ORGANIC CHEMISTRY –II

4. CARBOXYLIC ACIDS

- Saturated mono carboxylic acids are called fatty acids.
- Functional group is – COOH which is made up of carbonyl and hydroxy groups.
- General molecular formula is $CnH_{2n}O_2$ or $C_nH_{2n+1}COOH$.
- General representation is R – COOH
- Most of these fatty acids are derived from fats.

NAMING OF CARBOXYLIC ACIDS :

STRUCTURE	**COMMON NAME**	**IUPAC NAME**
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Aceticacid	Ethanoic acid
CH_3CH_2COOH	Propionic acid (or) Methyl acetic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid (or) Ethyl acetic acid	Butanoic acid
$CH_3-\underset{Cl}{\overset{\beta}{CH}}-\underset{CH_3}{\overset{\alpha}{CH}}-COOH$	β – chloro--α - methyl butyric acid	3-chloro – 2-methyl Butanoic acid
HOOC – COOH	Oxalic acid	Ethanedioic acid
HOOC – CH_2 - CH_2 - COOH	Succinic acid	Butanedioic acid
HOOC – CH_2 – COOH	Malonic acid	Propanedioic acid
HOOC – CH = CH – COOH	Maleic acid (or) Fumaric acid	But – 2 – ene – dioicacid
$CH_3-\underset{OH}{CH}-COOH$	α - Hydroxy propionic acid (or) Lactic acid	2 – Hydroxy propanoic acid

ISOMERISM IN FATTY ACIDS :

- The molecule formula $C_nH_{2n}O_2$ permits the existence of chain, functional , and metamerism.
- Mono carboxylic acids will exhibit chain and functional isomerism. They don't exhibit position isomerism as – COOH group is at chain terminal position.
- Carboxylic acids and esters having same molecular formula are functional isomers.

Example :

1) $C_2H_4O_2$: CH_3COOH, $HCOOCH_3$ } Functional

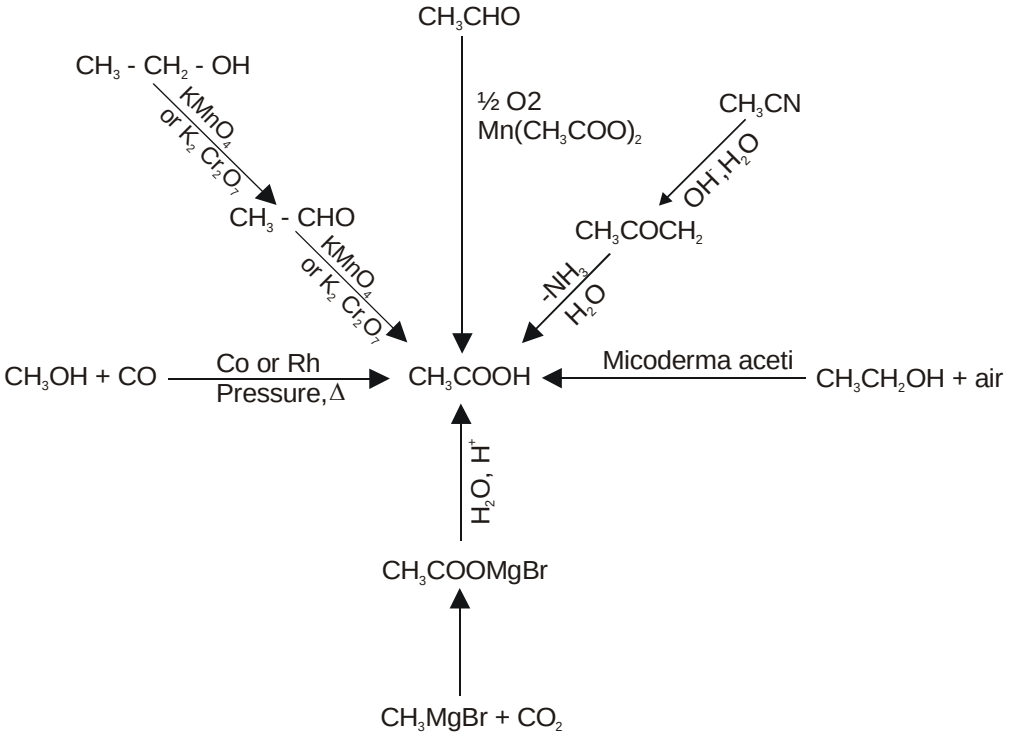
2) $C_3H_6O_2$: CH_3CH_2COOH } Functional

