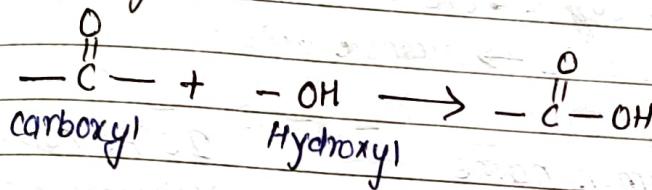


CHAPTER- 6 (- 1st lesson, ~~second~~ Friday)

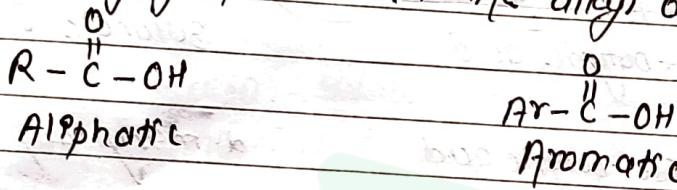
Carboxylic acids

DATE

Introduction → Organic compounds having one or more carboxyl group ($-C(=O)OH$) are called carboxylic acids. Carboxyl group is made by the combination of carboxyl and hydroxyl group and hence its name is carboxyl.



→ Carboxyl acid may be aliphatic or aromatic depending upon whether the carboxyl group is linked to the alkyl or aryl group.



→ Aliphatic monocarboxylic acid are also called fatty acids, because some of their higher members like palmitic acid, stearic acid etc are present in the natural fats as their esters.

I# Nomenclature →

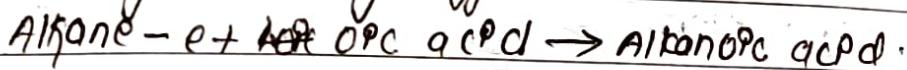
1. Common System →

In this system carboxylic acids are named on the basis of their source from which was obtained first time.

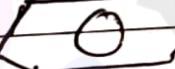
- $HCOOH$:- Named as formic acid, because it was first obtained by the distillation of formica (ants).
- CH_3COOH :- Named as acetic acid because it was obtained from acetum (vinegar).
- $CH_3CH_2CH_2COOH$ → Named as butyric acid because it was obtained from butyrum (butter).

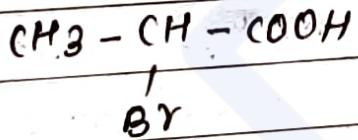
2) IUPAC system →

In this system carboxylic acids are known as alkanoic acid. The name is obtained by replacing terminal e of the corresponding alkane by suffix - OHC COOH .



Formula	Common name	IUPAC name
HCOOH	formic acid	Methanoic acid.
CH_3COOH	acetic acid	Ethanoic acid.
$\text{CH}_3\text{CH}_2\text{COOH}$	propionic acid	propanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	<i>n</i> -butyric acid	Butanoic acid
$\text{CH}_3 - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{COOH}$	<i>iso</i> -butyric acid	<i>d</i> -methyl propanoic acid
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\text{COOH}}{\text{CH}_2 - }$	<i>n</i> -valeric acid	pentanoic acid.

Example:-  , Benzoic acid

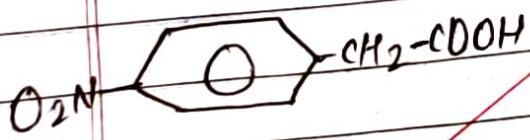


α-Bromo propanoic acid.



cyclohexane

carboxylic acid.

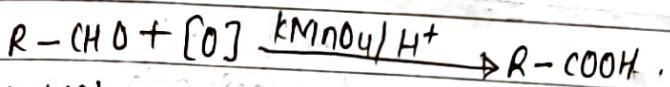


p-nitro benzoic acid.

1. General Methods of monocarboxylic acids

1. From aldehydes \rightarrow By this oxidation of aldehydes with acidicified KMnO₄ or K₂Cr₂O₇.

General reaction:-



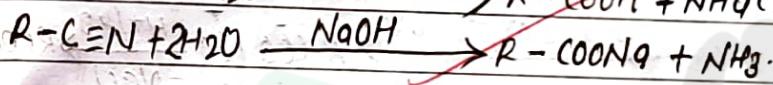
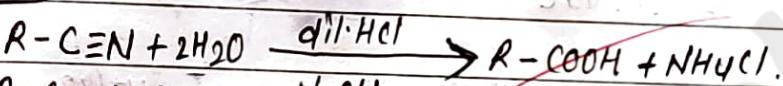
Example:-



