then α-hydrogen atom is replaced by halogen atom. In the presence of a base, poly-halogenation occurs. (Example: Haloform reaction)
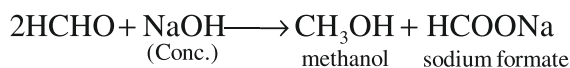
$$H_3C - CHO + Cl_2 \xrightarrow[-HCl]{} ClCH_2 - CHO$$

$$\xrightarrow[-HCl]{Cl_2} Cl_2CH - CHO \xrightarrow[-HCl]{Cl_2} \underset{\text{chloral}}{Cl_3C - CHO}$$

$$\xrightarrow{\text{NaOH}} \underset{\text{chloroform}}{CHCl_3} + HCOO\,Na$$

In the presence of acid, monohalogenated product is formed.

$$\underset{\text{acetaldehyde}}{H_3C - CHO} + Cl_2 \xrightarrow{CH_3COOH}$$

$$\underset{\alpha-\text{chloroacet aldehyde}}{Cl - CH_2 - CHO} + HCl$$

$$H_3C - CO - CH_3 + Br_2 \xrightarrow{CH_3COOH}$$

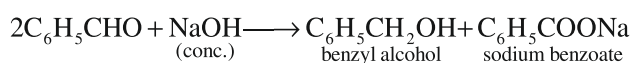$$\underset{\alpha-\text{bromoacetone}}{Br\,CH_2 - CO - CH_3} + HBr$$

In the excess of halogen, di and tri substituted products are formed.

3. Cannizzaro Reaction:

We know that at least one α-H atom take part in aldol condensation. Aldehydes, which do not contain α-hydrogen atom undergo Cannizzaro reaction in presence of concentrated base. In this reaction two molecules are used, out of which one molecule undergoes oxidation and another one undergoes reduction. Aldehyde, which is oxidized to form acid, while another molecule is reduced to alcohol. Formaldehyde (HCHO), benzaldehyde (C_6H_5CHO), chloral (CCl_3–CHO) and pivaldehyde ($(CH_3)_3C$–CHO).

$$2HCHO + \underset{\text{(Conc.)}}{NaOH} \longrightarrow \underset{\text{methanol}}{CH_3OH} + \underset{\text{sodium formate}}{HCOONa}$$

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$$2C_6H_5CHO + NaOH \xrightarrow{\text{(conc.)}} \underset{\text{benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{sodium benzoate}}{C_6H_5COONa}$$
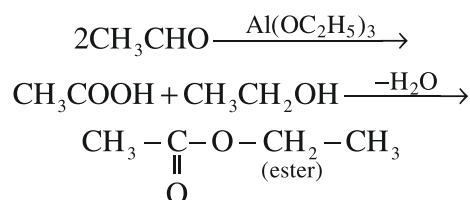
Crossed Cannizzaro reaction:

When Cannizzaro reaction takes place between two different aldehydes, then the aldehyde which can be easily oxidised gives acid and other aldehyde gives alcohol and this reaction is known as cross Cannizzaro reaction.

4. Tischenko Reaction-

Any aldehyde when reacts with aluminium ethoxide $Al(OC_2H_5)_3$ to form acid and alcohol (Cannizzaro reaction), which on reaction with each other to form ester, this reaction is known as Tischenko reaction.

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3}$$

$$CH_3COOH + CH_3CH_2OH \xrightarrow{-H_2O}$$

$$\underset{\text{(ester)}}{CH_3 - \underset{\underset{O}{\parallel}}{C} - O - CH_2 - CH_3}$$

12.1.5 Similarity and dissimilarity between aldehydes and ketones:

S.No.	Test	Aldehyde	Ketone
1.	Tollen's reagent	Form silver mirror	No reaction
2.	Fehling's solution	Red ppt. is obtained.	No reaction
3.	Reduction by $LiAlH_4$	Primary alcohols are formed	Secondary alcohols are formed
4.	Reaction with alcohol in of dry HCl gas	Acetal formed	Ketals are not easily formed
5.	Schiff's reagent	Pink colour obtained	No reaction
6.	Reaction with sodium nitroxide in presence of NaOH	No reaction	Red colour is obtained
7.	Reaction with m-dinitrobenzene in presence of NaOH	No reaction	Red-violet colour appears
8.	Reaction with NaOH	Brown resinous product formed	No reaction

$$C_6H_5CHO + HCHO \xrightarrow{NaOH\ Conc.}$$
$$C_6H_5CH_2OH + HCOONa$$

Similarity between aldehydes and ketones: Both contain cabonyl group, thus both show same type of nucleophilic addition and nucleophilic elimination reactions. These reaction are already explained in detail.

12.1.6 Uses of Aldehydes and Ketones:

(i) Formaldehyde (HCHO)

1. 40% solution of formaldehyde (formalin) is used for the preservation of biological or anatomical specimens.

2. Formaldehyde is used as insecticide.

3. Formaldehyde is used to prepare synthetic resins and B akelite plastic.

4. Formaldehyde forms urotropine, which is used in medicine for urological diseases. It forms many dyes as indigo, rosaniline, etc.

(ii) Acetaldehyde (CH_3CHO)

1. Acetaldehyde is used in preparation of dyes and resins. It is used for industral manufacturing of acetic acid.

2. It is used in silvering of mirrors and to open blocked nasal passages.

3. Used in medicine (Paraldehyde)

4. It is used in manufacturing of phenolic resin and as rubber accelerator.

(iii) Ketone:

1. Propanone is used in storage of acetylene.

2. It is used as a solvent for cellulose acetate, cellulose nitrate, celluloid, resin, etc.

3. Acetone is sued for synthesis of ketene, sulphonal which is used as medicine, chloritone, chloroform, iodoform and as nailpolish remover.

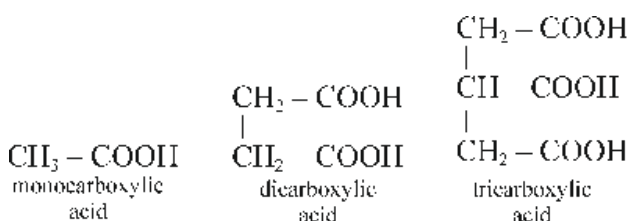4. Used as starting material for synthesis of synthetic rubber.

12.2 Carboxylic Acid

Organic compounds containing -COOH as the functional group are called carboxylic acid. These are caboxyl dervatives of hydrocarbon, in which one or more than one hydrogen atom of hydrocarbon chain is substituted by carboxylic group. Its general formula is $C_n H_{2n} O_2$. To show the presence of –COOH group, it can also be written as $C_n H_{2n+1}$ COOH or R–COOH.

From the structure of carboxylic group

$$(-\overset{\overset{\displaystyle O}{\|}}{C}-O-H)$$, it appears as it is made by combination

of two groups, $-\overset{\overset{\displaystyle O}{\|}}{C}-$ or carbonyl group and –OH or alcoholic group, but it does not show any properties of both carbonyl gourp and hydroxyl group.

