8 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

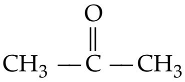
Topic-1

Aldehydes and Ketones: Methods of Preparation, Properties and Uses

Concepts Covered: *Classification of aldehydes and ketones, Nomenclature, Meth-ods of preparation, Physical and chemical properties uses*

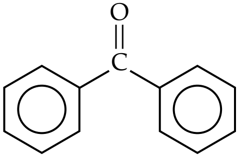
Revision Notes

- **Aldehydes and Ketones:**
  - (i) Aldehydes are those compounds in which carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one carbon containing group such as alkyl or aryl group with hydrogen atom. RCHO, e.g., HCHO, CH_3CHO, C_2H_5CHO, C_6H_5CHO, etc.
  - (ii) Ketones are those compounds in which carbonyl group is attached with two alkyl or two aryl or one alkyl and one aryl group. e.g., RCOR′ CH_3COCH_3, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$, etc.
- **Classification of aldehydes:**
  - **Aliphatic aldehyde:** An alkyl group or a H-atom is attached to an aldehydic (—CHO) group. e.g., formaldehyde (HCHO), acetaldehyde (CH_3CHO).
  - **Aromatic aldehdye:** An aryl group is attached to an aldehydic (—CHO) group. e.g., benzaldehdye (C_6H_5CHO).
- **Classification of ketones:**
  - **Simple or symmetrical:** Both the attached alkyl or aryl groups are similar. e.g.,



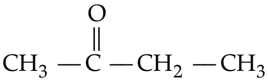
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Propanone



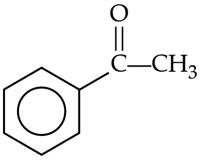
Diphenylmethanone

  - **Mixed or unsymmetrical:** Both the attached alkyl or aryl groups are different. e.g.,



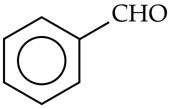
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

Butan-2-one

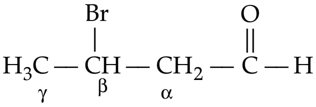


Phenylethanone

- **Nomenclature of Aldehydes and Ketones:**
  - Common names of aldehydes are derived from the common names of carboxylic acids by replacing the ‘ic’ with aldehyde. Greek letter α, β, γ and δ, etc. denote the location of the substitution in the carbon chain.



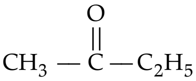
Benzaldehyde



$$\underset{\gamma}{H_3C}-\underset{\beta}{\overset{\overset{\displaystyle Br}{|}}{CH}}-\underset{\alpha}{CH_2}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

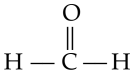
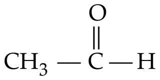
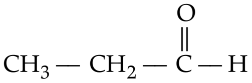
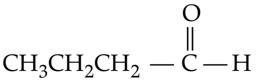
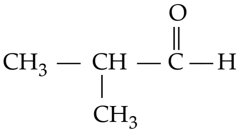
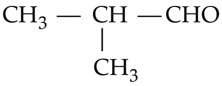
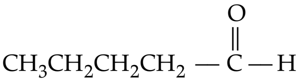
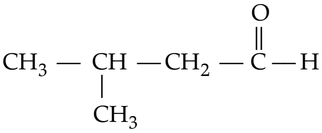
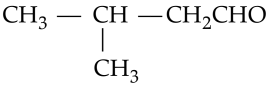
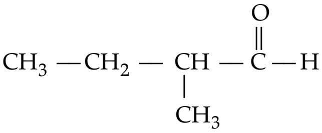
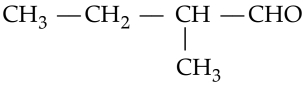
β-bromobutyraldehyde

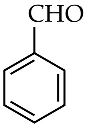
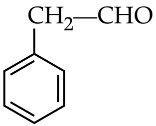
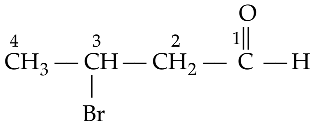
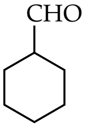
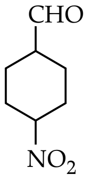
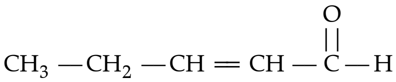
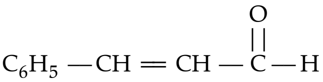
  - Common names of the ketones are derived by writing the names of alkyl groups attached to the $>C=O$ group in alphabetical order, followed by the word ketone.

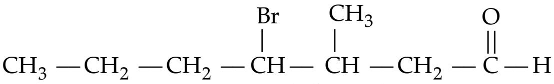


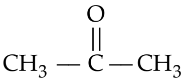
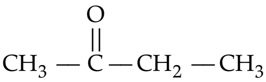
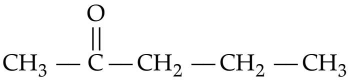
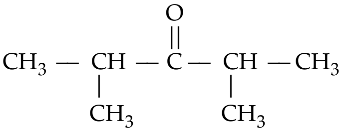
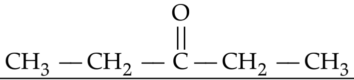
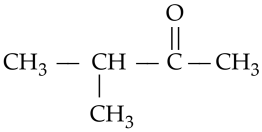
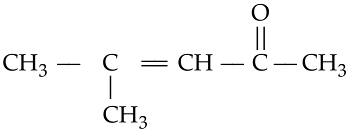
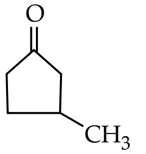
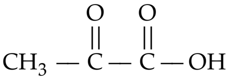
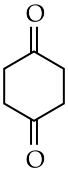
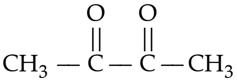
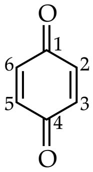
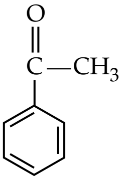
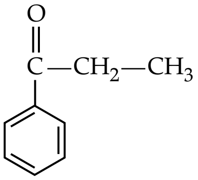
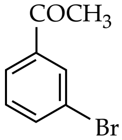
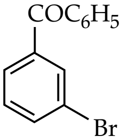
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$$ (Ethyl methyl ketone)

  - IUPAC names are written by replacing the word ‘e’ of corresponding alkanes by ‘al’ and ‘one’ of the open chain aliphatic aldehydes and ketones respectively.

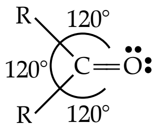
Aldehyde	**General formula:**  $R-\overset{O}{\overset{\|}{C}}-H$ **where** $R = C_nH_{2n+1}$		
Structural formula	**Condensed structural formula**	**Common name**	**IUPAC name**
 $H-\overset{O}{\overset{\|}{C}}-H$	HCHO	Formaldehyde	Methanal
 $CH_3-\overset{O}{\overset{\|}{C}}-H$	CH_3CHO	Acetaldehyde	Ethanal
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$	CH_3CH_2CHO	Propionaldehyde	Propanal
 $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$	$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal
 $CH_3-\underset{CH_3}{\underset{\|}{CH}}-\overset{O}{\overset{\|}{C}}-H$	 $CH_3-\underset{CH_3}{\underset{\|}{CH}}-CHO$	Isobutyraldehyde	2-Methylpropanal
 $CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$	$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
 $CH_3-\underset{CH_3}{\underset{\|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$	 $CH_3-\underset{CH_3}{\underset{\|}{CH}}-CH_2CHO$	Isovaleraldehyde	3-Methylbutanal
 $CH_3-CH_2-\underset{CH_3}{\underset{\|}{CH}}-\overset{O}{\overset{\|}{C}}-H$	 $CH_3-CH_2-\underset{CH_3}{\underset{\|}{CH}}-CHO$	α-Methylbutyraldehyde	2-Methylbutanal

