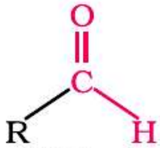
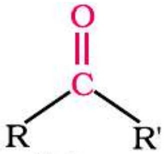
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

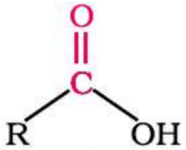
- Organic compounds containing Carbon-Oxygen double bond called carbonyl group.
- It is one of the most important functional group in Organic Chemistry.

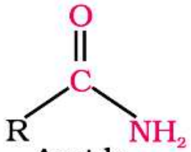
ALDEHYDES AND KETONES

- In aldehydes, the carbonyl group is bonded to a carbon and hydrogen.
- In ketones, the carbonyl group is bonded to two carbon atoms.
- The carbonyl compounds in which the carbonyl group is bonded to oxygen are known as carboxylic acids and their derivatives.
- The carbonyl compounds in which the carbon is attached to nitrogen are called amides.
- The carbonyl compounds in which the carbon is attached to halogens are called acyl halides.
- The general formulas of these classes of compounds are given below.

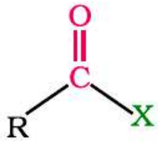

Aldehyde

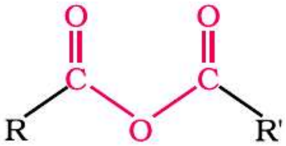

Ketone


Carboxylic acid


Amide


Ester


Acyl halide; X = (Halogen)


Acid anhydride

- Aldehydes, ketones and carboxylic acids are important in biochemical processes of life.
- They add fragrance and flavours to nature.
- Eg: Vannillin, Salicylaldehyde, Cinnamaldehyde etc.
- They are used in many food products and pharmaceuticals.
- Some of these compounds are used as solvents and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics etc.

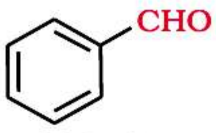
NOMENCLATURE OF ALDEHYDES AND KETONES

A. COMMON SYSTEM

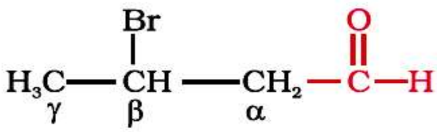
- Aldehydes are named by replacing the ending '–ic' acid of carboxylic acid with aldehyde.
- The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ etc.

CH_3CHO

Acetaldehyde



Benzaldehyde



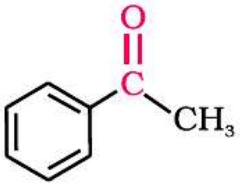
$$\underset{\gamma}{H_3C}-\underset{\beta}{\overset{Br}{CH}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H$$

β-Bromobutyraldehyde

- The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.
- The locations of substituents are indicated by Greek letters like α α ', β β' and so on.
- Some ketones have historical common names.

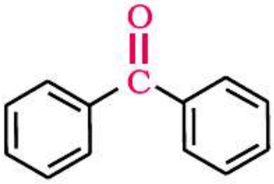
$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Acetone



Acetophenone

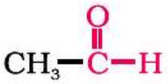
Propiophenone



Benzophenone

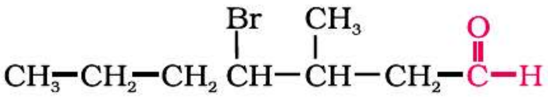
B. IUPAC NAMES

- The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending '–e' with '–al' and '–one' respectively.
- In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group.
- In the case of ketones, the numbering begins from the end nearer to the carbonyl group.
- The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain.
- In the case of cyclic ketones, the carbonyl carbon is numbered one.
- When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane.



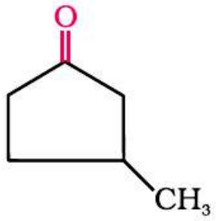
$$CH_3-\overset{O}{\overset{\|}{C}}-H$$

Ethanal

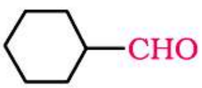


$$CH_3-CH_2-CH_2\,\overset{Br}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

4-Bromo-3-methylheptanal



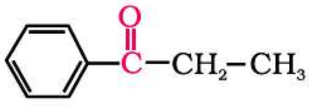
3-Methylcyclopentanone



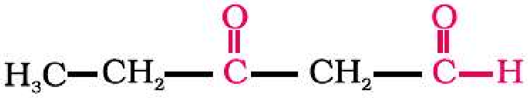
Cyclohexanecarbaldehyde

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

Pent-2-enal

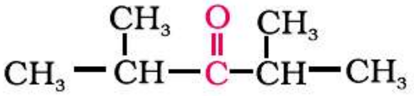


1-Phenylpropan-1-one



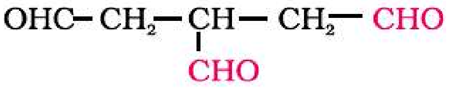
$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$

3-Oxopentanal



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

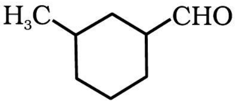
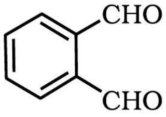
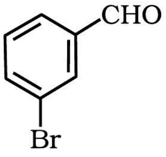
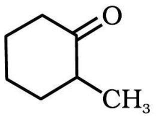
2,4-Dimethylpentan-3-one



