

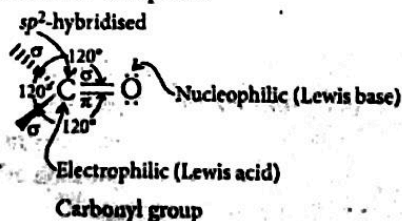
Aldehydes, Ketones and Carboxylic Acids

12.1 Introduction

- Aldehydes and ketones are organic compounds, containing a carbonyl group ($>C=O$). Hence, they are known as *carbonyl compounds*.
- Naturally occurring carbonyl compounds are present in nucleic acids, carbohydrates and proteins in plants and animals. They play an important role in biochemical processes to sustain life. They add fragrance and flavour to the nature and are also components of several pharmaceuticals and fabrics.
- Carboxylic acids occur widely throughout the plant and animal kingdoms. Acetic acid is the principle organic constituent of vinegar; butyric acid is responsible for the odour of rancid butter. Higher carboxylic acids such as palmitic acid, stearic acid and oleic acid are the components of animal fats and plant oils.

12.2 Structure of Carbonyl Functional Group

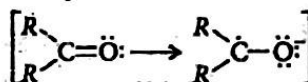
- The C atom of carbonyl group is sp^2 hybridised and forms three σ bonds and one π bond with O atom.
 - Carbonyl carbon and three atoms attached to it lie in the same plane with bond angle of 120° , trigonal coplanar structure and π -electron cloud lies above and below of this plane.



12.3 Aldehydes and Ketones

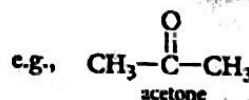
12.4 Carboxylic Acids

- The carbonyl bond is stronger, shorter and more polarized as compared to the double bond in alkenes. As oxygen is more electronegative than carbon, the double bond of carbonyl group is polar and shows dipole moment. Polarization contributes to the reactivity of aldehydes and ketones.

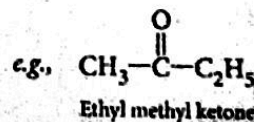


12.3 Aldehydes and Ketones

- These are the compounds with carbon-oxygen double bond ($>C=O$) called carbonyl group having general formula $C_nH_{2n}O$.
 - Aldehydes contain carbonyl group attached to either two H atoms or one H atom and one C atom of an alkyl/aryl group.
 - In ketones, the carbonyl group is attached to two C atoms of an alkyl/aryl group.
 - Simple or symmetrical ketones:** The ketones in which both alkyl groups attached to carbonyl carbon are identical are called *simple ketones*.



- Mixed or unsymmetrical ketones:** The ketones in which the two alkyl groups attached to carbonyl carbon are different are called *mixed ketones*.



12.3.1 Nomenclature

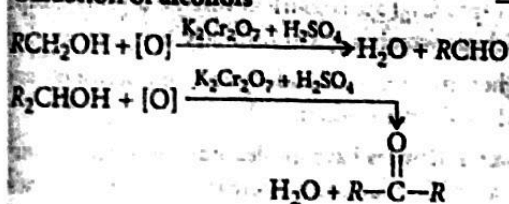
- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending $-ic$ of acid with aldehyde.
- The locations of the substituents in the carbon chain are indicated by Greek letters $\alpha, \beta, \gamma, \delta$, etc.
- The common names 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, α, β and so on beginning with the carbon atom next to the carbonyl group, indicate as α, β .
- 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.

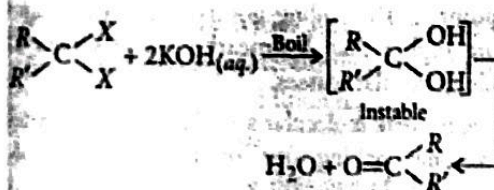
Compound	Common name	IUPAC name
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$	<i>n</i> -Butyraldehyde	Butanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CHO} \end{array}$	α -Methylbutyraldehyde	2-Methylbutanal
$\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	Methyl <i>n</i> -propylketone	Pentan-2-one
$\begin{array}{c} \text{Br} \\ \\ \text{CH}_3 - \text{CH} - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array}$	α -Bromoethyl <i>n</i> -propylketone	2-Bromohexan-3-one

12.3.2 Methods of preparation

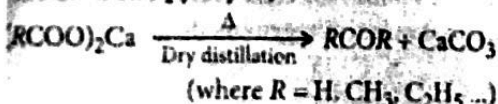
Oxidation of alcohols



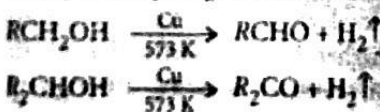
From geminal dihalides (By hydrolysis)



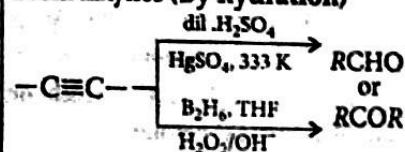
From calcium salts of fatty acids (By dry distillation or pyrolysis)