Carboxylic acids are classified as mono carboxylic acid, dicarboxylic acid, tricarboxylic acid, etc. according to number of carboxylic groups present in it. **For example–**

$$CH_3 - COOH$$
monocarboxylic acid

$$\begin{array}{c} CH_2 - COOH \\ | \\ CH_2 - COOH \end{array}$$
dicarboxylic acid

$$\begin{array}{c} CH_2 - COOH \\ | \\ CH - COOH \\ | \\ CH_2 - COOH \end{array}$$
tricarboxylic acid

Aliphatic monocarboxylic acids are known as Fatty acids because their higher members such as palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}$ COOH) are main component of fats.
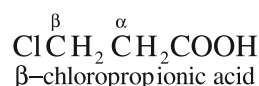
12.2.1 Nomenclature:

Generally, carboxylic acids are known by their common names. These common names are derived from Latin or Greek names of their natural sources. In english their names end with the suffix –ic acid.

For example–

(i) Formic acid (HCOOH) : It was first obtained from distillation of ants. In latin, formica means ant.

(ii) Acetic acid (CH$_3$OOH) : It was obtained from vinegar. In latin, acetum means vinegar.

(iii) Butyric acid (CH$_3$-CH$_2$-CH$_2$-COOH) : It was obtained from rancid butter. In Latin, butyrum means butter.

(iv) Propionic acid (C$_2$H$_5$COOH) : It is derived from the word Proton-Pion. In Latin, proton = first, pion = fat.

(v) Valeric acid (C$_4$H$_9$COOH) : It was obtained from roots of valerion plants, thus called valeric acid.

Position of other substituents in chain are indicated by Greek words α, β, γ, δ, etc. Carbon atom, attached with -COOH group is known as α-carbon atom and further as β, γ....etc.

For Example–
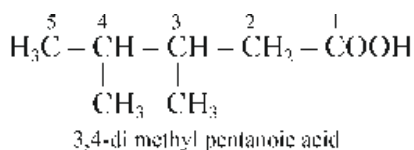
$$Cl\overset{\beta}{C}H_2 \overset{\alpha}{C}H_2COOH$$
$$\beta\text{–chloropropionic acid}$$

(II) IUPAC Nomenclature:

The IUPAC name of the monocarboxylic acids is alkanoic acid. Their names are derived by replacing the terminal 'e' from the name of the corresponding straight chain alkane by the suffix oic acid.

In substituted carboxylic acid, the longest carbon chain containing carboxylic group is chosen as parent chain and the chain is numbered in such a manner so that the carbon atom of the carboxyic group get the least number (1). Substituents are named in alphabetical order with their numerals as a prefix, before the name of root alkane. At the end suffix oic acid is added.

$$\overset{5}{H_3C}-\overset{4}{CH}-\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{COOH}$$
$$\quad\quad\quad |\quad\quad |$$
$$\quad\quad\quad CH_3\quad CH_3$$

3,4-di methyl pentanoic acid

For naming compounds containing more than one carboxylic group, the 'e' at the end of corresponding alkanes remains as it is. The number of carboxylic groups are indicated by adding the multiplicative prefix, before the word 'oic'. The position of –COOH groups are indicated by the arabic numeral before the multiplicative prefix.

Names and structure of some important carboxylic acids are:

Structure	General name	IUPAC name
HCOOH	formic acid	methanoic acid
CH_3-COOH	acetic acid	ethanoic acid
CH_3-CH_2-COOH	propionic acid	propanoic acid
CH_3-CH_2-CH_2-COOH	butyric acid	butanoic acid
$(CH_3)_2$CH COOH	isobutyric acid	2-methyl propanoic acid
HOOC-COOH	oxalic acid	ethane dioic acid
HOOC-CH_2-COOH	malonic acid	propanedi oic acid
HOOC-CH_2-CH_2-COOH	succinic acid	butanedioic acid
HOOC-CH_2-CH_2-CH_2-COOH	glutaric acid	pentanedioic acid
HOOC-$(CH_2)_4$-COOH	adipic acid	hexanedioic acid
HOOC-CH_2-CH-(COOH)-CH_2-COOH	–	propane-1, 2, 3- tricarboxylic acid
$\begin{array}{c}\quad Br \\ \quad | \\ H_3C-CH-CH-COOH \\ \quad\quad\quad | \\ \quad\quad\quad CH_3 \end{array}$	–	3-bromo-2-methyl butanoic acid

12.2.2 Formation methods of carboxylic acid

1. **By hydrolysis of alkane nitriles:** Acidic or alkaline hydrolysis of alkane nitriles yield the alkanoic acid.
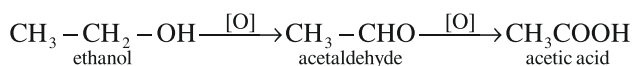
$$R-C\equiv N+2H_2O \xrightarrow[\overline{O}H]{H^+/} R-COOH+NH_3$$
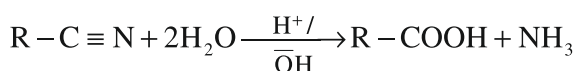
The starting material of reaction is alkane nitriles which can be prepared by the reaction of alkyl halide with alcoholic potassium cyanide.

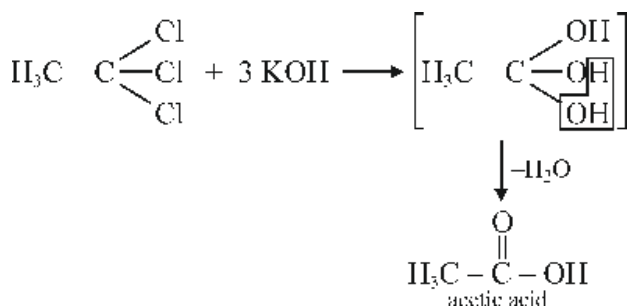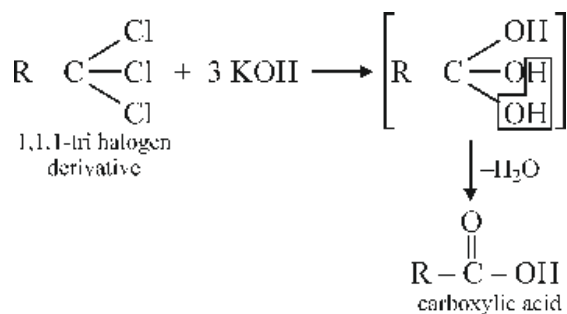$$\underset{\text{alkyl halide}}{R-X}+KCN \longrightarrow \underset{\text{alkane nitrile}}{R-CN}$$
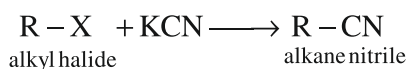
2. **By oxidation of primary alcohols or aldehydes:** The primary alcohols or aldehydes are readily oxidised to the corresponding alkanoic acids with oxidising agents such as acidic potassium dichromate ($K_2Cr_2O_7$)/potassium permanganate ($KMnO_4$).