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

Propane–1,2,3-tricarbaldehyde

EXAMPLES

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexane	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

STRUCTURE OF CARBONYL GROUP

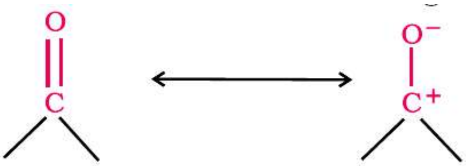
- The C=O bond is made up of one σ and one π-bond.
- In the formation of carbonyl group, Carbon uses sp^2-hybrid orbitals while Oxygen uses its unhybridised atomic orbitals.
- Carbon atom is joined to three atoms by σ-bonds.
- Since these bonds utilise sp^2 orbitals, they lie in the same plane and are 120^0

apart.

- Hence carbonyl group is planar.

NATURE OF C=O BOND

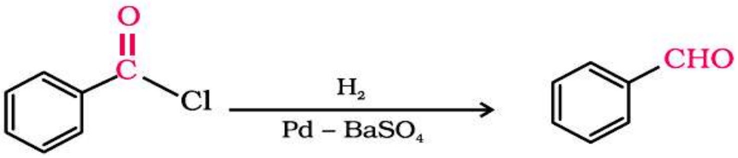
- The carbon—oxygen double bond is polarized due to higher electronegativity of oxygen relative to carbon.
- Hence the carbonyl carbon is an electrophilic centre and the carbonyl oxygen is a nucleophilic centre.
- Carbonyl compounds are polar.
- The high polarity of the carbonyl group is explained on the basis of resonance.



PREPARATION OF ALDEHYDES

1. FROM ACID CHLORIDE

- Acid chlorides when reduced by hydrogen in the presence of Palladium catalyst supported on $BaSO_4$ gives aldehydes.
- This reaction is known as **Rosenmund reduction.**



2. FROM NITRILES AND ESTERS

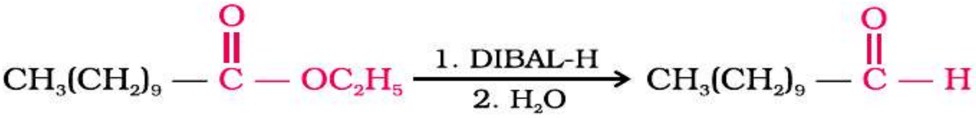
- Nitriles are reduced to corresponding imine with stannous chloride in the presence of HCl.
- Imine on hydrolysis give corresponding aldehyde.
- This reaction is known as **Stephen reaction.**

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

- Nitriles are selectively reduced by Di-isobutyl aluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes.

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

- Similarly esters are also reduced to aldehydes with DIBAL-H.

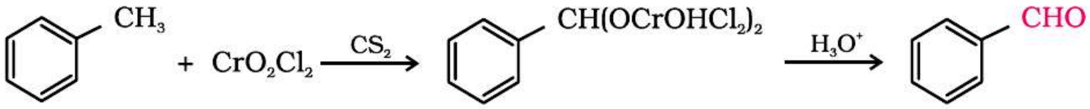


$$CH_3(CH_2)_9 - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9 - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

3. FROM HYDROCARBONS

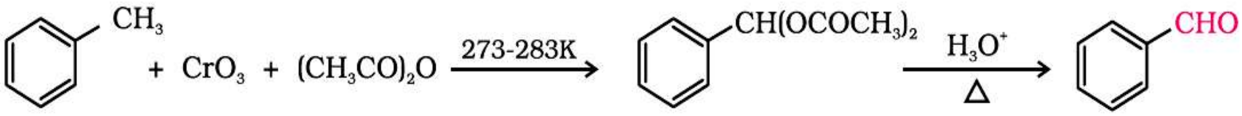
A) BY THE OXIDATION OF METHYLBENZENE

- Strong oxidising agents oxidize toluene and its derivatives to benzoic acids.
- Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.
- This reaction is called **Etard reaction.**



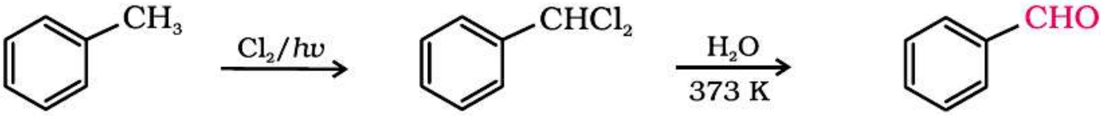
Toluene Chromium complex Benzaldehyde

- Toluene or substituted toluene on treating with chromic oxide in acetic anhydride gives is benzylidene diacetate.
- This on hydrolysis with aqueous acid gives benzaldehyde.



b) BY SIDE CHAIN CHLORINATION FOLLOWED BY HYDROLYSIS

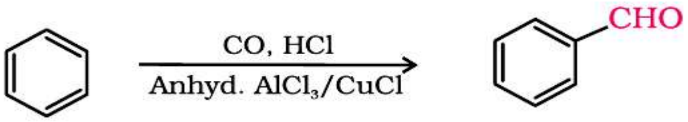
- Side chain chlorination of toluene gives benzal chloride.
- Benzal chloride on hydrolysis gives benzaldehyde.
- This is a commercial method of manufacture of benzaldehyde.



