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An Initiative by अमर उजाला

DISTINGUISHING OF ALDEHYDES & KETONES

Distinguishing tests for Aldehydes and Ketones

The mild oxidising agents are used to distinguish aldehydes from ketones

i) Tollen's test:

- **On warming an aldehyde with freshly prepared ammonical silver nitrate solution called Tollen's reagent, a bright silver mirror is produced due to the formation of silver metal.**

$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCO\bar{O} + 2Ag + 2H_2O + 4NH_3$$

ii) Fehling's test:

- **Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt).**
- **On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.**
- **Aldehydes are oxidised to corresponding carboxylate anion.**
- **Aromatic aldehydes do not respond to this test.**

$$R\text{-}CHO + 2Cu^{2+} + 3\bar{O}H \longrightarrow R\bar{C}O\bar{O} + Cu_2O + 3H_2O$$

Red-brown ppt

Reduction of Benedict's solution

It is an alkaline solution of copper sulphate complexed with sodium citrate and sodium carbonate.

This solution on warming with aldehydes gives reddish brown precipitate.

So all the organic compounds which give positive test with Fehling's solution, also give same test with Benedict's solution.

Reduction of Schiff's reagent

Schiff's regent is a dilute solution of rosaniline hydrochloride, whose red colour has been discharged by passing sulphur dioxide. Aldehydes when treated with Schiff's reagent

(magnenta solution in sulphurous acid, H_2SO_3) restores its pink colour.

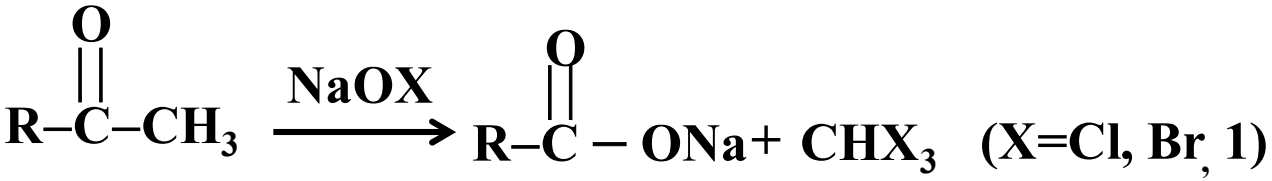
Note :

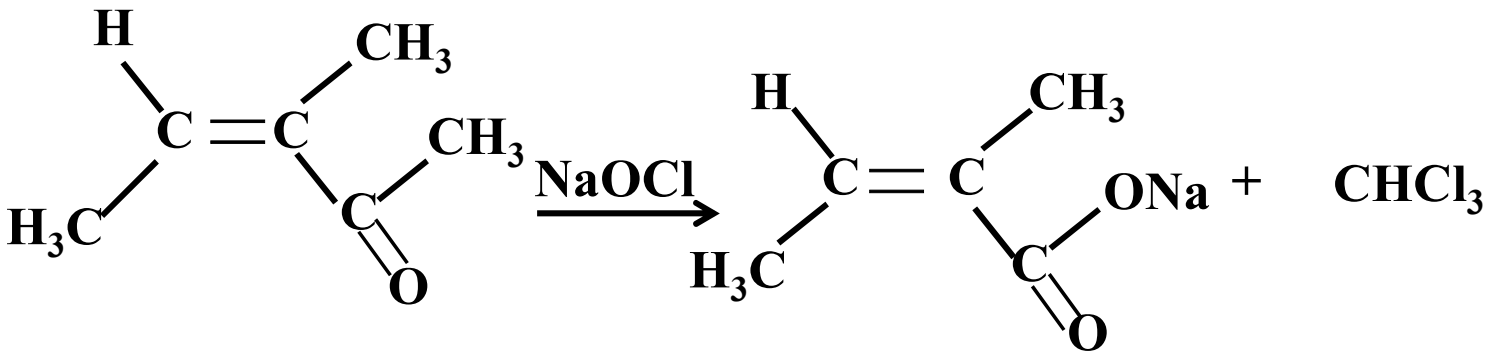
Ketones do not reduce Tollen's reagent, Fehling solution and Benedict's solution. Hence these reagents can be used to distinguish between aldehydes and ketones.

iii) Oxidation of methyl ketones by haloform reaction :

- **Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids.**

- **The methyl group is converted to haloform .**


O
R–C–CH3
NaOX
O
R–C – ONa+ CHX3
(X=Cl, Br, 1)


H
CH3
C
C
CH3
H3C
C
O
NaOCl
H
CH3
C
C
ONa
+
CHCl3
H3C
C
O

- **Iodoform test exhibited by following**

(i) Ethyl alcohol (2 – Alkanols)

(ii) Acetaldehyde

(iii) Acetone

(iv) Methylketones

(v) Acetophenone

(vi) α – hydroxy propionic acid (lactic acid)

(vii) Keto acid (Pyruvic acid)

(viii) 2- Amino alkanes

MCQs

1) Aldehydes can be oxidised by

a) Benedicts solution

b) Tollen's reagent

c) Fehling's solution

d) All the above ✔

2) Tollen's reagent is

a) Alkaline solution containing complex of copper nitrite

b) Ammonical curpous chloride solution

c) Ammonical $AgNO_3$ solution

d) Ammonical curpic chloride solution

3) Fehling's solution is

a) Alkaline $CuSO_4$ + Rochelle salt

b) Alkaline $CuSO_4$ complexed with nitrate ions

c) Ammonical $AgNO_3$ solution

d) Mageta solution in H_2SO_3

4) Schiff's reagent is

a) P-Rosaniline hydrochloride decolourised by passing SO_2

b) P-Rosaniline hydrochloride decolourised by chlorine

c) Acidic solution of phenolphthalein

d) Rochellie salt solution + $CuSO_4$ + NaOH

USES OF
ALDEHYDES AND KETONES
&
SOME IMPORTANT
CHEMICAL REACTIONS

Uses of Aldehydes And Ketones

- **Formalin is used to preserve biological specimens.**
- **Formaldehyde is used to prepare bakelite, urea-formaldehyde, glues and other polymeric products.**

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Uses of Aldehydes And Ketones

- **Acetaldehyde is used as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.**
- **Benzaldehyde is used in perfumery and in dye industries.**
- **Acetone is a common fingernail polish remover and is a solvent.**

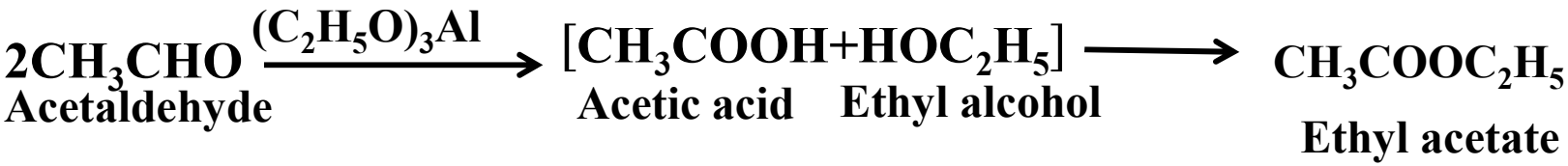
  Acetone is very flammable.