C_6H_5CHO or Benzaldehyde 	 Phenylacetaldehyde (2-Phenylethanal)	 $\overset{4}{CH_3}-\underset{Br}{\underset{\|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{O}{\overset{1\|}{C}}-H$ β-Bromobutyraldehyde (3-Bromobutanal)
$CH_2=CH-CHO$ Acrolein (Prop-2-en-1-al)  (Cyclohexanecarbaldehyde)	$CH_3-CH=CH-CHO$ Crotonaldehyde (But-2-en-1-al)  4-Nitrobenzaldehyde (4-Nitrophenylcarbaldehyde)	 $CH_3-CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-H$ Pent-2-enal  $C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-H$ Cinnamaldehyde (3-Phenylprop-2-en-1-al)  $\underset{CHO}{\underset{\|}{CHO}}$ Glyoxal (Ethane-1,2-dial)

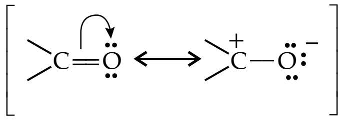
		 $CH_3-CH_2-CH_2-\overset{\overset{Br}{\vert}}{CH}-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-\overset{\overset{O}{\Vert}}{C}-H$ 4-Bromo-3-methylheptanal

Ketone	**General formula:** $R-\overset{\overset{O}{\Vert}}{C}-R'$ **and** $R' = C_nH_{2n'+1}$ $(n = n', n \neq 0)$		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_3$	CH_3COCH_3	Acetone	Propanone
 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_2-CH_3$	$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butan-2-one
 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_2-CH_2-CH_3$	$CH_3COCH_2CH_2CH_3$	Methyl *n*-Propyl ketone	Pentan-2-one
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethyl pentan-3-one
 $CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-CH_2-CH_3$	$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\overset{\overset{O}{\Vert}}{C}-CH_3$	$(CH_3)_2CHCOCH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
 $CH_3-\underset{\underset{CH_3}{\vert}}{C}=CH-\overset{\overset{O}{\Vert}}{C}-CH_3$	$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en -2-one
 β-Methylcyclopentanone (3-Methylcyclopentanone)	 $CH_3-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{O}{\Vert}}{C}-OH$ Pyruvic acid (2-Oxopropanoic acid)  Cyclohexan-1, 4-dione	 $CH_3-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{O}{\Vert}}{C}-CH_3$ Diacetyl (Butane-2-3-dione)	 *p*-Benzoquinone (Cyclohexa-2, 5-diene-1, 4-dione)
 Acetophenone (Phenylethanone)	 (Phenyl Propanone)	 *m*-Bromoacetophenone 1-(3-Bromophenyl) ethanone	 *m*-Bromobenzophenone (Bromediphenyl methanone)

- **Structure of Carbonyl group:** The carbon atom of the carbonyl group is sp^2 hybridised. All the three atoms attached to carbonyl carbon lie in the same plane.



It is polar in nature. Carbonyl compounds may be regarded as resonance hybrid of the two given structure.



- **Methods of preparation of Aldehydes and Ketones:**

(A) Preparation of Aldehydes:

(i) By oxidation of primary alcohols: Aldehydes can be prepared by the oxidation of primary alcohols.

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH}+[O]\xrightarrow{KMnO_4}\underset{\text{Aldehyde}}{R-CHO}+H_2O$$

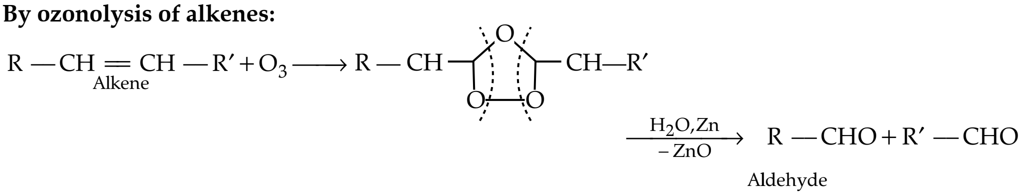
$$\underset{1^\circ\text{ alcohol}}{R-CH_2-OH}\xrightarrow{PCC/CH_2Cl_2}\underset{\text{Aldehyde}}{R-CHO}$$

(ii) By catalytic dehydrogenation of alcohols: In this method alcohol vapours are passed over heavy metal catalyst (Ag/Cu).

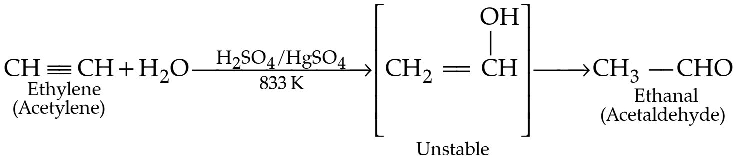
$$\underset{1^\circ\text{ alcohol}}{RCH_2OH}\xrightarrow{Cu/573\text{ K}}\underset{\text{Aldehyde}}{R-CHO}+H_2$$

(iii) From hydrocarbons:

(a) By ozonolysis of alkenes:

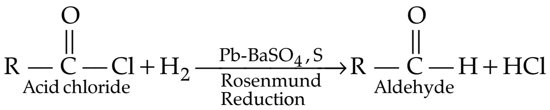


(b) By hydration of alkynes:



$$\underset{\substack{\text{Ethylene}\\\text{(Acetylene)}}}{CH\equiv CH}+H_2O\xrightarrow[833\text{ K}]{H_2SO_4/HgSO_4}\underset{\text{Unstable}}{\left[CH_2=\overset{\overset{\displaystyle OH}{|}}{CH}\right]}\longrightarrow\underset{\substack{\text{Ethanal}\\\text{(Acetaldehyde)}}}{CH_3-CHO}$$

(iv) From acid chloride (Rosenmund's reduction):



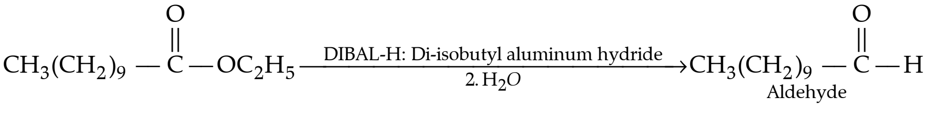
$$\underset{\text{Acid chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}+H_2\xrightarrow[\substack{\text{Rosenmund}\\\text{Reduction}}]{Pb\text{-}BaSO_4,S}\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}+HCl$$

Formaldehyde cannot be prepared by this method as HOCl is highly unstable.

(v) From nitriles and esters:

$$R-C\equiv N+HCl+SnCl_2\longrightarrow\underset{\text{Imine}}{R-CH=NH}\xrightarrow{H_3O^+}R-CHO+NH_3$$

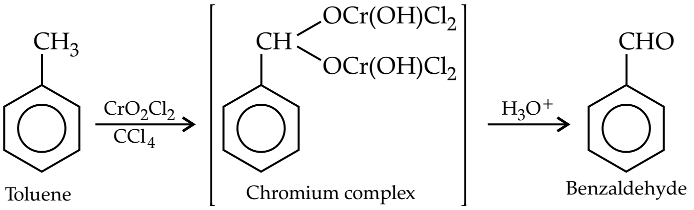
$$R-CN\xrightarrow[2.\ H_2O]{1.\ AlH(iBu)_2}\underset{\text{Aldehyde}}{R-CHO}$$



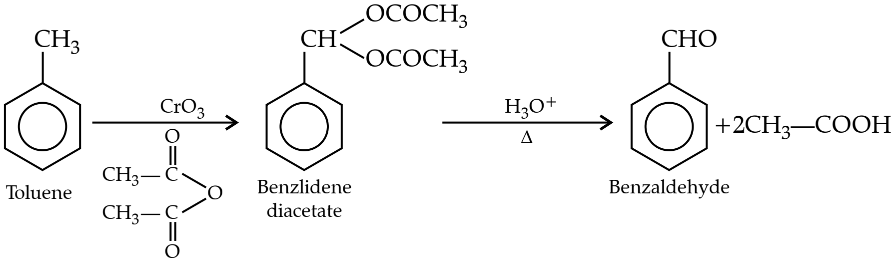
$$CH_3(CH_2)_9-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5\xrightarrow[2.\ H_2O]{\text{DIBAL-H: Di-isobutyl aluminum hydride}}\underset{\text{Aldehyde}}{CH_3(CH_2)_9-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

(B) Preparation of Benzaldehyde:

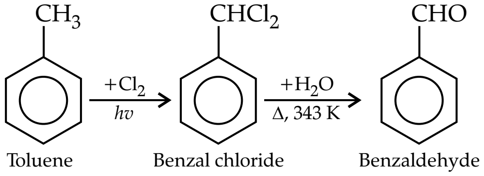
(i) By oxidation of toluene:



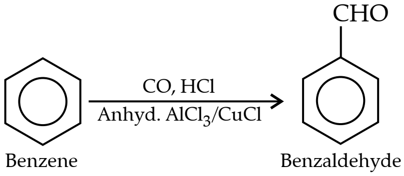
This reaction is called **Etard reaction**.