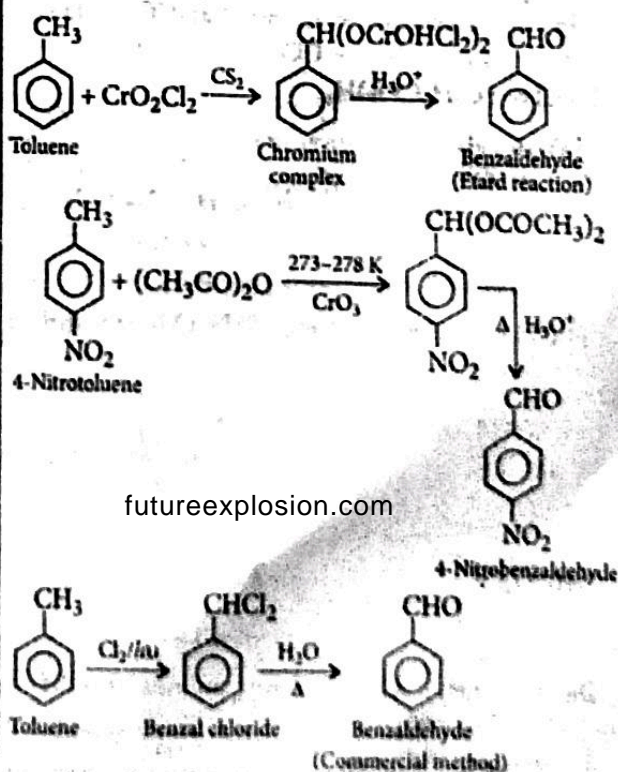
Catalytic dehydrogenation of alcohols

Aldehydes
and
Ketones

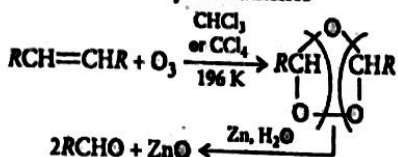
From alkynes (By hydration)



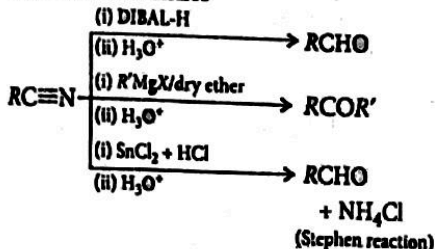
From aromatic hydrocarbons



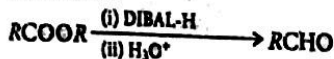
Reductive ozonolysis of alkenes



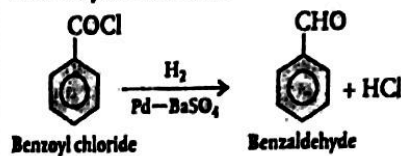
Reduction of nitriles



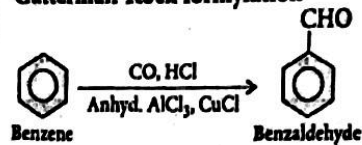
From esters



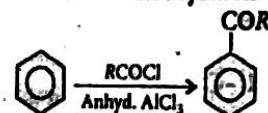
From acyl chlorides (Rosenmund reduction)



Gatterman-Koch formylation



Friedel-Crafts acylation



From Grignard reagent and Cadmium chloride

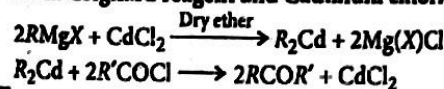
Aldehydes
&
Ketones

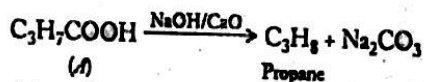
Illustration: Compound (A), $\text{C}_4\text{H}_8\text{O}_2$ has the following properties:

- It reacts with sodium bicarbonate to liberate CO_2 .
- On fusion with alkali it gives propane.
- With Ca(OH)_2 it gives $\text{C}_8\text{H}_{14}\text{O}_4\text{Ca}$ which on heating decomposes to di-*iso*-propyl ketone.

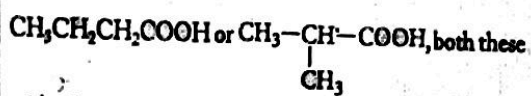
Identify the compound (A).

Soln.: (a) Since (A) reacts with NaHCO_3 to liberate CO_2 , it must contain a $-\text{COOH}$ group. Therefore (A) should be: $\text{C}_3\text{H}_7\text{COOH}$.

(b) With soda lime (A) gives propane:

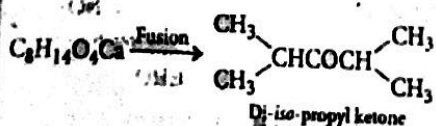


Thus, (A) could be:

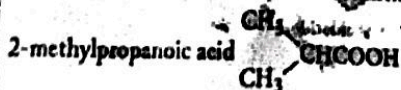


acids give propane on decarboxylation.

(c) The calcium salt $\text{C}_8\text{H}_{14}\text{O}_4\text{Ca}$ on heating gives di-*iso*-propyl ketone:



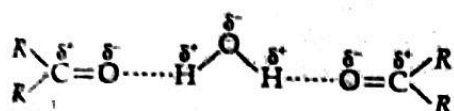
The structure of ketone above confirms that (A) is



12.3.3 Physical properties

- Physical state:** Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature.
 - Higher members of aldehydes and ketones are solids with fruity odour.
 - Lower aldehydes have unpleasant (pungent) odour but as molecular mass increases odour becomes less pungent and more fragrant. Ketones possess pleasant smell.
 - Boiling points:** 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 arising out of the dipole-dipole interactions.
 - Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
$$\begin{array}{c} \delta^+ \quad \delta^- \quad \delta^+ \quad \delta^- \quad \delta^+ \quad \delta^- \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{C}=\text{O} \cdots \cdots \text{C}=\text{O} \cdots \cdots \text{C}=\text{O} \cdots \cdots \end{array}$$

Intermolecular dipole-dipole interactions
 - Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.
- Solubility:** Lower members of aldehydes and ketones like formaldehyde, acetaldehyde and acetone (upto C_4) are soluble in water in all proportions due to H-bonding between polar carbonyl group and water.