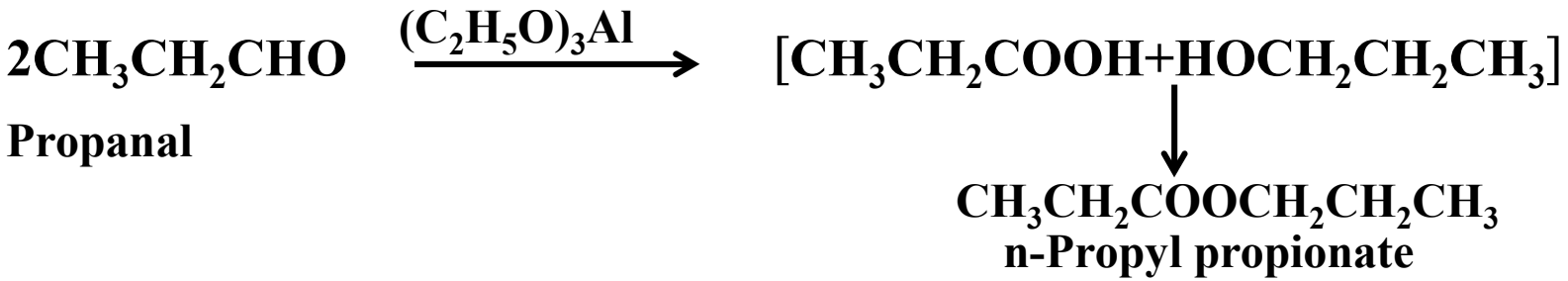
- **2-Butanone (Ethyl methyl k nt.**

Reaction with aluminium ethoxide (Tischenko's reaction):

This is a modified form of Cannizzaro's reaction. All aldehydes (with or without α - hydrogen atoms) undergo Cannizzaro's reaction on treatment with aluminium ethoxide to form an acid (by oxidation) and an alcohol (by reduction) which combines together to form esters.

For example





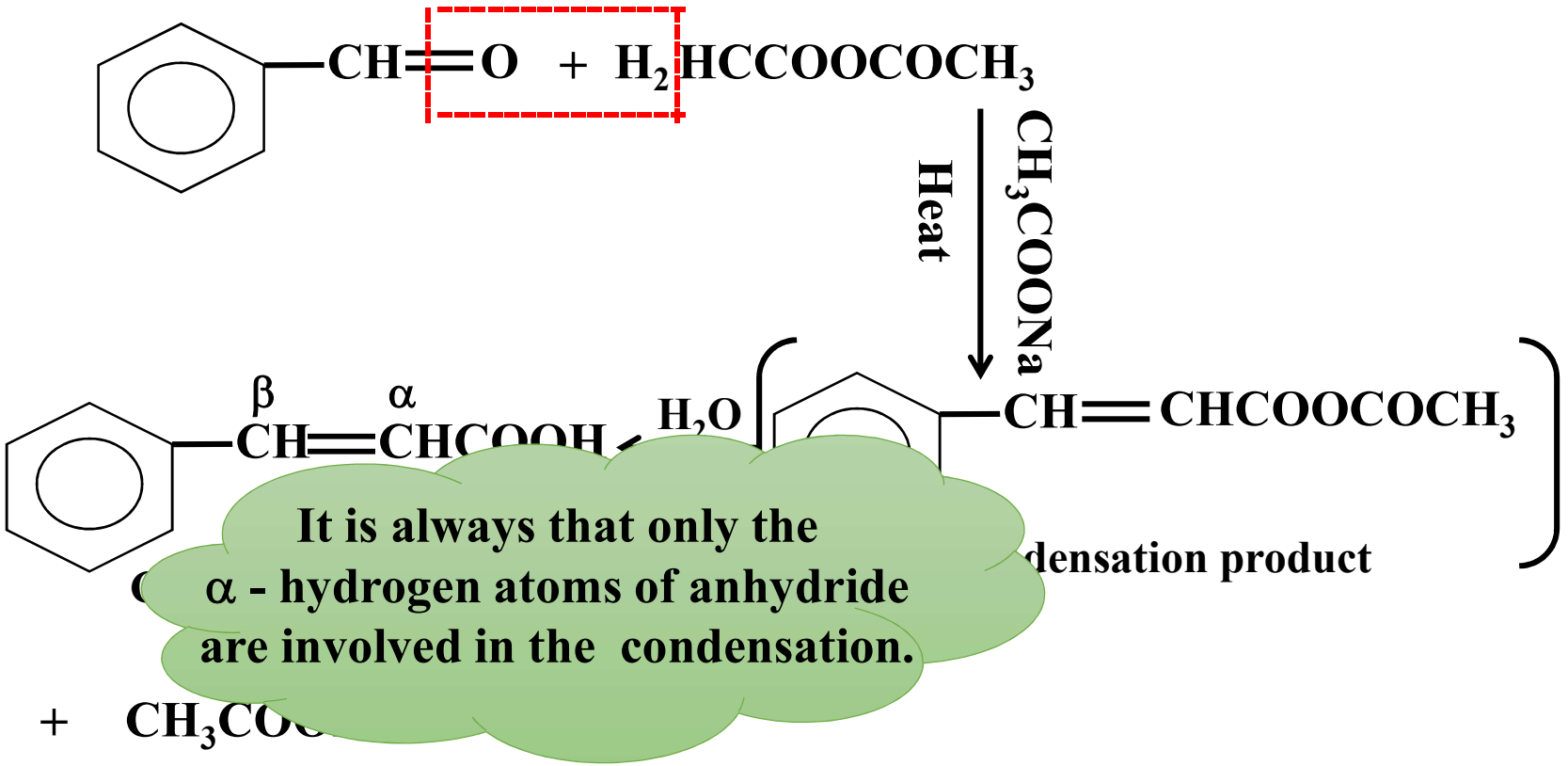
This is the reaction is called Tischenko's reaction

Perkin's reaction

In this reaction, an aromatic aldehyde, such as benzaldehyde, when heated with an aliphatic acid (base catalysed), condensation takes place and on hydrolysis α, β - unsaturated acid is formed.

Example

Benzaldehyde with acetic anhydride and sodium acetate upon hydrolysis yields cinnamic acid.