$$\underset{\text{primary alcohol}}{R-CH_2-OH}\xrightarrow{[O]}\underset{\text{aldehyde}}{R-CHO}\xrightarrow{[O]}\underset{\text{carboxylic acid}}{R-COOH}$$

$$\underset{\text{methanol}}{CH_3-OH}\xrightarrow{[O]}\underset{\text{formaldehyde}}{H-CHO}\xrightarrow{[O]}\underset{\text{formic acid}}{HCOOH}$$

$$\underset{\text{ethanol}}{CH_3-CH_2-OH}\xrightarrow{[O]}\underset{\text{acetaldehyde}}{CH_3-CHO}\xrightarrow{[O]}\underset{\text{acetic acid}}{CH_3COOH}$$
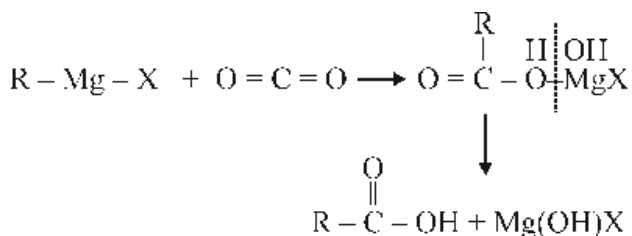
3. **By hydrolysis of 1, 1, 1-tri halogen derivative:** Alkanoic acids are prepared by the alkaline hydrolysis of 1, 1,1-trihalogen derivatives.
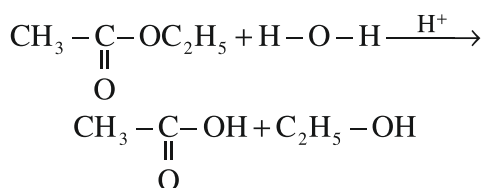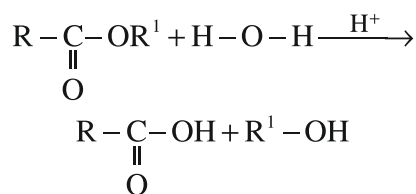
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$$R - C \underset{\overset{|}{Cl}}{\overset{Cl}{<}} Cl + 3\,KOH \longrightarrow \left[R - C \underset{\overset{|}{OH}}{\overset{OH}{<}} OH \right]$$

1,1,1-tri halogen derivative

$\downarrow -H_2O$

$$R - \underset{\overset{||}{O}}{C} - OH$$

carboxylic acid

$$H_3C - C \underset{\overset{|}{Cl}}{\overset{Cl}{<}} Cl + 3\,KOH \longrightarrow \left[H_3C - C \underset{\overset{|}{OH}}{\overset{OH}{<}} OH \right]$$

$\downarrow -H_2O$

$$H_3C - \underset{\overset{||}{O}}{C} - OH$$

acetic acid

4. **From Grignard reagents :** Grignard reagents react with carbon dioxide to form addition products, which on hydrolysis give alkanoic acids.

$$R - Mg - X + O=C=O \longrightarrow O = \overset{\overset{R}{|}}{C} - O\,\!:\!H\,|\,OH \, MgX$$

$$\downarrow$$

$$R - \underset{\overset{||}{O}}{C} - OH + Mg(OH)X$$

5. **From hydrolysis of acid derivatives :**

(i) **From esters:** Hydrolysis of esters by dilute mineral acids gives alkanoic acids.

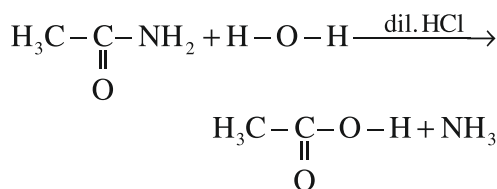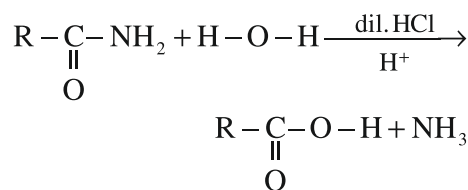$$R - \underset{\overset{||}{O}}{C} - OR^1 + H - O - H \xrightarrow{H^+}$$

$$R - \underset{\overset{||}{O}}{C} - OH + R^1 - OH$$

$$CH_3 - \underset{\overset{||}{O}}{C} - OC_2H_5 + H - O - H \xrightarrow{H^+}$$

$$CH_3 - \underset{\overset{||}{O}}{C} - OH + C_2H_5 - OH$$

(ii) **From alkanoyl halide:** Basic (alkaline) or acidic hydrolysis of alkanoyl chloride give alkanoic acids.

$$R - \underset{\overset{||}{O}}{C} - Cl + H - O - H \longrightarrow R - \underset{\overset{||}{O}}{C} - O - H + HCl$$

$$H_3C - \underset{\overset{||}{O}}{C} - Cl + H - O - H \longrightarrow CH_3 - \underset{\overset{||}{O}}{C} - O - H + HCl$$
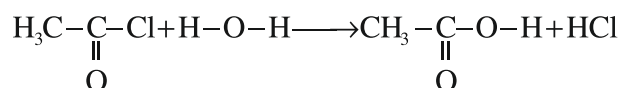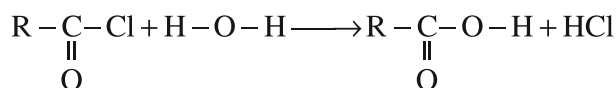
(iii) **From alkanoic anhydride:** Hydrolysis of alkanoic anhydride gives two molecules of alkanoic acids.

$$R - \underset{\overset{||}{O}}{C} - O - \underset{\overset{||}{O}}{C} - R \xrightarrow{H-O-H} R - \underset{\overset{||}{O}}{C} - OH + R - \underset{\overset{||}{O}}{C} - OH$$

$$H_3C - \underset{\overset{||}{O}}{C} - O - \underset{\overset{||}{O}}{C} - R \xrightarrow{H-O-H}$$

$$H_3C - \underset{\overset{||}{O}}{C} - OH + H - O - \underset{\overset{||}{O}}{C} - CH_3$$
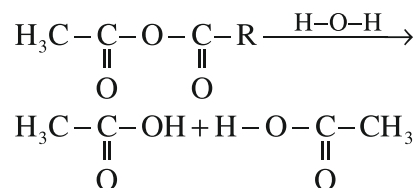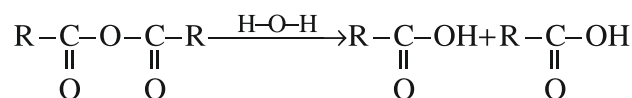
(iv) **From alkanamide:** In the presence of dilute HCl, alkanamide hydrolyse to give alkanoic acids.

$$R - \underset{\overset{||}{O}}{C} - NH_2 + H - O - H \xrightarrow[H^+]{dil.\,HCl}$$

$$R - \underset{\overset{||}{O}}{C} - O - H + NH_3$$

$$H_3C - \underset{\overset{||}{O}}{C} - NH_2 + H - O - H \xrightarrow{dil.\,HCl}$$

$$H_3C - \underset{\overset{||}{O}}{C} - O - H + NH_3$$

12.2.3 Physical Properties

(i) **Physical state:** Alkanoic acids upto C_{10} are colourless liquid. The higher members are colourless wax like solid.