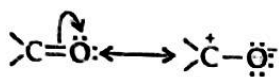
However, solubility decreases with increase in molecular weight.

Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.

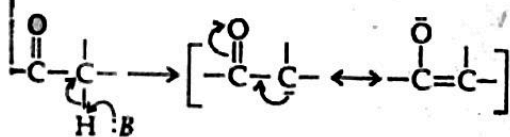
All carbonyl compounds are fairly soluble in organic solvents like alcohol, ether, benzene, chloroform etc.

4 Reactions of aldehydes and ketones

Polarity of carbonyl (C=O) group : Aldehydes and ketones undergo nucleophilic addition reactions in contrast to alkenes which undergo electrophilic addition reactions.



Acidity of α -hydrogen atoms : The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



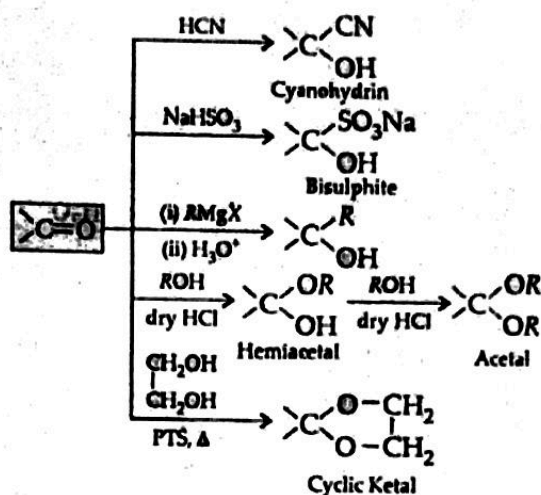
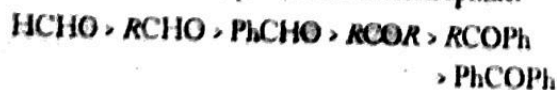
Nucleophilic Addition Reactions

Relative reactivities of aldehydes and ketones : Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

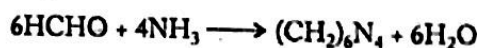
- Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

- Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively in ketones.

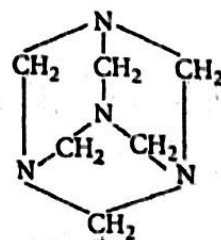
Aromatic aldehydes are less reactive than aliphatic aldehydes in nucleophilic addition reactions due to electron donating resonance effect of aromatic ring which makes carbonyl carbon less electrophilic.



Addition of ammonia and its derivatives: Formaldehyde reacts with excess of ammonia to give hexamethylene tetramine known as *Urotropine*. Urotropine is used as internal urinary antiseptic and against rheumatism and gout. It is also used in the production of plastics and drugs. When nitrated, it gives a high explosive known as *cyclonite*.

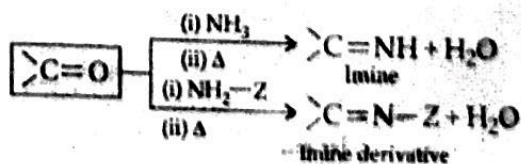
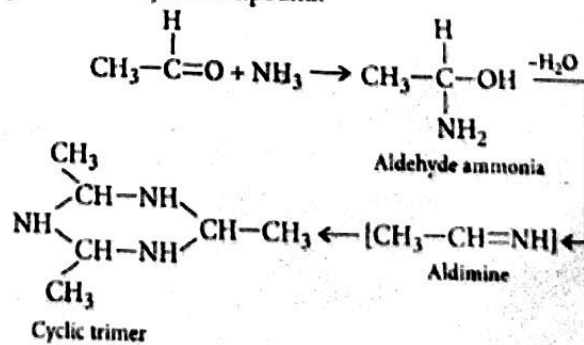


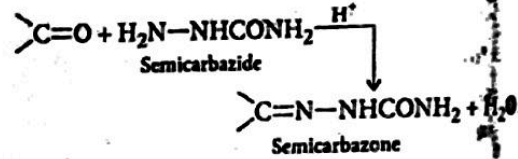
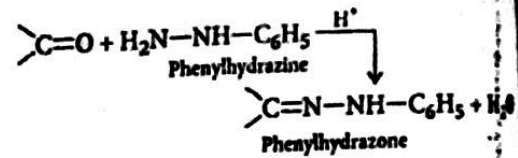
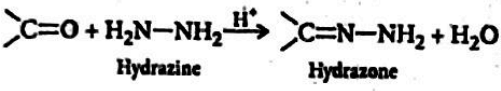
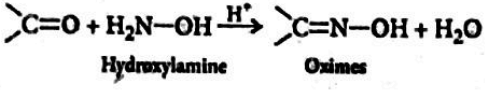
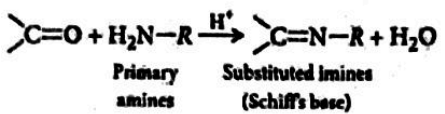
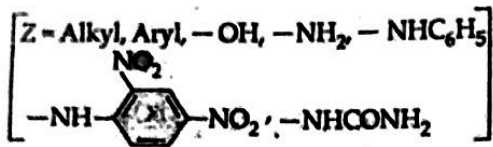
Hexamethylene tetramine has a cage like structure with three six membered rings, each in chair conformation.