3) $C_4H_8O_2$:

- CH_3COOCH_3
- $CH_3CH_2CH_2–COOH$
- $CH_3 – CH(CH_3) – COOH$ } Chain isomers
- $CH_3CH_2CH_2COOH$
- $CH_3CH_2COOCH_3$ } Functional
- $CH_3COOC_2H_5$
- $C_2H_5COOCH_3$ } Metamers

Acetic acid (or) Ethanoic acid (CH_3COOH)

Methods of preparation of Acetic acid :



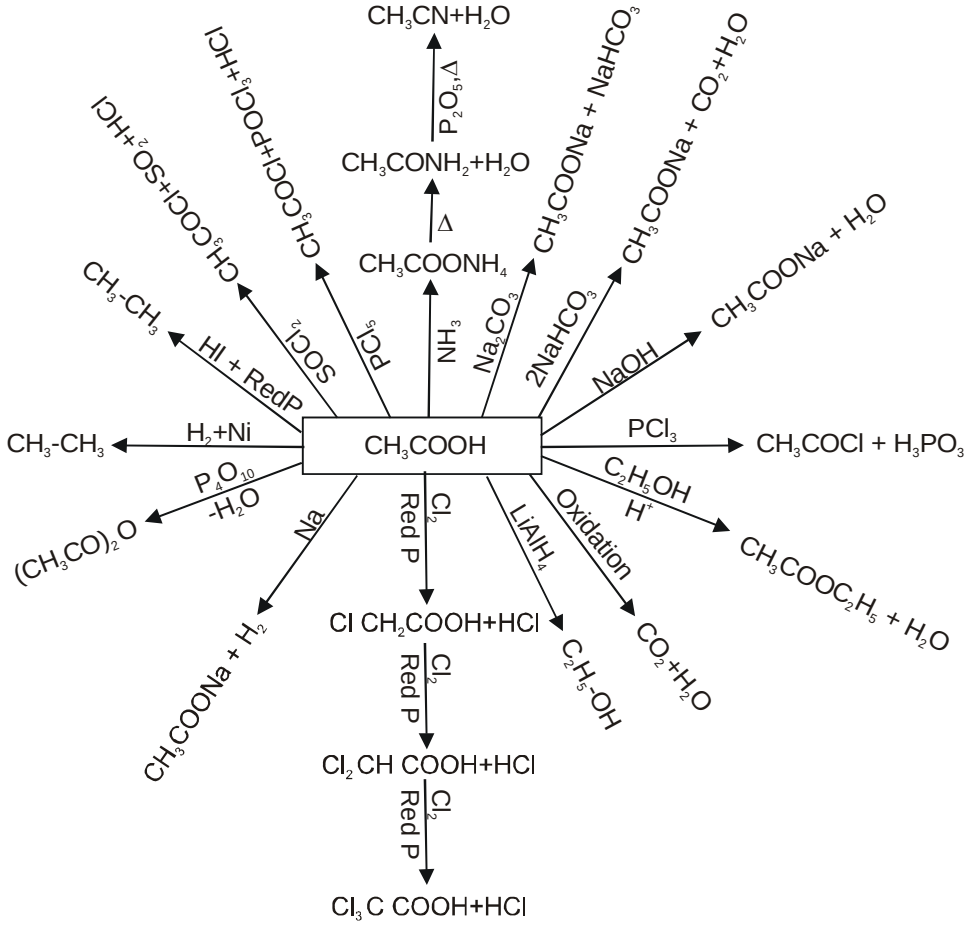
- Primary alcohols on oxidation give aldehydes which are easily oxidised to carboxylic acids in presence of acidified $K_2Cr_2O_7$ or $KMnO_4$.
- CH_3MgBr on addition of CO_2 gives an intermediate which on hydrolysis gives acetic acid.
- Alkyl cyanides on hydrolysis give carboxylic acids. Methyl cyanide or Acetonitrile on hydrolysis gives acetic acid and NH_3. The intermediate is acetamide.
- Acetic acid is mostly prepared from CH_3OH and CO in presence of Co or Rh catalyst.
- Commercially , acetic acid is prepared by the oxidation of ethanal with air in presence of Mn^{2+} catalyst.

