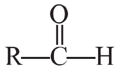
Chapter–12

Aldehydes, Ketones and Carboxylic Acids

basic concepts

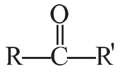
1. **The Carbonyl Group, $>C=O$:** The functional group $>C=O$ is called carbonyl group. Organic compounds containing carbonyl group are aldehydes, ketones, carboxylic acids and their derivatives. The general formulae of these compounds are given below:



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

Aldehyde

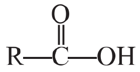
(where R may be H or any alkyl, aryl or aralkyl group)



$R-\overset{\overset{O}{\|}}{C}-R'$

Ketone

(where R and R' may be same or different alkyl, aryl or aralkyl group)

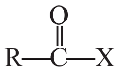


$R-\overset{\overset{O}{\|}}{C}-OH$

Carboxylic acid

(where R may be H or any alkyl, aryl or aralkyl group)

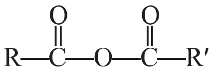
Derivatives of Carboxylic Acids:



$R-\overset{\overset{O}{\|}}{C}-X$

Acyl halide

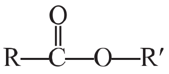
X = Halogen



$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$

Acid anhydride

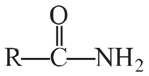
(where R and R′ may be same or different groups)



$R-\overset{\overset{O}{\|}}{C}-O-R'$

Ester

(where R and R′ may be same or different groups)



$R-\overset{\overset{O}{\|}}{C}-NH_2$

Acid amide

(where R may be H or any group)

The carbon atom of the carbonyl group is sp^2 hybridised. The structure of carbonyl group is shown in Fig. 12.1.

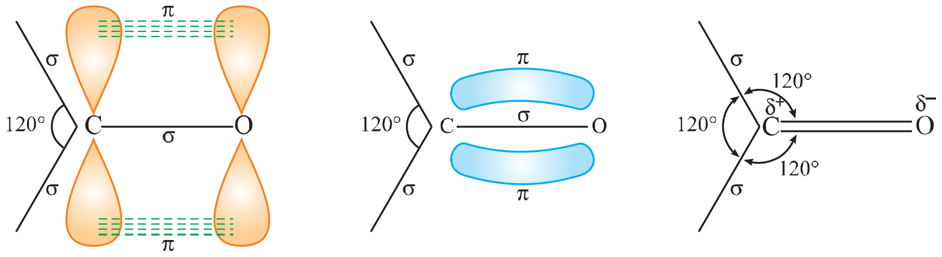


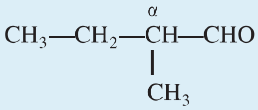
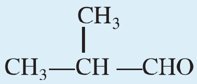
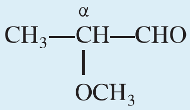
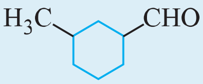
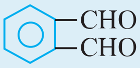
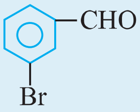
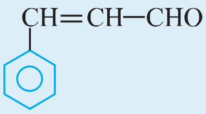
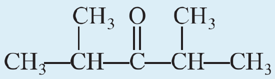
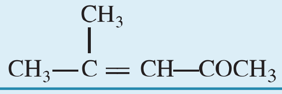
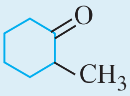
Fig. 12.1 Structure of Carbonyl Group ($>C=O$)

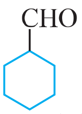
The $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond is polar due to higher electronegativity of oxygen atom as compared to carbon.

2. **Common and IUPAC Names of Some Aldehydes and Ketones:**

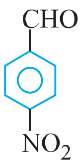
Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Common Name	Structural Formula	IUPAC Name
Formaldehyde	HCHO	Methanal
Acetaldehyde	CH_3-CHO	Ethanal

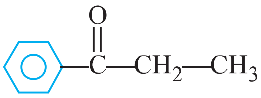
α-Methylbutyraldehyde	 $\overset{\alpha}{CH_3—CH_2—CH(CH_3)—CHO}$	2-Methylbutanal
Isobutyraldehyde	 $CH_3—CH(CH_3)—CHO$	2-Methylpropanal
Valeraldehyde	$CH_3—CH_2—CH_2—CH_2—CHO$	Pentanal
Acrolein	$CH_2{=}CH—CHO$	Prop-2-enal
α-Methoxypropionaldehyde	 $CH_3—\overset{\alpha}{C}H(OCH_3)—CHO$	2-Methoxypropanal
γ-Methylcyclohexane		3-Methylcyclohexanecarbaldehyde
Phthaldehyde		Benzene-1, 2-dicarbaldehyde
m-Bromobenzaldehyde		3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Crotonaldehyde	$CH_3—CH{=}CH—CHO$	But-2-enal
Cinnamaldehyde		3-Phenyl prop-2-enal
Acetone	CH_3COCH_3	Propanone
Diisopropyl ketone	 $CH_3—CH(CH_3)—CO—CH(CH_3)—CH_3$	2, 4-Dimethylpentan-3-one
Mesityl oxide	 $CH_3—C(CH_3){=}CH—COCH_3$	4-Methylpent-3-en-2-one
α-Methylcyclohexanone		2-Methylcyclohexanone



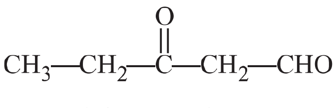
Cyclohexanecarbaldehyde



4-Nitrobenzenecarbaldehyde
or 4-Nitrobenzaldehyde

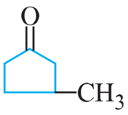


1-Phenyl propanone

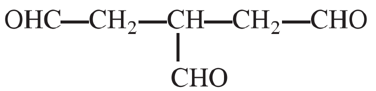


$$CH_3—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2—CHO$$

3-Oxopentanal

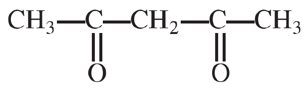


3-Methylcyclopentanone



$$OHC-CH_2-\underset{\underset{CHO}{|}}{CH}-CH_2-CHO$$

Propane-1,2,3-tricarbaldehyde



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Pentane-2,4-dione

3. Preparation of Aldehydes

(*a*) By oxidation of primary alcohols

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} + [O] \xrightarrow[\text{or } KMnO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\substack{\text{Aldehyde}\\ \text{(distilled out as soon}\\ \text{as formed)}}}{R-CHO} + H_2O$$

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Aldehyde}}{R-CHO}$$

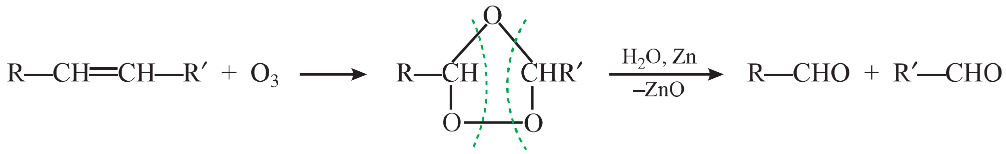
$$\underset{\text{But-2-en-1-ol}}{CH_3-CH=CH-CH_2-OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO}$$

(*b*) By dehydrogenation of primary alcohols

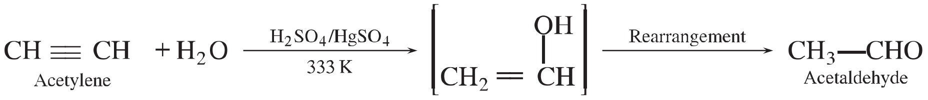
$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R-CHO} + H_2$$

(*c*) From hydrocarbons

(*i*) By ozonolysis of alkenes

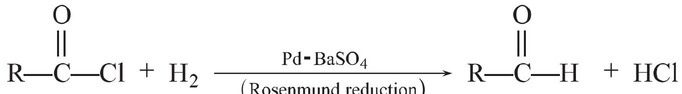


(*ii*) By hydration of alkynes

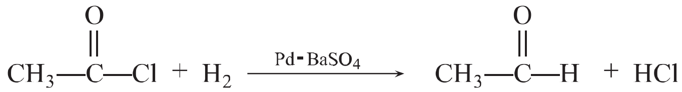


$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[333\text{ K}]{H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_2=\overset{\overset{OH}{|}}{CH}\right]} \xrightarrow{\text{Rearrangement}} \underset{\text{Acetaldehyde}}{CH_3-CHO}$$

(*d*) From acyl chloride



$$R-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{(Rosenmund reduction)}]{Pd\text{-}BaSO_4} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + HCl$$



$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + HCl$$

(*e*) From nitriles and esters

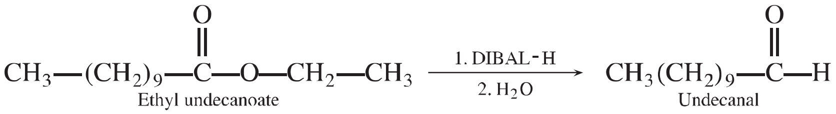
$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

$$R-C\equiv N + HCl + 2[H] \longrightarrow R-CH=NH.HCl \xrightarrow[-NH_4Cl]{+H_2O} \underset{\text{Aldehyde}}{R-CHO}$$

This reaction is called **Stephen reaction**

$$R-CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \underset{\text{Aldehyde}}{R-CHO}$$

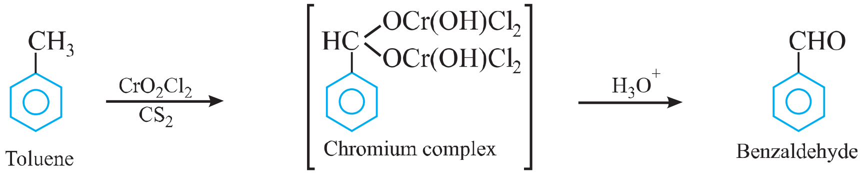
$$\underset{\text{Hex-4-enenitrile}}{CH_3-CH=CH-CH_2-CH_2-CN} \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \underset{\text{Hex-4-en-1-al}}{CH_3-CH=CH-CH_2-CH_2-CHO}$$



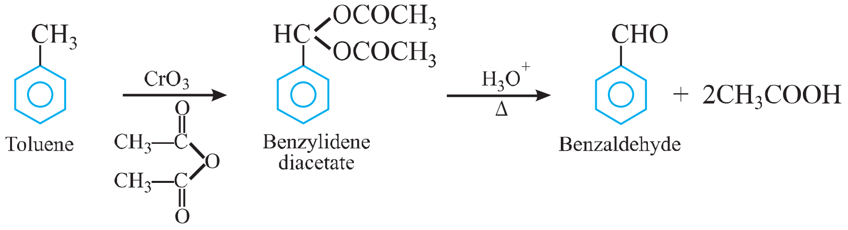
$$\underset{\text{Ethyl undecanoate}}{CH_3-(CH_2)_9-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3} \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} \underset{\text{Undecanal}}{CH_3(CH_2)_9-\overset{\overset{O}{\|}}{C}-H}$$

4. Preparation of Benzaldehyde

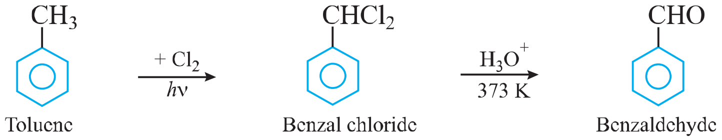
(*a*) By oxidation of toluene



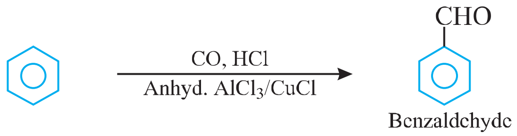
This reaction is called **Etard reaction**.



(*b*) By side chain chlorination followed by hydrolysis

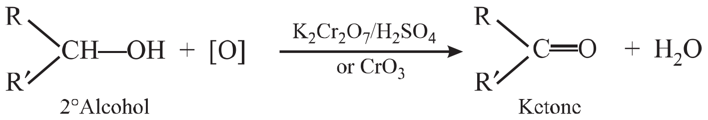


(*c*) By Gatterman–Koch reaction

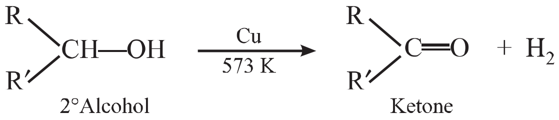


5. Preparation of Ketones

(*a*) By oxidation of secondary alcohols

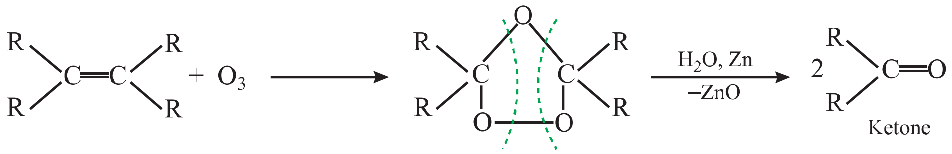


(*b*) By dehydrogenation of secondary alcohols

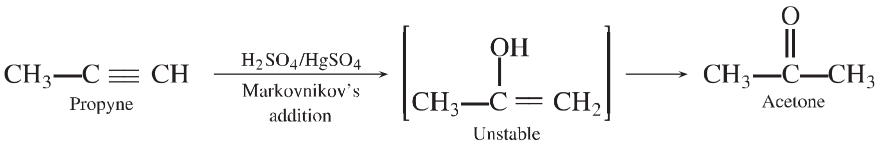


(*c*) From hydrocarbons

(*i*) By ozonolysis of alkenes

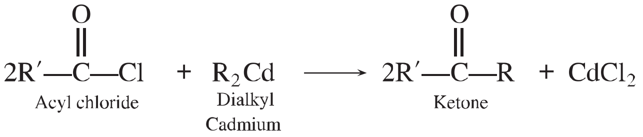


(*ii*) By hydration of alkynes



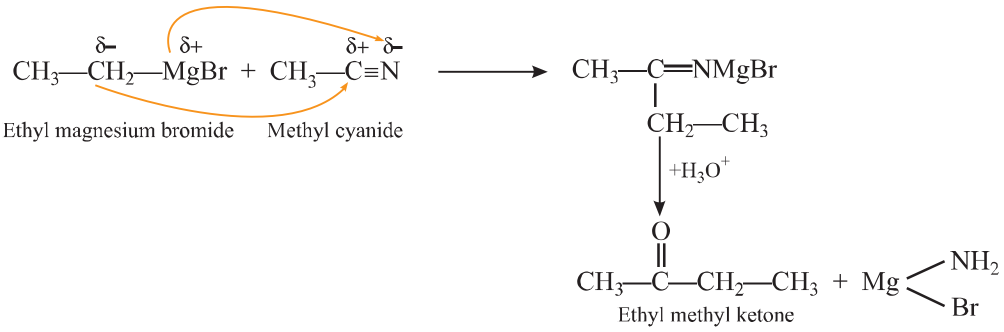
(*d*) From acyl chlorides

$$2R{-}MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$



$$\underset{\text{Acyl chloride}}{2R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} + \underset{\text{Dialkyl Cadmium}}{R_2Cd} \longrightarrow \underset{\text{Ketone}}{2R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R} + CdCl_2$$