futureexplosion.com

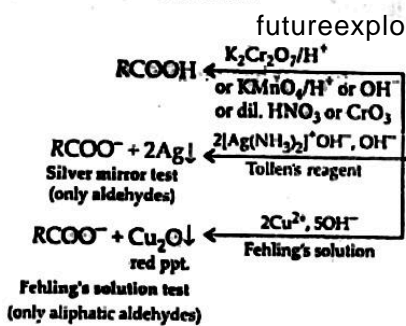
Acetaldehyde dissolved in ether reacts with ammonia gas to form solid **acetaldehyde ammonia**. It loses a water molecule to give an imine which further trimerises to give a heterocyclic compound.



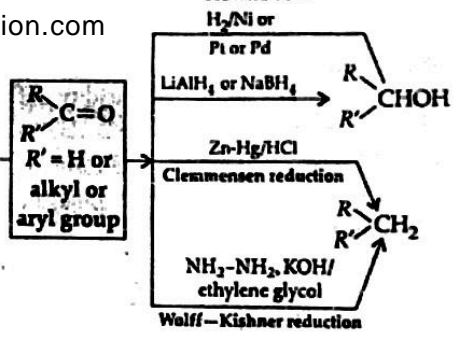


Oxidation and reduction reactions :

Oxidation



Reduction



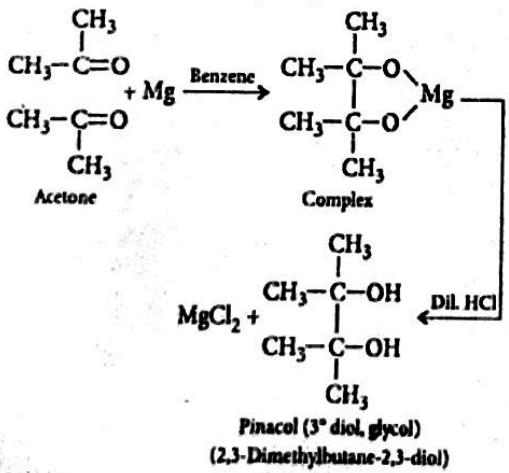
Schiff reagent

A colourless solution obtained by passing SO₂ gas through magenta coloured solution of *p*-rosaniline hydrochloride.

Aldehyde $\xrightarrow[\text{(Colourless)}]{\text{Schiff reagent}}$ Magenta colour is restored

Ketone $\xrightarrow[\text{(Colourless)}]{\text{Schiff reagent}}$ Remain colourless

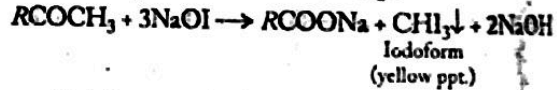
Reduction of ketones by magnesium :



It is a bimolecular reduction.

Haloform reaction :

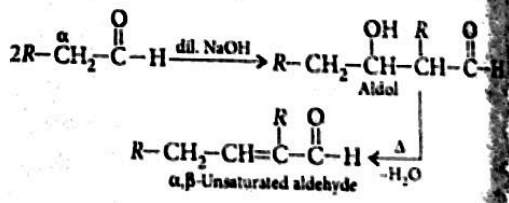
Given by methyl ketones and acetaldehyde.



Haloform test is also given by alcohols containing CH₃CHOH- group which can be easily oxidised to methylketone group e.g., ethanol, propan-2-ol, butan-2-ol.

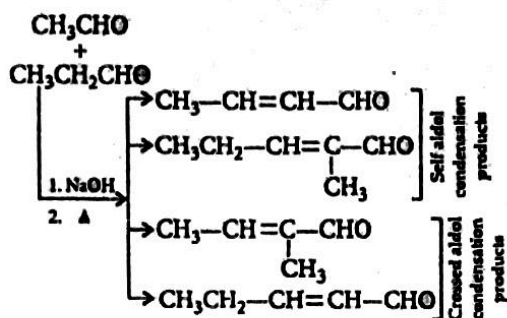
Reactions involving α-hydrogen atom :

Aldol condensation :

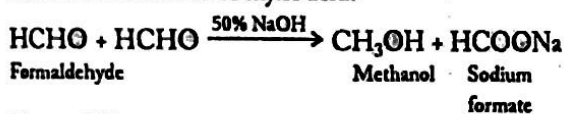


Crossed aldol condensation : Aldol condensation is carried out between two different carbonyl compounds.

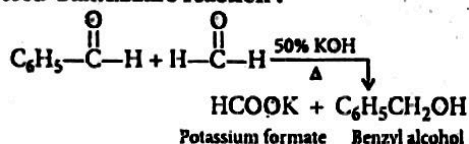
- If both the carbonyl compounds contain α-hydrogen atoms, it gives a mixture of four products.