Toluene Benzal chloride Benzaldehyde

c) BY GATTERMANN KOCH REACTION

- When benzene or its derivative is treated with CO and HCl in the presence of anhy. AlCl3 or CuCl, it gives benzaldehyde or substituted benzaldehyde.

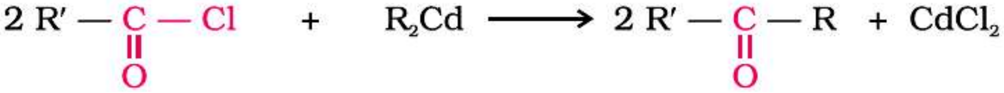


Benzene Benzaldehyde

PREPARATION OF KETONES

1. FROM ACID CHLORIDES

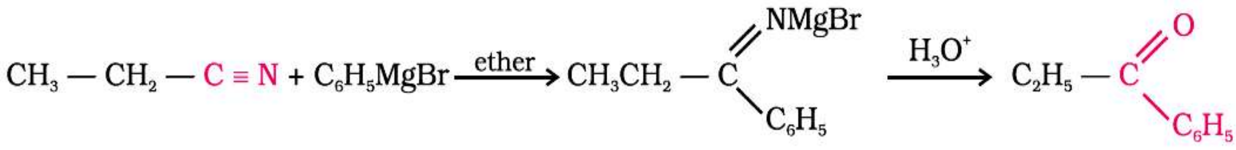
- Acyl chlorides on treatment with dialkyl cadmium give ketones.



$$2\,R'-\underset{\underset{O}{\|}}{C}-Cl \quad + \quad R_2Cd \longrightarrow 2\,R'-\underset{\underset{O}{\|}}{C}-R \; + \; CdCl_2$$

2. FROM NITRILES

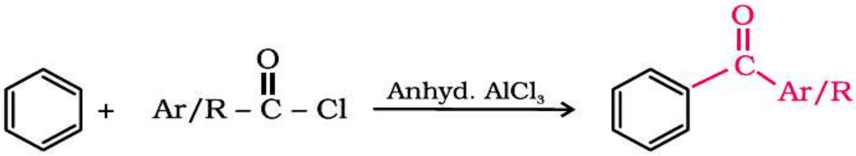
- Nitrile on treating with Grignard reagent followed by hydrolysis gives a ketone.



Propiophenone

3. FROM BENZENE OR SUBSTITUTED BENZENES

- When benzene or substituted benzene is treated with acid chloride in the presence of anhy. $AlCl_3$, it gives corresponding ketone.
- This reaction is known as **Friedel Crafts Acylation reaction.**



PHYSICAL PROPERTIES

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
- It is due to weak molecular association in aldehydes and ketones.
- The boiling points of aldehydes and ketones are lower than those of alcohols
- of similar molecular masses due to the absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water.
- The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

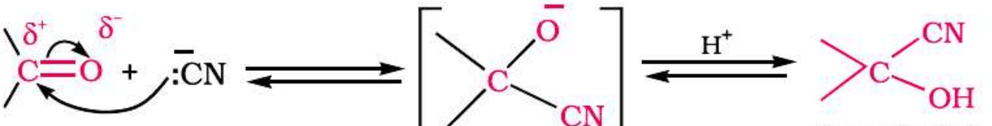
CHEMICAL REACTIONS

1. NUCLEOPHILIC ADDITION REACTIONS

A) ADDITION OF HYDROGEN CYANIDE

- Aldehydes and ketones react with HCN in presence of a base to yield cyanohydrins.

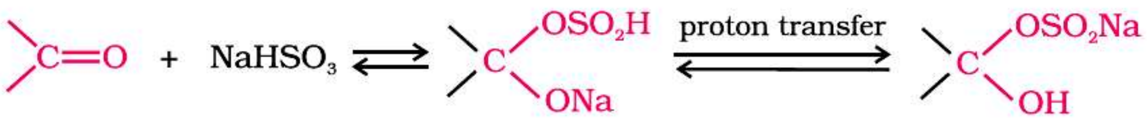
$$HCN + \overline{O}H \rightleftharpoons :\overline{C}N + H_2O$$



Cyanohydrin

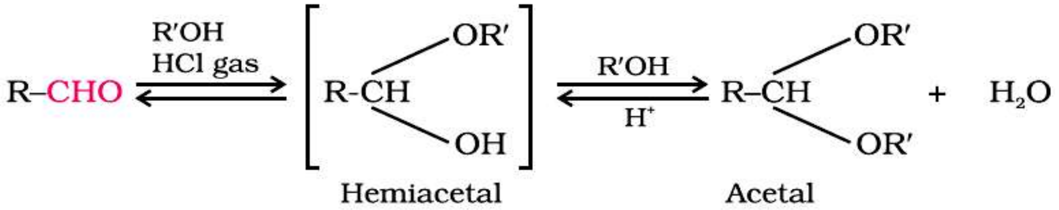
B. ADDITION OF SODIUM HYDROGEN SULPHITE

- Sodium hydrogen sulphite adds to aldehydes and ketones to form the addition products.