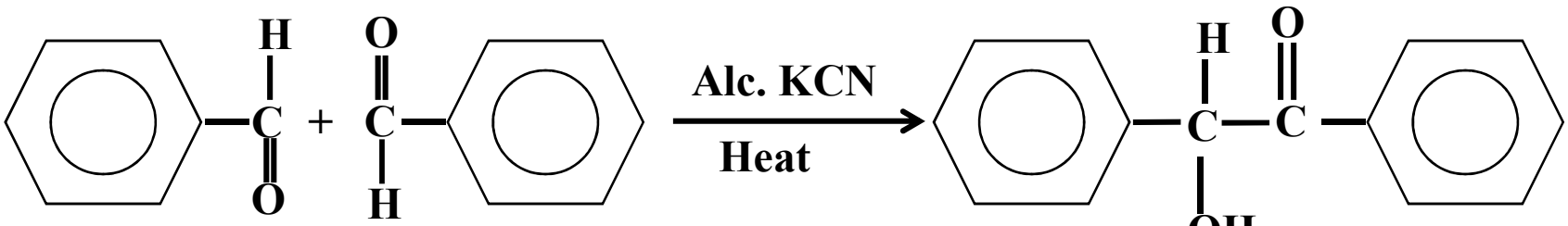

CH=O + H2HCCOOCOCH3
Heat
CH3COONa
β
α
CH=CHCOOH
H2O
CH=CHCOOCOCH3
densation product
It is always that only the
α - hydrogen atoms of anhydride
are involved in the condensation.
+ CH3CO

Miscellaneous reactions

Benzoin condensation (reaction with alcoholic potassium cyanide)

When aromatic aldehyde is heated with an ethanolic solution of KCN, two molecules of benzaldehyde undergo condensation to form benzoin. This reaction is called *Benzoin condensation.*

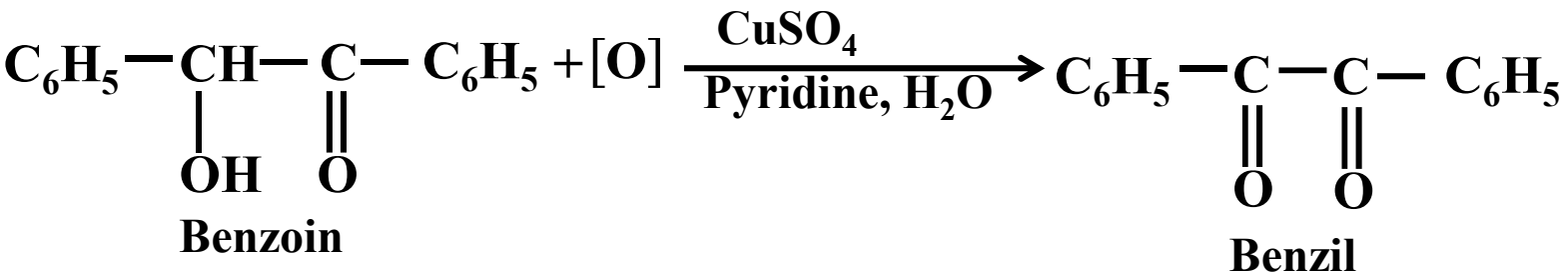
For example



Two molecules of benzaldehyde

Benzoin

Benzoin can be readily oxidises to a diketone, i.e., benzil.



Benzoin **Benzil**

MCQs

1) Formaldehyde is used as…

a) Preservative of biological specimens

b) Preparation of polymers like bakelite

c) Starting material in the manufacturing of acetic acid, ethyl acetate etc.

d) All of these ✓

2) Nail polish remover is…

a) Acetaldehyde

b) Acetone 

c) Propanaldehyde

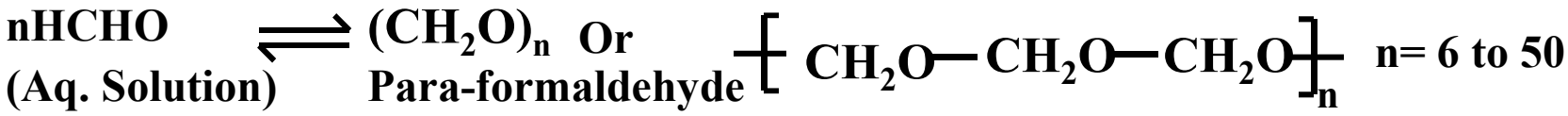
d) Benzaldehyde

ADDITIONAL INFORMATION OF ALDEHYDES & KETONES

Polymerisation of formaldehyde

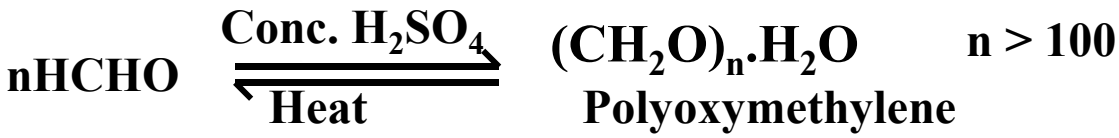
Paraformaldehyde

When an aqueous solution (40%) of formaldehyde is evaporated to dryness, a white crystalline solid with fishy odour is obtained. It is a long chain polymer.



On rapid heating it gives back gaseous formaldehyde.

When a formaldehyde solution (60%) is treated with conc. H_2SO_4, a white solid, polyoxymethylenes $(CH_2O)_n.H_2O$ are formed.

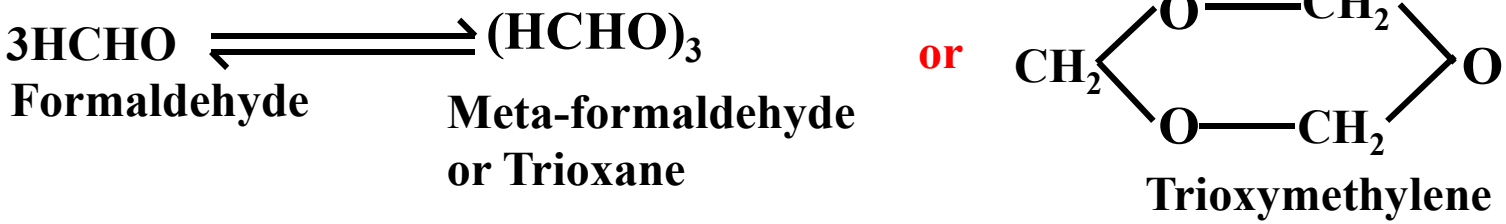


This is on heating gives back formaldehyde.

Metaformaldehyde

On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to meta formaldehyde, $(HCHO)_3$.

It is white solid (m.pt. 234 – 235 K). This on heating gives back gaseous formaldehyde.