• **Cannizzaro reaction** : Aldehydes which do not contain any α -hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and salt of carboxylic acid.



• **Crossed Cannizzaro reaction** :



Isobutyraldehyde undergoes Cannizzaro reaction even though it contains a α -hydrogen atom.

• **Electrophilic Substitution Reaction**

► Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

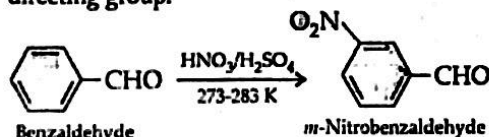
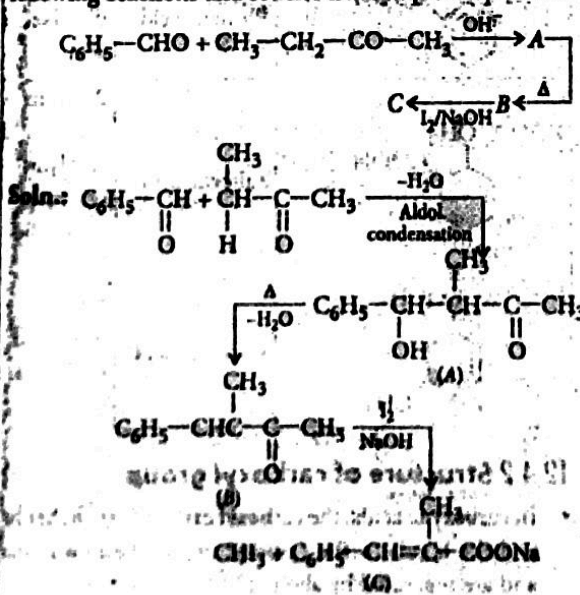


Illustration : Identify the compounds A, B and C in the following reactions and rewrite the complete equation :



12.3.5 Uses

- Formaldehyde is used as a disinfectant and as preservative for biological specimens.
 - It is used for silvering mirrors.
- Acetone is the most important commercial solvent.
 - It is also used in manufacture of explosives, lacquers, paint removers, plastics, drugs, perfumes, adhesives and disinfectants.
- Benzaldehyde is used in perfumery and in dye industry.

12.3.6 Distinction

• **Distinction between aldehydes and ketones**

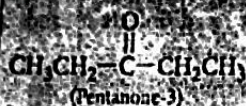
Test	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollen's reagent	Black precipitate of silver or silver mirror	No black ppt. or silver mirror
2,4-Dinitrophenylhydrazine	Orange-yellow or red well-defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
Sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test).	No reaction
Alkaline sodium nitroprusside	A deep red colour (formaldehyde does not respond to this test).	Red colour which changes to orange.

Illustration : Compound A, $\text{C}_5\text{H}_{10}\text{O}$, forms a phenylhydrazone, gives negative Tollens' and iodoform tests and is reduced to pentane. Identify A.

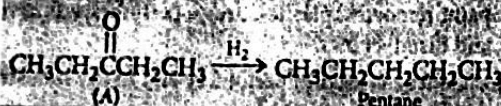
Soln.: Conclusion :

1. Compound (A) forms a hydrazone hence it has a carbonyl group.
2. It does not reduce Tollens' reagent, therefore it should be a ketone.
3. It does not give iodoform test hence ketone does not have a methyl group.

4. The structure of (A) will be:



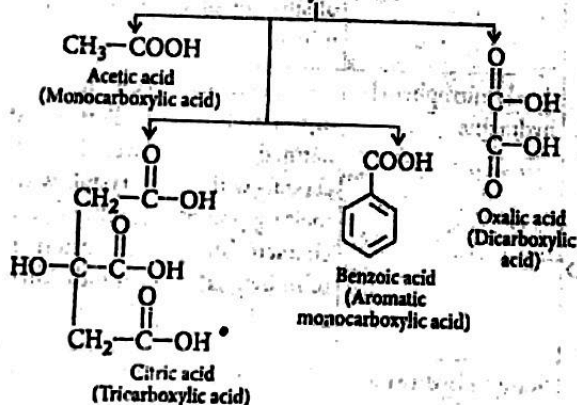
5. On reduction (A) gives pentane:



12.4 Carboxylic Acids

- Carboxylic acids are the compounds with $-\text{COOH}$ group having general formula $\text{C}_n\text{H}_{2n}\text{O}_2$.
- They are classified as mono, di, tri and polycarboxylic acids depending upon the number of carboxyl groups present in a molecule.

Carboxylic acids



- Aliphatic monocarboxylic acids and aliphatic esters are functional isomers. Some higher aliphatic monocarboxylic acids (C_{12} – C_{18}) are known as fatty acids because they occur in natural fats as esters of glycerol. e.g. palmitic acid and stearic acid are obtained on hydrolysis of fats.

2.4.1 Nomenclature of acids

The common names end with the suffix $-\text{ic acid}$ and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending $-\text{e}$ in the name of the corresponding alkane with $-\text{oic acid}$.

- In numbering the carbon chain, the carboxylic carbon is numbered one.