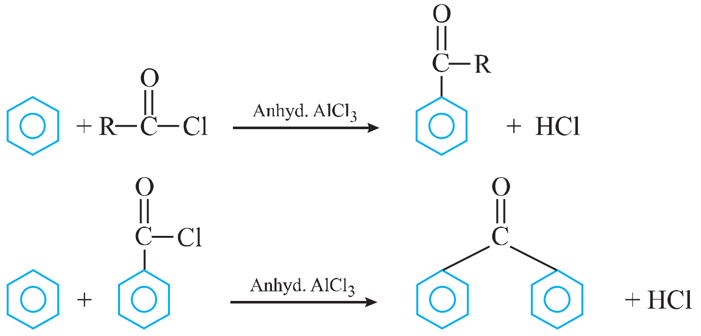
(*e*) From nitriles



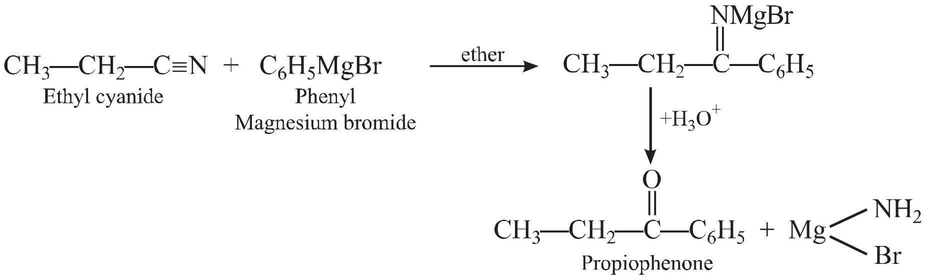
$$\underset{\text{Ethyl magnesium bromide}}{CH_3{-}\overset{\delta-}{CH_2}{-}\overset{\delta+}{MgBr}} + \underset{\text{Methyl cyanide}}{CH_3{-}\overset{\delta+}{C}{\equiv}\overset{\delta-}{N}} \longrightarrow CH_3{-}\underset{\displaystyle CH_2{-}CH_3}{\underset{|}{C}}{=}NMgBr \xrightarrow{+H_3O^+} \underset{\text{Ethyl methyl ketone}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3} + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

6. Preparation of Aromatic Ketones

(*a*) By Friedel-Crafts acylation



(*b*) From nitriles



$$\underset{\text{Ethyl cyanide}}{CH_3{-}CH_2{-}C{\equiv}N} + \underset{\text{Phenyl Magnesium bromide}}{C_6H_5MgBr} \xrightarrow{\text{ether}} CH_3{-}CH_2{-}\overset{\overset{\displaystyle NMgBr}{\|}}{C}{-}C_6H_5 \xrightarrow{+H_3O^+} \underset{\text{Propiophenone}}{CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5} + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

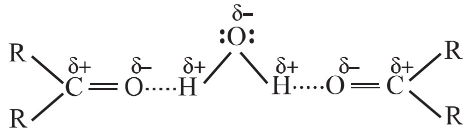
7. Physical Properties of Aldehydes and Ketones

(*a*) **Physical state:** Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell. The higher members are colourless solids. Aromatic ketones are usually solids with a pleasant smell.

(*b*) **Boiling points:** Aldehydes and ketones have relatively high boiling points as compared to hydrocarbons of comparable molecular masses. It is due to the reason that aldehydes and ketones contain polar carbonyl group and therefore, they have stronger dipole–dipole interactions between the opposite ends of C=O dipoles.

These dipole–dipole interactions are however, weaker than intermolecular H-bonding in alcohols. Consequently, boiling points of aldehydes and ketones are relatively lower than the alcohols of comparable molecular masses.

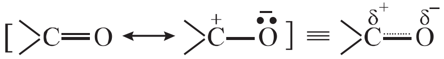
(*c*) **Solubility:** The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water. It is due to their capability to form hydrogen bonds with water molecules. The solubility of these compounds in water decreases with the increase in the size of alkyl group. It is because of the increase in the magnitude of non-polar part in the molecule. However, higher homologues are soluble in organic solvents.



8. Chemical Properties

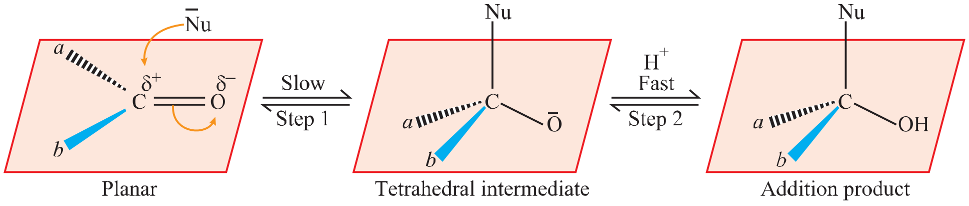
Aldehydes and ketones are highly reactive compounds. Both aldehydes and ketones undergo nucleophilic addition reactions.

Explanation: The reactive nature of aldehydes and ketones is because of the presence of a polar carbonyl group. As the oxygen atom is more electronegative, therefore, it pulls the electron around itself acquiring a partial negative charge (δ^-) whereas a partial positive charge (δ^+) is developed on the carbon atom.



Resonating forms

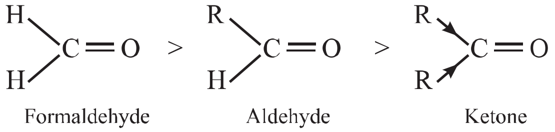
The positively charged carbon atom of carbonyl group is then readily attacked by the nucleophilic species for initiation of the reaction. This leads to the formation of an intermediate anion which further undergoes the attack of (H^+) ion or other positively charged species to form the final product. The nucleophilic reactions may be catalysed by acids or bases. The reaction in general, may be represented as:



Relative Reactivity of Aldehydes and Ketones

In general, ketones are less reactive than aldehydes on account of the following facts:

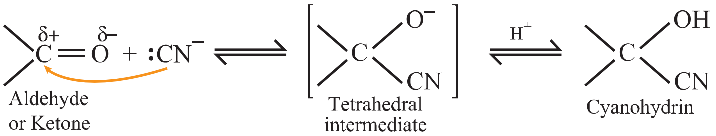
Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

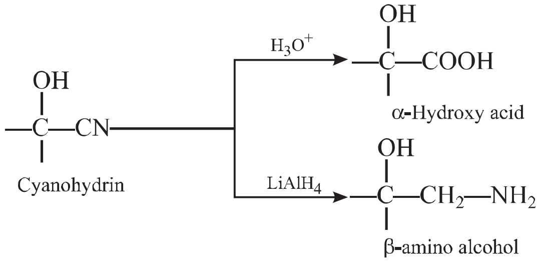


Some Important Nucleophilic Addition Reactions

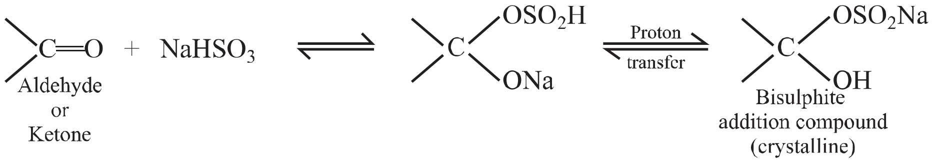
(*a*) **(*i*) Addition of hydrogen cyanide (HCN)**

$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



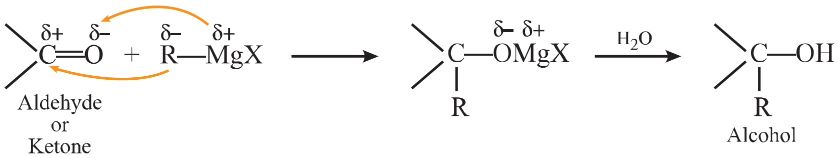


(*ii*) Addition of sodium hydrogensulphite ($NaHSO_3$)

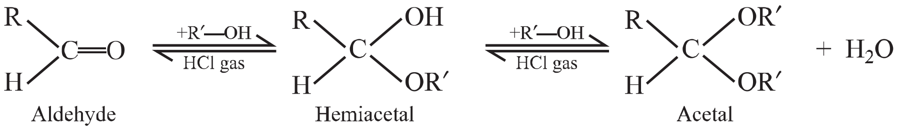


This reaction is useful for separation and purification of aldehydes and ketones.

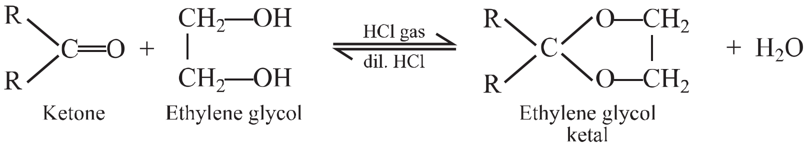
(*iii*) Addition of Grignard reagent



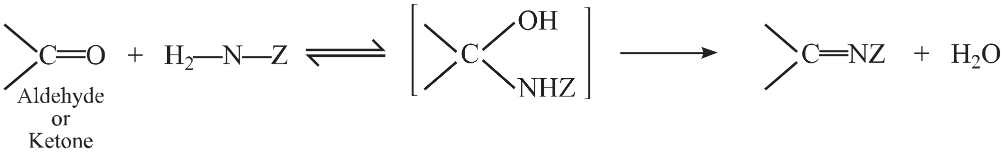
(*iv*) Addition of alcohols

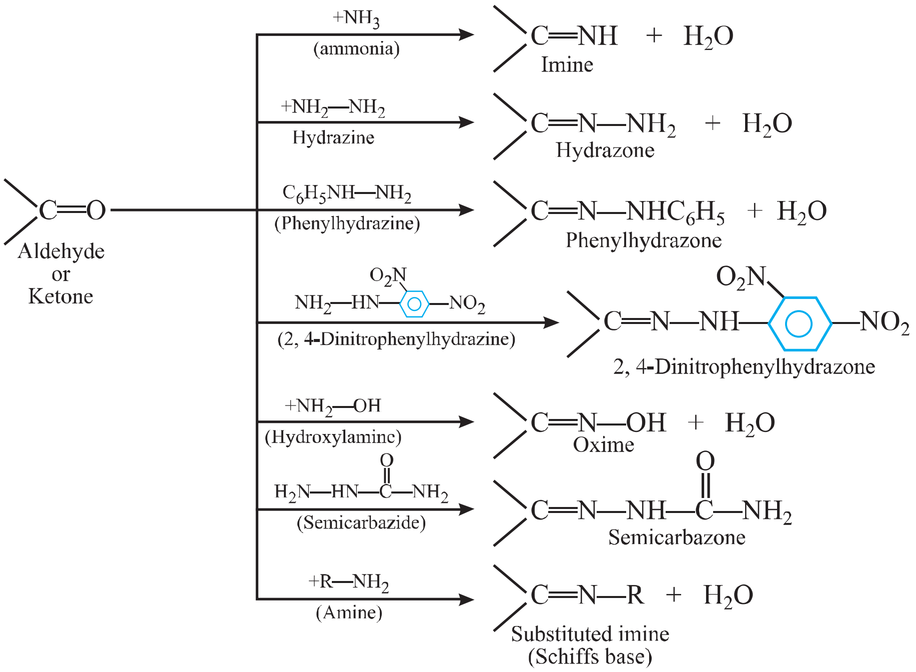


Ketones do not react with monohydric alcohols but react with dihydric alcohols to give ketals.



(*b*) Addition of ammonia and its derivatives

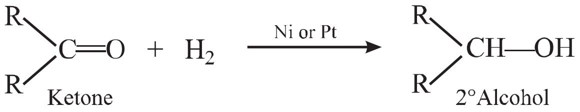




(*c*) Reduction

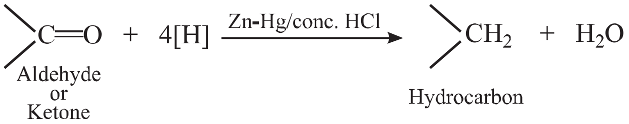
(*i*) Reduction to alcohols: Aldehydes and ketones are reduced to primary and secondary alcohols, respectively, by $LiAlH_4$ or $NaBH_4$ or H_2 in the presence of Ni or Pt.

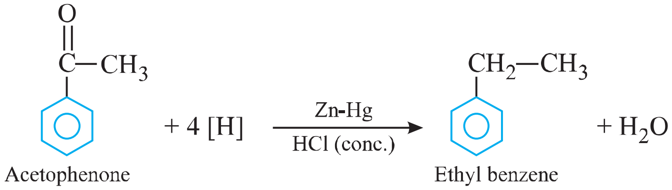
$$\underset{}{R—CHO} + 2[H] \xrightarrow[\text{or NaBH}_4]{\text{LiAlH}_4} \underset{1^\circ\ \text{Alcohol}}{R—CH_2—OH}$$



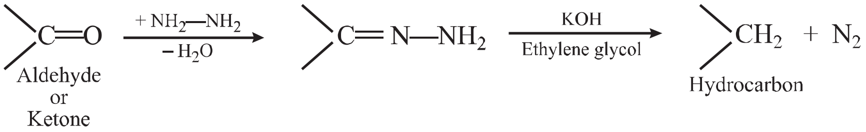
(*ii*) Reduction to hydrocarbons

(Clemmensen reduction)





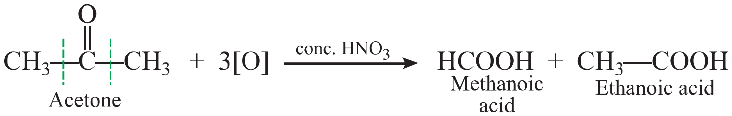
(Wolff–Kishner reduction)



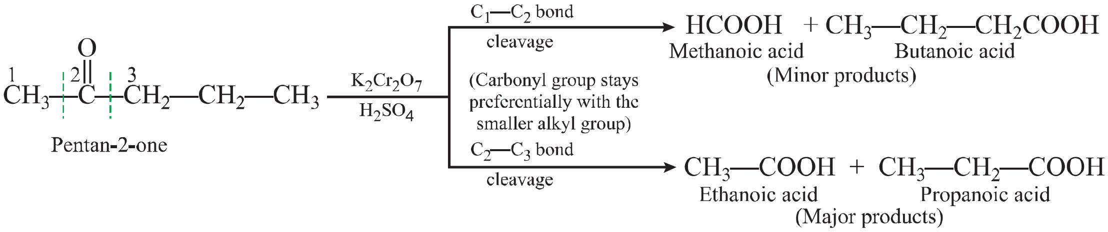
(*d*) Oxidation: Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollens' reagent or Fehling's solution.

$$\underset{\text{Aldehyde}}{R—CHO} + [O] \xrightarrow[\text{KMnO}_4/\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4 \text{ or}} \underset{\text{Carboxylic acid}}{R—COOH}$$

Ketones undergo oxidation under vigorous conditions with cleavage of carbon–carbon bond.



$$\underset{\text{Acetone}}{CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3} + 3[O] \xrightarrow{\text{conc. HNO}_3} \underset{\text{Methanoic acid}}{HCOOH} + \underset{\text{Ethanoic acid}}{CH_3—COOH}$$

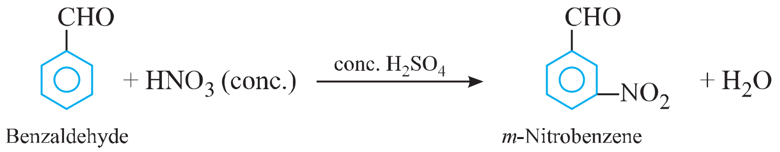


As ketones are not oxidised by mild oxidising agents such as Tollens' reagent and Fehling's solution, these reagents are used to distinguish aldehydes from ketones.