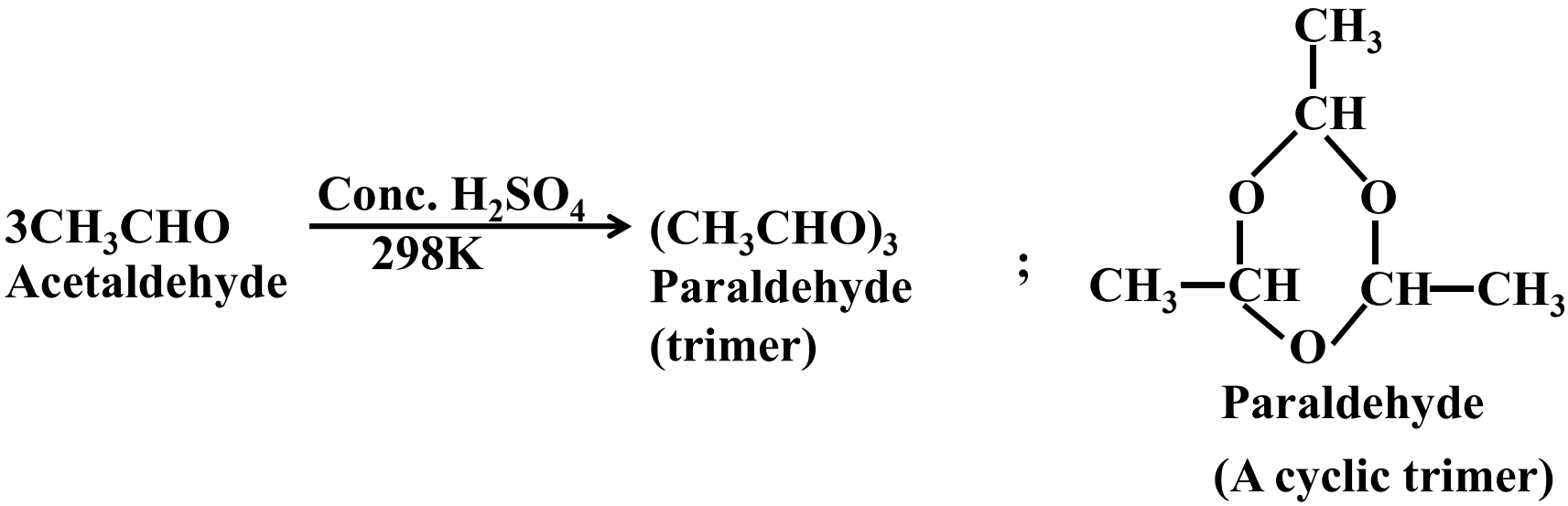
Polymerisation of acetaldehyde

Acetaldehyde undergoes polymerisation forming different products under different conditions.

Paraldehyde

It is formed, when anhydrous acetaldehyde is treated with conc. Sulphuric acid it changes again into acetaldehyde.

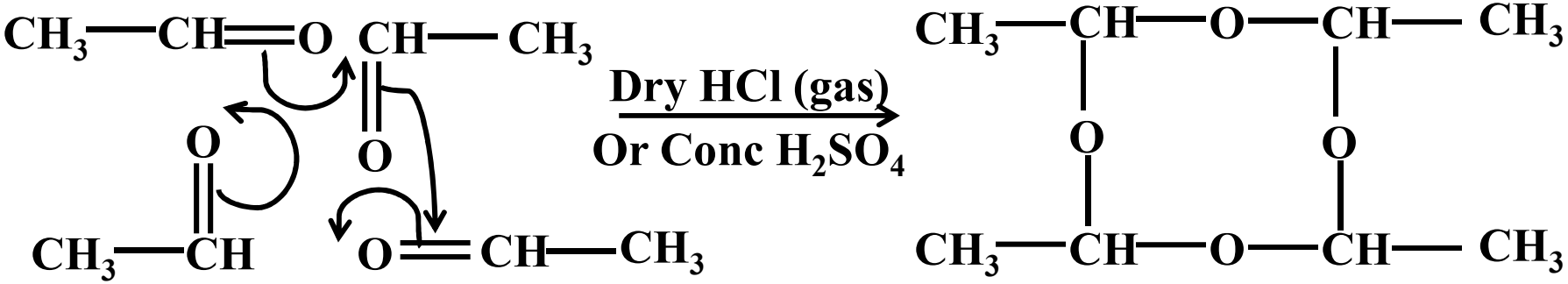
It is used in medicines as a hypnotic and soporific (sleep producing) agent.


3CH3CHO
Acetaldehyde
Conc. H2SO4
298K
(CH3CHO)3
Paraldehyde
(trimer)
;
CH3
CH
O
O
CH3—CH
CH—CH3
O
Paraldehyde
(A cyclic trimer)

Metaldehyde

Acetaldehyde on treatment with dry HCl gas or a few drops of conc. H_2SO_4 at 273 K, is converted into metaldehyde $(CH_3CHO)_4$.

It is a white solid (m.pt. 518 K). On heating it sublimes but changes again into acetaldehyde when distilled with dilute sulphuric acid. It is used as a solid fuel.



Acetaldehyde (Four molecules)

Metaldehyde (A cyclic tetramer)

It is used for killing slugs and snails.

MCQs

1) Metaformaldehyde is a…

a) Tetraoxime

b) Trioxymethylene

c) Trioxane

d) Both b & c ✓

2) Monomer of metaldehyde is…

a) Acetone

b) acetaldehyde ✓

c) Formaldehyde

d) Meta – nitro benzaldehyde

INTRODUCTION & NOMENCLATURE OF CARBOXYLIC ACIDS

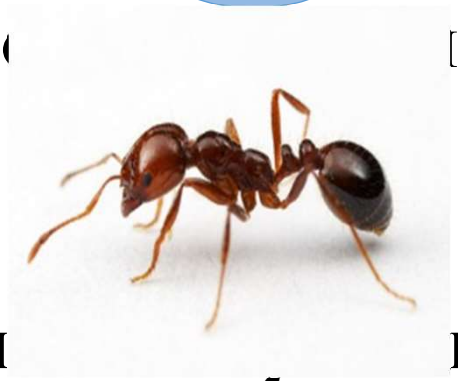
Carboxylic Acids

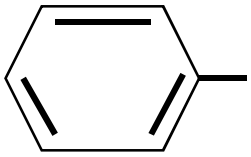
- **The general formula of carboxylic acid is C_nH_{2n+1}.COOH**
- **Carbon compounds containing a carboxyl functional group, -COOH are called carboxylic acids.**
- **The carboxyl group, consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl.**
- **Some higher members of aliphatic carboxylic acids (C_{12}- C_{18}) known as fatty acids, occur in natural fats as esters of glycerol.**