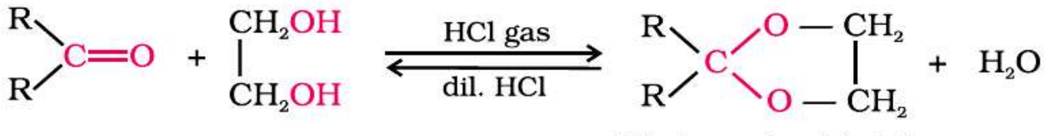


C. ADDITION OF ALCOHOLS

- Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield hemiacetals.
- It further reacts with one more molecule of alcohol to give a gem dialkoxy compound known as acetals.

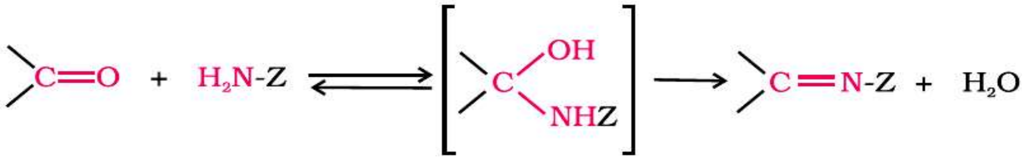


- Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.


Ethylene glycol ketal

D. ADDITION OF AMMONIA AND ITS DERIVATIVES

- Nucleophiles such as ammonia and its derivatives $H_2N\text{-}Z$ add to the carbonyl group of aldehydes and ketones to form =C=N−Z.
- [Z= Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$ etc.]



2. REDUCTION

A. REDUCTION TO ALCOHOLS

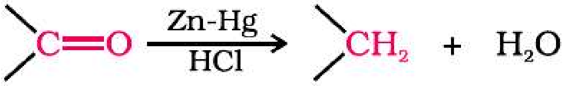
- Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$ as well as catalytic hydrogenation.

B. REDUCTION TO HYDROCARBONS

1. CLEMMENSEN REDUCTION

- Aldehydes and ketones on reduction with zinc amalgam and conc. HCl gives corresponding hydrocarbons.

- This reaction is known as Clemmensen reduction.



2. WOLF KISHNER REDUCTION

- Aldehydes and ketones can be reduced to the corresponding hydrocarbons by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.
- This reaction is called **Wolf Kishner Reduction.**

3. OXIDATION

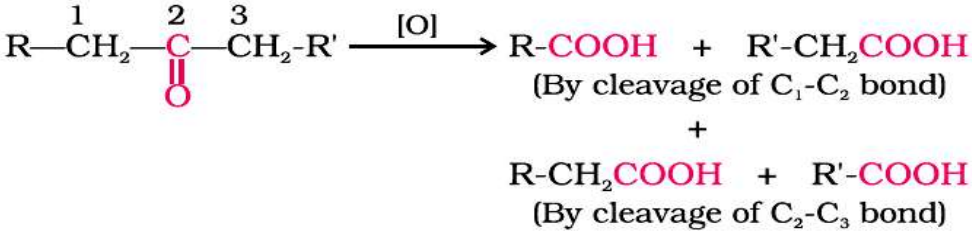
a) OXIDATION OF ALDEHYDES

- Aldehydes are easily oxidized to carboxylic acids on treatment with common oxidising agents like nitric acid, $KMnO_4$, $K_2Cr_2O_7$ etc.

$$\text{R-CHO} \xrightarrow{[O]} \text{R-COOH}$$

b) OXIDATION OF KETONES

- Ketones are generally oxidized under vigorous conditions.
- i.e., strong oxidising agents and at elevated temperatures.
- It involves the carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



$$\text{R}-\overset{1}{\text{CH}_2}-\underset{\|\atop \text{O}}{\overset{2}{\text{C}}}-\overset{3}{\text{CH}_2}\text{-R}' \xrightarrow{[O]} \underset{\text{(By cleavage of } C_1\text{-}C_2 \text{ bond)}}{\text{R-COOH} + \text{R}'\text{-CH}_2\text{COOH}} + \underset{\text{(By cleavage of } C_2\text{-}C_3 \text{ bond)}}{\text{R-CH}_2\text{COOH} + \text{R}'\text{-COOH}}$$

TESTS TO DISTINGUISH ALDEHYDES FROM KETONES

1. TOLLENS' TEST

- Aldehyde on warming with freshly prepared ammoniacal silver nitrate solution, a bright silver mirror is produced due to the formation of silver metal.
- Aldehydes are oxidized to corresponding carboxylate anion.

$$\text{RCHO} + 2[\text{Ag(NH}_3)_2]^+ + 3\,\bar{\text{O}}\text{H} \longrightarrow \text{RCO}\bar{\text{O}} + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$$

b) FEHLING'S TEST

- Aldehydes on heating with Fehling's solution, a reddish brown precipitate is obtained.