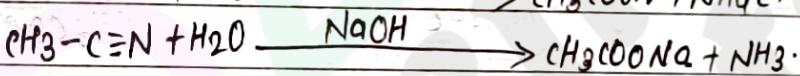
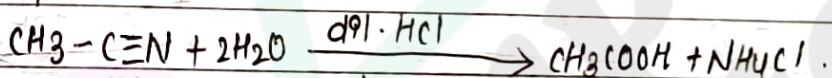
~~group~~

2. From nitriles \rightarrow By the hydrolysis of alkyl cyanides with dilute acids or alkalis gives carboxylic acids.

C.R

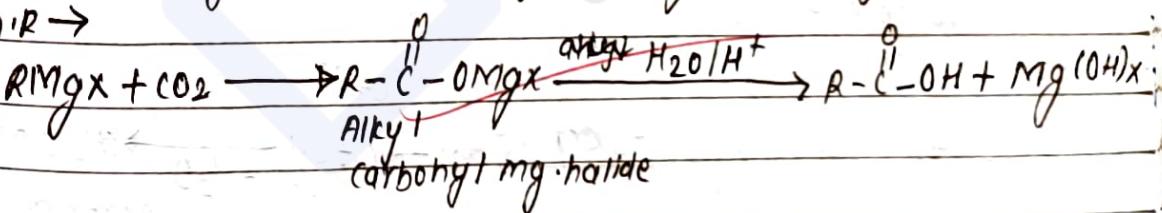


Example

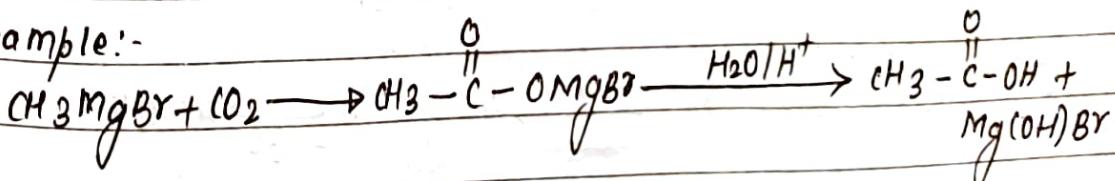


3. From Grignard reagents \rightarrow By carbonation of Grignard reagent - when CO₂ is passed through ethereal solution of Grignard reagent on addition of compound is formed which on hydrolysis gives carboxylic acids.

C.R \rightarrow



Example:-



2

DAT

From dicarboxylic acids → By heating dicarboxylic acids both carboxyl group is linked to the same - carbon atom.



مکالمہ

Ethanol and

6

From sodium alkoxide \rightarrow when sodium alkoxide are treated with carbon monoxide give sodium carboxylate which on acidic hydrolysis gives carboxylic acid.

$$R\ddot{O}Na + CO \xrightarrow{\Delta, \text{ under pressure}} RCOONa \xrightarrow{H^+ / H_2O} RCOOH$$

Sod. Alkoxyde carbon monoxide Sod. Carboxylate = NaCl

$$\text{CH}_3\text{CH}_2\bar{\text{O}}\text{Na}^+ \xrightarrow[\Delta]{} \text{CH}_3\text{COONa}^+ \text{H}^+/\text{H}_2\text{O}$$

Q. From ~~terhaloalkane~~ → By hydrolysis of ~~terhaloalkane~~ in which all halogen atoms are linked to the same carbon with aqueous alkali.

Example :-

12

$$\text{CH}_3\text{C}-\overset{\text{OH}}{\underset{\text{H}_2\text{O}}{\text{C}}}+\text{KOH} \xrightarrow{-\text{KCl}} \text{CH}_3\text{COOK}$$

Acetic acid

$$\begin{array}{c}
 \text{(II)} \\
 \text{H} - \overset{\text{C}^1}{\underset{\text{C}^1}{\text{C}}} - \text{C}^1 + \text{aq } 3\text{ROH} \xrightarrow{-3\text{KCl}} \text{H} - \overset{\text{C}^1}{\underset{\text{C}^1}{\text{C}}} - \text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{HCOOH} \\
 \text{C}^1 - \overset{\text{C}^1}{\underset{\text{C}^1}{\text{C}}} - \text{C}^1 \\
 \text{HO} - \overset{\text{C}^1}{\underset{\text{C}^1}{\text{C}}} - \text{OR} \\
 \text{COOH}
 \end{array}$$

(III)

$$\text{Cyclohexene Oxide} + \text{aq. } 35\% \text{ H}_2\text{O}_2 \rightarrow \text{Cyclohexadienyl Cation} \xrightarrow{-\text{H}_2\text{O}} \text{Cyclohexadiene}$$

classmate

Physical properties →
Physical state: →

- 1) first three members → colorless pungent smelling liquid
Acet - 6 members → oily liquid with pungent odour.
The rest are: colorless and odourless waxy solids.