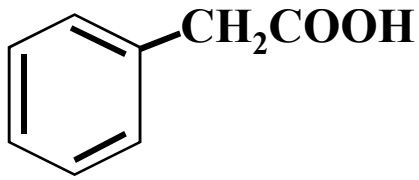
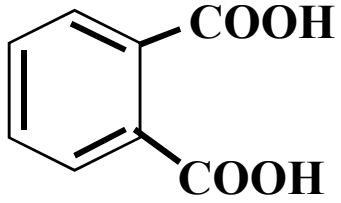
Nomenclature Of Carboxylic Acids

Common name of most of the carboxylic acid based on their sources

IUPAC name: alk + an +oic acid

Structure	Common name	I.U.P.A.C. name
	Propionicacid	Propanoic acid
	Butyric acid	Butanoic acid
	Isobutyric acid	2-methylpropanoic acid
	Oxalic acid	Ethanedioic acid
	Malonic acid	Propane-1,3-dioic acid

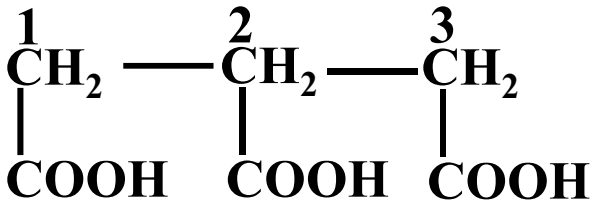
Structure	Common name	I.U.P.A.C. name
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butane –1,4 – dioicacid
$HOOC-(CH_2)_3-COOH$	Glutaric acid	Pentane –1,5 – dioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	Hexane –1,6 – dioic acid
$HOOC-CH_2-CH(COOH)-CH_2-COOH$	——	Propane -1, 2, 3- tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (benzenoic acid)

Structure	Common name	I.U.P.A.C. name
	Phenylacetic acid	2-phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

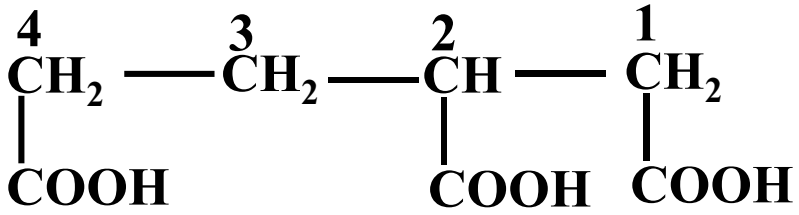
Tricarboxylic acids

According to the recommendations for IUPAC nomenculture of three (or more) —COOH groups, the acid is named as a derivative of parent alkane which does not include the carbon atoms of the carboxylic groups. These are named by use of suffix tricarboxylic acid (for three —COOH groups).

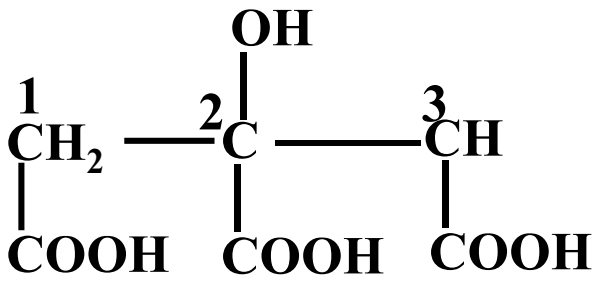
Some Example are



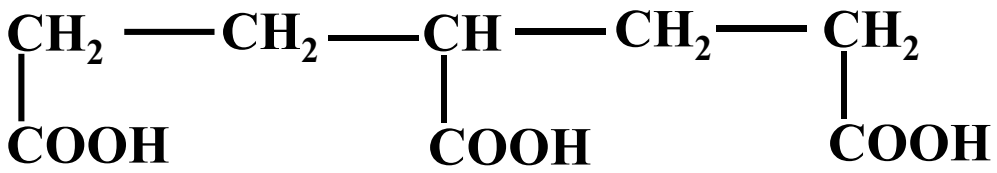
Propane–1,2,3-tricarboxylic acid
(3-carboxy pentane-1,5-dioic acid)



Butane- 1,2,4-tricaroxylic acid (formerly 3-carboxy hexane-1, 6-dioic acid)



2-Hydroxy propane-1,2,3-tricarboxylic acid (citric acid)



Pentane -1,3,5-tricarboxylic acid

(formerly 4- carboxy heptane-1,7-dioic acid)

MCQs

1) A compound of general formula $C_nH_{2n}O_2$ could be

a) an acid

b) a diketone

c) an ether

d) an aldehyde

2) Which of the following is extracted from the roots of valerian plant?

a) $CH_3 – (CH_2)_3 - COOH$

b) $CH_3 – CH_2 - COOH$

c) $CH_3 – (CH_2)_2 - COOH$

d) $CH_3 – (CH_2)_4 - COOH$

3) The carboxylic acid includes the functional groups

a) carbonyl & amine groups

b) carbonyl & hydroxyl groups

c) hydroxyl & carbonyl groups

d) carbonyl, hydronyl & alkyl groups

4) Which of the following is called ethanoic acid

a) $HCOOH$

b) CH_3COOH ✓

c) CH_3CH_2COOH

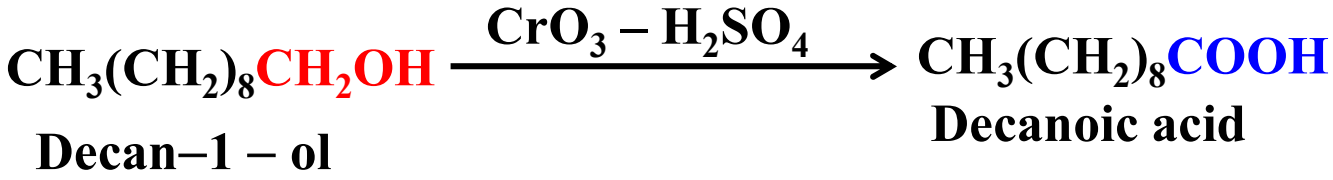
d) $CH_3CH_2CH_2COOH$

PREPARATION OF CARBOXYLIC ACIDS (PART-1)