- The Aldehydes are oxidized to corresponding carboxylate anion.
- Aromatic aldehydes do not respond to this test.

$$R\text{-}CHO + 2Cu^{2+} + 5\bar{O}H \longrightarrow RCO\bar{O} + \underset{\text{Red-brown ppt}}{Cu_2O} + 3H_2O$$

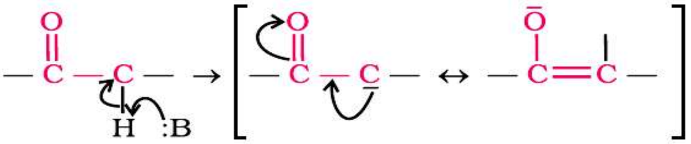
c) HALOFORM REACTION

- Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom are oxidized by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of the carbonyl compound.
- The methyl group is converted to **Haloform.**

$$R{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 \xrightarrow{NaOX} R{-}\overset{\overset{\large O}{\|}}{C}{-}ONa + CHX_3 \quad (X{=}Cl, Br, I)$$

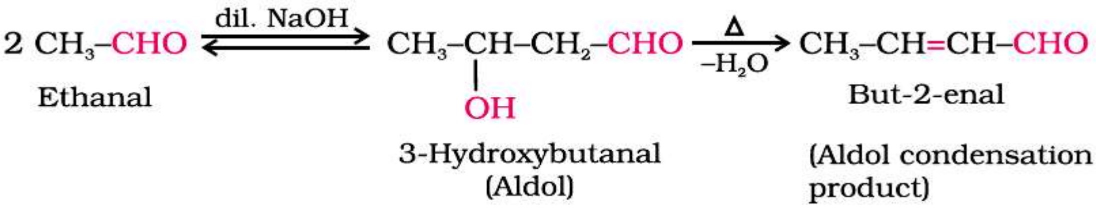
4. REACTIONS DUE TO α-HYDROGEN

- The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-hydrogen.
- The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilization of the conjugate base.



a) ALDOL CONDENSATION

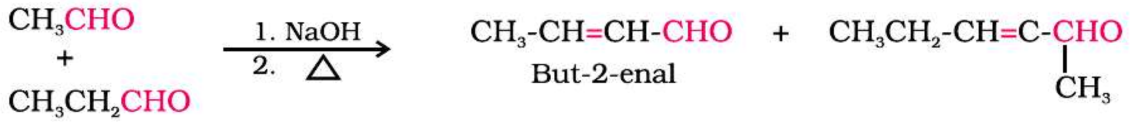
- Aldehydes and ketones having at least one α-hydrogen atom undergo condensation in presence of dilute alkalie as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (Ketol) respectively.
- This reaction is known as **aldol condensation.**



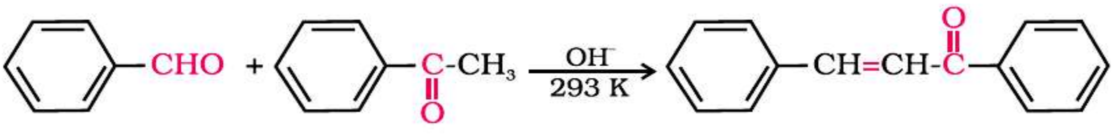
$$\underset{\text{Ethanal}}{2\,CH_3{-}CHO} \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} \underset{\substack{\text{3-Hydroxybutanal}\\\text{(Aldol)}}}{CH_3{-}\underset{\underset{\large OH}{|}}{CH}{-}CH_2{-}CHO} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{But-2-enal}\\\text{(Aldol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

b) CROSSED ALDOL CONDENSATION

- When aldol condensation is carried out between two different aldehydes or ketones, it is called Crossed Aldol Condensation.



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

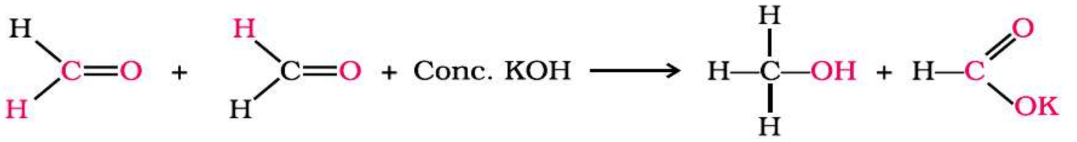


1, 3-Diphenylprop-2-en-1-one

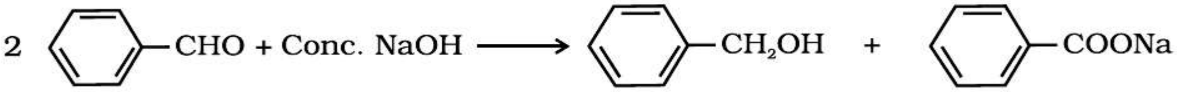
5. OTHER REACTIONS

a) CANNIZZARO REACTION

- In the Presence of a base, aldehydes which do not have an α-hydrogen atom undergo self-oxidation and reduction reaction and salt of carboxylic acid and an alcohol are produced.
- This reaction is known as **Cannizzaro reaction.**



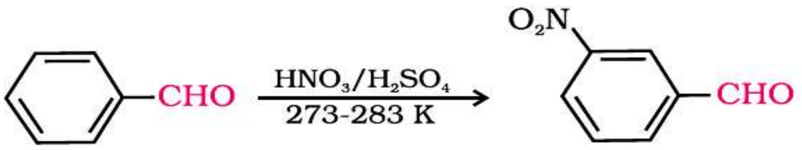
Formaldehyde Methanol Potassium formate



Benzaldehyde Benzyl alcohol Sodium benzoate

b) ELECTROPHILIC SUBSTITUTION REACTION

- Aromatic aldehydes and ketones undergo electrophilic substitution at the ring.
- The carbonyl group acts as a deactivating and meta directing group.