V.B.P.

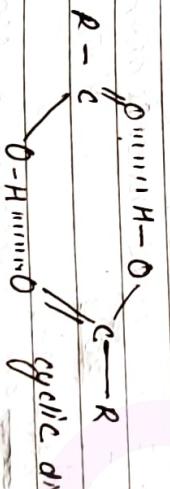
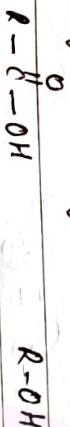
2) Boiling point: → carboxylic acids have higher boiling point than that of alcohols of comparable molecular mass. For ex:- Acetic acid at 118°C and propanal boils at 97°C although they have same molecular mass.

6. The reasons are:-

1) The $-\text{OH}$ bond of carboxylic acids is more strongly polarised than that of alcohol due to presence of carboxyl group adjacent to H^+ . Hence carboxylic acids form stronger H-bond compared to alcohols.

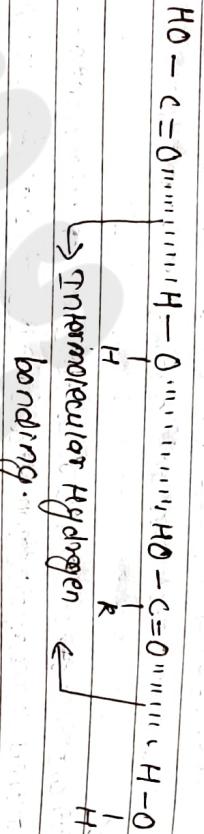


II) The alcohol can form H-bonding only through $-\text{OH}$ group but carboxylic acids can form H-bondings through $-\text{OH}$ group and carboxyl group leading to the dimeric structure. Hence the observed molecular mass becomes double the actual molecular mass. Hence it makes carboxylic acids of higher boiling than alcohol.



→ The boiling point of high aliphatic and aromatic carboxylic acids increase with increase in molecular size due to a corresponding increasing Vander waals force of attraction.

3. Solubility: 4 - member one soluble in water due to formation of intermolecular H-bonding with water molecule.

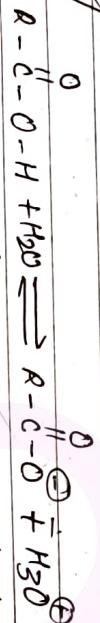


→ The solubility in water decrease with increase in the size of alkylic groups. All carboxylic acid are soluble in organic solvents.

Chemical properties →

1. Acidic nature → Reactions due to H-atoms of the -OH group carboxylic acids are weaker than mineral acids but stronger than water, alcohol, phenol and carbonic acid. The acidity of carboxylic acids can be explained in the following terms:

(A) Ionization constant → When a carboxylic acids in dissolved in water it ionizes to give carboxylate anion and hydronium ions. These ions are in dynamic equilibrium with the carboxylic acid molecules.



The equilibrium constant for the process is given by

$$\text{K}_{\text{eq}} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

Water is present in large excess therefore its concentration is taken as constant.

$$\therefore \text{K}_{\text{eq}} \times [\text{H}_2\text{O}] = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

where K_a = ionization constant or acid dissociation constant.

→ A larger value of K_a signifies higher degree of dissociation of the acids and stronger the acid. The acid strength is also described by the pK_a value,

$$pK_a = -\log K_a$$

∴ Stronger acids will have larger value of K_a and smaller value of pK_a .

⑥ Resonance stabilization → In aqueous solution the basic one equilibrates with the undissociated acid molecule.

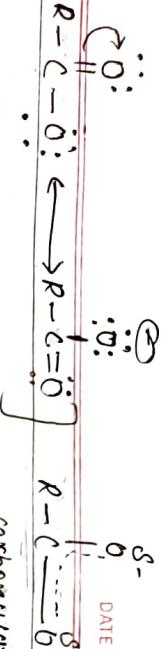


The carboxylic acids are stabilized by resonance as follows:-



The positive charge on the carbon atom of the $-OH$ group of acids make the release of H -atoms as hydrogen bond easier. Hence carboxylic acids are acidic in nature.