Methods of Preparation of Carboxylic Acids

1) From primary alcohols and aldehydes

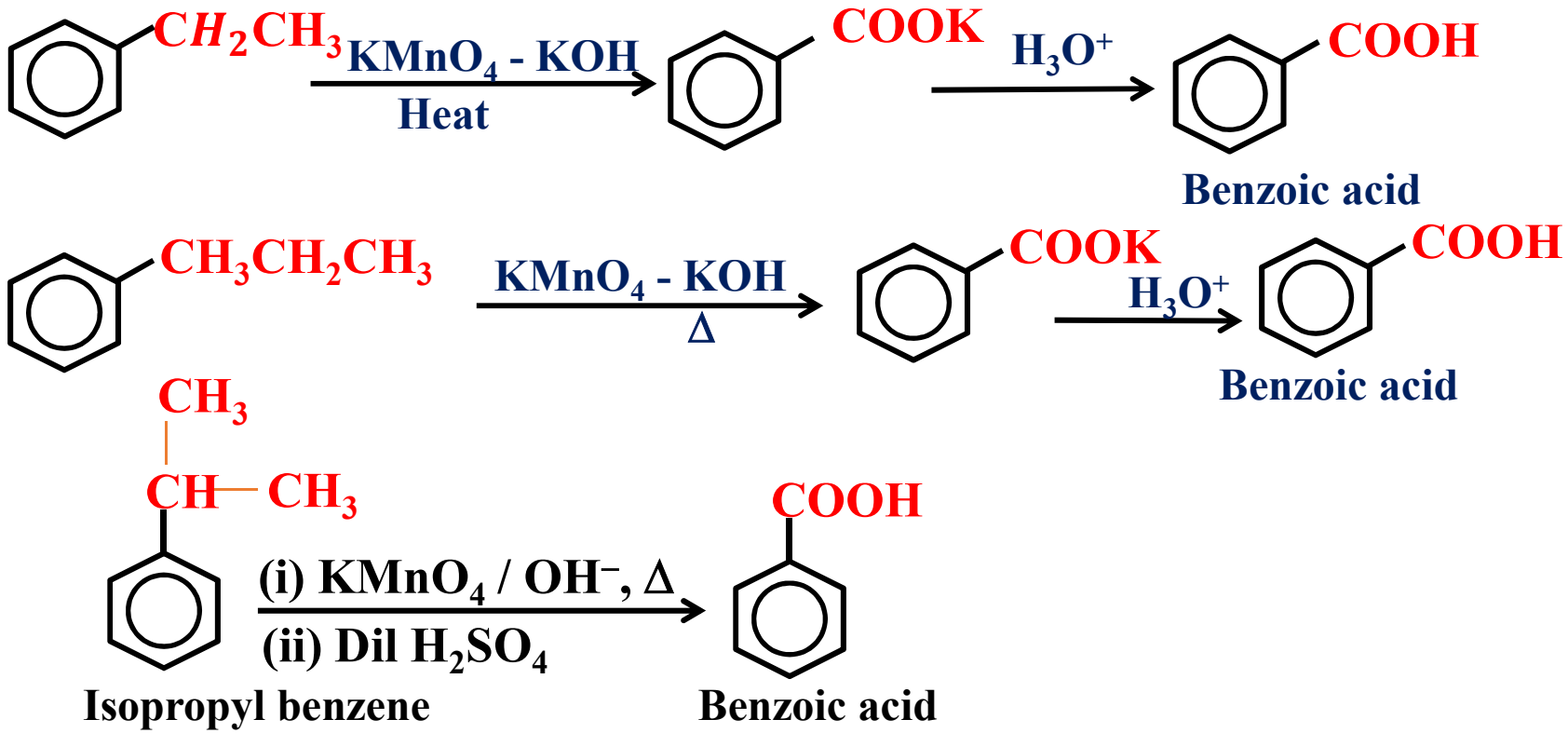
Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate in neutral, acidic or alkaline media.

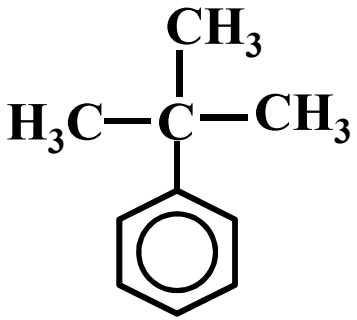


2) From alkylbenzenes

- **Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.**

- **The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain.**
- **Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.**


CH2CH3
KMnO4 - KOH
Heat
COOK
H3O+
COOH
Benzoic acid
CH3CH2CH3
KMnO4 - KOH
Δ
COOK
H3O+
COOH
Benzoic acid
CH3
CH
CH3
(i) KMnO4 / OH−, Δ
(ii) Dil H2SO4
COOH
Isopropyl benzene
Benzoic acid



(i) $KMnO_4$ / OH^-, Δ

(ii) Dil H_2SO_4

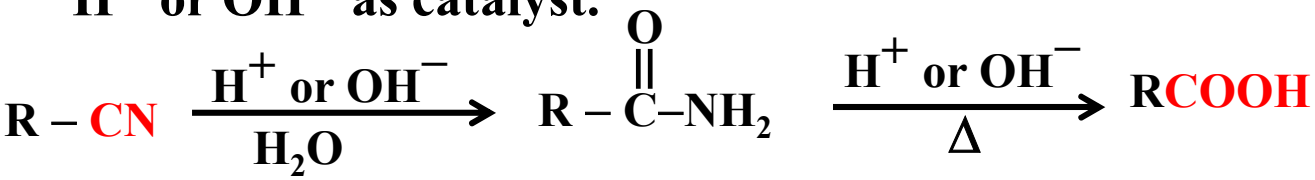
No reaction

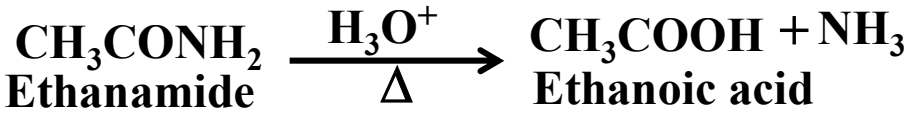
Tert. butyl benzene

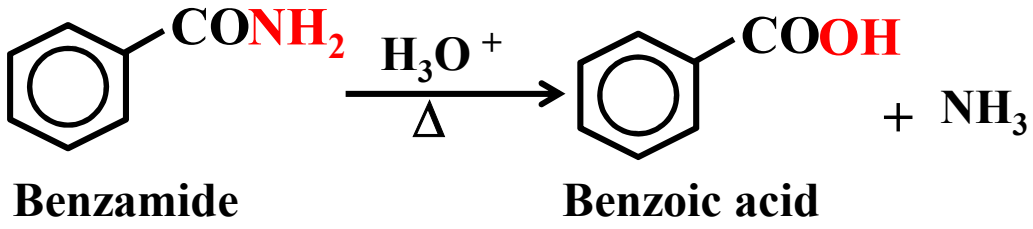
(3^0 alkyl chain, contains no benzylic hydrogen)

3) From nitriles and amides

- Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst.