- Biochemical oxidation of ethylalcohol inpresence of Micoderma aceti bacteria yield 6 to 10% acetic acid, called vinegar.

Physical properties :

- It is colorless liquid with pungent smell.
- It is corrosive liquid
- It's boiling point is higher than even H_2O due to formation of stronger hydrogen bonds [118°C]. It's b.p. is higher than the b.p of corresponding alcohols, ethers, alkylhalides, alkanes, alkenes, alkynes.
- It is miscible with H_2O, alcohol, ether.
- Due to hydrogen bonding it exists as dimer in vapour state or in aqueous solution and polymer in liquid state.

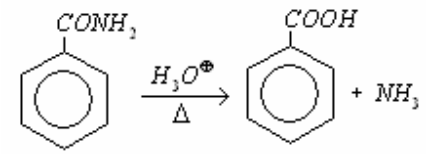
CHEMICAL PROPERTIES :



- **Reactions of salts of acetic acid :**
  1) De carboxylation : $CH_3COONa+NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
  2) Kolbe's electrolysis : $2CH_3COONa + 2H-OH \xrightarrow[(anode)\ (cathode)]{electrolysis} C_2H_6 + 2CO_2 + 2NaOH + H_2$
  3) Dry distillation of calcium acetate :
     i) $(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3 + CaCO_3$
     ii) $(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2CH_3CHO + 2CaCO_3$
- With any active metal like Na, K, Zn it liberates H_2 gas.
- It neutrlises bases basic salts NaOH, Na_2CO_3, $NaHCO_3$.
- With ethyl alcohol, it forms fruity smelling ester.
- With chlorinating agents like PCl_3, PCl_5, $SOCl_2$ it gives ethanoyl chloride.
- With ammonia it first gives ammonium acetate and on heating it gives acetamide.
- With excess of Cl_2 and in presence of red P it gives trichloro acetic acid. It is α - chlorination and is called HVZ reaction.
- In the reaction of CH_3COOH with metals, bases, metal carbonates and bicarbonates and NH_3 , O–H bond is cleaved.
- In the reaction of CH_3COOH with alcohol, PCl_3, PCl_5, $SOCl_2$ C – OH bond is cleaved.

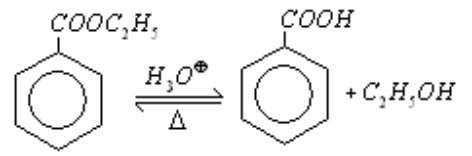
PREPARATION OF BENZOIC ACID

- **FROM AMIDES :**



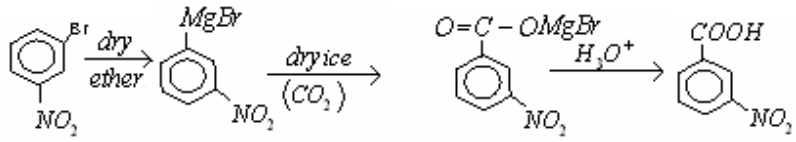
Benzamide Benzoic acid

- **FROM ESTERS :**



Ethyl benzoate Benzoic acid

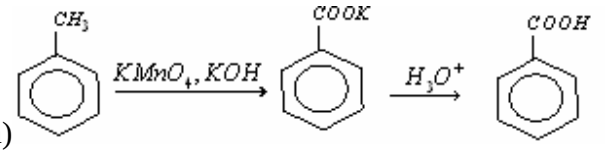
FROM CO_2 AND GRIGANARD REAGENT :



FROM ALKYL BENZENE :

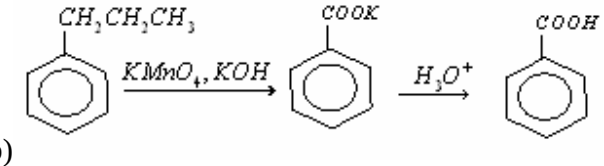
- Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid (or) acidic (or) alkaline potassium permaganate. The entire side chain is oxidised to the carbonyl group irrespecitve of length of the side chain.
- Primary (or) secondary alkyl groups are oxidised in this manner tertiary group is not effected.

a)



Toluene Benzoic acid

b)



Propylbenzene Benzoic acid

Uses of acetic acid :

- As solvent in industry
- For curing meat and fish
- As vinegar in food stuffs
- In the Preparation of perfumes , dyes and drugs.
- In the preparation of acetone, ester, acetic anhydride, acetamide etc