→ Carboxylate anion is also stabilized by resonance as follows:-



carboxylate anion is more stabilized by resonance than carboxylic acid. It is because the resonance structures of carboxylate anion are potential and involve dispersal of negative charge whereas that of carboxylic acid are not. Potential and involve charge separation as a result the equilibrium first proceeds in forward direction producing more hydronium ion. Hence carboxylic acids behaves as fairly strong acids.

Carboxylic acids are stronger acids than alcohols & water.



In alcohol neither alcohol nor alkoxide ion are stabilized by resonance. Hence alcohol is weaker acid than carboxylic acids.

Effects of substituent on the acid strength of carboxylic acids:-

The electron releasing substituent like a light group (CH_3 , $(\text{CH}_3)_2\text{CH}_2$, etc) decreases the acid strength of the carboxylic acids because it increases electron density at the oxygen atom of $-\text{OH}$ group and makes release of H^+ ion difficult.

\rightarrow It also destabilizes the carboxylate anion by the concentration of negative charge on the oxygen atom. Let us consider formic acid and acetic acid.



\rightarrow - CH_3 group makes the release of H^+ difficult to bear.

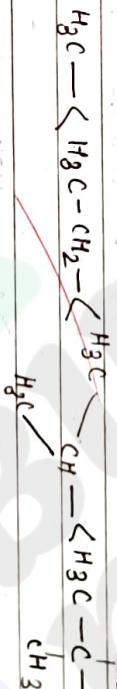
use e- density is high at O- atom of -OH group and cannot pull the bond electron pair strongly and H⁺ cannot be released.

$\ddot{\ominus} \ddot{O}$:



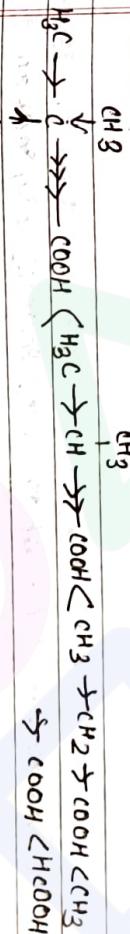
∴ Hence formic acid is more stronger acid than all the acids.

∴ The electron releasing effect of alkyl group is described as σ effect. The σ effect alkyl group increase in this order:-



Therefore, the acid strength carboxylic acids increase in the

order:-



2,2-dimethylpropanoic acid.

→ The electron with drawing group such as Halogen, -NO₂, -CN etc. increase the acid strength of the carboxylic acid. It decreases electron density at the O-atom of -OH group and make release of H⁺ easier.

It stabilizes the carboxylate ion by the dispersal of negative charge.

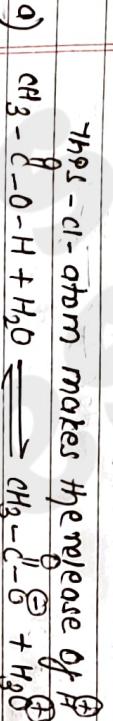
tive charge.

For eg:-

Longer acetic acid and monochloro-acetic acid.



The $\text{C} - \text{Cl}$ - atom makes the release of H^+ - ion easier.

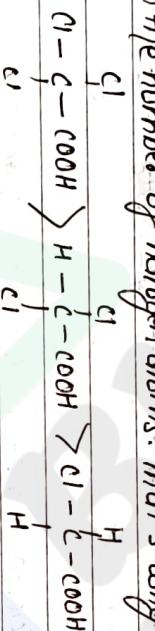


Less stable.



More stable

j) The acid strength of carboxylic acids increases with increase in the number of halogen atoms. That is why



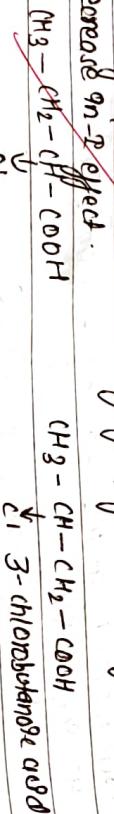
p,p'-chloroacetic o,p'-chloroacetic mono-chloroacetic acid

pp) The acid strength of carboxylic acid increases with increase in electronegativity of halogen atoms

$\text{F} > \text{Cl} > \text{Br} > \text{I}$ Then order of strength is :-



iii) The acid strength of carboxylic acid decreases with increase in distance of the electonegative drawing group from -COOH group due to decrease in P^{δ} effect.