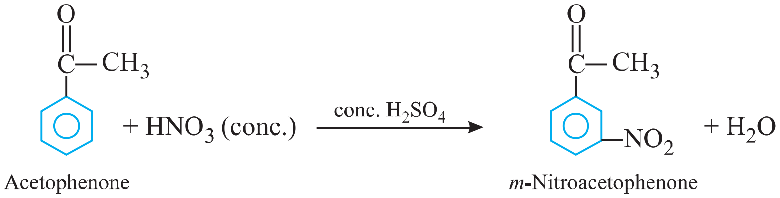
Electrophilic substitution reactions:

As, $—\overset{\overset{\displaystyle O}{\|}}{C}—H$ or $—\overset{\overset{\displaystyle O}{\|}}{C}—R$ group are electron-withdrawing and, therefore they are deactivating and *m*-directing.

Nitration:



Benzaldehyde *m*-Nitrobenzene



Acetophenone *m*-Nitroacetophenone

9. Uses of Aldehydes and Ketones

(*i*) A 40% aqueous solution of formaldehyde is known as formalin and is used to preserve biological specimens and to prepare bakelite.

(*ii*) Acetaldehydes are used as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.

(*iii*) Benzaldehyde is used in perfumery and in dye industries.

(*iv*) Acetone and ethyl methyl ketone are common industrial solvents.

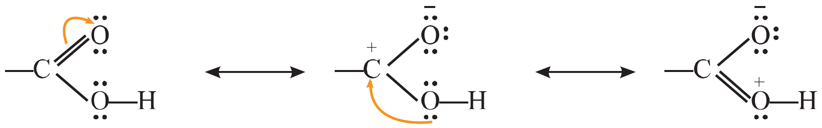
10. Carboxylic Acid

Organic compounds containing carboxyl group $-C\begin{smallmatrix} \nearrow O \\ \searrow OH \end{smallmatrix}$ possess sufficient acidic character and are called carboxylic acids. The carboxyl group is made up of carbonyl, $>C=O$ and hydroxyl, —OH group, hence, its name is carboxyl group (carb from carbonyl and oxyl from hydroxyl). Carboxylic acids may be aliphatic (R—COOH) or aromatic (Ar—COOH) depending upon whether —COOH group is attached to aliphatic alkyl chain or aryl groups, respectively.

Aliphatic monocarboxylic acids are known as fatty acids because some of their higher members (C_{12}—C_{18}) like palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) exist in natural fats as esters of glycerol and are obtained by their hydrolysis.

Structure of Carboxyl Group

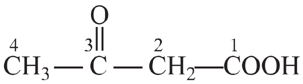
In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



11. In IUPAC system, the name of carboxylic acid is derived by replacing terminal **e** of the alkane with **oic acid**. For example,

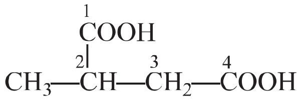
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}OOH$

Propanoic acid



$\overset{4}{C}H_3-\overset{\overset{O}{\|}}{\underset{3}{C}}-\overset{2}{C}H_2-\overset{1}{C}OOH$

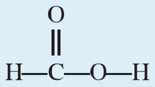
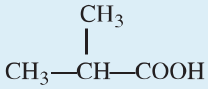
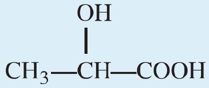
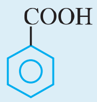
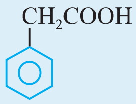
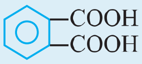
3-Oxobutanoic acid

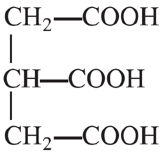


$CH_3-\overset{\overset{\overset{1}{COOH}}{|}}{\underset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}OOH$

2-Methyl butane-1, 4-dioic acid

Table 12.2: Common and IUPAC Names of Some Carboxylic Acids

Common Name	Structural Formula	IUPAC Name
Formic acid	 $H-\overset{\overset{O}{\|}}{C}-O-H$	Methanoic acid
Acetic acid	CH_3-COOH	Ethanoic acid
Isobutyric acid	 $CH_3-\overset{\overset{CH_3}{\mid}}{CH}-COOH$	2-Methyl propanoic acid
Oxalic acid	$HOOC-COOH$	Ethanedioic acid
Malonic acid	$HOO\overset{3}{C}-\overset{2}{C}H_2-\overset{1}{C}OOH$	Propane-1, 3-dioic acid
Succinic acid	$HOOC-(CH_2)_2-COOH$	Butane-1, 4-dioic acid
Glutaric acid	$HOOC-(CH_2)_3-COOH$	Pentane-1, 5-dioic acid
Adipic acid	$HOOC-(CH_2)_4-COOH$	Hexane-1, 6-dioic acid
Lactic acid	 $CH_3-\overset{\overset{OH}{\mid}}{CH}-COOH$	2-Hydroxy propanoic acid
Acrylic acid	$CH_2=CH-COOH$	Prop-2-enoic acid
Crotonic acid	$CH_3-CH=CH-COOH$	But-2-enoic acid
Benzoic acid		Benzene carboxylic acid(Benzoic acid)
Phenyl acetic acid		2-Phenylethanoic acid
Phthalic acid		Benzene-1, 2-dicarboxylic acid



$$\begin{array}{l} CH_2-COOH \\ \mid \\ CH-COOH \\ \mid \\ CH_2-COOH \end{array}$$

Propane-1, 2, 3-tricarboxylic acid

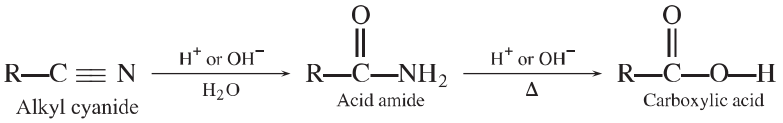
12. Methods of Preparation of Carboxylic Acids

(*a*) By oxidation of primary alcohols and aldehydes.

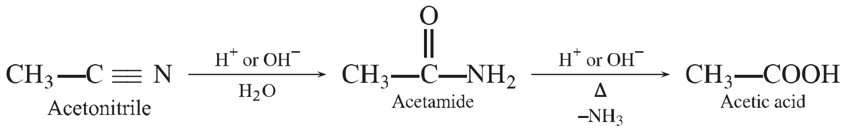
$$\underset{1^\circ\text{ Alcohol}}{R-CH_2-OH} \xrightarrow[(ii)\ H_3O]{(i)\ \text{Alk. }KMnO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[\substack{\text{or} \\ CrO_3/H_2SO_4 \\ \text{(Jones reagent)}}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

(*b*) From alkyl cyanides and amides.



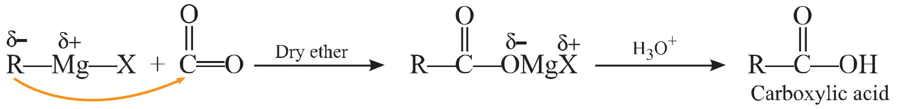
$$\underset{\text{Alkyl cyanide}}{R-C\equiv N} \xrightarrow[H_2O]{H^+\text{ or }OH^-} \underset{\text{Acid amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\Delta]{H^+\text{ or }OH^-} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-O-H}$$



$$CH_3-C\equiv N \xrightarrow[H_2O]{H^+ \text{ or } OH^-} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\Delta,\ -NH_3]{H^+ \text{ or } OH^-} CH_3-COOH$$

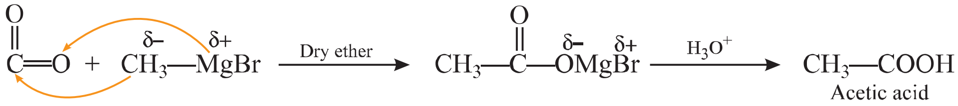
Acetonitrile — Acetamide — Acetic acid

(*c*) From Grignard reagent



$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-X + \overset{\overset{\displaystyle O}{\|}}{C}=O \xrightarrow{\text{Dry ether}} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\delta-}{O}\overset{\delta+}{MgX} \xrightarrow{H_3O^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

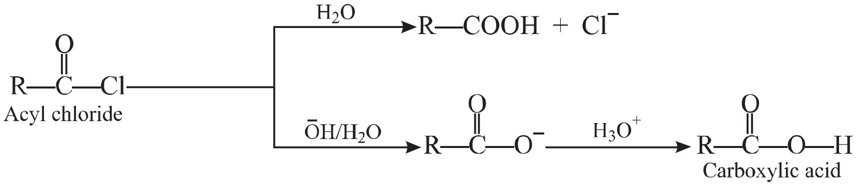
Carboxylic acid



$$\overset{\overset{\displaystyle O}{\|}}{C}=O + \overset{\delta-}{CH_3}-\overset{\delta+}{MgBr} \xrightarrow{\text{Dry ether}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\delta-}{O}\overset{\delta+}{MgBr} \xrightarrow{H_3O^+} CH_3-COOH$$

Acetic acid

(*d*) By hydrolysis of acyl halides and acid anhydrides



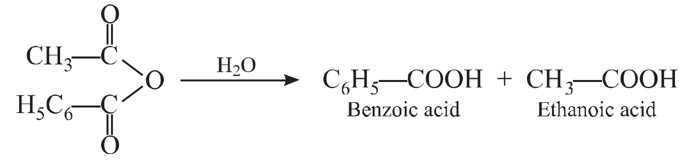
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{H_2O} R-COOH + Cl^-$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{\bar{O}H/H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \xrightarrow{H_3O^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

Acyl chloride — Carboxylic acid

$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5-COOH$$

Benzoic anhydride — Benzoic acid



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow{H_2O} C_6H_5-COOH + CH_3-COOH$$

Benzoic ethanoic anhydride

Benzoic acid — Ethanoic acid

(*e*) By hydrolysis of esters

$$CH_3-CH_2-CH_2-COOCH_2-CH_3 \xrightleftharpoons{NaOH} CH_3-CH_2-CH_2-CO\overset{-}{O}\overset{+}{Na} + CH_3-CH_2-OH$$

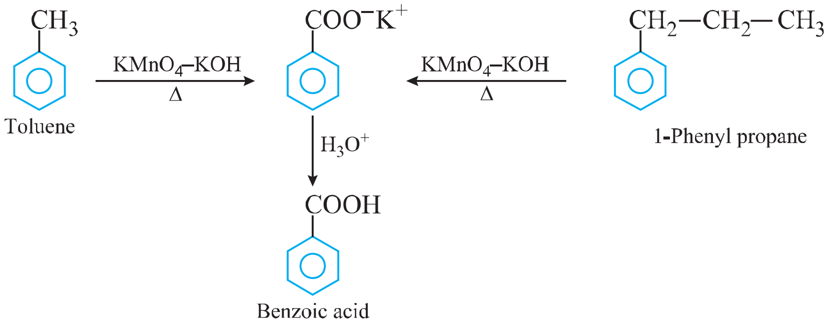
Ethyl butyrate

$$CH_3-CH_2-CH_2-CO\overset{-}{O}\overset{+}{Na} \xrightarrow{H_3O^+} CH_3-CH_2-CH_2-COOH$$

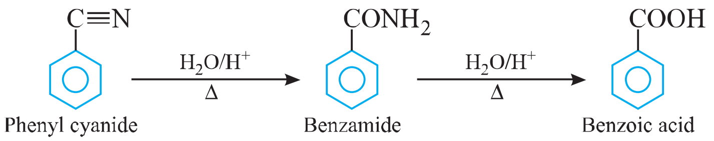
Butanoic acid

Preparation of benzoic acid

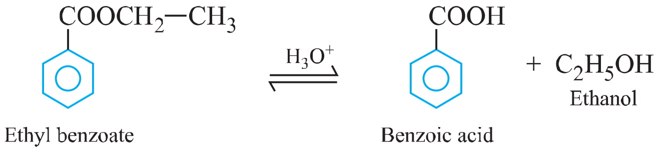
(*i*) From alkyl benzene



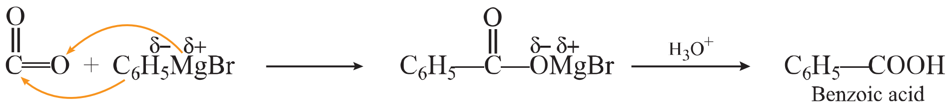
(*ii*) From nitriles and amides



(*iii*) By hydrolysis of esters



(*iv*) From Grignard reagent



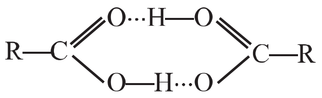
13. Physical Properties of Carboxylic Acids

(*a*) **Physical state:** The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids with an odour of rancid butter while the higher members are colourless, odourless, waxy solids. Benzoic acid is a crystalline solid.

(*b*) **Solubility:** Carboxylic acid molecules are polar, like alcohols, and can form intermolecular hydrogen bonds. The first four acids are miscible with water, the $C_5H_{11}COOH$ is partly soluble and the higher acids are insoluble. It is because of the increase in the magnitude of non-polar part in the molecule. Benzoic acid is practically insoluble in water.

Carboxylic acids are soluble in less polar solvents like ether, benzene, alcohol, etc.

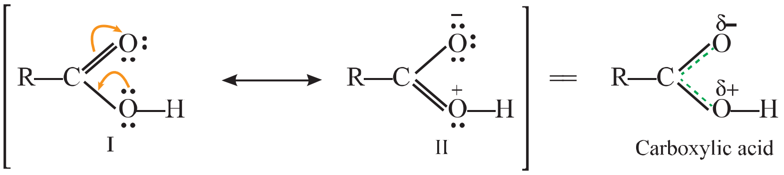
(*c*) **Boiling points:** Because of their ability to form intermolecular hydrogen bonding, carboxylic acids have high boiling points. The hydrogen bonds formed by the carboxylic acids are stronger than those in alcohols because O—H bond in COOH is strongly polarised due to the presence of electron-withdrawing carbonyl group in adjacent position than the O—H bond of alcohols. Therefore, the boiling points of carboxylic acids particularly lower members are higher than alcohols of comparable molecular masses.