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(ii) **Odour:** The first three members (C_1-C_3) have pungent smell, from C_4-C_9 have smell like rotten butter and higher members are practically odourless.

(iii) **Solubility:** First four members of aliphatic carboxylic acid are soluble in water. Pentanoic acid and hexanoic acids are partially soluble in water. Higher members are insoluble in water because as the molecular weight increases, hydrocarbon part increases which decreases the polarity of –COOH group. All alkanoic acids are soluble in organic solvents, like, ethanol, ether, benzene, carbon tetra chloride, etc. Solubility of carboxylic acid in water in due to hydrogen bonding.

(iv) **Boiling point:** Alkanoic acids have higher boiling point.

As the molecular weight increases their boiling point increases. Carboxylic acids have higher boiling point than alkane, ethers and alcohols of comparable molecular masses.

ether $\cong$ alkane < alcohol < carboxylic acid

Compound	CH_3COOH	$CH_3CH_2CH_2OH$	CH_3-O-CH_2-CH_3
	acetic acid	propanol	ethyl methyl ether
Mol. Wt.	60	60	60
b.p.	391 K	370 K	280 K

This means , intermolecular hydrogen bonding between molecules of carboxylic acids are stronger than H– bonding between molecules of alcohols because in acid, carbonyl group is present adjacent to $O-H$ bond so $O-H$ bond of acid is more polar than $O-H$ bond of alcohol. Due to polarity of carboxylic acid molecule, oxygen atom of carbonyl group get negative charge, this negatively charged oxygen atom makes hydrogen bond with positively charged hydrogen atom of other molecules. This is the reason that carboxylic acid molecules exist as dimer not only in solid or liquid state but in the vapour phase also. For example in acetic acid, its two molecules are associated by hydrogen bonding to form dimer.
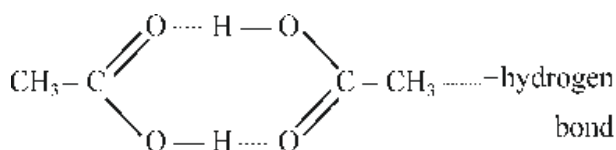

The existence of such dimer is supported by the fact that when molecular mass of acetic acid was determined by measurement of colligative properties, it was found to be 120 whereas actually it is 60.

(v) **Melting point:** Melting points of aliphatic carboxylic acid (upto C_{10}) show regular changes or oscillation effect. The melting point of carboxylic acids containing even number of carbon atoms is higher than the carboxylic acids containing odd number of carbon atoms.
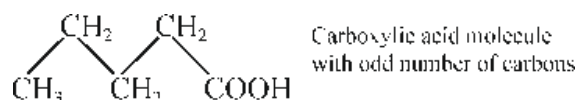
It has been shown by X-ray diffraction studies that carboxylic acids with odd number of carbon atoms, have the carboxyl group and terminal methyl groups on the same side. So this molecules fit poorly in the crystal lattice and have weak inter molecular forces of attraction. On the other hand, carboxylic acids containing even number of carbon atoms, have carboxyl group and terminal methyl groups on the opposite sides of the zig-zag carbon chain, as a result they fit closely in the crystal lattice, there by, increasing inter molecular forces of attraction resulting in higher melting point.
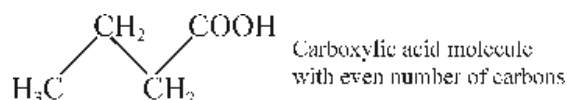
Carboxylic acids having more than ten carbon atoms do not show this changes or oscillation effect.

12.2.4 Chemical Properties

Alkanoic acids have both alkyl group and carboxylic group. Thus, its chemical reactions can be classified into two groups:
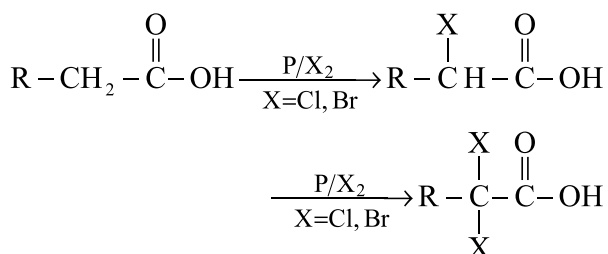
(I) Reactions of alkyl group.

(II) Reactions of carboxylic group $(-\overset{\overset{\displaystyle O}{\|}}{C}-OH)$.

(I) **Reactions of Alkyl group as whole :**

Halogenation, Hell-volhard-Zelinsky reaction: Carboxylic acids having an α-hydrogen, on treatment with chlorine or bromine in the presence of small amount of red phosphrous give α-halocarboxylic acid. The reaction is carried out at high temerature. At low temperature, reaction is very slow. Red phosphorous convert carboxylic acid into acyl halide, which is more reactive than acid and can be easily halogenated. As methanoic acid has no α-hydrogen, it does not undergoes Hell-Volhard-Zelinsky reaction (HVZ).

$$R - CH_2 - \overset{\overset{O}{\|}}{C} - OH \xrightarrow[X=Cl,\,Br]{P/X_2} R - \overset{\overset{X}{|}}{C}H - \overset{\overset{O}{\|}}{C} - OH$$

$$\xrightarrow[X=Cl,\,Br]{P/X_2} R - \overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}} - \overset{\overset{O}{\|}}{C} - OH$$

If halogen is taken in excess, all α-H atoms are replaced by halogen atoms.

(II) **Chemical Reactions of** $-\overset{\overset{O}{\|}}{C}-OH$ **group:**

(A) Reaction of carboxylic group $(-\overset{\overset{O}{\|}}{C}-OH)$:

(i) **Reduction:** By red phophourous and HI : Alkanoic acids are reduced to alkane, when react with red phosphourous and HI at 433K temperature and at high pressure.

$$R - COOH + 6HI \xrightarrow[433\,K]{red\,P} R - CH_3 + 3I_2 + 2H_2O$$
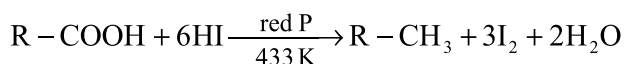
Alkanoic acids are reduced to primary alcohols, by lithium aluminium hydride (LiAlH$_4$) or diborane.

$$R - COOH + 6HI \xrightarrow{LiAlH_4} R - CH_2 + OH + H_2O$$
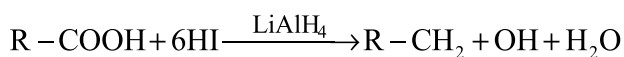
(ii) **Decarboxylation:** When sodium salts of carboxylic acid is heated with sodalime (mixture of NaOH and CaO; 3: 1), hydrocarbons are formed. In this reaction carbon dioxide gas is released so it is known as decarboxylation.