Benzaldehyde *m*-Nitrobenzaldehyde

USES OF ALDEHYDES AND KETONES

- Aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products.
- Formalin is used to preserve biological specimens and to prepare bakelite, urea formaldehyde resins and other polymeric products.
- Acetaldehyde is used as a starting material in the manufacture of acetic acid,

ethyl acetate, vinyl acetate, polymers and drugs.

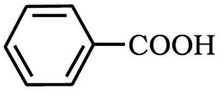
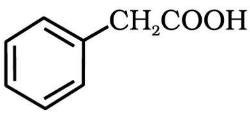
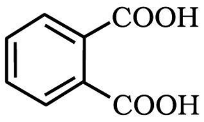
- Benzaldehyde is used in perfume industry and in dye industries.
- Acetone and ethyl methyl ketone are common industrial solvents.

CARBOXYLIC ACIDS

- The carbonyl compounds in which carbonyl group is bonded to a hydroxyl group is called carboxylic acids.

NOMENCLATURE

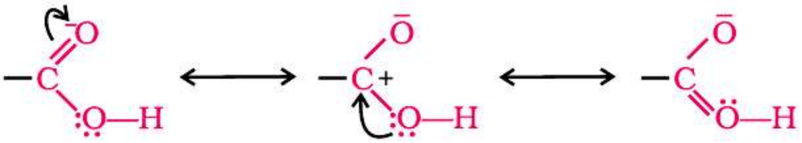
- The common names end with the suffix –ic acid.
- In the IUPAC System, aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with –oic acid.

Structure	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$HOOC\text{-}COOH$	Oxalic acid	Ethanedioic acid
$HOOC\ \text{-}CH_2\text{-}COOH$	Malonic acid	Propanedioic acid
$HOOC\ \text{-}(CH_2)_2\text{-}COOH$	Succinic acid	Butanedioic acid
$HOOC\ \text{-}(CH_2)_3\text{-}COOH$	Glutaric acid	Pentanedioic acid
$HOOC\ \text{-}(CH_2)_4\text{-}COOH$	Adipic acid	Hexanedioic acid
$HOOC\ \text{-}CH_2\text{-}CH(COOH)\text{-}CH_2\text{-}COOH$	–	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

STRUCTURE OF CARBOXYL GROUP

- In carboxylic acids, the bonds to the carbonyl carbon lie in one plane and are separated by about 120°.
- The carboxylic carbon is less electrophilic than carbonyl carbon because of the

resonance structure.



METHODS OF PREPARATION OF CARBOXYLIC ACIDS

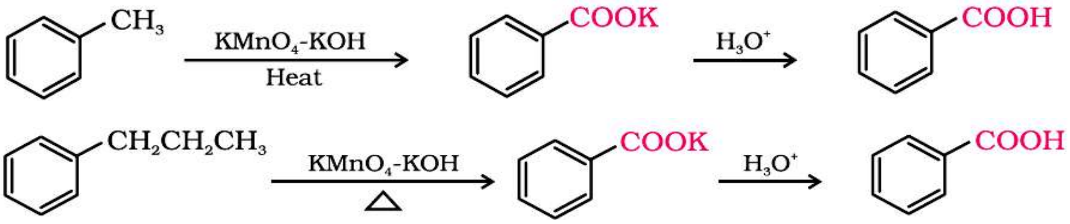
1. FROM PRIMARY ALCOHOLS AND ALDEHYDES

- Primary alcohols are readily oxidized to carboxylic acids with common oxidising agents such as $KMnO_4$ in neutral, acidic or alkaline media or by $K_2Cr_2O_7$ and CrO_3 in acidic media.

$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

2. FROM ALKYL BENZENES

- Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline $KMnO_4$.
- The entire side chain is oxidized to the carboxyl group.

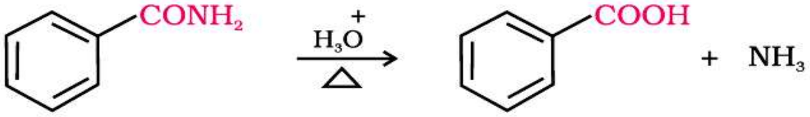


3. FROM NITRILES AND AMIDES

- Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst.
- Mild reaction conditions are used to stop the reaction at the amide stage.