Intermolecular hydrogen bonding in carboxylic acids

14. Chemical Properties of Carboxylic Acids

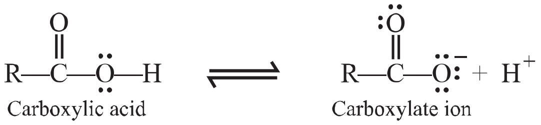
Carboxylic acids are resonance hybrid of the following structures:



From these structures, it is clear that the carbonyl parts of the carboxyl group have a reduced double bond character. Thus, it does not give the reactions of the carbonyl group. Also it is evident that the two contributing structures of carboxylic acid are not equivalent, therefore, they are less resonance stabilized. Moreover, oxygen atom of —OH group has positive charge in structure II, this indicates its electron deficient nature. Hence, the shared pair of electrons of O—H bond will be strongly pulled towards oxygen and this makes the O—H bond quite polar. Thus, the reactions of carboxylic acids are characteristic of the carboxyl group and alkyl group.

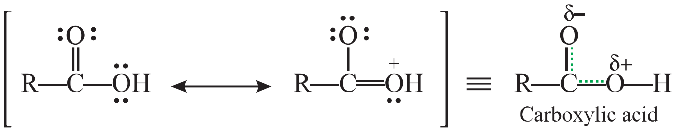
Acidic Nature

Carboxylic acids are quite strong acids because of the presence of polar O—H group. They ionise to give hydrogen ions and hence behave as acids.

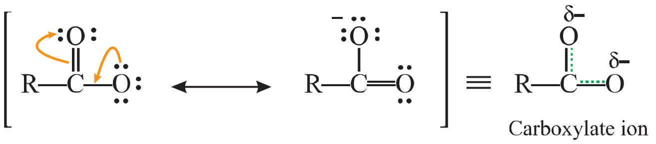


Carboxylic acids behave as fairly strong acids: This can be explained as follows:

Carboxylic acids as well as carboxylate ion both are stabilised by resonance. However, carboxylate ion is more stabilised by resonance because its contributing structures are exactly identical. On the other hand, the contributing structures of carboxylic acid involve charge separation. Since carboxylate ion is more stabilised by resonance than carboxylic acid, therefore, equilibrium lies very much in forward direction, *i.e.*, in favour of ionised form. Hence, carboxylic acids behave as fairly strong acids.



Less stabilised



More stabilised

Acidity of carboxylic acids: Both carboxylic acid and carboxylate ion are resonance stabilised but stabilisation is far greater for the carboxylate ion than for the acid. Thus, carboxylic acids get ionised due to gain in the stability in going from carboxylic acid to the more stable carboxylate ion. Any factor that stabilises the carboxylate ion more would facilitate the release of protons and increase the acidity. Thus, electron-withdrawing substituents (Cl, NO_2, CN, etc.) in a carboxylic acid would disperse the negative charge of the COO^-, stabilise it and thus enhance the acid strength. On the other hand, the presence of an electron-donating substituent such as alkyl group, would intensify the negative charge on the COO^- ion and thus destabilise it, making the carboxylic acid less acidic.

The effect of some substituents is as follows:

(*i*) Effect of electron withdrawing substituents: The electron withdrawing substituents decrease the electron density on the O—H bond thus facilitating the release of H^+ ions and also stabilise the carboxylate anion by dispersal of negative charge. Thus, an electron-withdrawing group increases the strength of the acid.

(*ii*) Effect of electron releasing substituents—alkyl groups: The presence of electron releasing substituent intensifies the electron density in O—H bond. As a result, it adversely affects the release of H^+ ions and thus decreases the acidic character.

(*iii*) Acidity decreases with larger alkyl groups as the +I effect of the alkyl group increases with size of alkyl group. For example, Formic acid > Acetic acid > Propanoic acid.

(*iv*) Acidity increases with increasing number of electron-withdrawing substituents on the α-carbon. For example, Acetic acid < Chloroacetic acid < Dichloroacetic acid (Cl_2CH—COOH) < Trichloroacetic acid (Cl_3C—COOH).

(*v*) Acidity increases with increasing electronegativity of substituents. Thus,

Iodoacetic acid (ICH_2—COOH) < Bromoacetic acid ($BrCH_2$—COOH) < Chloroacetic acid ($ClCH_2$—COOH) < Fluoroacetic acid (FCH_2—COOH).

(*vi*) Acidity declines with increasing distance between electron-withdrawing group and COOH group. For example, 2-Chlorobutanoic acid > 3-Chlorobutanoic acid > 4-Chlorobutanoic acid.

(*vii*) Unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids. Benzoic acid is a stronger acid than acetic acid. Further, since formic acid does not contain any alkyl group, therefore, it is a stronger acid than benzoic acid. Thus,

Formic acid > Benzoic acid > Acetic acid

Effect of substituents on the acidic strength of benzoic acid.

(*i*) The electron-releasing groups such as, —CH_3, —OH, —NH_2, etc., tend to decrease the acid strength of benzoic acid. The electron-withdrawing groups such as —Cl, —NO_2, etc., tend to increase the strength of benzoic acid.

(*ii*) Ortho isomer of benzoic acid is the strongest of all the isomers irrespective of the nature of the substituent. This is called ortho effect. This effect may be due to a combination of steric and electronic factors.

(*iii*) The acid-strengthening effect of electron-withdrawing group (*e.g.*, —Cl, —NO_2, etc.) is more pronounced at *p*-position than at *m*-position.

(*iv*) The acid-weakening effect of an electron-releasing substituent (*e.g.*, —OH, —CH_3, —NH_2, etc.) is more pronounced at *p*-position than at *m*-position.

15. Chemical Reactions

The reaction of carboxylic acids are classified as follows:

(*a*) Reactions involving cleavage of O—H bond: Reaction with metals and alkalis.

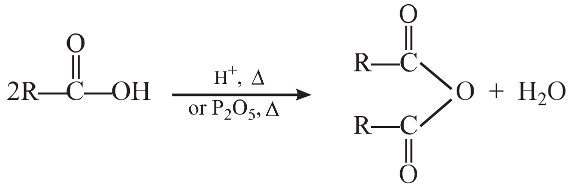
$$2R\text{—}COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{—}CO\overset{-}{O}\overset{+}{Na}} + H_2$$

$$R\text{—}COOH + NaOH \longrightarrow R\text{—}CO\overset{-}{O}\overset{+}{Na} + H_2O$$

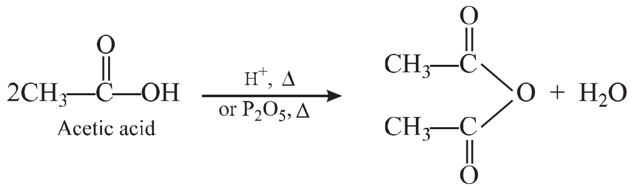
$$R\text{—}COOH + NaHCO_3 \longrightarrow R\text{—}CO\overset{-}{O}\overset{+}{Na} + H_2O + CO_2\uparrow$$

(*b*) Reactions involving cleavage of C—OH bond

(*i*) Formation of anhydride



Acid anhydride



Acetic acid

Acetic anhydride

(*ii*) Esterification:

$$R\text{—}COOH + R'\text{—}OH \xrightleftharpoons{H^+} R\text{—}COOR' + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3\text{—}COOH} + CH_3\text{—}CH_2\text{—}OH \xrightleftharpoons{H^+} \underset{\text{Ethyl acetate}}{CH_3\text{—}COOCH_2\text{—}CH_3} + H_2O$$

(*iii*) Reactions with PCl_5, PCl_3 and $SOCl_2$

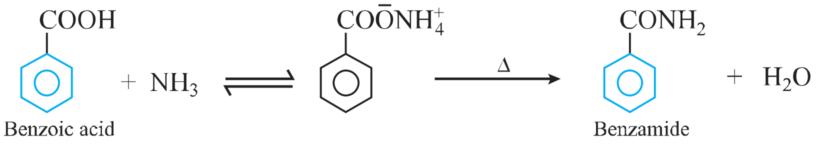
$$\underset{}{R{-}COOH} + PCl_5 \longrightarrow \underset{\text{Acyl chloride}}{RCOCl} + POCl_3 + HCl$$

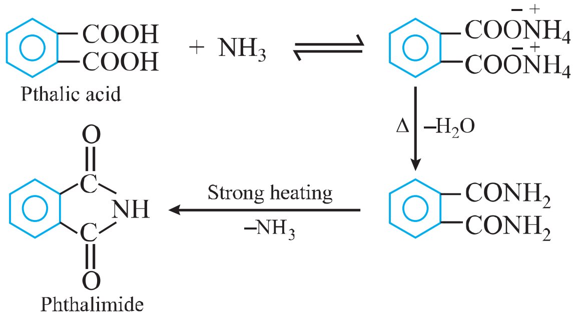
$$3R{-}COOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$R{-}COOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

(*iv*) Reaction with ammonia:

$$R{-}COOH + NH_3 \rightleftharpoons R{-}CO\bar{O}\overset{+}{N}H_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acid amide}}{R{-}CONH_2}$$





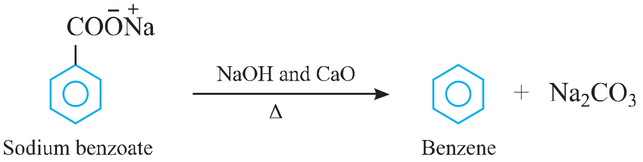
(*c*) Reaction involving —COOH group

(*i*) Reduction:

$$R{-}COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/\text{ether or } B_2H_6} \underset{1°\ \text{Alcohol}}{R{-}CH_2{-}OH}$$

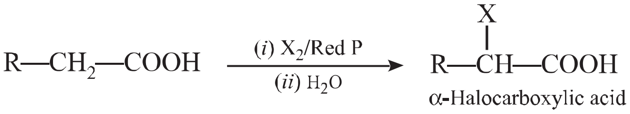
(*ii*) Decarboxylation:

$$\underset{\text{Sodium carboxylate}}{R{-}CO\overset{-}{O}\overset{+}{N}a} \xrightarrow[\Delta]{\text{NaOH and CaO}} R{-}H + Na_2CO_3$$



(*iii*) Halogenation:

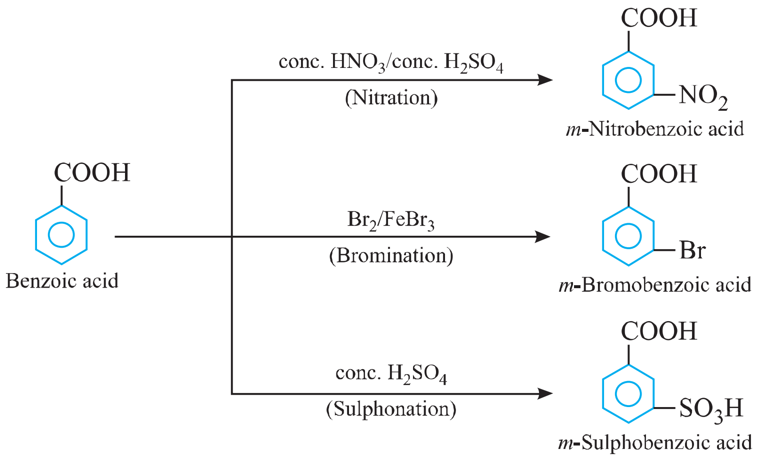
(Hell-Volhard Zelinsky reaction)



$$R{-}CH_2{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid}}{R{-}\overset{X}{\overset{|}{C}H}{-}COOH}$$

(X = Cl, Br)

(*d*) **Ring substitution reaction:** Aromatic carboxylic acids undergo electrophilic substitution reactions in which —COOH group acts as a deactivating and meta-directing group. They however do not undergo Friedel–Crafts reaction because the carboxyl group is deactivating and the catalyst $AlCl_3$ (Lewis acid) gets bonded to the carboxyl group.



16. Uses of Carboxylic acids:

(*i*) Formic acid is used in rubber, textile, dyeing, leather and electroplating industry.

(*ii*) Acetic acid is used as solvent and as vinegar in food industry.

(*iii*) Adipic acid is used in the manufacture of nylon-6, 6.

(*iv*) Sodium benzoate is used as preservative.

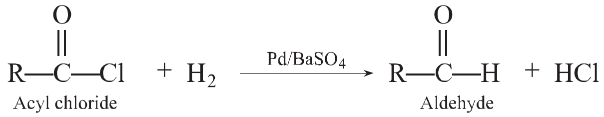
(*v*) Higher fatty acids are used for the manufacture of soaps and detergents.

(*vi*) Esters of benzoic acid are used in perfumery.

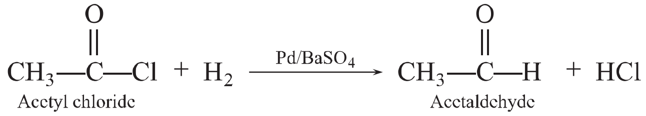
17. Some Important Name Reactions

(*a*) Rosenmund Reduction:

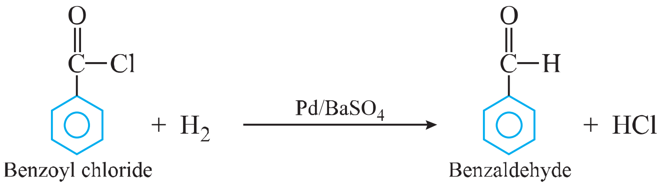
Acid chloride are converted to corresponding aldehydes by catalytic reduction. The reaction is carried out by passing H_2 gas through a hot solution of acid chloride in the presence of Pd deposited over $BaSO_4$ (partially poisoned with sulphur or quinoline).



$$\underset{\text{Acyl chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$



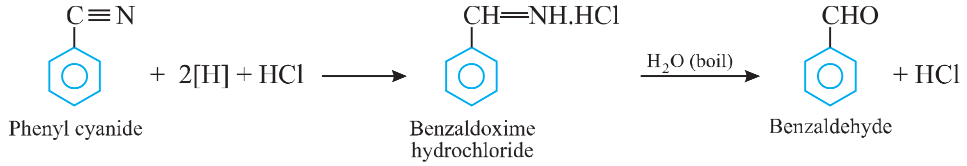
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$



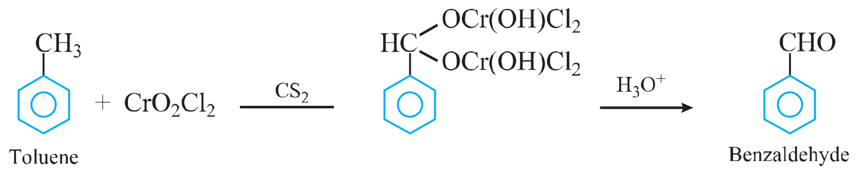
(*b*) **Stephen reaction:** Nitriles are reduced to corresponding imines with $SnCl_2$ in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

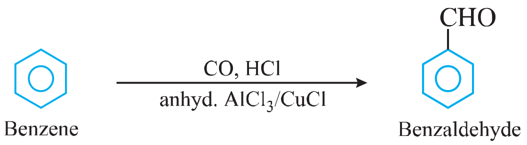
$$\underset{\text{Ethanenitrile}}{CH_3-C\equiv N} + 2[H] + HCl \longrightarrow \underset{\text{Acetaldoxime hydrochloride}}{CH_3-CH=NH.HCl} \xrightarrow{H_2O\text{ (boil)}} \underset{\text{Acetaldehyde}}{CH_3-CHO} + NH_4Cl$$



(*c*) **Etard reaction:** Chromyl chloride oxidises toluene to chromium complex which on hydrolysis gives benzaldehyde.