(ii) By side chain chlorination followed by hydrolysis:

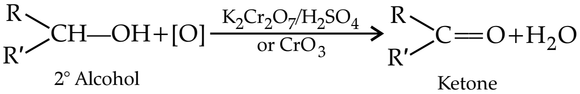


(iii) By Gatterman – Koch reaction:

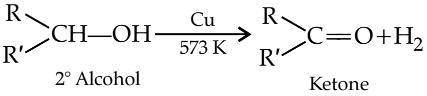


(C) Preparation of Ketones:

(i) By oxidation of secondary alcohols:

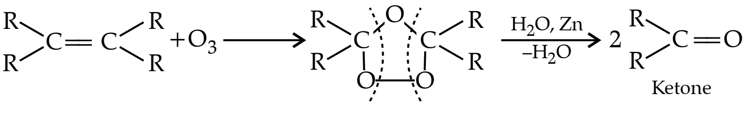


(ii) By catalytic dehydrogenation of secondary alcohols:

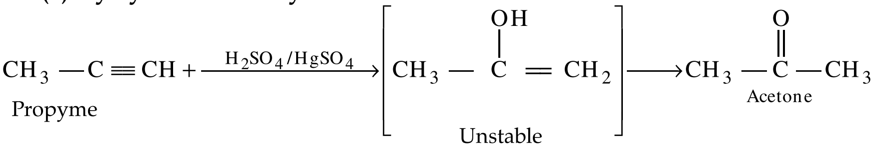


(iii) From Hydrocarbons:

(1) By catalytic ozonolysis of alkenes:



(2) By hydration of alkynes:



$$CH_3-C\equiv CH+\xrightarrow{H_2SO_4/HgSO_4}\left[CH_3-\overset{\overset{\large OH}{|}}{C}=CH_2\right]\longrightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$$

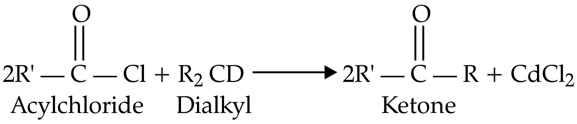
Propyme

Unstable

Acetone

(iv) From acyl chlorides and Grignard's reagent:

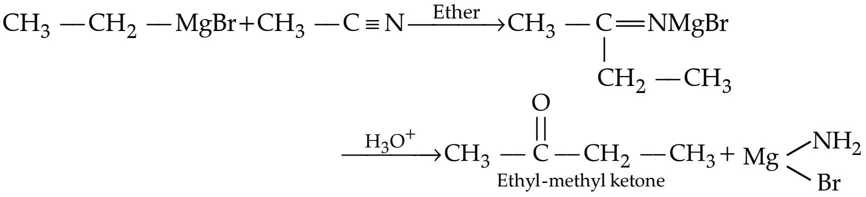
$2R-MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$



$$2R'-\overset{\overset{\large O}{\|}}{C}-Cl + R_2\,CD \longrightarrow 2R'-\overset{\overset{\large O}{\|}}{C}-R + CdCl_2$$

Acylchloride Dialkyl Ketone

(v) From nitriles:



$$CH_3-CH_2-MgBr+CH_3-C\equiv N\xrightarrow{Ether}CH_3-\underset{\underset{\large CH_2-CH_3}{|}}{C}=NMgBr$$

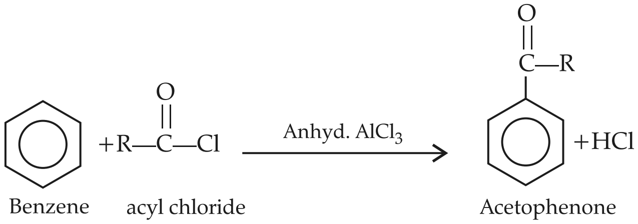
$$\xrightarrow{H_3O^+}CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_3+Mg\begin{matrix}NH_2\\Br\end{matrix}$$

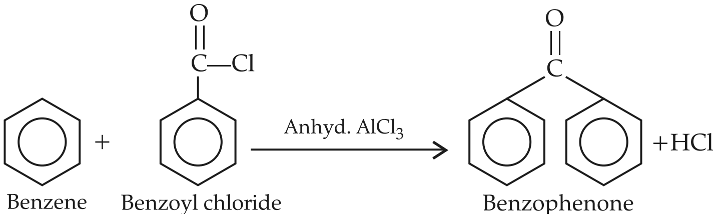
Ethyl-methyl ketone

$$\underset{2^\circ\text{Alcohol}}{R_2CHOH} + (CH_3)_2\,C=O \xrightarrow{[(CH_3)_3CO]_3Al} \underset{\text{Ketone}}{R_2C=O} + \underset{\text{Isopropyl alcohol}}{(CH_3)_2\,CHOH}$$

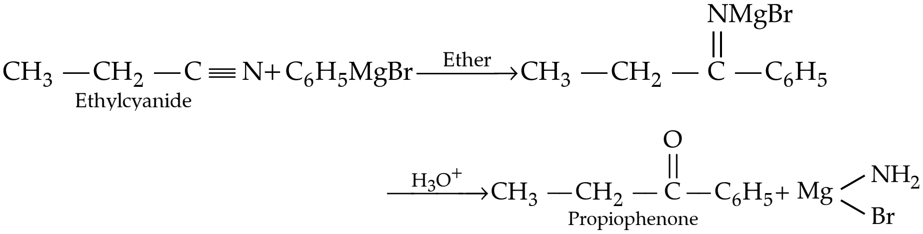
(D) Preparation of Aromatic ketones:

(i) By Friedel-Crafts acylation:





(ii) From nitriles:



$$\underset{\text{Ethylcyanide}}{CH_3-CH_2-C\equiv N} + C_6H_5MgBr \xrightarrow{\text{Ether}} CH_3-CH_2-\overset{\overset{\displaystyle NMgBr}{||}}{C}-C_6H_5$$

$$\xrightarrow{H_3O^+} \underset{\text{Propiophenone}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-C_6H_5} + Mg\begin{cases}NH_2\\ Br\end{cases}$$

- **Physical properties of Aldehydes and Ketones:**

  (i) 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.

  (ii) Both of these have relatively high boiling point as compared to hydrocarbons of comparable molecular masses. But they have lower boiling point than alcohols of comparable molecular masses due to absence of intermolecular hydrogen bonding.

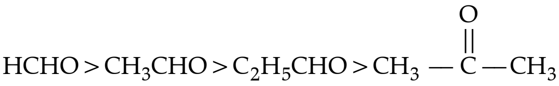
  (iii) The lower members of aldehydes and ketones (upto four carbon atoms) are soluble in water in all proportions due to hydrogen bonding capacity. In water, their solubility decreases with increase in the size of alkyl group.

  (iv) Aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.

  (v) Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

- **Chemical properties of Aldehydes and Ketones:** Aldehydes and ketones are highly reactive compounds. Both undergo nucleophilic addition reaction.

  Some important nucleophilic addition reactions: Reactivity order is:

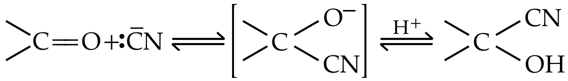


$$HCHO > CH_3CHO > C_2H_5CHO > CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

It is due to +I effect of alkyl groups which decrease the positive charge on carbonyl carbon and steric hindrance.