Compound	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	<i>n</i> -Butyric acid	Butanoic acid
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{COOH} \end{array}$	Isobutyric acid (α -Methylpropionic acid)	2-Methylpropanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	<i>n</i> -Valeric acid	Pentanoic acid
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{COOH} \end{array}$	Isovaleric acid (β -Methylbutyric acid)	3-Methylbutanoic acid
$\text{HOOC}-\text{COOH}$	Oxalic acid	Ethanedioic acid
$\text{HOOC}-\text{CH}_2-\text{COOH}$	Malonic acid	Propanedioic acid
$\text{HOOC}(\text{CH}_2)_2\text{COOH}$	Succinic acid	Butanedioic acid
$\text{HOOC}(\text{CH}_2)_3\text{COOH}$	Glutaric acid	Pentanedioic acid
$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	Adipic acid	Hexanedioic acid
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{COOH} \\ \\ \text{OH} \end{array}$	Lactic acid	2-Hydroxypropanoic acid
$\text{CH}_2=\text{CH}-\text{COOH}$	Acrylic acid	Propenoic acid
$\begin{array}{c} \text{HOOC}-\text{CH}-\text{CH}_2\text{COOH} \\ \\ \text{OH} \end{array}$	Malic acid	2-Hydroxybutanedioic acid
	Phthalic acid	Benzene-1,2-dicarboxylic acid
	Salicylic acid	2-Hydroxybenzoic acid (2-Hydroxybenzenecarboxylic acid)
	<i>m</i> -Toluic acid	3-Methylbenzoic acid

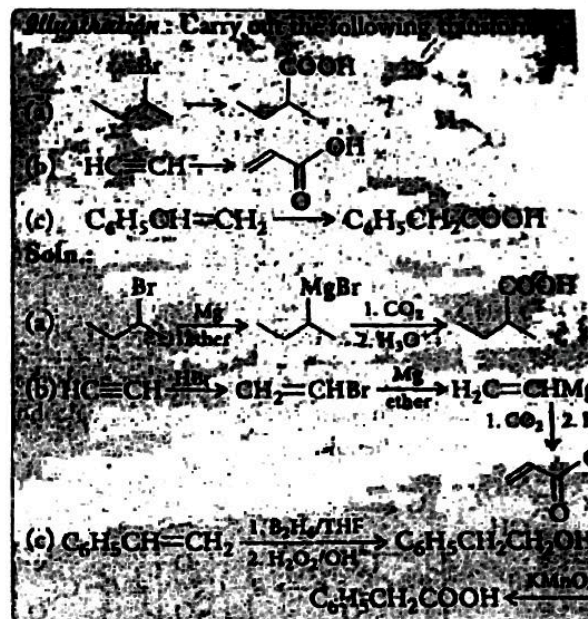
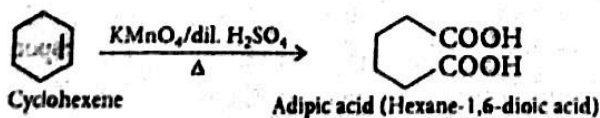
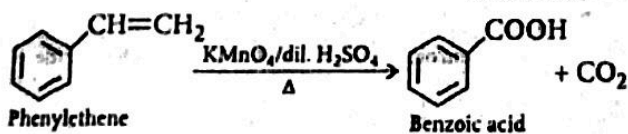
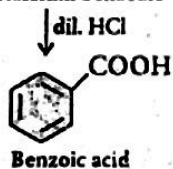
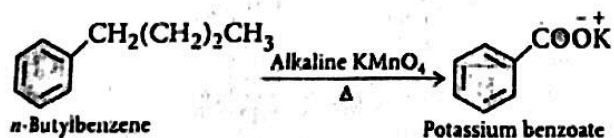
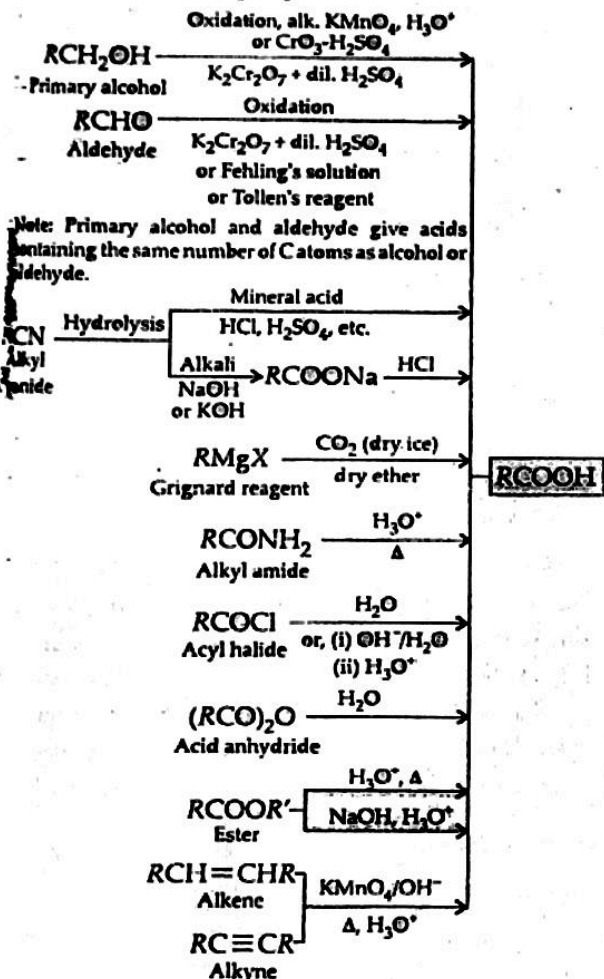
12.4.2 Structure of carboxyl group