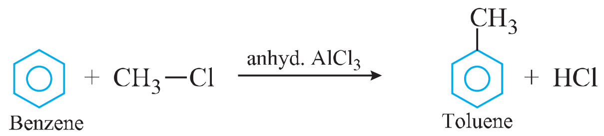


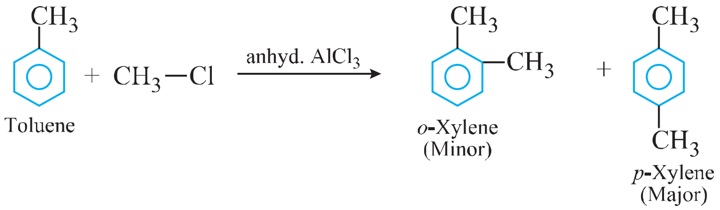
(*d*) **Gatterman–Koch reaction:** When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous $AlCl_3$ and CuCl, it gives benzaldehyde or substituted benzaldehyde.



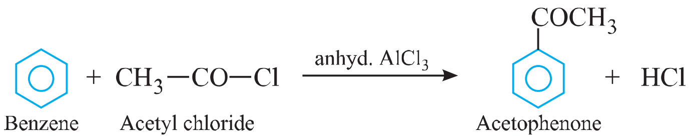
(*e*) **Friedel–Crafts reactions:**

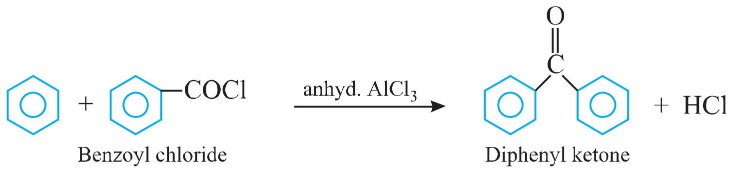
Friedel–Crafts alkylation: Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous $AlCl_3$ to form alkyl benzenes.

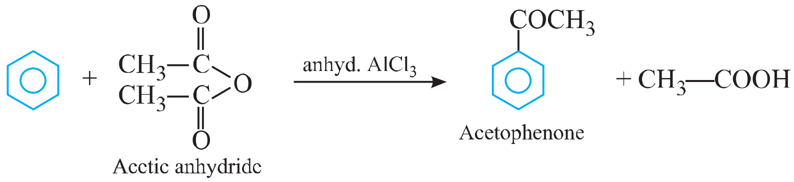




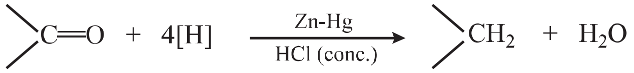
Friedel–Crafts acylation: Benzene and other aromatic compounds react with acylchlorides or acid anhydrides in the presence of anhyd. $AlCl_3$ to form aromatic ketone.





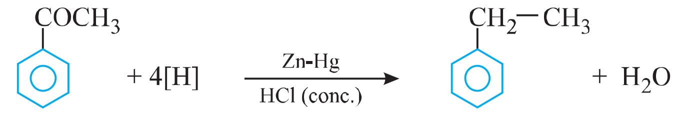


(*f*) **Clemmensen reduction:** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.



$$CH_3-CH_2-CH_2-CHO + [H] \xrightarrow[\text{HCl (conc.)}]{\text{Zn-Hg}} CH_3-CH_2-CH_2-CH_3 + H_2O$$

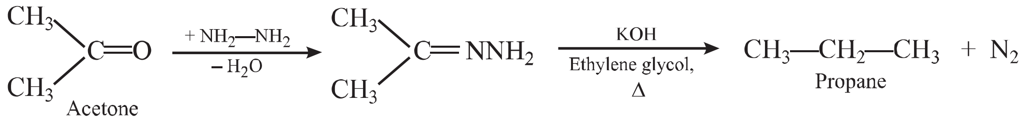
Butyraldehyde n-Butane



Acetophenone Ethyl benzene

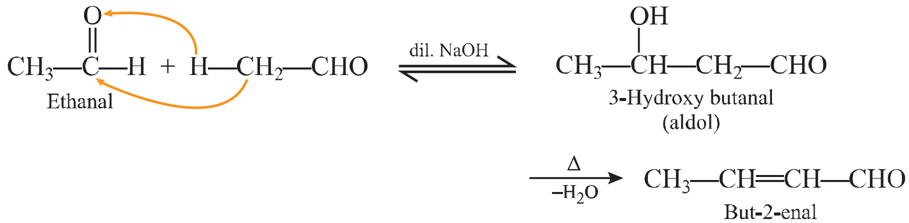
(*g*) **Wolff–Kishner reduction:** The carbonyl group of aldehydes and ketones is reduced to —CH_2 group on treatment with hydrazine followed by heating with potassium or sodium hydroxide in a high boiling solvent such as ethylene glycol.

Hydrazone



Acetone Propane

(*h*) **Aldol condensation:** Two molecules of aldehydes or ketones containing at least one α-hydrogen atom on treatment with dilute alkali undergo condensation to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (Ketol).

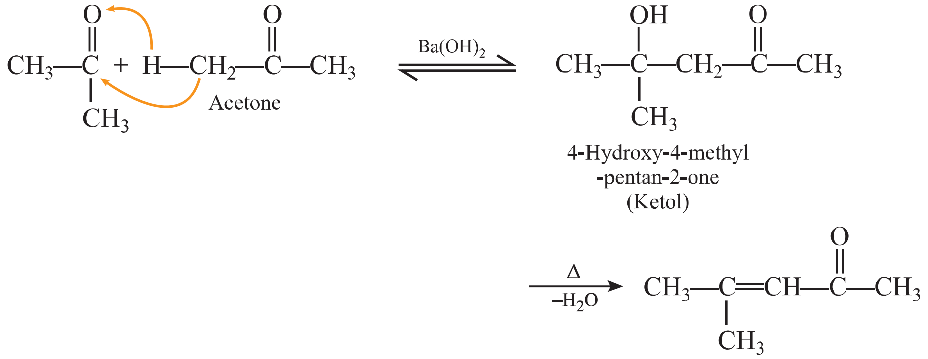


$$CH_3-\overset{\overset{O}{\|}}{C}-H + H-CH_2-CHO \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

Ethanal

3-Hydroxy butanal
(aldol)

But-2-enal



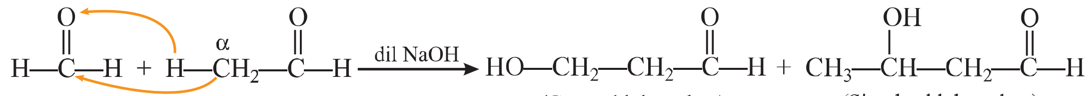
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}} + H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetone

4-Hydroxy-4-methyl
-pentan-2-one
(Ketol)

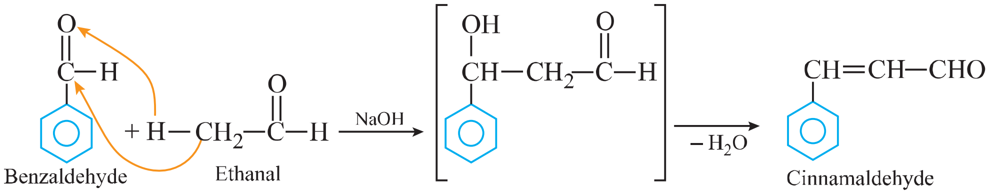
4-Methyl pent-3-en-2-one

(*i*) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation.

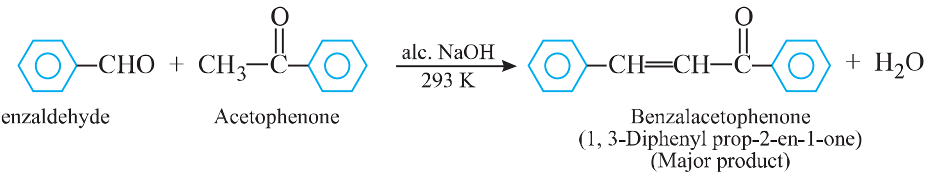


$$H-\overset{\overset{O}{\|}}{C}-H + H-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{dil NaOH}} HO-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

Formaldehyde Acetaldehyde (Cross aldol product) (Simple aldol product)



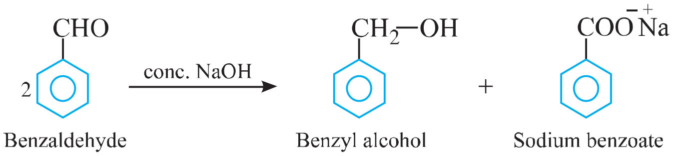
Benzaldehyde Ethanal Cinnamaldehyde



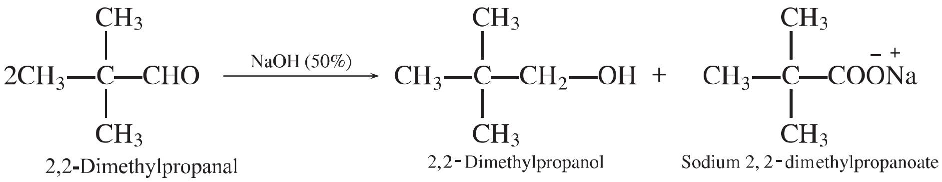
Benzaldehyde Acetophenone Benzalacetophenone (1, 3-Diphenyl prop-2-en-1-one) (Major product)

(*j*) **Cannizzaro reaction:** Aldehydes which do not have an α-hydrogen, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

$$\underset{\text{Formaldehyde}}{2HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methyl alcohol}}{CH_3-OH} + \underset{\text{Potassium formate}}{HCOO^-K^+}$$

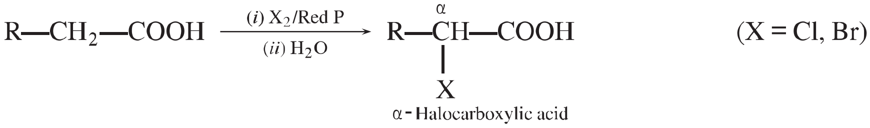


Benzaldehyde Benzyl alcohol Sodium benzoate

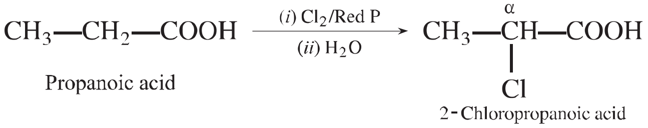


$$\underset{\text{2,2-Dimethylpropanal}}{2CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO} \xrightarrow{\text{NaOH (50\%)}} \underset{\text{2,2-Dimethylpropanol}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-OH} + \underset{\text{Sodium 2, 2-dimethylpropanoate}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COO^-Na^+}$$

(*k*) **Hell-Volhard-Zelinsky reaction:** Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine, or bromine in the presence of red phosphorus to give α-halo-carboxylic acids.



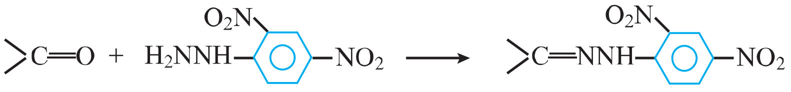
$$R-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid}}{R-\underset{X}{\overset{\alpha}{CH}}-COOH} \qquad (X = Cl, Br)$$



$$\underset{\text{Propanoic acid}}{CH_3-CH_2-COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{Red P}} \underset{\text{2-Chloropropanoic acid}}{CH_3-\underset{Cl}{\overset{\alpha}{CH}}-COOH}$$

18. Chemical Tests for Aldehydes and Ketones

(*a*) **Test for carbonyl group (2, 4-Dinitrophenyl hydrazine test):** Both aldehydes and ketones contain carbonyl group. Hence, they react with 2, 4-dinitrophenyl hydrazine to form yellow, or orange precipitate of 2, 4-dinitrophenyl hydrazone.



2, 4-Dinitrophenylhydrazine 2, 4-DNP-derivative (Yellow, orange ppt.)

(*b*) (*i*) **Tollens' test:** When aldehydes are heated with Tollens' reagent (ammoniacal silver nitrate solution), they form silver mirror on the inner side of the test tube. Ketones do not respond to this test.

$$\mathrm{R{-}CHO} + \underset{\text{Tollens' reagent}}{2[\mathrm{Ag(NH_3)_2}]^+} + 3\mathrm{OH^-} \longrightarrow \mathrm{R{-}COO^-} + \underset{\text{(Silver mirror)}}{2\mathrm{Ag}\downarrow} + 2\mathrm{H_2O} + 4\mathrm{NH_3}$$

(*ii*) **Fehling's test:** Aliphatic aldehydes when warmed with a few drops of Fehling's solution give a reddish brown precipitate of cuprous oxide. Ketones do not respond to this test.

$$\mathrm{R{-}CHO} + \underset{\text{Fehling solution}}{2\mathrm{Cu^{2+}}} + 5\mathrm{OH^-} \longrightarrow \mathrm{R{-}COO^-} + \underset{\text{Red brown ppt.}}{\mathrm{Cu_2O}\downarrow} + 3\mathrm{H_2O}$$

(*iii*) **Iodoform test:** Acetaldehyde, acetone or any ketone having at least one —CH_3 group when heated with alkaline solution of iodine form yellow coloured precipitate of iodoform.

$$2\mathrm{NaOH} + \mathrm{I_2} \longrightarrow \mathrm{NaOI} + \mathrm{NaI} + \mathrm{H_2O}$$

$$\mathrm{R{-}COCH_3} \xrightarrow[-\mathrm{NaOH}]{+3\mathrm{NaOI}} \mathrm{R{-}COCI_3} \xrightarrow{\mathrm{NaOH}} \mathrm{R{-}COO^-\overset{+}{Na}} + \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{\mathrm{CHI_3}\downarrow}$$

(*c*) Tests for Carboxylic Acids

(*i*) **Litmus test:** Aqueous solutions of carboxylic acids turn blue litmus red. Phenols also give this test. Alcohols do not respond to this test.

(*ii*) **Sodium bicarbonate test:** When carboxylic acid is added to an aqueous solution of sodium bicarbonate, brisk effervescence of CO_2 is evolved.

$$\underset{\text{Carboxylic acid}}{\mathrm{RCOOH}} + \mathrm{NaHCO_3} \longrightarrow \underset{\substack{\text{Sodium}\\ \text{carboxylate}}}{\mathrm{RCOONa}} + \mathrm{H_2O} + \mathrm{CO_2}\uparrow$$

Phenols and alcohols do not give this test.