$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H} \text{ or } \overset{-}{O}H} R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\triangle]{\overset{+}{H} \text{ or } \overset{-}{O}H} RCOOH$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\triangle]{H_3\overset{+}{O}} \underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3$$



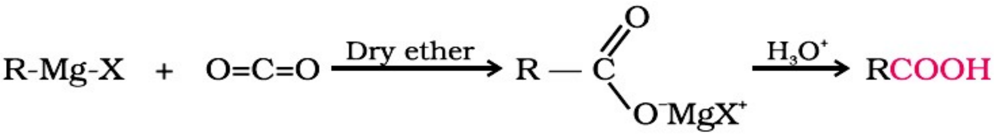
Benzamide

Benzoic acid

4. From Grignard reagents

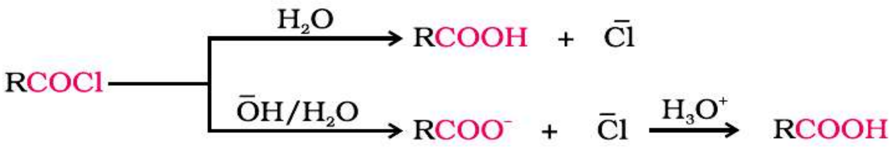
- Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids.
- Carboxylic acids in turn give corresponding carboxylic acids after acidification

with mineral acid.



5. From acyl halides and anhydrides

- Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids.
- Anhydrides are hydrolysed to corresponding acids with water.

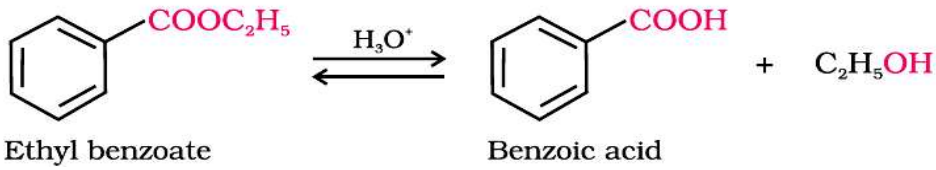


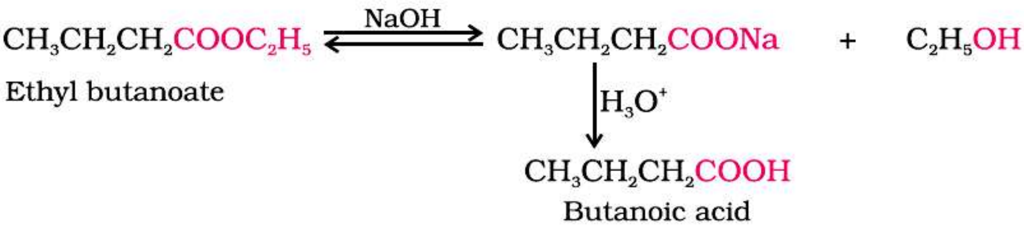
$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2\ C_6H_5COOH$$

Benzoic anhydride Benzoic acid

6. From esters

- Acid hydrolysis of esters directly gives carboxylic acids.
- Base hydrolysis gives carboxylates, which on acidification gives corresponding carboxylic acids.





PHYSICAL PROPERTIES

- Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours.
- The higher acids are wax like solids and are odourless due to their low volatility.
- Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molar masses.
- This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

- In the vapour phase carboxylic acids exist as a dimmer because hydrogen bonds are not broken completely even in this phase.

CHEMICAL REACTIONS

1. REACTIONS INVOLVING CLEAVAGE OF O–H BONDS

A. REACTION WITH METALS AND ALKALIES

- The carboxylic acids evolve hydrogen with electropositive metals and form salts with alkalies.
- They react with weaker bases such as carbonates and hydrogen carbonates to evolve carbon dioxide.
- This reaction is used to detect the presence of carboxyl group in an organic compound.

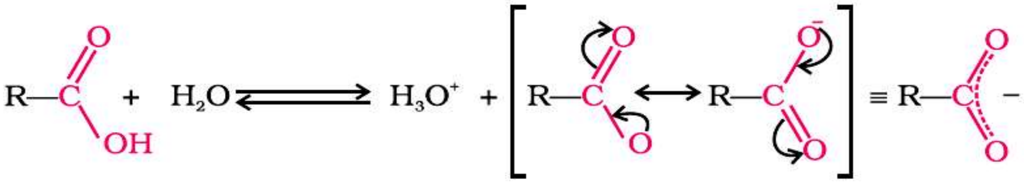
$$2R\text{-}COOH + 2Na \longrightarrow 2R\text{-}CO\bar{O}Na^{+} + H_2$$

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}CO\bar{O}Na^{+} + H_2O$$

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}CO\bar{O}Na^{+} + H_2O + CO_2$$

B. Acidity

- Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.



- Carboxylic acids are weaker than mineral acids.
- But they are stronger acids than alcohols and many simple phenols.
- The conjugate base of carboxylic acid is a carboxylate ion.
- The carboxylate ion is stabilized by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom.
- The conjugate base of phenol is phenoxide ion.
- Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.
- Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion.
- The negative charge is delocalized over two electronegative oxygen atom in carboxylate ion.
- But in phenoxide ion, the negative charge is less effectively delocalized over

one oxygen atom and less electronegative carbon atoms.

- Thus the carboxylate ion is more stabilized than phenoxide ion.
- So carboxylic acids are more acidic than phenols.