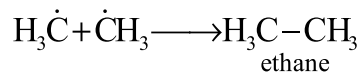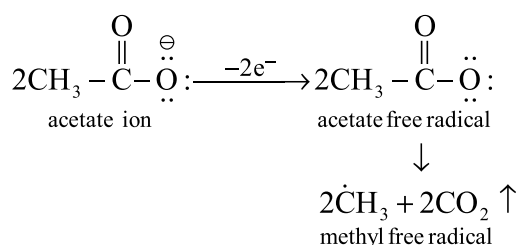$$RCOONa + (NaOH + CaO) \xrightarrow[\text{sodalime}]{\Delta} R - H + Na_2CO_3$$
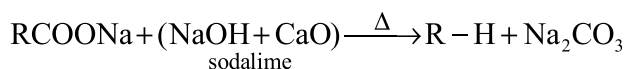
Kolbe's electrolysis: Alkali metal salts of carboxylic acids undergo decarboxylation on electrolysis of their aquous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.
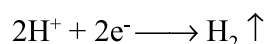
$$2CH_3COONa + 2H_2O \xrightarrow{\text{electrolysis}}$$
$$CH_3 - CH_3 + 2CO_2 + H_2 + 2NaOH$$
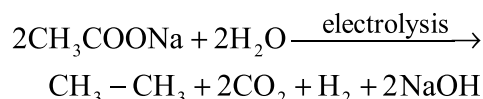
Reaction takes place by free radical mechanism:

At Anode–

$$2CH_3 - \overset{\overset{O}{\|}}{C} - \overset{\ominus}{\underset{..}{\overset{..}{O}}}: \xrightarrow{-2e^-} 2CH_3 - \overset{\overset{O}{\|}}{C} - \overset{..}{\underset{..}{O}}:$$

acetate ion   acetate free radical

$$\downarrow$$

$$2\dot{C}H_3 + 2CO_2 \uparrow$$
methyl free radical

$$H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C - CH_3$$
ethane

At Cathode– At cathode, hydrogen gas is evolved.
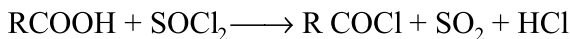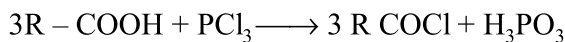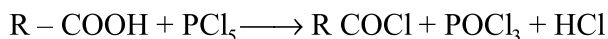
$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

(iii) **Schmidt Reaction : Formation of Primary alkane amine:** Carboxylic acids react with hydrazoic acid N$_3$H to give primary alkane amine, having one carbon atom less than the alkanoic acid.

$$R - COOH + N_3H \xrightarrow{dil.\ H_2SO_4} R - NH_2$$
$$+ CO_2 + N_2$$
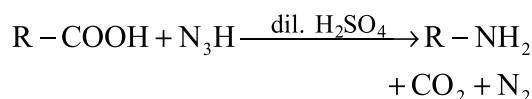
(B) **Reactions involving clevage of C–OH bond of carboxylic group:**

**(i)** **Reaction with PCl$_5$, PCl$_3$ and SOCl$_2$ formation of acyl halide:** When carboxylic acids react with phosphorous pentachloride (PCl$_5$), Phosphorous trichloride (PCl$_3$) and thionyl chloride (SOCl$_2$) the –OH group is replaced by chlorine atom.

$$R - COOH + PCl_5 \longrightarrow R\,COCl + POCl_3 + HCl$$

$$3R - COOH + PCl_3 \longrightarrow 3\,R\,COCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow R\,COCl + SO_2 + HCl$$

(ii) Esterification: Carboxylic acids react with alcohols in presence of mineral acid catalyst (sulphuric acid, hydrochloric acid) to form alkyl alkanoate (esters). This reaction is known as esterification reaction.

$$\underset{\text{alkanoic acid}}{R - COOH} + \underset{\text{alcohol}}{R^1 - OH} \xrightarrow{H^+} \underset{\text{ester}}{R - COOR^1} + H_2O$$
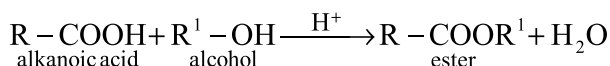
(iii) Formation of alkanoic anhydride: Carboxylic acid when heated with concentrated H_2SO_4 or P_2O_5, form anhydrides by elimination of a water molecule from two molecules of acid.
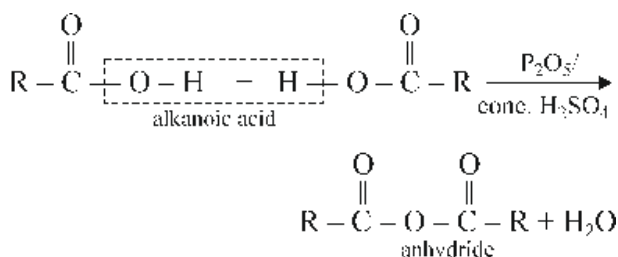
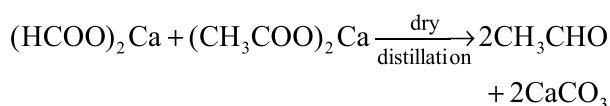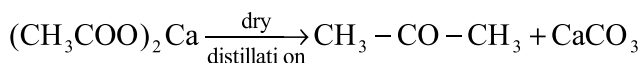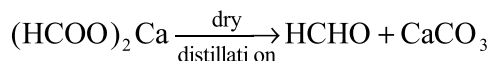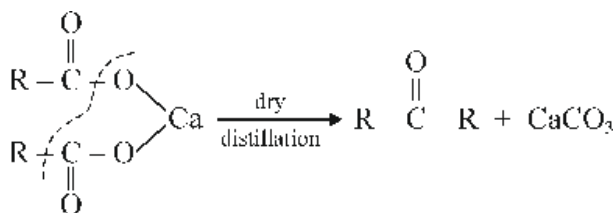**(iv) Reaction with ammonia-formation of alkanamide:** Alkanoic acids react with ammonia (NH_3) to form ammonium salts. These salts on further heating at high temperature eliminate one molecule of water and form amides.
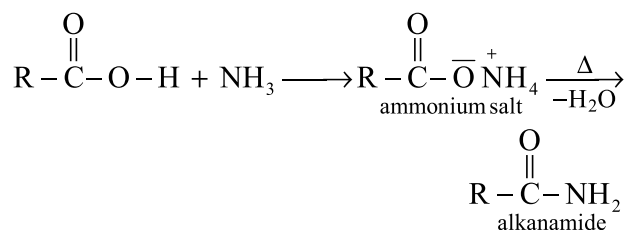
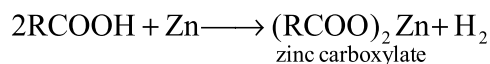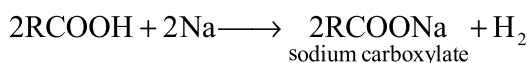Alkanamides, when heated in the presence of P_2O_5 give alkyl cyanide by removal of one molecule of water.
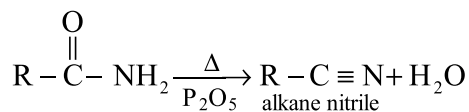
(v) Formation of Carbonyl compounds: By dry distillation of calcium salts of alkanoic acid, carbonyl compounds are obtained.
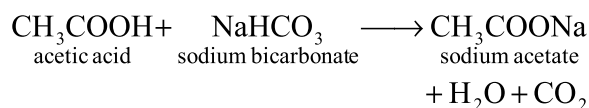

$$(HCOO)_2\,Ca \xrightarrow[\text{distillation}]{\text{dry}} HCHO + CaCO_3$$

$$(CH_3COO)_2\,Ca \xrightarrow[\text{distillation}]{\text{dry}} CH_3 - CO - CH_3 + CaCO_3$$