(*iii*) **Ester formation test:** On warming carboxylic acids with an alcohol (*e.g.*, ethanol) in presence of a small amount of sulphuric acid, a fruity smell of ester is obtained.

$$\underset{\text{Carboxylic acid}}{\mathrm{RCOOH}} + \underset{\text{Alcohol}}{\mathrm{R'OH}} \xrightarrow{\mathrm{H_2SO_4}} \underset{\substack{\text{Ester}\\ \text{(Fruity smell)}}}{\mathrm{RCOOR'}} + \mathrm{H_2O}$$

(*iv*) **Distinction between formic acid and acetic acid.**

Tollens' reagent test: Formic acid reduces Tollens' reagent to metallic silver but acetic acid does not.

$$\underset{\text{Formic acid}}{\mathrm{HCOOH}} + 2[\mathrm{Ag(NH_3)_2}]^+ + 2\mathrm{OH^-} \longrightarrow \underset{\substack{\text{(Silver}\\ \text{mirror)}}}{2\mathrm{Ag}\downarrow} + \mathrm{CO_2}\uparrow + 2\mathrm{H_2O} + 4\mathrm{NH_3}$$

$HgCl_2$ test: Formic acid reduces $HgCl_2$ to give white ppt. of Hg_2Cl_2 while acetic acid does not give this test.

$$\underset{\text{Formic acid}}{\mathrm{HCOOH}} + \underset{\substack{\text{Mercuric}\\ \text{chloride}}}{2\mathrm{HgCl_2}} \longrightarrow \underset{\substack{\text{Mercurous}\\ \text{chloride}\\ \text{(white ppt.)}}}{\mathrm{Hg_2Cl_2}\downarrow} + 2\mathrm{HCl} + \mathrm{CO_2}\uparrow$$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write the structures of the following compounds:

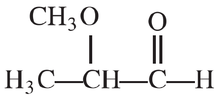
(*i*) α-Methoxypropionaldehyde **(*ii*) 3-Hydroxybutanal**

(*iii*) 2-Hydroxycyclopentane carbaldehyde

(*iv*) 4-oxopentanal **(*v*) Di-sec. butyl ketone**

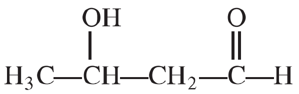
(*vi*) 4-Fluoroacetophenone

Ans. (*i*)



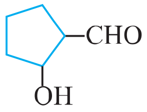
$H_3C{-}\overset{\overset{\displaystyle CH_3O}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$

(*ii*)

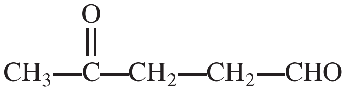


$H_3C{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$

(*iii*)

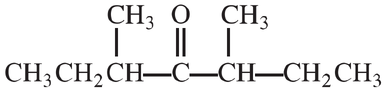


(*iv*)



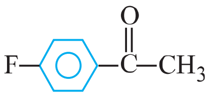
$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}CHO$

(*v*)



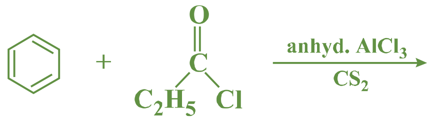
$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2CH_3$

(*vi*)



Q. 2. Write the structures of products of the following reactions:

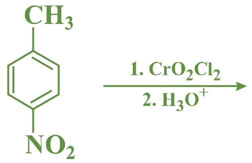
(*i*)



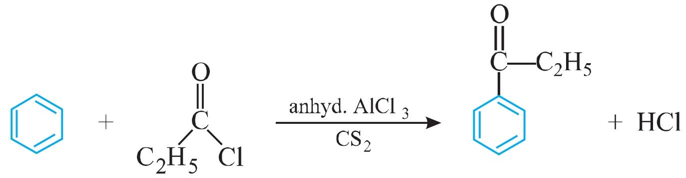
(*ii*) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

(*iii*) $H_3C{-}C\equiv C{-}H \xrightarrow{Hg^{2+}, H_2SO_4}$

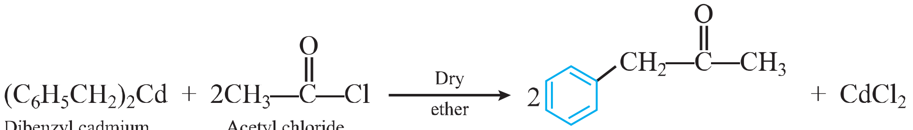
(*iv*)



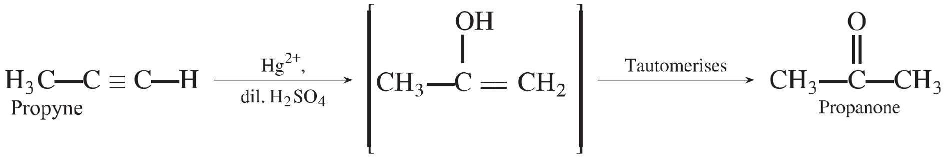
Ans. (*i*)



(*ii*)

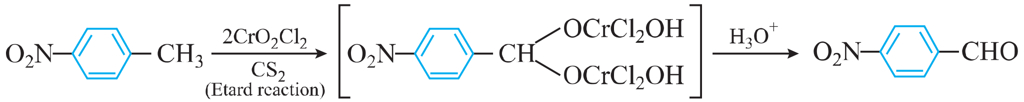


(*iii*)



$$\underset{\text{Propyne}}{H_3C{-}C\equiv C{-}H} \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+},} \left[CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}=CH_2\right] \xrightarrow{\text{Tautomerises}} \underset{\text{Propanone}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$$

(*iv*)



Q. 3. Arrange the following compounds in increasing order of their boiling points.

$CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Q. 4. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(*i*) Ethanal, Propanal, Propanone, Butanone

(*ii*) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

Ans. (*i*) The reactivity in nucleophilic addition reactions increases in the order:

Butanone < Propanone < Propanal < Ethanal

(*ii*) Acetophenone is a ketone. All the other three compounds are aldehydes. Hence, acetophenone is least reactive.

p-Tolualdehyde has an electron-donating methyl group at the para position of the benzene ring whereas *p*-nitrobenzaldehyde has an electron-withdrawing nitro group at the para position. Thus, *p*-tolualdehyde is less reactive and *p*-nitrobenzaldehyde is more reactive than benzaldehyde.

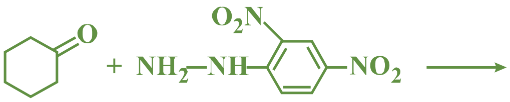
Therefore, the required order is as follows:

Acetophenone < *p*-Tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

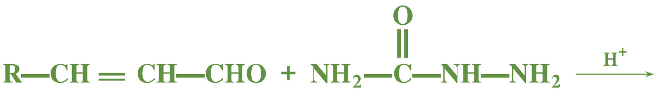
Q. 5. Predict the products of the following reactions:

(*i*)

(*ii*)

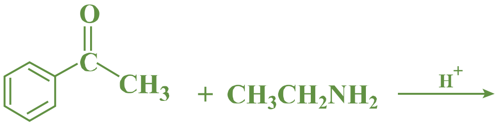


(*iii*)

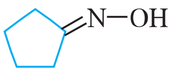


$$R—CH = CH—CHO + NH_2—\overset{\overset{O}{\|}}{C}—NH—NH_2 \xrightarrow{H^+}$$

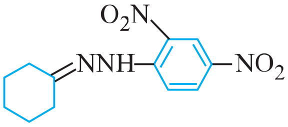
(*iv*)



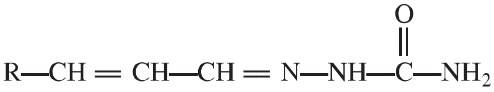
Ans. (*i*)



(*ii*)

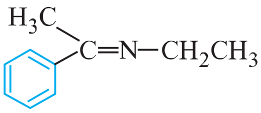


(*iii*)



$$R—CH = CH—CH = N—NH—\overset{\overset{O}{\|}}{C}—NH_2$$

(*iv*)

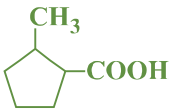


Q. 6. Give the IUPAC names of the following compounds:

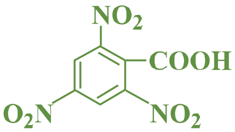
(*i*) $PhCH_2CH_2COOH$

(*ii*) $(CH_3)_2C{=}CHCOOH$

(*iii*)



(*iv*)



Ans. (*i*) 3-Phenylpropanoic acid

(*ii*) 3-Methylbut-2-enoic acid

(*iii*) 2-Methylcyclopentanecarboxylic acid

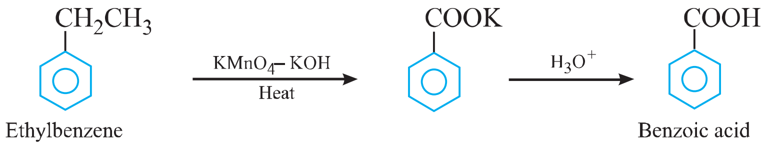
(*iv*) 2, 4, 6-Trinitrobenzoic acid.

Q. 7. Show how each of the following compounds can be converted to benzoic acid:

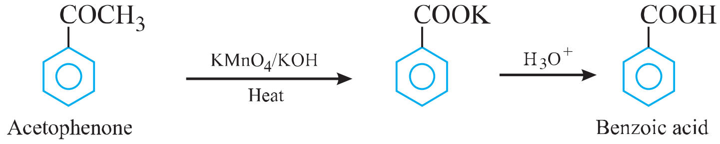
(*i*) Ethylbenzene **(*ii*) Acetophenone**

(*iii*) Bromobenzene **(*iv*) Phenylethene (Styrene)**

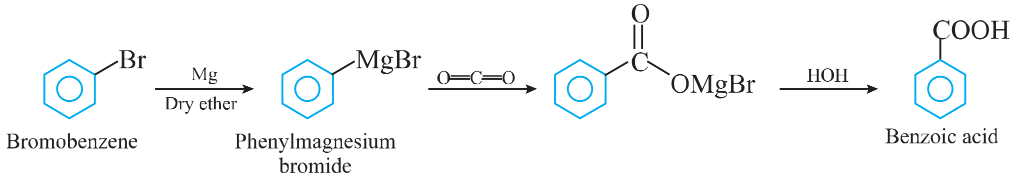
Ans. (*i*)



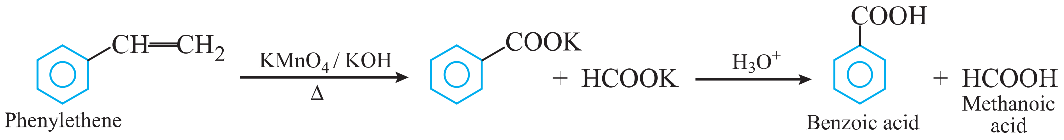
(*ii*)



(*iii*)



(*iv*)



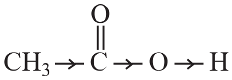
Q. 8. Which acid of each pair shown here would you expect to be stronger?

(*i*) CH_3CO_2H or CH_2FCO_2H **(*ii*) CH_2FCO_2H or CH_2ClCO_2H**

(*iii*) $CH_2FCH_2CH_2CO_2H$ or $CH_3—CHF—CH_2CO_2H$

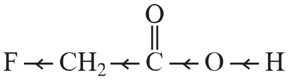
(*iv*)

Ans. (*i*)



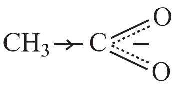
$CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H$

The release of a proton is difficult because +I-effect of CH_3 group increases the electron density in the O—H bond.

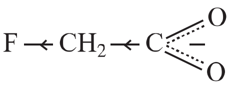


$F \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

The release of a proton is easier because –I-effect of F decreases the electron density in the O—H bond.



By intensifying the negative charge , +I-effect destabilises the carboxylate ion.

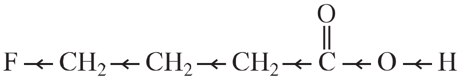


By dispersing the negative charge, –I-effect stabilises the carboxylate ion.

Therefore, due to lesser electron density in the O—H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion, FCH_2COOH is a stronger acid than CH_3COOH.

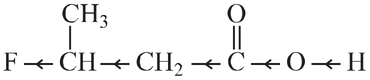
(*ii*) The FCH_2COO^- ion is much more stable than $ClCH_2COO^-$ ion due to much stronger –I effect of F than Cl and thus FCH_2COOH is a stronger acid than $ClCH_2COOH$.

(*iii*)



$F \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

4-Fluorobutanoic acid

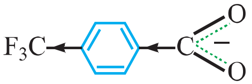


$F \leftarrow \overset{\overset{CH_3}{|}}{CH} \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

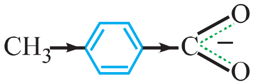
3-Fluorobutanoic acid

Inductive effect decreases with distance, therefore, –I effect of F is somewhat stronger in 3-fluorobutanoic acid than in 4-fluorobutanoic acid. Hence, CH_3CHFCH_2COOH is a stronger acid than $FCH_2CH_2CH_2COOH$.

(*iv*)



CF_3 has a strong –I-effect, it stabilises the carboxylate ion by dispersing the –ve charge



CH_3 has a weak +I-effect, it destabilises the carboxylate ion by intensifying the –ve charge

Hence, due to greater stability of $F_3C—C_6H_4—COO^-$ (*p*) ion than $CH_3—C_6H_4COO^-$ (*p*) ion, $F_3C—C_6H_4—COOH$ (*p*) is a much stronger acid than $CH_3—C_6H_4—COOH$ (*p*).

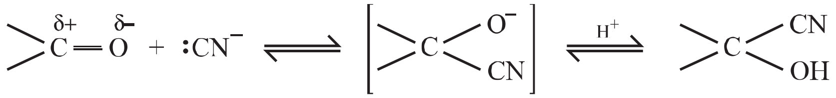
NCERT Textbook Exercises

Q. 1. What is meant by the following terms? Give an example of the reaction in each case.

(*i*) Cyanohydrin **(*ii*) Acetal** **(*iii*) Semicarbazone**
(*iv*) Aldol **(*v*) Hemiacetal** **(*vi*) Oxime**
(*vii*) Ketal **(*viii*) Imine** **(*ix*) 2, 4-DNP derivative**
(*x*) Schiff's base

Ans. (*i*) gem-Hydroxynitriles, *i.e.*, compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. It is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

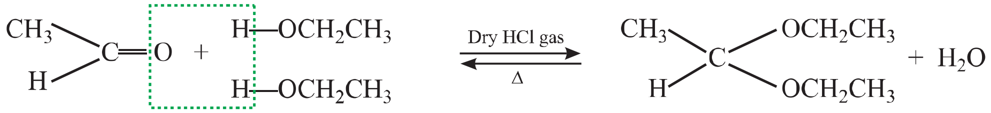
$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



Tetrahedral intermediate

Cyanohydrin

(*ii*) gem-Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.