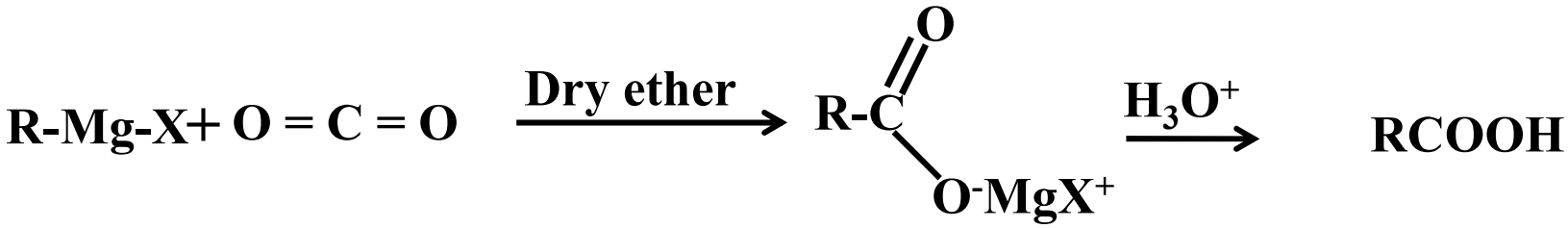






4) From Grignard reagents

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which give corresponding carboxylic acids after acidification with mineral acid.



MCQs

1) Methyl cyanide on hydrolysis gives following

a) acetic acid

b) acetaldehyde

c) acetone

d) methyl amine

2) The reaction of CH_3MgBr on dry ice followed by acid hydrolysis gives

a) acetic acid

b) formic acid

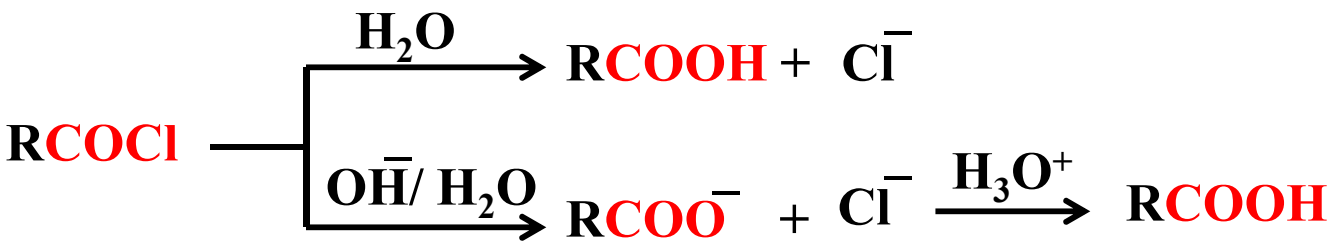
c) acetone

d) acetaldehyde

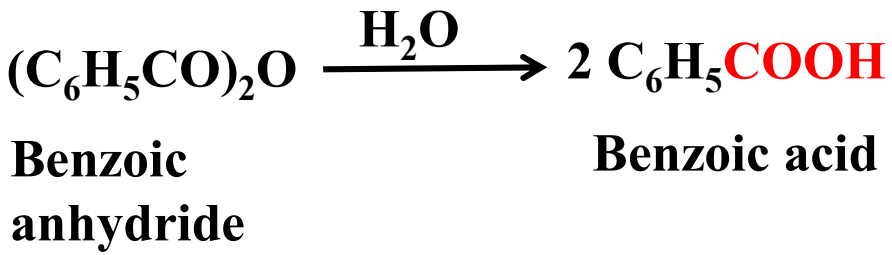
PREPARATION OF CARBOXYLIC ACIDS (PART-2)

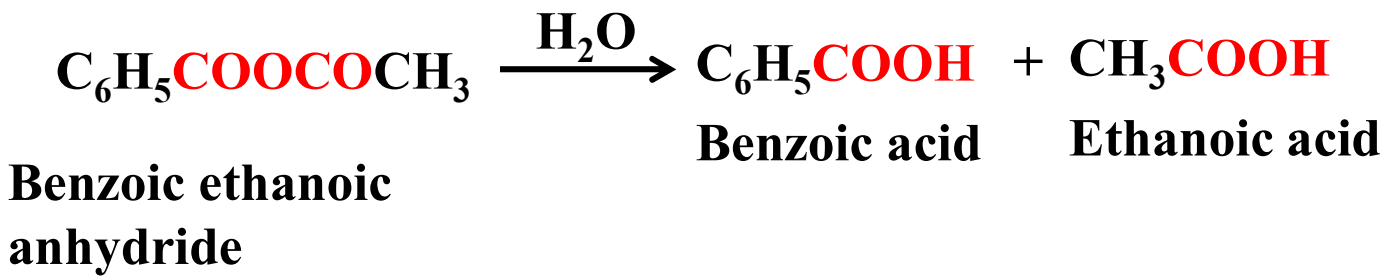
5) From acyl halides and anhydrides

- **Acid chlorides when hydrolysed with water give carboxylic acids**



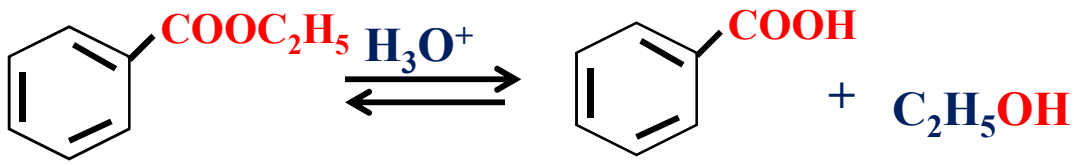
- **Anhydrides are hydrolysed to corresponding acid(s) with water**