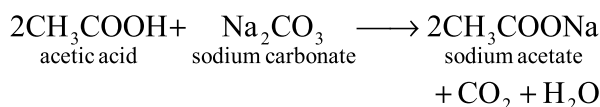$$(HCOO)_2\,Ca + (CH_3COO)_2\,Ca \xrightarrow[\text{distillation}]{\text{dry}} 2CH_3CHO + 2CaCO_3$$

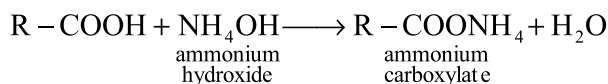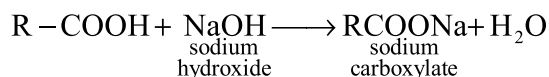**III Reactions involving clevage of (O – H) bond of carboxyl group :**

(i) Reaction with metals: Carboxylic acids react with active metals like Na, K, Mg, Ca, Zn, etc. to form salt and hydrogen gas is released.

$$2RCOOH + 2Na \longrightarrow \underset{\text{sodium carboxylate}}{2RCOONa} + H_2$$

$$2RCOOH + Zn \longrightarrow \underset{\text{zinc carboxylate}}{(RCOO)_2\,Zn} + H_2$$

(ii) Reaction with carbonate and bicarbonate: Carboxylic acids release carbon dioxide gas, when react with carbonate and bicarbonate.

$$\underset{\text{acetic acid}}{2CH_3COOH} + \underset{\text{sodium carbonate}}{Na_2CO_3} \longrightarrow \underset{\text{sodium acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{sodium bicarbonate}}{NaHCO_3} \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + H_2O + CO_2$$

(iii) Reaction with bases: Carboxylic acids react with base to form salts.

$$R - COOH + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{NaOH} \longrightarrow \underset{\substack{\text{sodium}\\\text{carboxylate}}}{RCOONa} + H_2O$$

$$R - COOH + \underset{\substack{\text{ammonium}\\\text{hydroxide}}}{NH_4OH} \longrightarrow \underset{\substack{\text{ammonium}\\\text{carboxylate}}}{R - COONH_4} + H_2O$$

Above three reactions (i), (ii) and (iii) show the acidic nature of carboxylic acids.

12.2.5 Acidity of Caroboxylic acid

Acidity of an acid depends on its proton giving capacity. Carboxylic acid when dissolved in water, it dissociates to give carboxylate anion and hydronium ion.
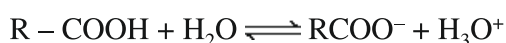
$$R - COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

According to law of mass action, equilibrium constant can be given as–

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[RCOOH][H_2O]}$$

$$K_{eq}[H_2O] = K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

K_{eq} = equilibrium constant
K_a = dissociation constant of acid

The value of K_a is dependent on temperature and from the above equation it is clear that value of K_a is directly proportional to H$^+$ concentration. Thus, value of K_a is a measure of strength of acid.

The value of K_a will be greater if concentration of H$^+$ ions is more i.e. the dissociation of acid will be increased and the acid will be stronger. Thus, by comparing the values of K_a , the strength of various acids can be compared. For more convenient, pK_a is used in place of K_a. pK_a value is a negative logrithm of the dissociation constant K_a.

$$pK_a = - \log_{10}K_a$$

Smaller the numerical value of pK_a, stronger is the acid.

Fatty acids are weak acids. As the molecular masses increases, acidic nature decreases.

$$HCOOH > CH_3COOH > C_2H_5COOH$$

Ka(25ºC) 17.7×10^{-5} 1.75×10^{-5} 1.4×10^{-5}

K_a value of carboxylic acids are in between 10^{-4} –10^{-5} (pKa = 4–5) so these are weaker acid than mineral acids like Nitric, Sulphuric, Hydrochloric, and sulphonic acid but more acidic than phenol and alcohols.

Cause of acidic nature of carboxylic acids:

Molecule of carboxylic acids may be regarded as a resonance hybrid of the following two structures.
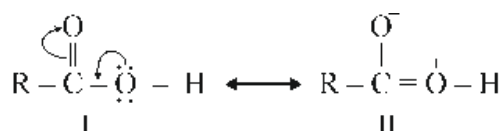

In structure (II) due to electron deficiency on oxygen atom of O-H bond, oxygen atom attracts the electrons of the O-H bond towards itself. As a result, the O-H bond weakens and ultimately breaks to split off a proton.

After the removal of proton, carboxylate anion is formed. This carboxylate anion is stabilized by resonance.


resonance in carboxylate anion
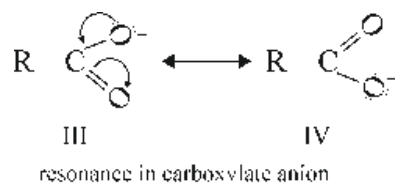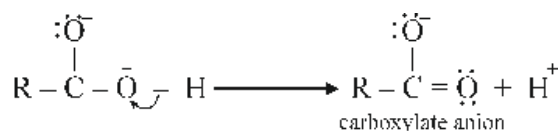
Carboxylic acid and carboxylate anion, both are stabilised by resonance but the resonance energy of carboxylate anion is more because its both resonating strucutres III and IV are equivalent and in these structures charges are not separated. Whereas in carboxylic acid, its resonating structures (I) and (II) are not equivalent and charges are separate as positive and negative charge. Thus, carboxylate anion is more stable than carboxlic acid molecule. Carboxylic acid molecules dissociate to form more stable carboxylate anions and show acidic character. In carboxylate anion, charge is not transferred to oxygen atom but delocalized between both oxygen and carbon atoms. Due to resonance both the oxygen-carbon bond lengths are equal. Their values are between C-O and C=O bond length.

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resonance hybrid of
carboxylate anion
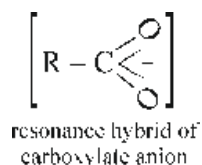
From the above discussion, it is clear that due to resonance in both carboxylic acid and carboxylate anion, carbon and oxygen double bond character decreases. Thus, they do not show characteristic reactions of carboxyl compounds like, nucleophilic addition- elimination reactions.