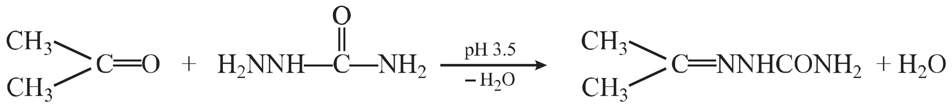
Acetaldehyde

Ethyl alcohol

Acetaldehyde diethyl acetal

These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehydic group in organic synthesis.

(*iii*) Semicarbazones are derivatives of aldehydes and ketones and are produced by the action of semicarbazide on them in weak acidic medium.



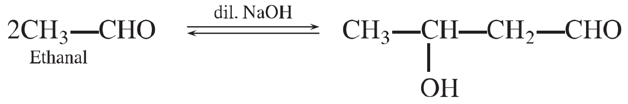
Acetone

Semicarbazide

Acetone semicarbazone

These are used for identification and characterisation of aldehydes and ketones.

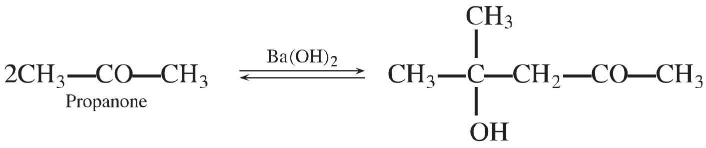
(*iv*) Aldols are β-hydroxy aldehydes or ketones and are produced by the condensation two same or different molecules of aldehyde or ketones.



$$2CH_3—CHO \xrightleftharpoons{\text{dil. NaOH}} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—CHO$$

Ethanal

3-Hydroxybutanal (Aldol)



$$2CH_3—CO—CH_3 \xrightleftharpoons{Ba(OH)_2} CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_2—CO—CH_3$$

Propanone

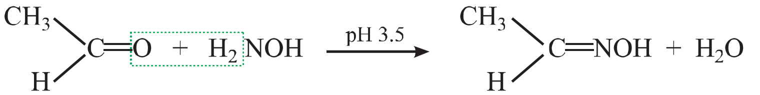
4-Hydroxy-4-methylpentan-2-one

(*v*) gem-Alkoxyalcohols are called hemiacetals. These are produced by addition of one molecule of a monohydric alcohol to an aldehyde in presence of dry HCl gas.

Ethanal

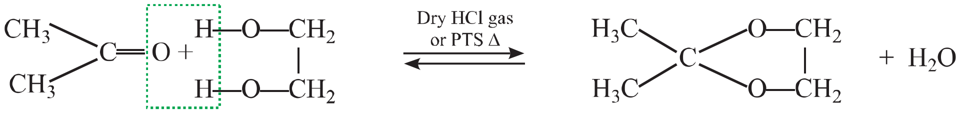
Methyl alcohol

1-Hydroxy-1-methoxyethane (A hemiacetal) (*vi*) Oximes are produced when aldehydes or ketones react with hydroxylamine in weak acidic medium.



Acetaldehyde Hydroxylamine Acetaldoxime

(*vii*) gem-Dialkoxyalkanes are called ketals. In ketals, the two alkoxy groups are present on the same carbon within the chain. These are produced when a ketone is heated with ethylene glycol in presence of dry HCl gas or *p*-toluenesulphonic acid (PTS).



Acetone Ethylene glycol Acetone ethylene ketal

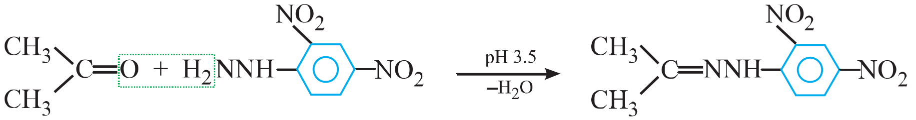
These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for protection of keto groups in organic synthesis.

(*viii*) Compounds containing $>C=N-$ group are called imines. These are produced when aldehydes and ketones react with ammonia derivatives.

$$\underset{\text{Aldehyde/Ketone}}{>C=O} + \underset{\text{Ammonia derivative}}{H_2N-Z} \longrightarrow \underset{\text{Imines}}{>C=N-Z} + H_2O$$

$Z = H$, Alkyl, aryl, $-NH_2$, $-OH$, $-C_6H_5NH$, $-NHCONH_2$, etc.

(*ix*) 2, 4-Dinitrophenylhydrazones (2, 4-DNP derivatives) are produced when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in weakly acidic medium.



2, 4-Dinitrophenyl hydrazine

Acetone 2, 4-dinitrophenylhydrazone

2, 4-DNP derivatives are used for identification and characterisation of aldehydes and ketones.

(*x*) Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.

$$\underset{\text{Aldehyde}}{R-CH=O} + \underset{1^\circ\text{ Amine}}{H_2N-R'} \xrightarrow[\text{Heat}]{\text{Trace of }H^+} \underset{\text{Schiff's base}}{R-CH=N-R'} + H_2O$$

Q. 2. Name the following compounds according to IUPAC system of nomenclature.

(*i*) $CH_3CH(CH_3)CH_2CH_2CHO$ **(*ii*) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$**

(*iii*) $CH_3CH=CHCHO$ ***[CBSE 2019(56/5/2)]***

(*iv*) $CH_3COCH_2COCH_3$ **(*v*) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$**

(*vi*) $(CH_3)_3CCH_2COOH$ **(*vii*) $OHCC_6H_4CHO$-*p***

Ans. (*i*) 4-Methylpentanal (*ii*) 6-Chloro-4-ethylhexan-3-one

(*iii*) But-2-en-1-al (*iv*) Pentane-2, 4-dione

(*v*) 3, 3, 5-Trimethylhexan-2-one (*vi*) 3, 3-Dimethylbutanoic acid

(*vii*) Benzene-1, 4-dicarbaldehyde

Q. 3. Draw the structures of the following compounds:

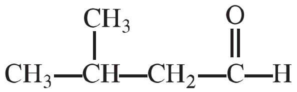
(*i*) 3-Methylbutanal **(*ii*) *p*-Nitropropiophenone**

(*iii*) *p*-Methylbenzaldehyde **(*iv*) 4-Methylpent-3-en-2-one**

(*v*) 4-Chloropentan-2-one **(*vi*) 3-Bromo-4-phenylpentanoic acid**

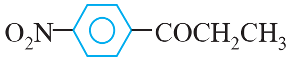
(*vii*) *p-p'*-Dihydroxybenzophenone **(*viii*) Hex-2-en-4-ynoic acid**

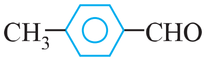
Ans. (*i*)

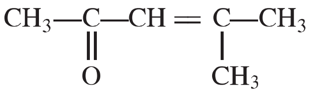


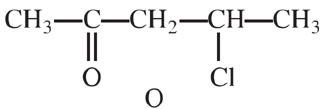
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

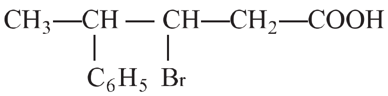
(*ii*)

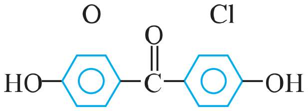


(*iii*) 

(*iv*) 
$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$

(*v*) 
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

(*vi*) 
$CH_3-\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_2-COOH$

(*vii*) 

(*viii*) $CH_3-C\equiv C-CH=CH-COOH$

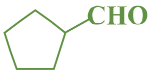
Q. 4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

(*i*) $CH_3CO(CH_2)_4CH_3$

(*ii*) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(*iii*) $CH_3(CH_2)_5CHO$

(*iv*) Ph—CH=CH—CHO

(*v*) 

(*vi*) PhCOPh

Ans.

S.No.	IUPAC Name	Common Name
(*i*)	Heptan-2-one	Methyl *n*-pentyl ketone
(*ii*)	4-Bromo-2-methylhexanal	γ-Bromo-α-methylcaproaldehyde
(*iii*)	Heptanal	—
(*iv*)	3-Phenylprop-2-enal	β-Phenylacrolein
(*v*)	Cyclopentanecarbaldehyde	Cyclopentanecarbaldehyde
(*vi*)	Diphenylmethanone	Benzophenone

Q. 5. Draw structures of the following derivatives:

(*i*) The 2, 4-dinitrophenylhydrazone of benzaldehyde

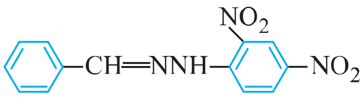
(*ii*) Cyclopropanone oxime

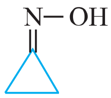
(*iii*) Acetaldehydedimethylacetal

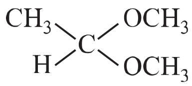
(*iv*) The semicarbazone of cyclobutanone

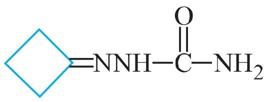
(*v*) The ethylene ketal of hexan-3-one

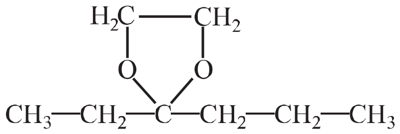
(*vi*) The methyl hemiacetal of formaldehyde.

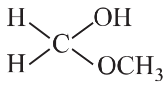
Ans. (*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

Q. 6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents:

(*i*) PhMgBr and then H_3O^+

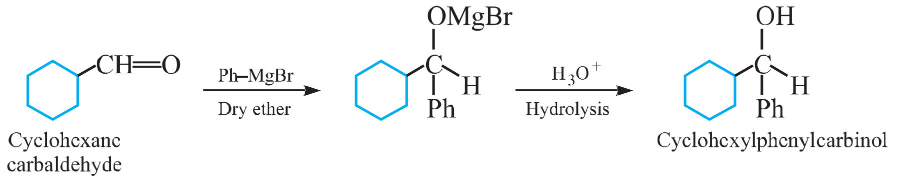
(*ii*) Tollens' reagent

(*iii*) Semicarbazide and weak acid

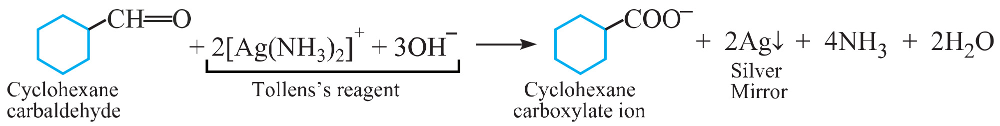
(*iv*) Excess ethanol and acid

(*v*) Zinc amalgam and dilute hydrochloric acid.

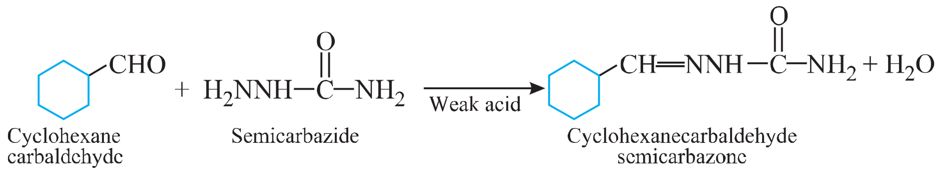
Ans. (*i*)



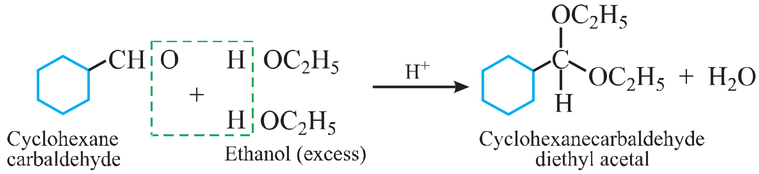
(*ii*)



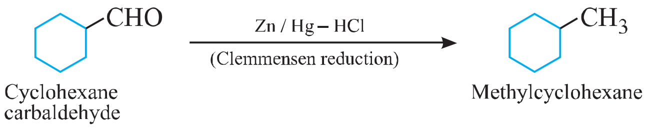
(*iii*)



(*iv*)



(*v*)



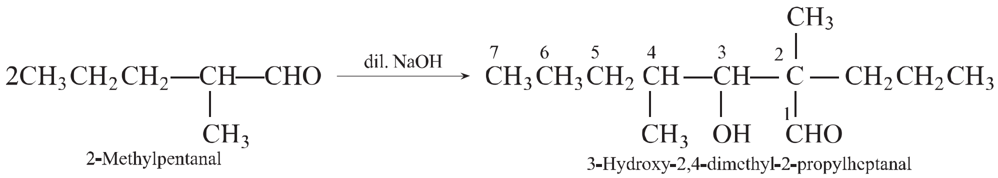
Q. 7. Which of the following compounds will undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(*i*) Methanal **(*ii*) 2-Methylpentanal**
(*iii*) Benzaldehyde **(*iv*) Benzophenone**
(*v*) Cyclohexanone **(*vi*) 1-Phenylpropanone**
(*vii*) Phenylacetaldehyde **(*viii*) Butan-1-ol**
(*ix*) 2, 2-Dimethylbutanal.

Ans. (*i*) Methanal does not contain α-hydrogen and hence undergoes cannizzaro reaction.

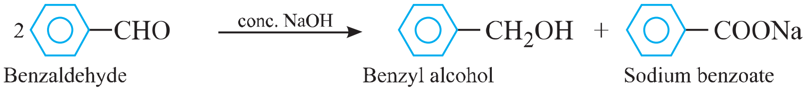
$$\underset{\text{Methanal}}{2HCHO} \xrightarrow{\text{conc. NaOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium methanoate}}{HCOONa}$$

(*ii*) 2-Methylpentanal, contains α-hydrogens and hence undergo aldol condensation.



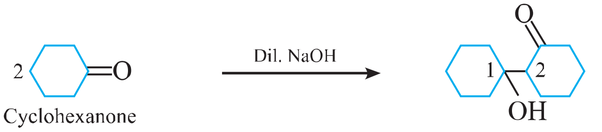
$$\underset{\text{2-Methylpentanal}}{2CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO} \xrightarrow{\text{dil. NaOH}} \underset{\text{3-Hydroxy-2,4-dimethyl-2-propylheptanal}}{\overset{7}{C}H_3\overset{6}{C}H_3\overset{5}{C}H_2\,\underset{CH_3}{\underset{|}{\overset{4}{C}H}}-\underset{OH}{\underset{|}{\overset{3}{C}H}}-\underset{CHO}{\underset{|1}{\overset{CH_3}{\overset{|}{\overset{2}{C}}}}}-CH_2CH_2CH_3}$$

(*iii*) Benzaldehyde does not contain α-hydrogen and hence undergoes cannizzaro reaction.



(*iv*) Benzophenone is a ketone having no α-hydrogen. It neither undergoes aldol condensation nor Cannizzaro reaction.

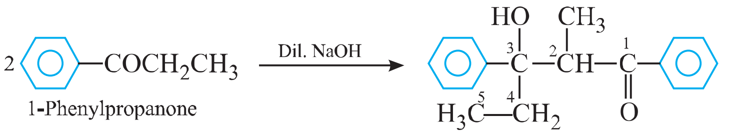
(*v*) Cyclohexanone contains α-hydrogens and hence undergo aldol condensation.