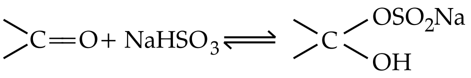
(i) Addition of hydrogen cyanide (HCN):

$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$



Cyanohydrin

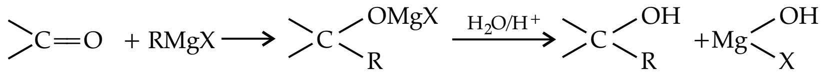
(ii) Addition to sodium hydrogen sulphite:



Bisulphite
(additon compound)—White crystalline solid

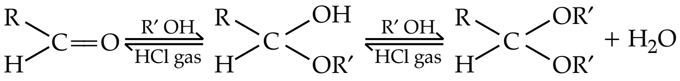
This reaction is used for the separation and purification of aldehydes and ketones.

(iii) Addition of Grignard reagent:



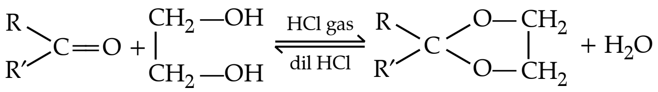
Carbonyl compound Grignard reagent Alcohol

(iv) Addition of alcohol:



Aldehyde Hemiacetal Acetal

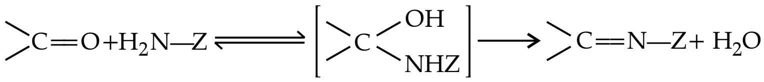
Ketones do not react with monohydric alcohols but react with dihydric alcohols to give ketals.



Ketone Ethylene glycol Ethylene glycol ketal

$RCHO + RHN_2 \rightarrow \underset{\text{(Schiff's Base)}}{RCH=NHR}$

(v) Addition of ammonia and its derivatives:



Ethylene glycol ketal

$RCHO + RHN_2 \rightarrow \underset{\text{(Schiff's Base)}}{RCH=NHR}$

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

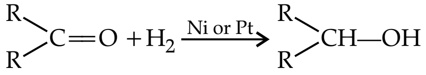
$$6HCHO + 4NH_3 \rightarrow \underset{\text{(Urotropine)}}{(CH_2)_6N_4} + 6H_2O$$

Urotropine on controlled nitration gives the well known explosive RDX (Research and Development explosive).

- **Reduction:** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.

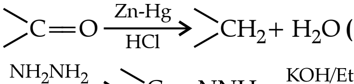
(i) Reduction to alcohols:

$$\underset{\text{Aldehyde}}{R-CHO} + 2[H] \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{1^\circ \text{ Alcohol}}{R-CH_2-OH}$$

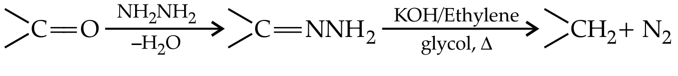


Ketone 2° Alcohol

(ii) Reduction to hydrocarbons:



(Clemmensen reduction)

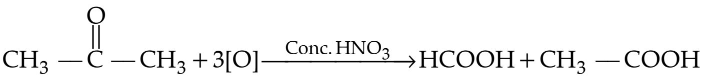


(Wolff-Kishner reduction)

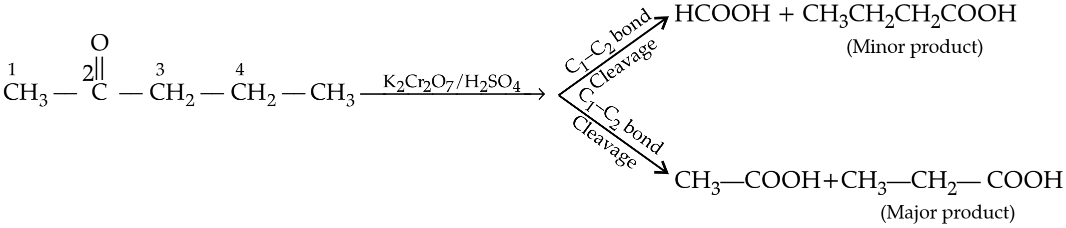
- **Oxidation:** Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollen's reagent or Fehling's solution.

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[KMnO_4/H_2SO_4]{K_2Cr_2O_7/H_2SO_4 \text{ or}} \underset{\text{Carboxylic acid}}{R-COOH}$$

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



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3[O] \xrightarrow{\text{Conc. } HNO_3} HCOOH + CH_3-COOH$$



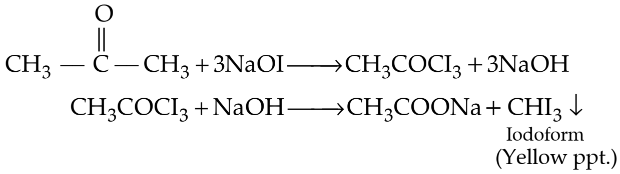
(a) Tollen's test – Aldehydes give bright silver mirror with tollen's reagent:

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + \underset{\substack{\text{silver}\\\text{mirror}}}{2\,Ag\downarrow} + 2H_2O + 4NH_3$$

(b) Fehling's test – Fehling solution gives a reddish brown precipitate with aldehydes except benzaldehyde.

$$R{-}CHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + \underset{\text{red ppt}}{Cu_2O\downarrow} + 3H_2O$$

- **Iodoform reaction:** When the reaction takes place with sodium hypoiodite, NaOI (NaOH + I_2), the iodoform formed is a bright yellow precipitate.



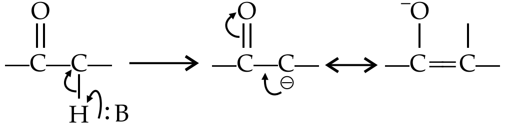
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3NaOI \longrightarrow CH_3COCI_3 + 3NaOH$$

$$CH_3COCI_3 + NaOH \longrightarrow CH_3COONa + \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow}$$

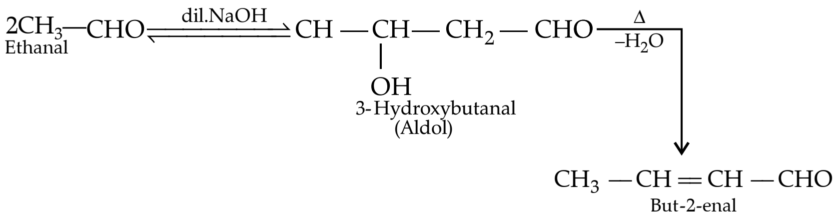
Among aldehydes, this test is given by only acetaldehyde as other aldehydes do not possess $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ group. Among ketones, all methyl ketones give this test.

- **Reaction due to α-hydrogen.**

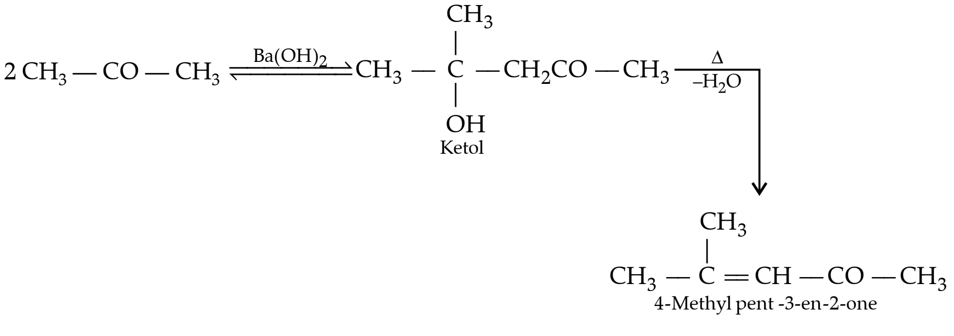
α-hydrogen in aldehydes and ketones is acidic in nature due to strong electron withdrawing effect of carbonyl group. As a result, aldehydes and ketones undergo a number of reactions.



(i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen react in the presence of dilute alkali to form β-hydroxy aldehdyes (aldol) or β-hydroxy ketones (Ketol).