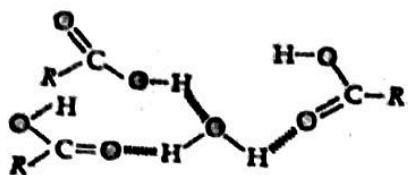
- In carboxylic acids, the carboxyl carbon is sp^2 hybridised and the bonds to the carboxyl carbon lie in one plane and are separated by about 120° .

The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



12.4.3 Methods of preparation

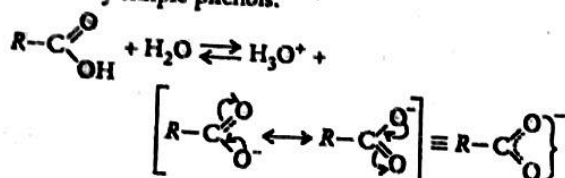




(Hydrogen bonding of RCOOH with H₂O)
Vinegar is 6-8% solution of acetic acid in water.
Pure acetic acid is called *glacial acetic acid*.

12.4.5 Reactions of carboxylic acids

- **Acidic nature:** Carboxylic acids are weaker acids than mineral acids, but they are stronger acids than alcohols and many simple phenols.

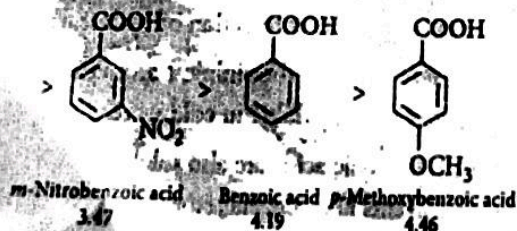
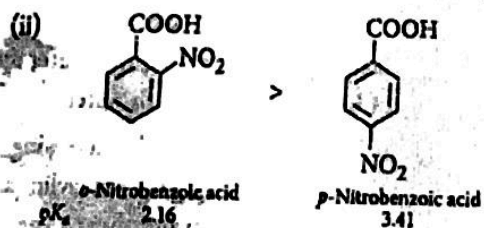
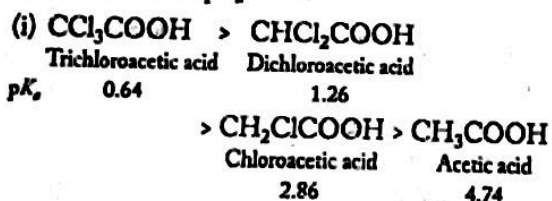


- **Effect of substituents on acidic strength:**

- ▶ Presence of electron withdrawing groups, increases the acidic strength.
 - More the number of electron withdrawing groups, more will be the acidic strength.
 - More is the distance between the carboxyl group and electron withdrawing group, lesser will be the acidic strength.

- ▶ Presence of electron releasing groups, decreases the acidic strength.

- ▶ The example with order of decreasing acidity are given below with pK_a values.



- ▶ Direct attachment of phenyl or vinyl group to a carboxyl group increases the acidity of corresponding acids. This is due to the greater electronegativity of the sp² hybridized carbon atom to which the carboxyl group is attached. The inductive effect of following groups in the decreasing order of acidity is

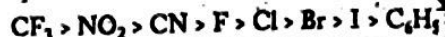


Illustration: Arrange the following in order of increasing acidity:

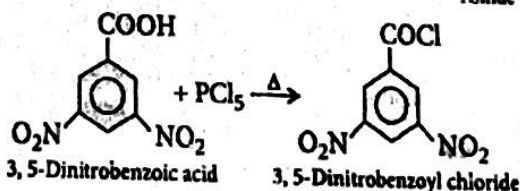
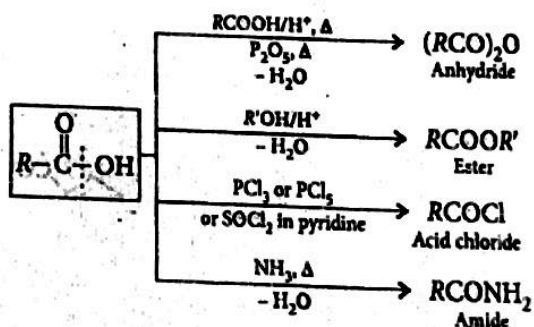
- HCOOH, ClCH₂COOH, CH₃COOH
- CH₃COOH, (CH₃)₂CHCOOH, (CH₃)₃CCOOH
- ClCH₂COOH, CH₃CH₂COOH, ClCH₂CH₂COOH, (CH₃)₂CHCOOH, CH₃COOH

- Soln.:** (i) CH₃COOH < HCOOH < ClCH₂COOH
 (ii) (CH₃)₃CCOOH < (CH₃)₂CHCOOH < CH₃COOH
 (iii) (CH₃)₂CHCOOH < CH₃CH₂COOH < CH₃COOH < ClCH₂CH₂COOH < ClCH₂COOH

Illustration: Formic acid is a stronger acid than acetic acid. Explain, why?