EFFECT OF SUBSTITUENTS ON THE ACIDITY OF CARBOXYLIC ACIDS

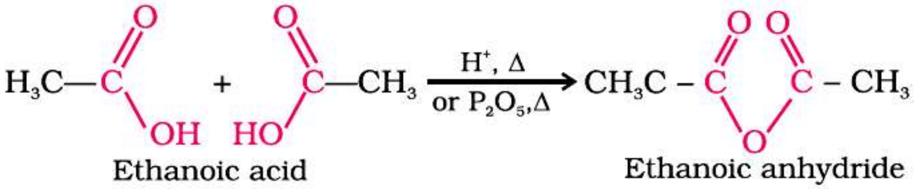
- Electron withdrawing groups increase the acidity of carboxylic acids.
- This is by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects.
- Electron donating groups decrease the acidity by destabilizing the conjugate base.
- The effect of the following groups in increasing acidity order is

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

2. REACTIONS INVOLVING CLEAVAGE OF C–OH BONDS

A. FORMATION OF ANHYDRIDE

- Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.



B. ESTERIFICATION

- Carboxylic acids react with alcohols in the presence of conc. H_2SO_4 or dry HCl to form esters.
- This reaction is called **esterification.**

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

C. REACTIONS WITH PCl_5, PCl_3 AND $SOCl_2$

- Carboxylic acids on treating with PCl_5, PCl_3 and $SOCl_2$ gives corresponding acid chlorides by replacing the hydroxyl groups by chlorine atom.

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$

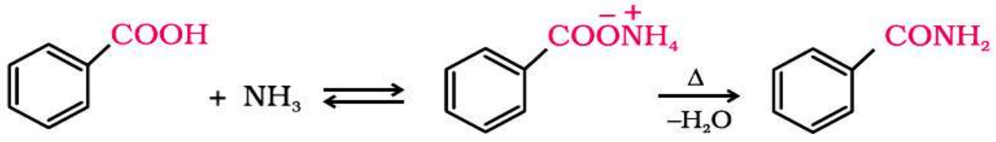
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

D. REACTION WITH AMMONIA

- Carboxylic acids react with ammonia to give ammonium salt, which on further heating at high temperature gives amides.

$$\underset{}{CH_3COOH + NH_3} \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3CO\overset{-}{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$



Ammonium benzoate Benzamide

3. REACTIONS INVOLVING –COOH GROUP

A. REDUCTION

- Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or with diborane.
- Diborane does not easily reduce functional groups such as ester, nitro, halo etc.
- Sodium borohydride does not reduce the carboxyl group.

$$\text{R-COOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether} \quad \text{or } B_2H_6} \text{R-}CH_2OH$$

B. DECARBOXYLATION

- Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3:1).
- The reaction is known as decarboxylation.

$$\text{R-COONa} \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} \text{R-H} + Na_2CO_3$$

C. KOLBE'S ELECTROLYSIS

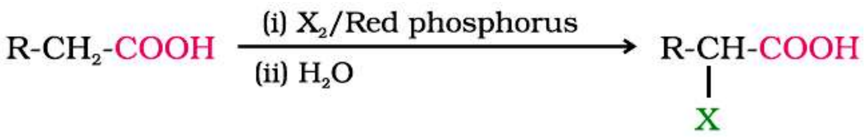
- Alkali metal salts of carboxylic acids undergo decarboxylation, on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.
- This reaction is known as **Kolbe electrolysis.**

$$2CH_3COONa + 2H_2O \longrightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2NaOH$$

SUBSTITUTION REACTIONS IN THE HYDROCARBON PART

A. HALOGENATION

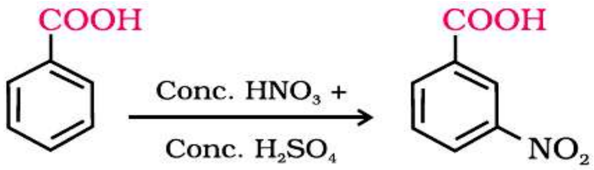
- Carboxylic acids having α-hydrogen atoms when treated with chlorine or bromine in presence of small amount of red phosphorous gives α -chloro or α-bromo carboxylic acids.
- This reaction is known as **Hell-Volhard Zelinsky reaction.**

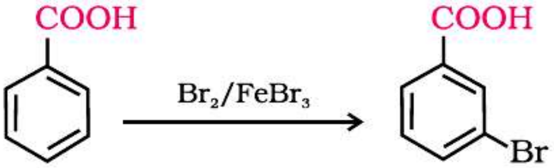


$$\text{R-}CH_2\text{-COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} \text{R-}\underset{\displaystyle X}{\underset{|}{\text{CH}}}\text{-COOH}$$

B. RING SUBSTITUTION

- Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta directing group.





USES OF CARBOXYLIC ACIDS

- Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.
- Ethanoic acid is used as solvent and as vinegar in food industry.
- Hexadienoic acid is used in the manufacture of nylon-6, 6.
- Esters of benzoic acid are used in perfume industry.
- Sodium benzoate is used as a food preservative.
- Higher fatty acids are used for the manufacture of soaps and detergents.