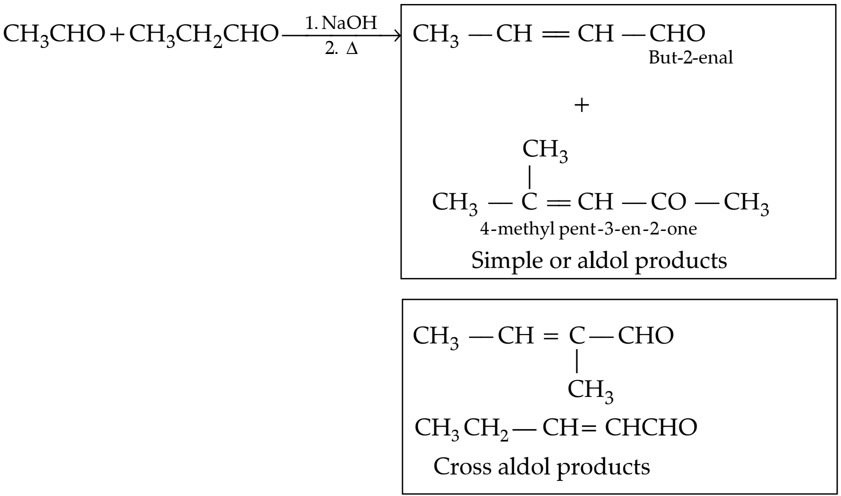
$$\underset{\text{Ethanal}}{2CH_3-CHO} \underset{}{\overset{\text{dil.NaOH}}{\rightleftharpoons}} \underset{\substack{\text{3-Hydroxybutanal}\\\text{(Aldol)}}}{CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$



$$2\,CH_3-CO-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} \underset{\text{Ketol}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CO-CH_3} \xrightarrow[-H_2O]{\Delta} \underset{\text{4-Methyl pent -3-en-2-one}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CO-CH_3}$$

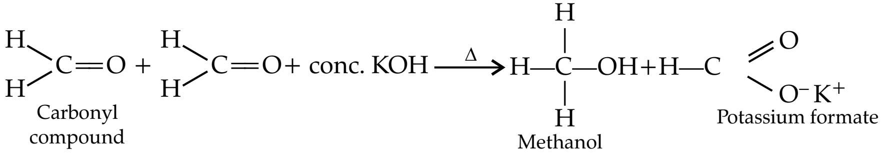
(ii) Cross aldol condensation: When two different aldehydes and/or ketones undergo aldol condensation, it is called cross aldol condensation.

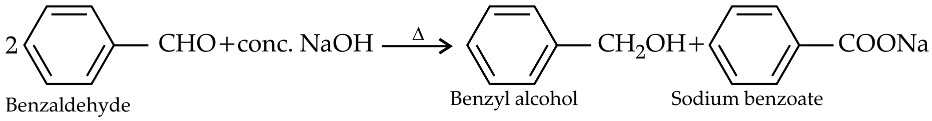
Base catalysed cross aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen reaction** or **Claisen–Schmidt condensation**.



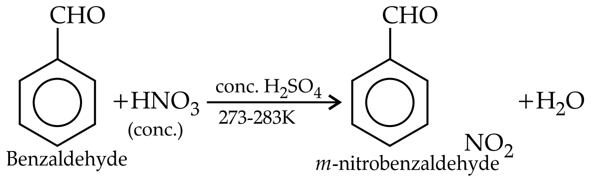
$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH} \boxed{\begin{array}{c} CH_3-CH=CH-CHO \\ + \\ CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH-CO-CH_3 \end{array}} \quad \boxed{\begin{array}{c} CH_3-CH=\underset{\underset{\large CH_3}{|}}{C}-CHO \\ CH_3CH_2-CH=CHCHO \end{array}}$$

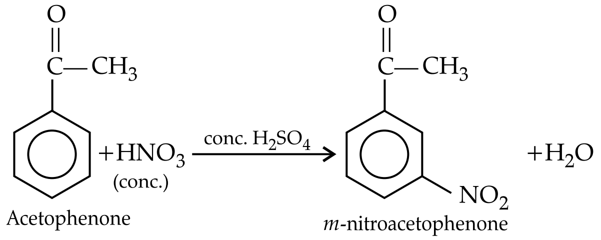
(iii) Cannizzaro Reaction: Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not have α-hydrogen undergo this reaction.

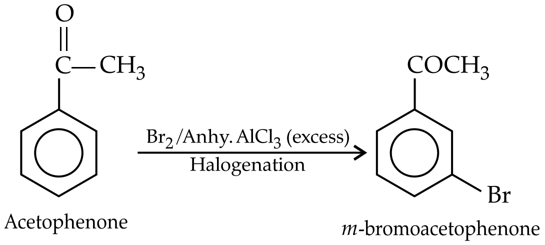




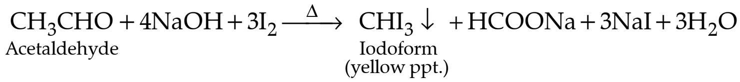
- **Electrophilic substitution reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows +R effect, therefore acts as a deactivating and *meta* directing group.







- **Test to distinguish between formaldehyde and acetaldehyde by Iodoform test:**
  Acetaldehyde gives a yellow precipitate of iodoform on heating with iodine in the presence of an alkali.



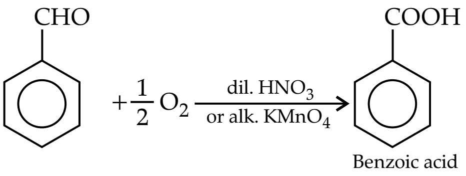
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4NaOH + 3I_2 \xrightarrow{\Delta} \underset{\substack{\text{Iodoform} \\ \text{(yellow ppt.)}}}{CHI_3 \downarrow} + HCOONa + 3NaI + 3H_2O$$

Formaldehyde does not give this test.

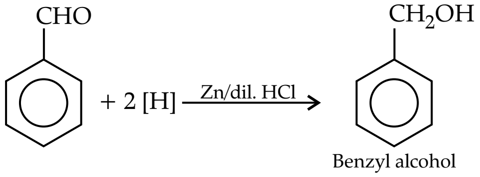
- **Test to distinguish between aldehydes and ketones:**

Test	Aldehydes	Ketones
Tollen's reagent	Gives silver mirror	No reaction
Fehling's solution	Gives reddish brown precipitate	No reaction
Schiff's reagent	Restores pink colour	No reaction
Reaction with $LiAlH_4$	Forms primary alcohol	Forms secondary alcohol

- **Uses of Aldehydes and Ketones:**
  - Formaldehdye is used as disinfectant and germicide.
  - Formaldehdye is used in the manufacture of Bakelite, resin and other polymers.
  - Formaldehyde is used to manufacture medicine for urine infection.
  - Acetaldehyde is used as a starting material for synthesis of acetic acid, drugs and polymers.
  - Acetone is a constituent of liquid nail polish.
  - Paraldehyde is used as a hypnotic in medicine.
- **Physical properties of benzaldehyde:**
  - Colourless liquid with a characteristic almond like odour:
  - Highly reactive.
  - Boiling point of 452 K.
- **Chemical properties of benzaldehyde:**
  - **Oxidation:**

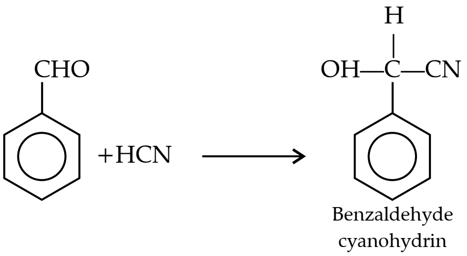


Reduction:

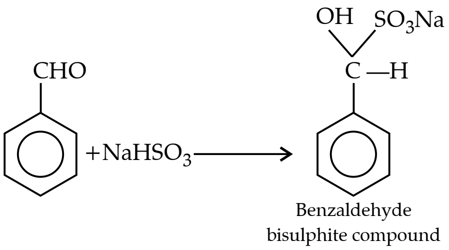


- **Nucleophilic Addition Reaction:**

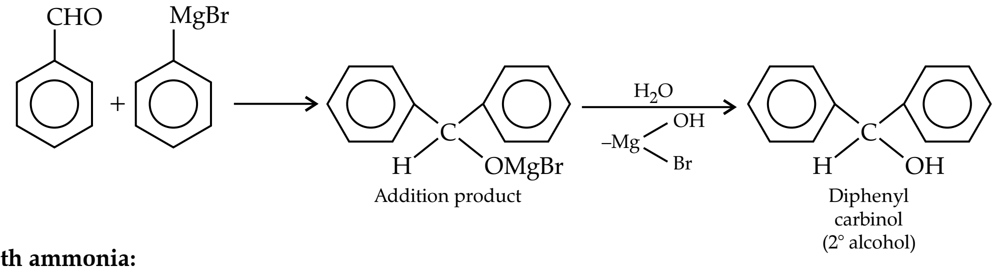
(i) With HCN:



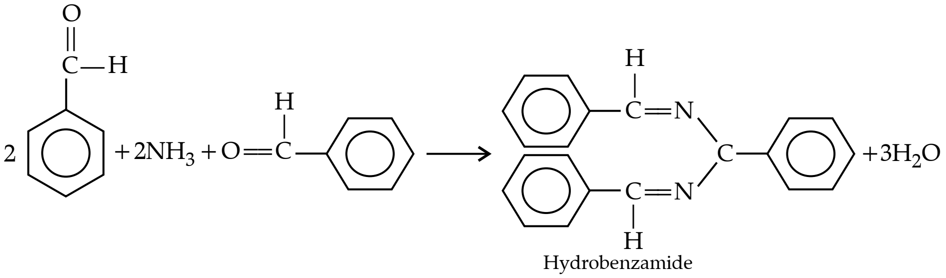
(ii) With $NaHSO_3$:



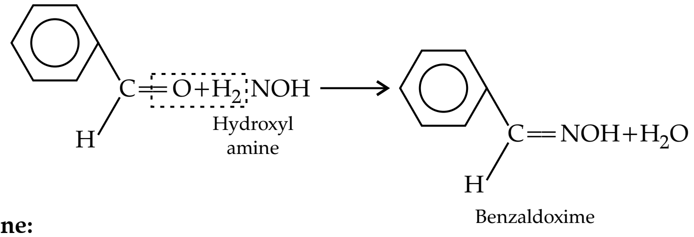
(iii) With Grignard's reagent:



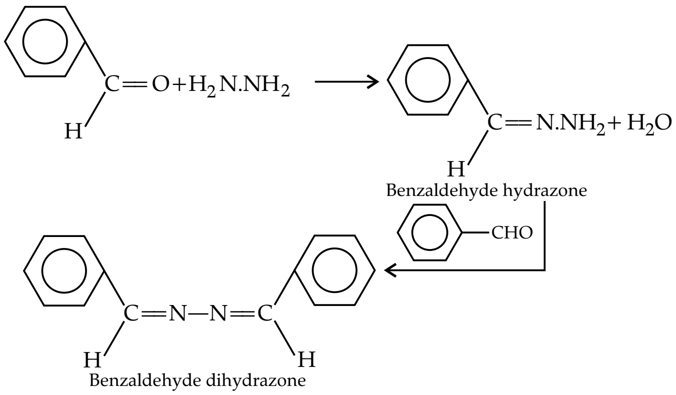
(iv) With ammonia:



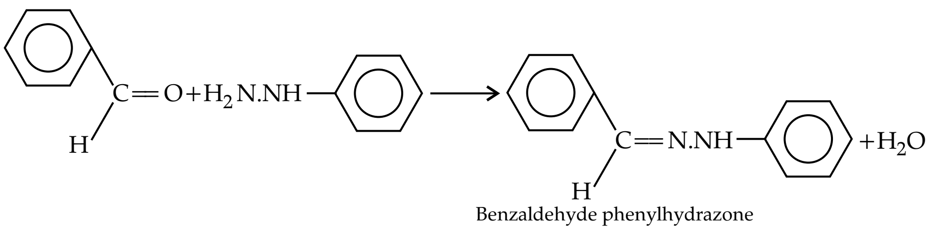
(v) With hydroxyl amine:



(vi) With hydrazine:



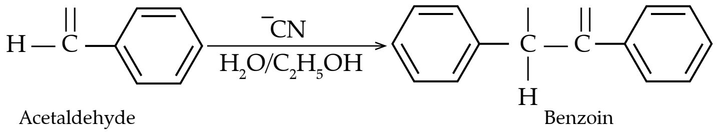
(vii) With phenyl hydrazine:



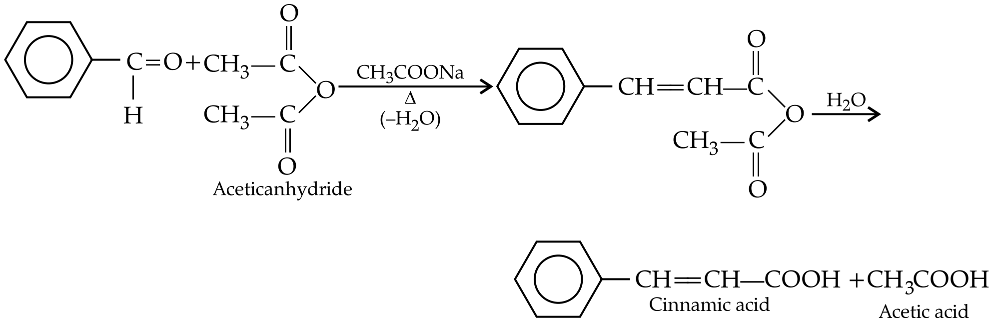
(viii) With PCl_5:

$$C_6H_5CHO + PCl_5 \longrightarrow \underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + POCl_3$$

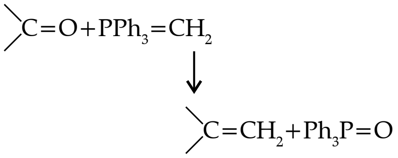
(ix) Benzoin condensation:



(x) Perkin's reaction:

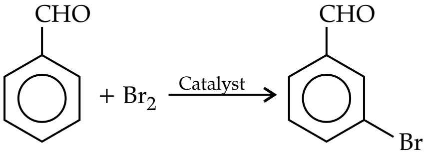


(xi) Wittig reaction:



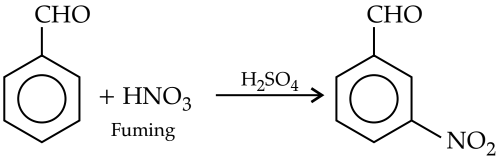
- **Electrophilic Substitution Reaction:**

(i) Halogenation:



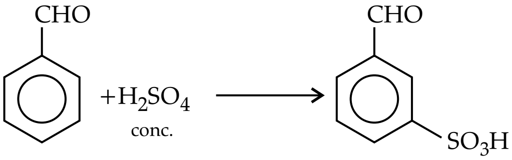
m-bromobenzaldehyde

(ii) Nitration:



m-nitrobenzaldehyde

(iii) Sulphonation:



m-benzaldehyde
sulphonic acid

- Test to distinguish between benzaldehyde and acetaldehyde by Iodoform test:

  Acetaldehyde gives a yellow precipitate of iodoform when heated with iodine, in the presence of alkali.

$$CH_3CHO + 4NaOH + 3I_2 \xrightarrow{\Delta} \underset{\substack{\text{Iodoform} \\ \text{(yellow ppt.)}}}{CHI_3\downarrow} + HCOONa + 3NaI + 3H_2O$$

  Benzaldehyde does not give iodoform test.

- **Uses of benzaldehyde:**
  - Manufacturing of dyes.
  - As a flavouring essence in perfumery.
  - Synthesis of cinnamic acid, cinnamaldehyde, etc.

Key Terms

- **Hydroformylation:** In this process, alkenes give aldehydes by the reaction of hydrogen and CO.
- **Collin's reagent:** This reagent can be prepared by mixing pyridine (C_5H_5N), CrO_3 and HCl in the presence of dichloromethane. This reagent is used to prepare aldehydes, by controlled oxidation process.
- **Baeyer-Villiger oxidation:** In this process, when ketones are treated with peroxy acids (per acetic acid), e.g., in the presence of an acid catalyst give carboxylic esters by insertion of esters.
- **MPV-reduction:** It is Meerwein Ponndorf Verley reduction. In this process, ketones are reduced to secondary alcohols with isopropyl alcohol in the presence of aluminium isopropoxide.
- **Oppenauer oxidation:** It is the reverse process of MPV-reduction.
- **Urotropine:** It is hexamethylenetetramine and used as a urinary antiseptic.
- **Formalin:** 40% aqueous solution of formaldehyde.