Comparison of acidic strength of carboxylic acids, alcohols and phenols:

Both carboxylic acids and alcohols contain $O-H$ group but carboxylic acids show strong acidic character due to resonance stabilization of carboxylate ion. On the contrary, alchols and alkoxide ions do not show resonance.

$$R-\ddot{O}-H + H_2O \longrightarrow R-\ddot{O}^- + H_3O^+$$
alcohol   alkoxide ion
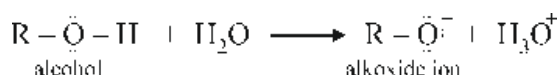
In alcohols, O-H bond is attached to alkyl group, it has electron relasing inductive effect. (+I effect), thus it push the electrons of R-O bond towards oxygen atom, therefore, polarity of O-H bond decreases hence it makes the release of proton difficult. On releasing the proton, alkoxide ion formed is also less stable than alcohol. The +I effect of R, increases electron density on oxygen, making it unstable. Thus alcohol molecules and alkoxide ions both are less stable than carboxlic acid and carboxlate ions, so alcohols show very weak acidic behaviour than carboxylic acids.

Phenols and carboxylic acids both have acidic nature. Phenols are more acidic than alcohols. The conjugate base of carboxylic acid, a carboxylate ion, is stabilized by two equivalent resonating structures and it has negative charge at more electronegative oxygen atom.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

I   II
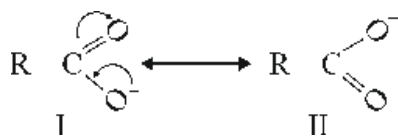
The cunjugate base of phenol, a phenoxide ion, has non-equivalent resonating structures. It has negative charge at less electronegative carbon atom.

III   IV   V   VI   VII
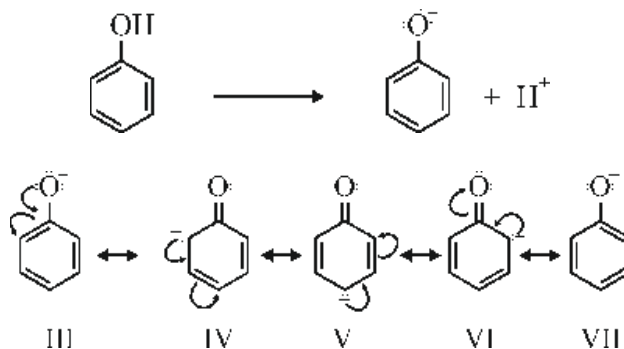
Therefore, resonance in phenoxide ion is not as important as in carboxylate ion. In carboxylate ion negative charge is delocalized over two electronegative oxygen atoms.

In phenoxide ion negative charge is less effectively delocalized over one oxygen atom and less electronegative carbon atom. Thus, the carboxylate ion is more stabilized than phenoxide ion and carboxylic acids are more acidic than phenols.

## Effect of substituents on the acidity of carboxylic acids:

Substituents other than main functional group may affect the acidity of carboxylic acids. If substituents make it easy to remove H^+ ion from acid molecule and stabilize the carboxylate ion through resonance or inductive effect then presence of such groups on carboxylic acids increases its acidity. For example, acidity increases by the presence of groups having -I effect. The effect of the following groups in increasing acidity order is

Phenyl $< I < Br < Cl < F < CN < NO_2 < CF_3$

The groups having –I effect attract electrons of O-H bond towards itself. It will decrease the electron density on O-H bond and O-H bond becomes weaker and releases proton easily. Groups having -I effect also stabilize the carboxylate ion by delocalisation of negative charge, formed after removal of H^+ ion.

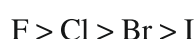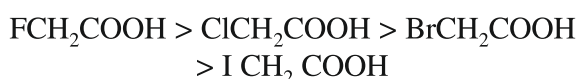For example– Chloroacetic acid

273
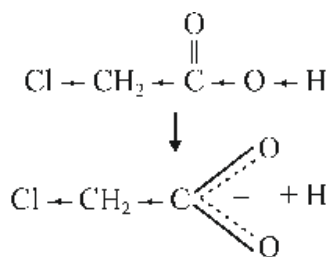
-I effect of chlorine increase acidity

Order of electron withdrawing inductive effect (-I effect) of halogens is–

$$F > Cl > Br > I$$

Thus , the order of α-halo acids will be:

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > I\,CH_2\,COOH$$

As the number of electron withdrawing groups increases, the acidity of carboxylic acid also increases. For example:

$$Cl_3C\,COOH > Cl_2\,CH\,COOH > Cl\,CH_2\,COOH$$

The inductive effect decreases as the distance increases. As the distance of group having -I effect, increases from carboxyl group, acidity decreases. On this basis the order of acidity of α-chloro, β-chloro, γ-chloro follows the order–
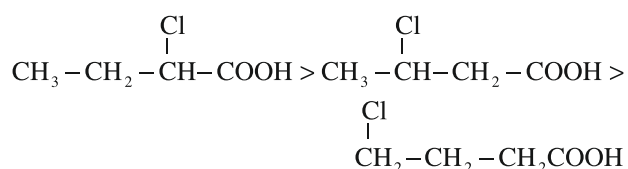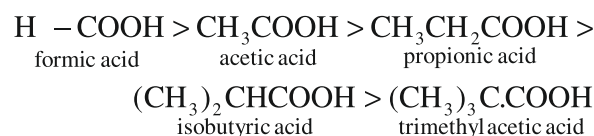

If in carboxylic acid molecule, the substituent make it difficult to remov H$^+$ ion and destabilise the carboxylate ion formed after removal of H$^+$ ion, then it decrease the strength of the acid. For example, in the presence of electron releasing group (+I inductive effect), acidity of carboxylic acid decreases.
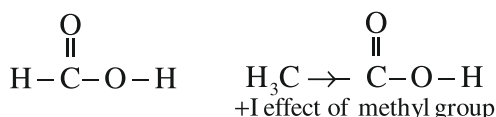
The order of +I effect of alkyl groups is as follows:

$$CH_3 - < CH_3CH_2 - < (CH_3)_2CH - < (CH_3)_3C -$$

On this basis the order of acidity of carboxylic acids will be–

$$H - COOH > CH_3COOH > CH_3CH_2COOH >$$
$$\text{formic acid} \qquad \text{acetic acid} \qquad\qquad \text{propionic acid}$$

$$(CH_3)_2CHCOOH > (CH_3)_3C.COOH$$
$$\text{isobutyric acid} \qquad\qquad \text{trimethyl acetic acid}$$

Formic acid is more acidic than acetic acid.