Cyclohexanone

2-(1-Hydroxy-1-cyclohexyl)
cyclohexan-1-one

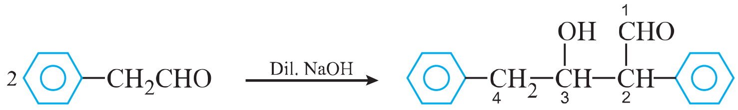
(*vi*) 1-Phenylpropanone contains α-hydrogens and hence undergo aldol condensation.



1-Phenylpropanone

3-Hydroxy-2-methyl-1,3-diphenylpentan-1-one

(*vii*) Phenylacetaldehyde contains α-hydrogen and hence undergoes aldol condensation.

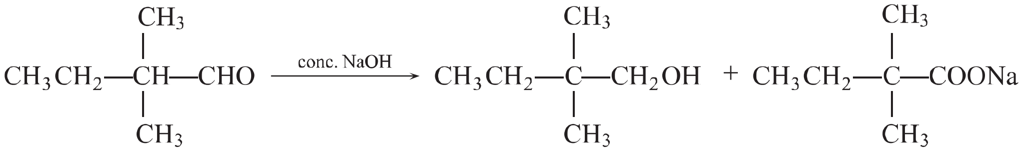


Phenylacetaldehyde

3-Hydroxy-2, 4-diphenylbutanal

(*viii*) Butan-1-ol is an alcohol, so it neither undergoes aldol condensation nor Cannizzaro reaction.

(*ix*) 2, 2-dimethylbutanal does not contain α-hydrogen and hence undergo Cannizzaro reaction.



$$CH_3CH_2\text{—}\underset{CH_3}{\overset{CH_3}{C}}H\text{—}CHO \xrightarrow{\text{conc. NaOH}} CH_3CH_2\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}CH_2OH + CH_3CH_2\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}COONa$$

2, 2-Dimethylbutanal   2, 2-Dimethylbutan-1-ol   Sodium 2, 2-Dimethylbutanonate

Q. 8. How will you convert ethanal into the following compounds?

(*i*) Butane-1, 3-diol (*ii*) But-2-enal (*iii*) But-2-enoic acid.

Ans. (*i*) $$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3\overset{3}{C}HOH\text{—}\overset{2}{C}H_2\text{—}\overset{1}{C}HO} \xrightarrow[\text{(Reduction)}]{NaBH_4} \underset{\text{Butane-1, 3-diol}}{\overset{4}{C}H_3\text{—}\overset{3}{C}HOH\text{—}\overset{2}{C}H_2\overset{1}{C}H_2OH}$$

(*ii*) $$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3\text{—}\overset{3}{C}HOH\text{—}\overset{2}{C}H_2\text{—}\overset{1}{C}HO} \xrightarrow[-H_2O]{H_3O^+/\text{Heat}} \underset{\text{But-2-enal}}{CH_3\text{—}CH=CH\text{—}CHO}$$

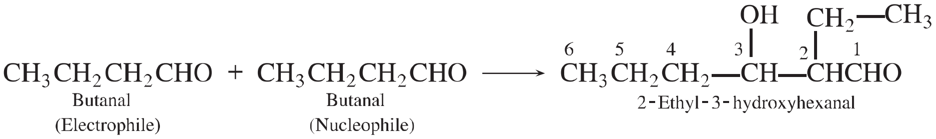
(*iii*) $$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[(ii)\ H^+,\Delta]{(i)\ \text{dil. NaOH}} \underset{\text{But-2-enal}}{CH_3CH=CHCHO} \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH=CHCO_2H}$$

Q. 9. Write structural formula and names of four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.

Ans. (*i*) Propanal serves as nucleophile and also as electrophile.

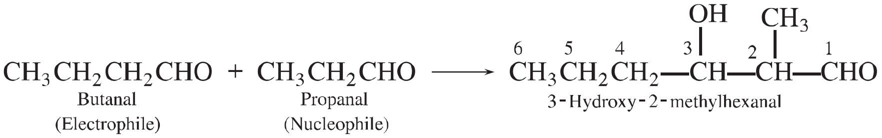
$$\underset{\substack{\text{Propanal}\\\text{(Nucleophile)}}}{CH_3CH_2CHO} + \underset{\substack{\text{Propanal}\\\text{(Electrophile)}}}{CH_3CH_2CHO} \longrightarrow \underset{\text{3-Hydroxy-2-methylpentanal}}{\overset{5}{C}H_3\overset{4}{C}H_2\overset{OH}{\overset{3}{C}H}\text{—}\overset{CH_3}{\overset{2}{C}}\text{—}\overset{1}{C}HO}$$

(*ii*) Butanal serves both as nucleophile and an electrophile.



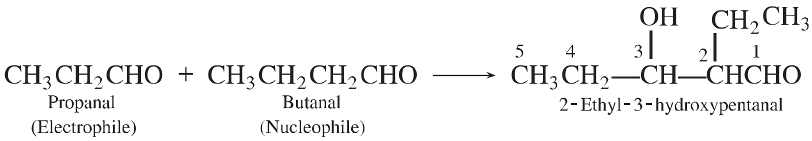
$$\underset{\substack{\text{Butanal}\\\text{(Electrophile)}}}{CH_3CH_2CH_2CHO} + \underset{\substack{\text{Butanal}\\\text{(Nucleophile)}}}{CH_3CH_2CH_2CHO} \longrightarrow \underset{\text{2-Ethyl-3-hydroxyhexanal}}{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\text{—}\overset{OH}{\overset{3}{C}H}\text{—}\overset{CH_2\text{—}CH_3}{\overset{2}{C}H}\overset{1}{C}HO}$$

(*iii*) Butanal as electrophile and propanal as nucleophile.



$$\underset{\substack{\text{Butanal}\\\text{(Electrophile)}}}{CH_3CH_2CH_2CHO} + \underset{\substack{\text{Propanal}\\\text{(Nucleophile)}}}{CH_3CH_2CHO} \longrightarrow \underset{\text{3-Hydroxy-2-methylhexanal}}{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\text{—}\overset{OH}{\overset{3}{C}H}\text{—}\overset{CH_3}{\overset{2}{C}H}\text{—}\overset{1}{C}HO}$$

(*iv*) Propanal as electrophile and butanal as nucleophile.



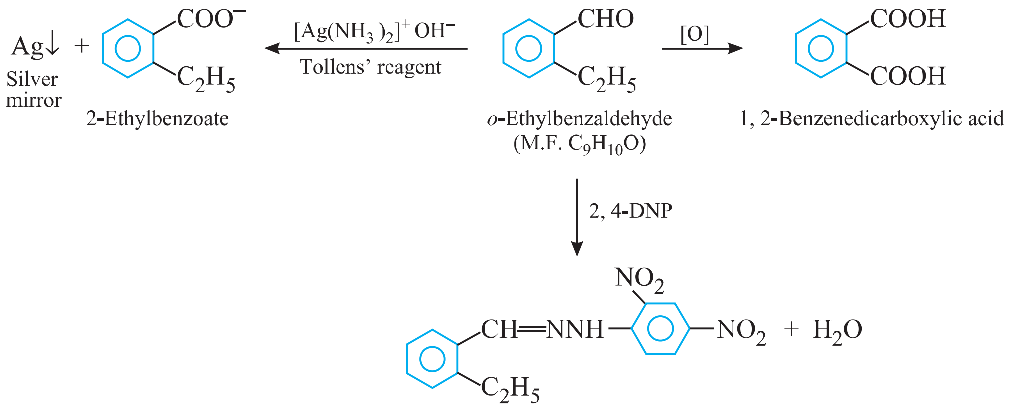
$$\underset{\substack{\text{Propanal}\\\text{(Electrophile)}}}{CH_3CH_2CHO} + \underset{\substack{\text{Butanal}\\\text{(Nucleophile)}}}{CH_3CH_2CH_2CHO} \longrightarrow \underset{\text{2-Ethyl-3-hydroxypentanal}}{\overset{5}{C}H_3\overset{4}{C}H_2-\overset{\overset{OH}{|}}{\overset{3}{C}}H-\overset{\overset{CH_2CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}HO}$$

Q. 10. An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound. ***[HOTS]***

Ans. (*i*) The given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollens' reagent, it must be an aldehyde.

(*ii*) As it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.

(*iii*) On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. The only *o*-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is *o*-ethylbenzaldehyde. All the reactions can be explained on the basis of this structure.



2, 4-DNP derivative

Q. 11. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved. ***[CBSE Delhi 2010; (AI) 2009] [HOTS]***

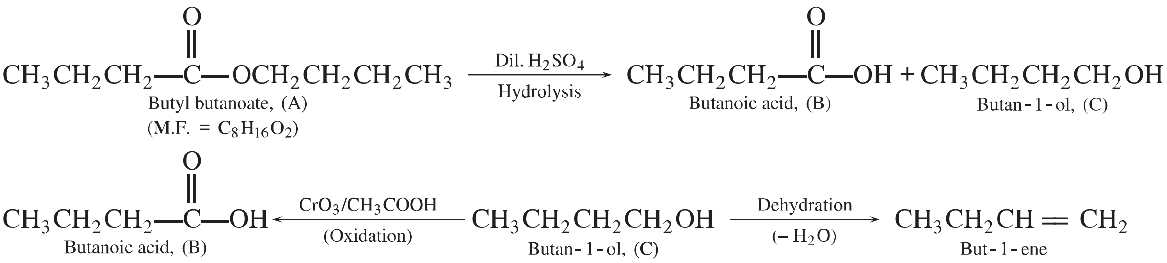
Ans. As the organic compound (*A*) with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid (*B*) and the alcohol (*C*) therefore (*A*) must be an ester and oxidation of (*C*) with chromic acid produces the acid (*B*), therefore, both the carboxylic acid (*B*) and alcohol (*C*) must contain the same number of carbon atoms.

Now ester (*A*) contains eight carbon atoms, therefore, both the carboxylic acid (B) and the alcohol (C) must contain four carbon atoms each.

As the alcohol (*C*) on dehydration gives but-1-ene, therefore, (*C*) must be a straight chain alcohol, *i.e.*, butan-1-ol.

If *C* is butan-1-ol, then the acid (*B*) which it gives on oxidation must be butanoic acid and the ester (*A*) must be butyl butanoate.

The relevant equations for all the reactions involved may be explained as follows:



$$\underset{\substack{\text{Butyl butanoate, (A)}\\\text{(M.F. = }C_8H_{16}O_2)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3} \xrightarrow[\text{Hydrolysis}]{\text{Dil. }H_2SO_4} \underset{\text{Butanoic acid, (B)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Butan-1-ol, (C)}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\text{Butanoic acid, (B)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} \xleftarrow[\text{(Oxidation)}]{CrO_3/CH_3COOH} \underset{\text{Butan-1-ol, (C)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[(-H_2O)]{\text{Dehydration}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

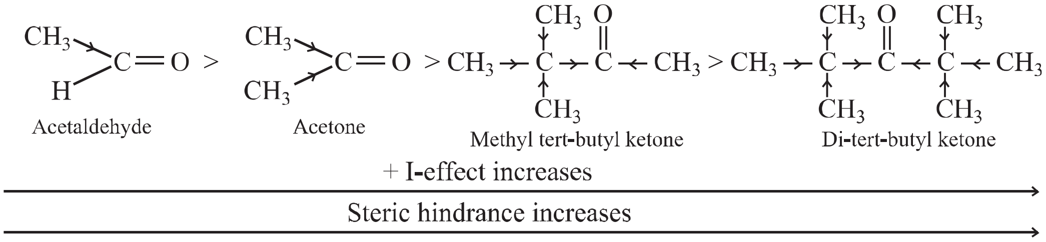
Q. 12. Arrange the following compounds in increasing order of their property as indicated:

(*i*) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN).

(*ii*) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength).

(*iii*) Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid (acid strength).

Ans. (*i*) The reactivity towards HCN addition decreases as the +I-effect of the alkyl group/s increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon increases. Hence, the reactivity decreases in the order:

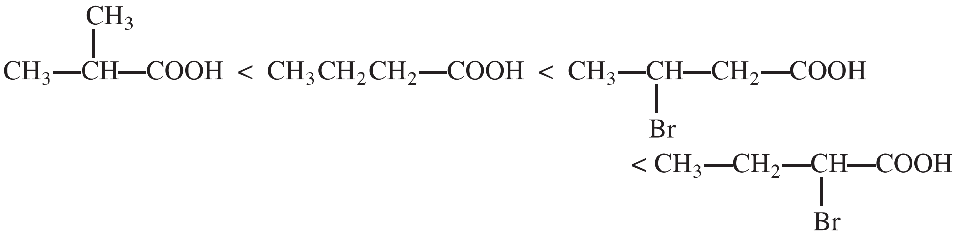


Thus, di-tert-butyl ketone < methyl tert-butyl ketone < Acetone < Acetaldehyde.

(*ii*) As we know + I-effect decreases while – I-effect increases the acid strength of carboxylic acids. As +I-effect of isopropyl group is more than that of *n*-propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Now –I-effect decreases with distance, therefore, $CH_3CH_2CH(Br)COOH$ is a stronger acid than $CH_3CH(Br)CH_2COOH$.

Therefore, the overall acid strength increases in the order:



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-COOH < CH_3CH_2CH_2-COOH < CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_2-COOH$$
$$< CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{C}H}-COOH$$

(*iii*) As electron-donating groups decrease the acid strength, therefore 4-methoxybenzoic acid is a weaker acid than benzoic acid.

Now electron-withdrawing groups increase the acid strength, therefore, both 4-nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acids than benzoic acid. Further due to the presence of an additional NO_2 groups at *m*-position w.r.t. COOH group, 3, 4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid. Therefore, the overall acid strength increases in the following order:

4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4-dinitrobenzoic acid.

Q. 13. Give simple chemical tests to distinguish between the following pairs of compounds: **[*CBSE 2019*(*56/2/1*)]**

(*i*) Propanal and Propanone

(*ii*) Acetophenone and Benzophenone

(*iii*) Phenol and Benzoic acid

(*iv*) Benzoic acid and Ethyl benzoate

(*v*) Pentan-2-one and Pentan-3-one

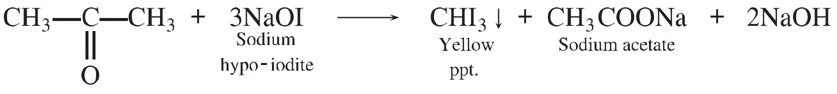
(*vi*) Benzaldehyde and Acetophenone

(*vii*) Ethanal and Propanal

Ans. (*i*) **Propanal and propanone:**

Iodoform test: This test is given by propanone and not by propanal. Propanone on reacting with hot $NaOH/I_2$ gives a yellow precipitate of CHI_3 while propanal does not.

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$



$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + \underset{\text{Sodium hypo-iodite}}{3NaOI} \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + \underset{\text{Sodium acetate}}{CH_3COONa} + 2NaOH$$