Mnemonics

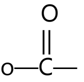
Concept: Detection Test

Mnemonics: TASte FAAR IMLy

Interpretation:

TASte → Tollen's test, Aldehyde group, Silver Morror

FAAR → Fehling's Aliphatic Aldehyde, Red-Brown ppt.

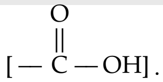
IMLy → Iodoform test, Methyl group linked to  $—\overset{\displaystyle O}{\overset{\|}{C}}—$, Yellow ppt

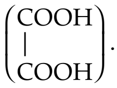
Topic-2

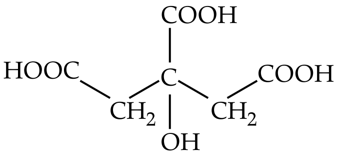
Carboxylic Acids: Methods of Preparation, Properties and Uses

Concepts Covered: *Classification of carboxylic acid, Methods of preparation, Physical and chemical properties, Test to identify carboxylic acid uses*

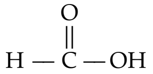
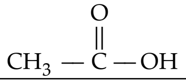
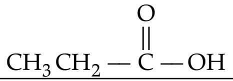
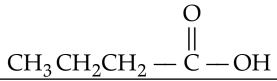
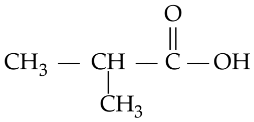
Revision Notes

- Carboxylic acids are the organic compounds which contain the carboxyl group  $[—\overset{\displaystyle O}{\overset{\|}{C}}—OH]$.
- **Classification of carboxylic acid:**
  (i) **Based on nature of group attached to the carboxyl group:**
    - **Aliphatic carboxylic acids:** Alkyl group or hydrogen atom is attached to carboxylic group. e.g., acetic acid (CH_3COOH), formic acid (HCOOH).
    - **Aromatic carboxylic acids:** Aryl group is attached to carboxylic group. e.g., benzoic acid (C_6H_5COOH).

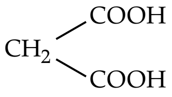
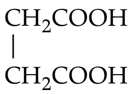
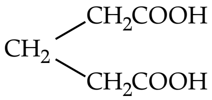
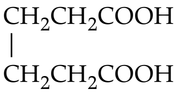
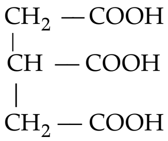
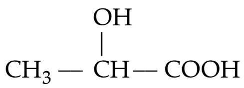
  (ii) **Based on number of carboxyl group:**
    - **Monocarboxylic acid:** If carboxylic acid contains one —COOH group, it is termed as monocarboxylic acid. e.g., acetic acid (CH_3COOH).
    - **Dicarboxylic acid:** If carboxylic acid contains two —COOH groups, it is termed as dicarboxylic acid. e.g., oxalic acid  $\left(\begin{array}{l}COOH\\ |\\ COOH\end{array}\right)$.
    - **Tricarboxylic acid:** If carboxylic acid contains three —COOH groups, it is termed as tricarboxylic acid. e.g., citric acid.

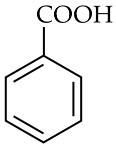


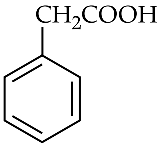
- **Nomenclature of carboxylic acid:** Monocarboxylic acids are named as alkanoic acids, i.e., name of parent alkane + oic acid. Dicarboxylic acids are termed as alkanedioic acids.

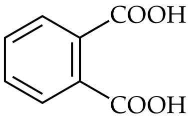
Carboxylic acid	**General Formula: $R-\overset{O}{\overset{\|}{C}}-OH$, where $R = C_nH_{2n+1}$**		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
 $H-\overset{O}{\overset{\|}{C}}-OH$	HCOOH	Formic acid	Methanoic acid
 $CH_3-\overset{O}{\overset{\|}{C}}-OH$	CH_3COOH	Acetic acid	Ethanoic acid
 $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$	CH_3CH_2COOH	Propionic acid	Propanoic acid
 $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$	$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
 $CH_3-\underset{\underset{CH_3}{\|}}{CH}-\overset{O}{\overset{\|}{C}}-OH$	$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid

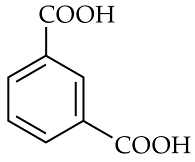
Dicarboxylic Acids

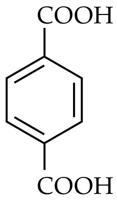
 (Oxalic acid) Ethane-1, 2-dioic acid	 (Malonic acid) Propane-1, 3-dioic acid	 (Succinic acid) Butane-1, 4-dioic acid	 (Glutaric acid) Pentane-1, 5-dioic acid
 (Adipic acid) Hexane-1, 6-dioic acid	 Propane-1,2-3- tricarboxylic acid	$CH_3-CH=CH-COOH$ (Crotonic acid) But-2-en-1-oic acid	 $CH_3-\overset{OH}{\overset{\|}{C}H}-COOH$ (Lactic acid) 2-Hydroxypropanoic acid


Benzoic acid or Benzene carboxylic acid

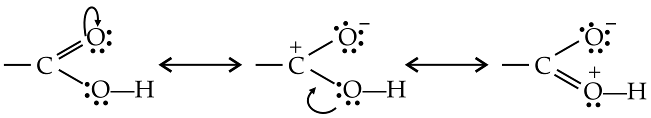

Phenylacetic acid or 2-Phenylethanoic acid


Phthalic acid or Benzene-1, 2-dicarboxylic acid


Isophthalic acid or Benzene-1, 3-dicarboxylic acid


Terephthalic acid or Benzene-1, 4-dicarboxylic acid

- **Structure of —COOH group:** In the carboxyl group, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. It exhibits resonance due to the presence of lone pair of electrons present on the O-atoms.



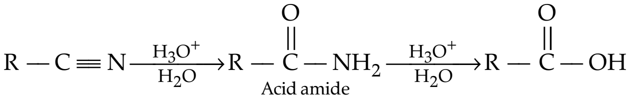
- **Methods of preparation of Carboxylic acids:**

(i) By oxidation of primary alcohols and aldehydes:

$$R-CH_2-OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alk. } KMnO_4} R-COOH$$

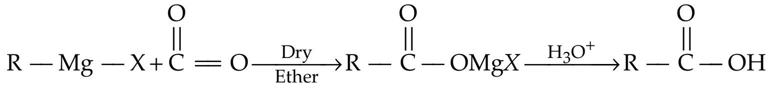
$$R-CHO+[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} R-COOH$$

(ii) From alkyl cyanides and amides:



$$R-C\equiv N \xrightarrow[H_2O]{H_3O^+} \underset{\text{Acid amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[H_2O]{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH$$

(iii) From Grignard reagent:

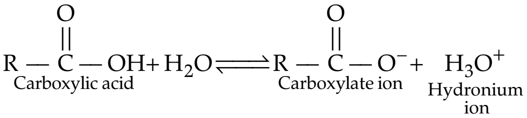


$$R-Mg-X+\overset{\overset{\displaystyle O}{\|}}{C}=O\xrightarrow[\text{Ether}]{\text{Dry}}R-\overset{\overset{\displaystyle O}{\|}}{C}-OMgX\xrightarrow{H_3O^+}R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

- **Physical properties of Carboxylic acids:**
  - **(i)** Lower members are colourless liquid with pungent smell, while higher members are odourless waxy solid. Benzoic acid is a crystalline solid.
  - **(ii)** First four members are water miscible due to tendency to form hydrogen bond. Higher acids are insoluble.
  - **(iii)** Carboxylic acid have higher boiling point due to their ability to form intermolecular hydrogen bonding.
- **Chemical Properties:** Chemical properties of carboxylic acids are classified as follows:

(i) Reduction involving H atom:

(a) Acidic nature:



$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH}+H_2O\rightleftharpoons\underset{\text{Carboxylate ion}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-}+\underset{\text{Hydronium ion}}{H_3O^+}$$

Greater the extent of ionisation, greater is the strength of the acid. The presence of an electron releasing group decreases the acidic strength of the carboxylic acid while the presence of electron withdrawing group increases the acidic strength of the carboxylic acid.