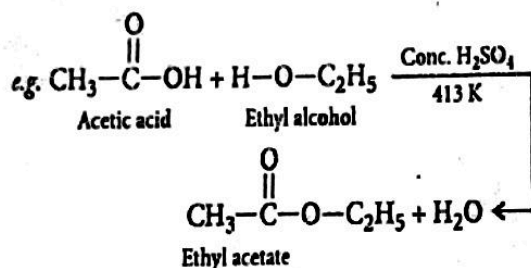
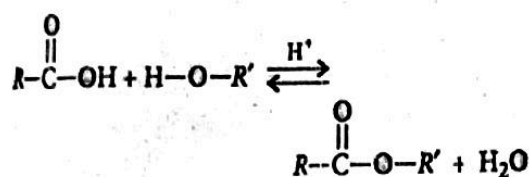
Soln.: Acetic acid contains a methyl group (which releases electrons due to +I-effect) which increases the concentration of negative charge of acetate ion, making it unstable hence there is slow liberation of H⁺ or it is a weaker acid. On the other hand in formic acid no such electron release occurs hence formate ion forms easily, making it a stronger acid.

- **Reactions involving cleavage of C—OH bond:**



- **Fischer esterification:** A carboxylic acid is heated with an alcohol in the presence of concentrated sulphuric acid or dry hydrogen chloride, to give corresponding ester.

- This reaction is reversible and accumulation of water may reverse the reaction.
- Forward reaction is esterification and reverse reaction is hydrolysis of ester.
- Ester formation may be favoured by using excess of alcohol in presence of concentrated sulphuric acid. Concentrated sulphuric acid furnishes H⁺ ions and accelerates the esterification by removing water molecules formed. Thus, concentrated sulphuric acid acts as catalyst as well as dehydrating agent.



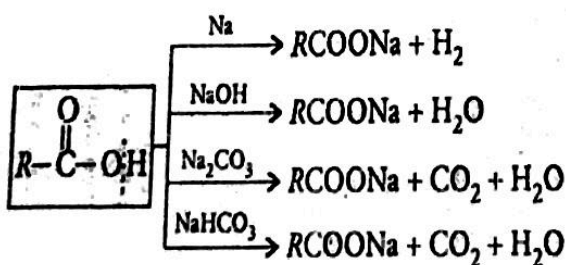
- Fischer esterification is acid catalyzed nucleophilic acyl substitution reaction of carboxylic acids.
- The presence of bulkier groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification. This is due to steric hindrance. The order of reactivity in esterification is as follows:

Alcohols : $\text{CH}_3\text{OH} > 1^\circ \text{ alcohols} > 2^\circ \text{ alcohols} > 3^\circ \text{ alcohols}$

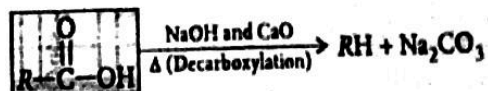
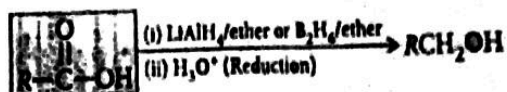
Carboxylic acids : $\text{HCOOH} > \text{CH}_3\text{COOH} >$

$\text{RCH}_2\text{COOH} > \text{R}_2\text{CHCOOH} > \text{R}_3\text{CCOOH}$

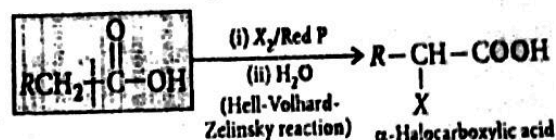
Reactions involving cleavage of O—H bond :



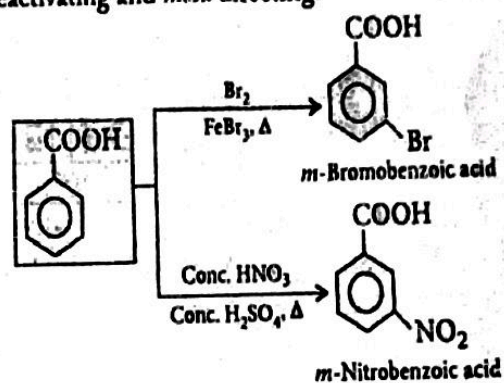
Reaction involving —COOH group :



• Reaction involving α -halogenation :



• Ring substitution in aromatic acids : —COOH group is deactivating and *meta* directing.



Distinction

• Distinction test between Phenol and Carboxylic acid

Test	Phenol	Carboxylic acid
NaHCO ₃ test	No reaction	Brisk effervescence of CO ₂ gas.
FeCl ₃ test	Violet colour	Buff coloured ppt.

12.4.6 Uses of carboxylic acids

- Formic acid is used in rubber, textile, dyeing leather and electroplating industries.
- Acetic acid is chief constituent of vinegar.
 - ▶ It is used as solvent.
- Adipic acid is used in the preparation of nylon -6,6.
- Esters of benzoic acid are used in perfumery.
 - ▶ Sodium benzoate is used as food preservative.
- Higher fatty acids are used for the manufacture of soaps and detergents.