+I effect of methyl group

In acetic acid, the methyl group has +I effect so it increases the electron density at O – H bond. Thus make removal of proton difficult, with this, due to electron releasing nature of methyl group, negative charge can not be dispersed in acetate ion. Therefore, stability of acetate ion decreases.
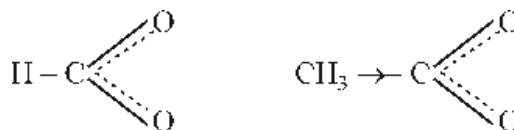
Phenyl group has electron withdrawing (-I) effect if it is directly attached with carboxyl group, then it increses acidity.

formic acid > benzoic acid > acetic acid

In aromatic carboxylic acid, presence of electron withdrawing (-I) group on phenyl ring, increases acidity and presence of electron donating group decreases acidity.

benzoic acid
(p^{Ka} – 4.19)

4-methoxy
benzoic acid
(p^{Ka} – 4.46)

4-nitro
benzoic acid
(p^{Ka} –3.41)
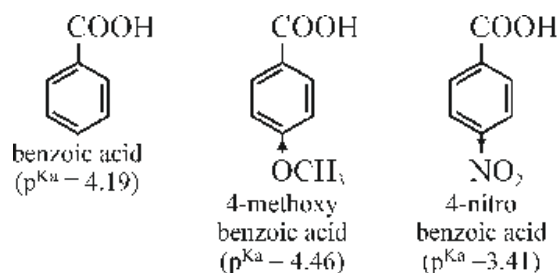
12.2.5 Applications of carboxylic Acids–

(i) Formic acid (HCOOH)

    (a) In the preparation of carbon monoxide in laboratory.

    (b) In textile colour industry.

(c) In preservation of fruits.

(d) In the tanning of leathers.

(e) In the preparation of oxalic acid.

(f) As a reducing agent.

(g) In the coagulation of latex.

(ii) Acetic Acid (CH_3COOH)

(a) As a laboratory reagent and solvent.

(b) As constituent of Vinegar.

(c) In preparation of cellulose ester and other esters.

(d) In the preparation of various carbonyl compounds like acetic anhydride, acetone, acetyl chloride, acetamide, etc.

Imortant points

(1) Aldehydes and ketones are functional group isomers, these contain carbony group ($> C = O$). so these are called carbonyl compounds.

(2) According to IUPAC, aliphatic aldehydes are called alkanals and ketones are known as alkanones.

(3) Due to presence of polar carbonyl group in aldehydes and ketones, they have sufficient dipole moments.

(4) Secondary alcohols are oxidized to ketones by Oppenauer oxidation.

(5) Stephen's Reaction is used to form aldehydes from alkane nitrile.

(6) The synthesis of aldehyde by reduction of alkanoyl chloride is calles Rosenmund reduction.

(7) Due to presence of polar carbonyl group in aldehyde and ketones, most of the reactions shown by them are nucleophilic addition reactions.

(8) Ketones do not give any reaction with Tollen's Reagent and Fehling solution.

(9) The important reaction related to α-hydrogen is Aldol Condensation.

(10) Formaldehyde can not be prepared by Rosenmund Reduction.

EXERCISE QUESTIONS

Multiple Choice Questions

(1) The hybridization of carbon in carbonyl carbon of carbonyl compounds is:
(a) sp^2 d
(b) sp^3
(c) sp^2
(d) sp

(2) Which of the following can not be synthesized by Stephens reaction ?
(a) CH_3CHO
(b) CH_3CH_2CHO
(c) C_6H_5CHO
(d) CH_3COCH_3

(3) Which isomerism is shown by pentanone?
(a) Position isomerism
(b) Chain isomerism
(c) Functional isomerism
(d) All these

(4) Which of the following is used for reduction of aldehydes and ketones in Clemmenson's reduction?
(a) Zinc amalgam and conc. HCI
(b) Red P and HI
(c) $LiA1H_4$
(d) odium ethoxide

(5) The reduction of acetone by Mg-Hg gives:
(a) Aldol
(b) Propane
(c) Pinacol
(d) Propanol

(6) Aldehydes and ketones do not react with :
(a) Sodium bisulphide
(b) Pheny1 hydrazine
(c) Dihydrogen Sodium Phosphate
(d) Semicarbazide

(7) When ethanol is heated with Fehling's solution, then the precipitate obtained is of:
(a) Cu
(b) CuO
(c) Cu_2O
(d) Cu + CuO

(8) Which of the following is not synthesized by Rosenmund Reduction :
(a) Formaldehyde
(b) Acetaldehyde
(c) Butyraldehyde
(d) Formaldehyde and Acetaldehyde

(9)   Which of the following undergo Aldol Condensation ?

    (a) $CH_3 CH_2 CHO$ (b) C_6H_5CHO

    (c) $CH\equiv CCHO$ (d) $CH_2=C(Cl)CHO$

(10) Which of the following method is used for conversion of ketone to hydrocarbon?

    (a)   Wolff-Kishner reduction

    (b)   Clemenson reduction

    (c)   Cannizzaro reaction

    (d)   Aldol condensation

Very Short Answer Questions

(11) Write the IUPAC name of :

    (a)   Acetaldehyde   (b)   Isobutyraldehyde

(12) Write the IUPAC name of :

    (a)   Methyl propyl ketone

    (b)   Ethyl methyl ketone

(13) What is the singnificance of Oppenauer oxidation?

(14) Formaldehyde cannot be prepared by Rosenmund Reduction ? Give reasons.

(15) What are the main reactions shown by carbonyl compounds?

(16) Write the following nucleophiles in increasing order.

    $CH_3CHO, CH_3COCH_3, HCHO, C_2H_5COCH_3$

(17) What is Tolllen's Reagent and Fehling's solution.

(18) Name one aldehyde which gives Fehling's test.

Short Answer Type Questions

(19) Ozonolysis of ethene gives which product. Also write the equation.

(20) Explain Stephen's reaction and Rosenmund reaction.

(21) "Aldehydes are good reducing agents". Explain it by giving two reactions.

(22) Complete the following reactions and write product also:

    (i) $CH_3 - CH_2 - OH \xrightarrow{Cu/573K}$?

    (ii) $R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + H_2 \xrightarrow{Pd/BaSO2}$?
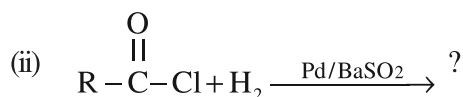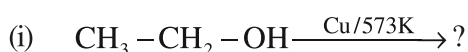
(23) What is Meerwein- Ponndorf – Verley reduction (MPV).

(24) Explain the reason for acidity of α-hydrogen atom in aldehydes.

(25) Explain the commercial importance of formaldehyde and acetaldehyde.

(26) Write the method of preparation of pinacol from ketone.

(27) The acidity of formic acid is more than acetic acid. Explain.

Long Answer Questions

(28) Explain the similarity and dissimilarity between aldehydes and ketones.

(29) Which methods is used for preparation of both aldehydes and ketones. Give chemical equations.

(30) Aldehydes are more active towards nucleohilic addition reactions. Explain.

(31) Explain the following reactions and give equations also:

    (i)   Preparation of Alcohols from carbonyl compounds.

    (ii)   Addition product obtained by addition of carbonyl compound and Alcohols.

    (iii) Reduction of Tollen's Reagent.

    (iv)   Baeyer-Villiger oxidation.

    (v)   Cannizzaro Reaction.

    (vi)   Kolbe's electrolysis.

    (vii) Hunsdiecker reaction.

Answers (Multiple Choice Questions)

1. (c),   2. (d),   3. (d),   4. (a),

5. (c),   6. (c),   7. (c),   8. (a),

9. (a),   10. (b)