(b) Reactions showing acidic character:

$$2RCOOH+2Na\longrightarrow 2RCOONa+H_2$$

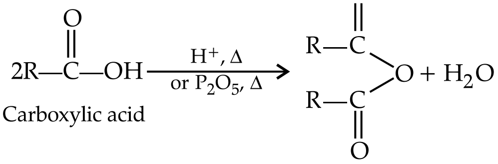
$$R-COOH+NaOH\longrightarrow R-COONa+H_2O$$

$$R-COOH+NaHCO_3\longrightarrow R-COONa+H_2O+CO_2\uparrow$$

$$2R-COOH+Na_2CO_3\longrightarrow 2RCOONa+CO_2\uparrow+H_2O$$

(ii) Reaction involving —OH group:

(a) Formation of acid anhydride:



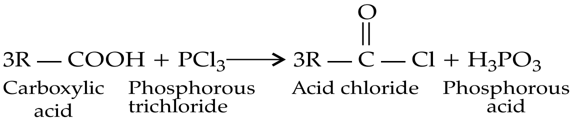
Acid anhydride

(b) Esterification:

$$\underset{\text{carboxylic acid}}{R-COOH}+\underset{\text{alcohol}}{R'-OH}\overset{H^+}{\rightleftharpoons}\underset{\text{esters}}{R-COOR'}+H_2O$$

(c) Reaction with PCl_5, PCl_3 and $SOCl_2$

$$\underset{\text{Carboxylic acid}}{R-COOH}+\underset{\text{Phosphorous pentachloride}}{PCl_5}\longrightarrow\underset{\text{Acylchloride}}{RCOCl}+POCl_3+HCl$$



$$\underset{\text{Carboxylic acid}}{3R-COOH}+\underset{\text{Phosphorous trichloride}}{PCl_3}\longrightarrow\underset{\text{Acid chloride}}{3R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}+\underset{\text{Phosphorous acid}}{H_3PO_3}$$

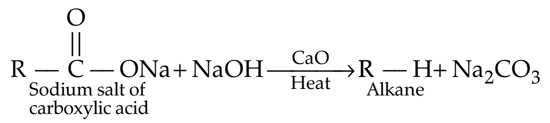
$$\underset{\text{Carboxylic acid}}{R-COOH}+\underset{\text{Thionyl chloride}}{SOCl_2}\longrightarrow\underset{\text{Acylchloride}}{RCOCl}+SO_2\uparrow+HCl\uparrow$$

(d) Reaction with ammonia:

$$\underset{\text{Carboxylic acid}}{R-COOH}+NH_3\rightleftharpoons R-COO-NH_4\xrightarrow[-H_2O]{\Delta}\underset{\text{Acid amide}}{R-CONH_2}$$

(iii) Reaction involving carboxyl group:

Decarboxylation (Removal of —CO_2)



$$\Rightarrow \quad \underset{\text{Sodium salt of carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa}+NaOH\xrightarrow[\text{Heat}]{\text{CaO}}\underset{\text{Alkane}}{R-H}+Na_2CO_3$$

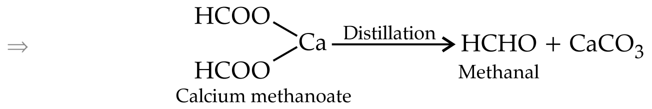
- **Electrolysis of aqueous solution of sodium or potassium salt:**

$$2RCOONa \longrightarrow \underset{\text{Carboxylate ion}}{2RCOO^-}+2Na^+$$

At anode: $\underset{\text{Carboxylate ion}}{2RCOO^-} \longrightarrow \underset{\text{Alkane}}{R-R}+2CO_2+2e^-$

At cathode: $2H_2O \rightleftharpoons 2H^+ + 2OH^- (2H^+ + 2e^- \longrightarrow H_2)$

This process is known as **Kolbe's electrolysis**.



$$\Rightarrow \quad \underset{\text{Calcium methanoate}}{(HCOO)_2Ca} \xrightarrow{\text{Distillation}} \underset{\text{Methanal}}{HCHO} + CaCO_3$$

$$\Rightarrow \quad \underset{\text{Silver ethanoate}}{CH_3COOAg}+Br_2 \xrightarrow{CCl_4,\text{Reflux}} \underset{\text{Bromomethane}}{CH_3Br}+CO_2+AgBr$$

This is called as **Hunsdiecker reaction**.

(b) Reduction:

$\Rightarrow$ **Partial reduction to alcohols:**

$$RCOOH+2H_2 \xrightarrow[\text{(or } LiAlH_4\text{)}]{\text{Copper chromite}} \underset{\text{Alcohol}}{RCH_2OH}+H_2O$$

$\Rightarrow$ **Complete reduction to alkanes:**

$$RCOOH+6HI \xrightarrow[\text{Heat}]{\text{Red P}} \underset{\text{Alkane}}{RCH_3}+3I_2+2H_2O$$

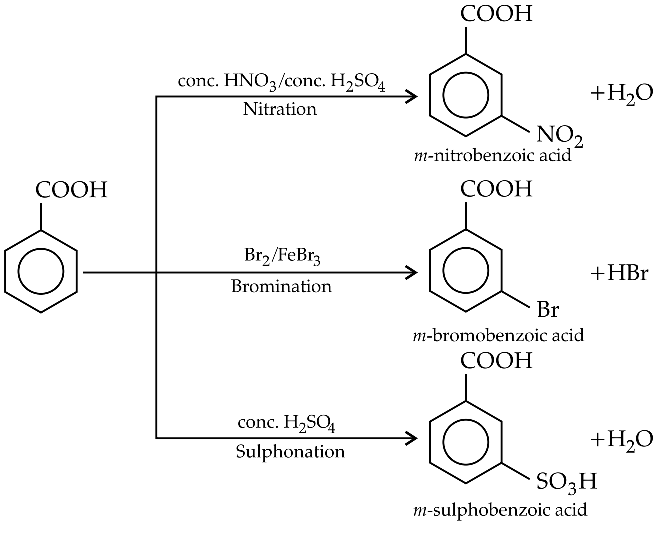
(iv) Reaction involving alkyl group

- **Halogenation**

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[(-HCl)]{Cl_2,\text{Red P}} \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} \xrightarrow[(-HCl)]{Cl_2,\text{Red P}} \underset{\text{Dichloro acetic acid}}{CHCl_2COOH} \xrightarrow[(-HCl)]{Cl_2,\text{Red P}} \underset{\text{Trichloro acetic acid}}{CCl_3COOH}$$

This is called as **Hell-Volhard-Zelinsky (HVZ) reaction**.

(v) Electrophilic substitution in aromatic carboxylic acids:



- **Test for carboxylic acid:**

Test	**Formic acid**
Tollen's reagent	Gives silver mirror or black precipitate.
Fehling's solution	Gives red precipitate.
With acidified $KMnO_4$	Decolourises pink colour.

Test	**Acetic acid**
With bicarbonates and carbonates	Liberates CO_2 gas.
With ferric chloride	Forms wine red colour.
On warming with ethyl alcohol and conc. H_2SO_4	Pleasant fruity odour of ethyl acetate is formed.

Test	**Benzoic acid**
On boiling	Dissolves in water.
On cooling	Separates out in the form of white shining leaflets.
With ferric chloride	Gives buff coloured precipitate.
On warming with a little alcohol and conc. H_2SO_4	A fragrant odour of ethyl benzoate is formed.

- **Uses of Formic acid:**
  - As an antiseptic.
  - As coagulating agent in rubber industry.
  - For dye baths in textiles.
- **Uses of acetic acid:**
  - As vinegar.
  - Solvent for resins, cellulose, etc.
  - Production of esters, perfumes, acetone, etc.
  - Manufacture of cellulose acetate.
- **Uses of benzoic acid:**
  - Food preservative.
  - As urinary antiseptic in medicine.
  - Manufacture of antiseptics and dyes.
  - Esters of benzoic acid are used in perfume.

Key Terms

- **Electron withdrawing group:** An atom or functional group that withdraws electron density from neighbouring atoms towards itself by resonance or indicative effects.
- **Electron donating group:** An atom or functional group that releases electron density to neighbouring atoms from itself by resonance or inductive effects.

❑❑