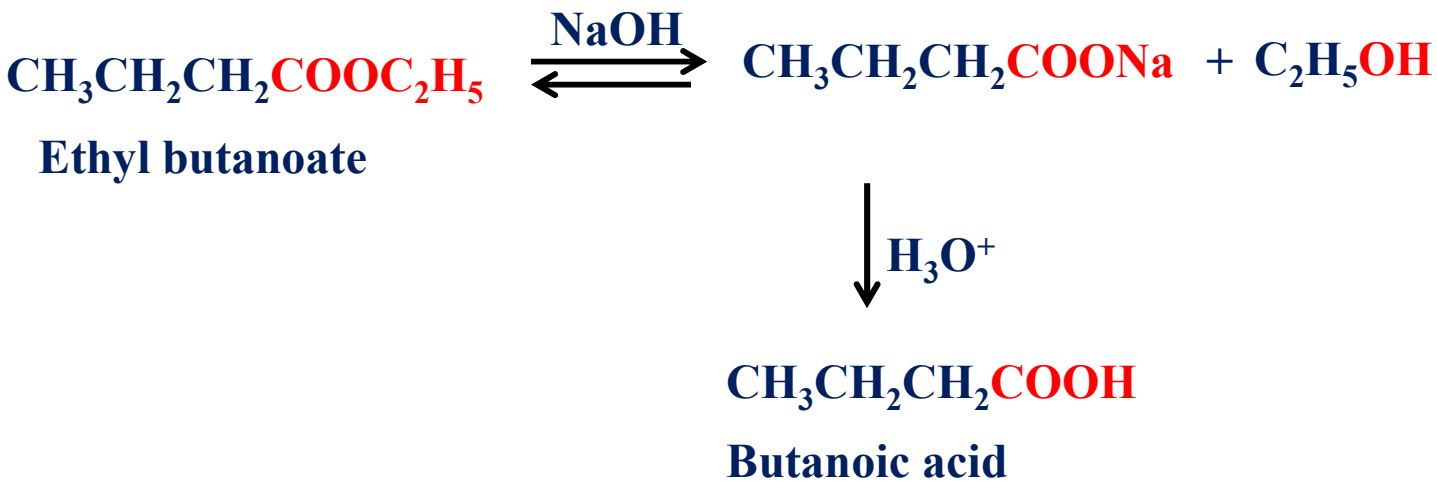
6) From esters

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates which on acidification gives corresponding carboxylic acids.



Ethyl benzoate

Benzoic acid


NaOH
CH3CH2CH2COOC2H5
CH3CH2CH2COONa + C2H5OH
Ethyl butanoate
H3O+
CH3CH2CH2COOH
Butanoic acid

1) $C_6H_5COOC_2H_5 \xrightarrow[\Delta]{H_3O^+} A + C_2H_5OH$ what is A?

a) C_6H_5

b) $C_6H_5NH_2$

c) $C_6H_5C_2H_5$

d) C_6H_5COOH ✓

2) On hydrolysis of acetylchloride gives…

a) Acetaldehyde

b) Acetic acid ✔

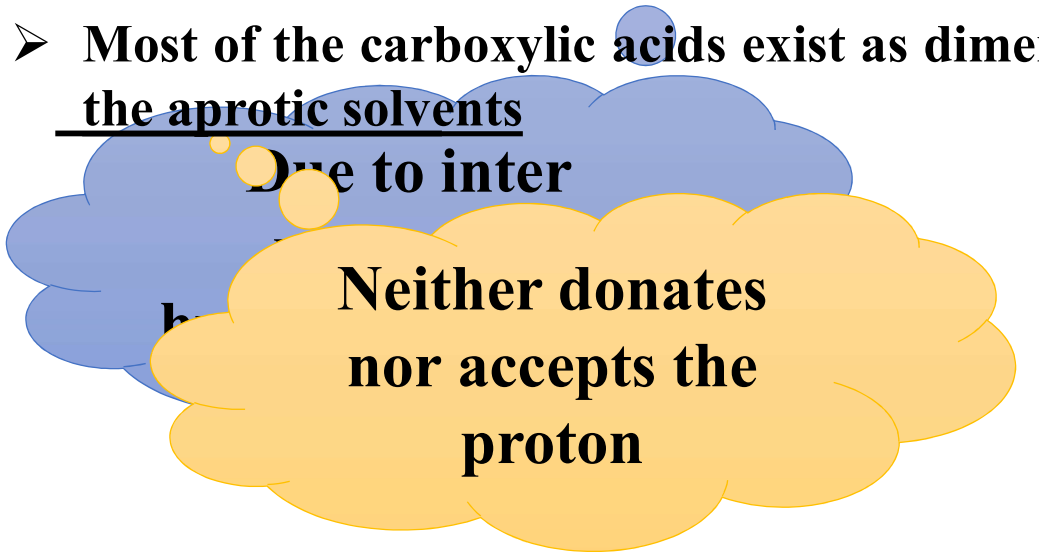
c) Formic acid

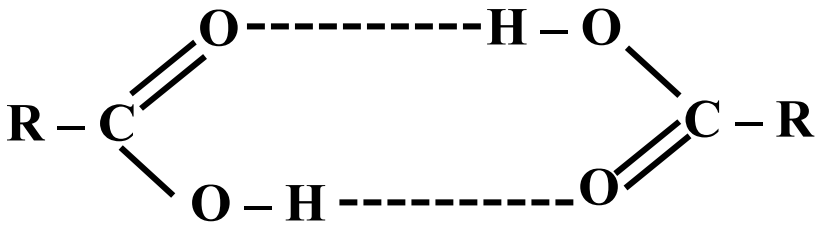
d) Propanoic acid

PHYSICAL PROPERTIES OF CARBOXYLIC ACID

Physical Properties

- **Carboxylic acids have higher boiling points than aldehydes,ketones and even alcohols of comparable molecular masses.**
- **Most of the carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents**





dimer

In vapour state

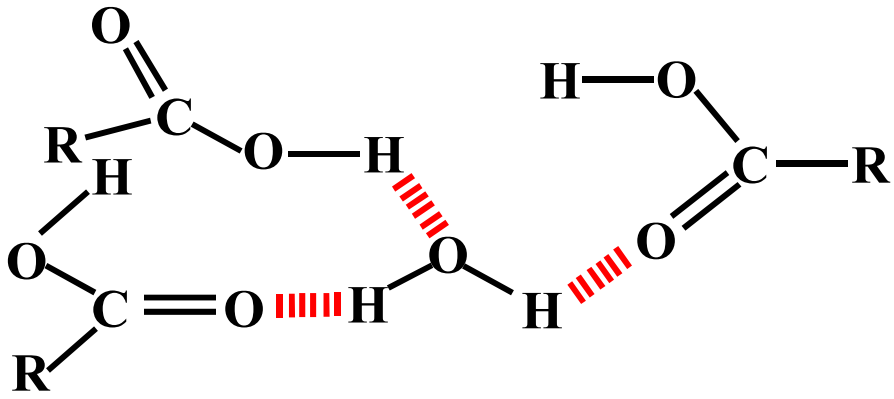
or

in aprotic solvent

Due to inter molecular hydrogen bonding

Solubility

- **Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.**



Hydrogen bonding of RCOOH with H_2O

Solubility

- **The solubility decreases with increasing number of carbon atoms.**
- **Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.**
- **Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc**

MCQs

1) Carboxylic acids have higher boiling point than… of comparable molecular masses…

a) Aldehydes

b) Ketones

c) alcohols

d) All of these ✓

2) Aprotic solvents…

a) Proton donors

b) Proton acceptors

c) Proton donors but not Proton acceptors

d) Neither Proton donors nor Proton acceptors ✓

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