o-chlorobutanoic acid

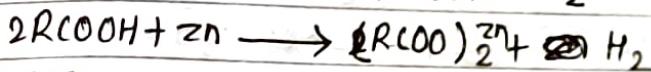
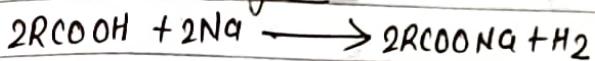
classmate



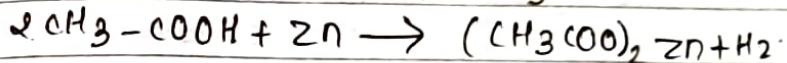
4-chlorobutanoic acid

PAGE

(A) Reaction with Metals \rightarrow Carboxylic acids reacts with metals like Zn, Na, K etc to liberate H₂ gas.



Example:-

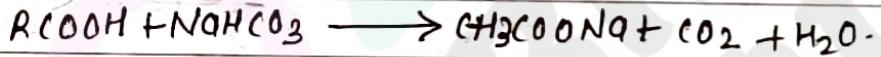
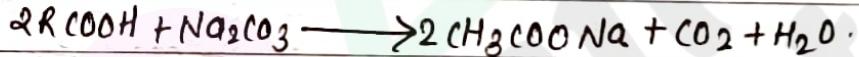


(B) Reaction with alkalis \rightarrow Carboxylic acids reacts with alkalis to give salt and water.



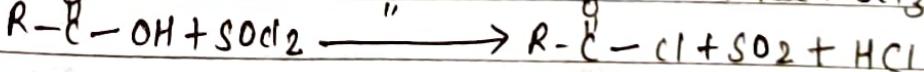
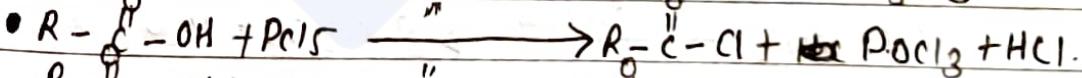
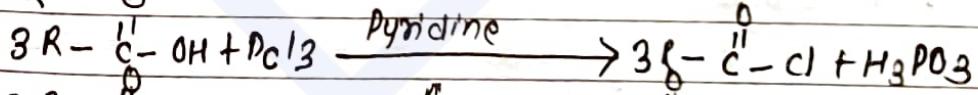
(C) Reaction with carbonates and bicarbonates \rightarrow carboxylic acids give carbon dioxide gas from carbonates and bicarbonates.

G.R

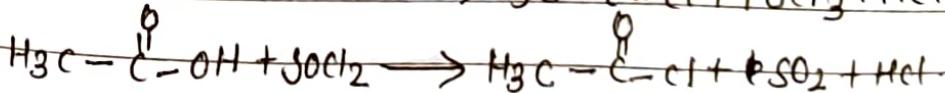
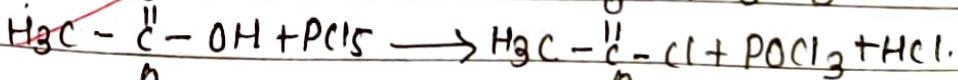
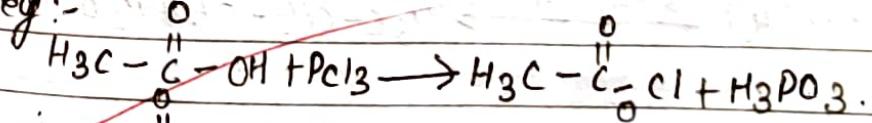


(D) Reaction with PCl_3 , PCl_5 or SOCl_2 \rightarrow carboxylic acid reacts with PCl_3 , PCl_5 , SOCl_2 to give acid chloride.

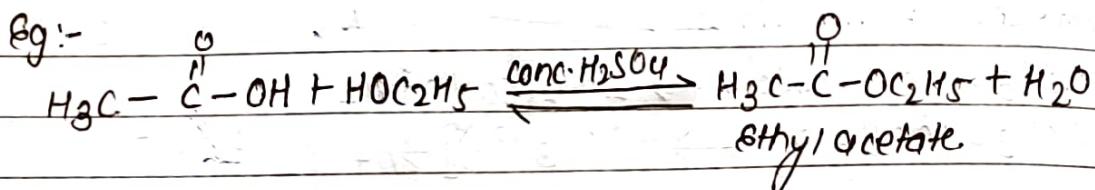
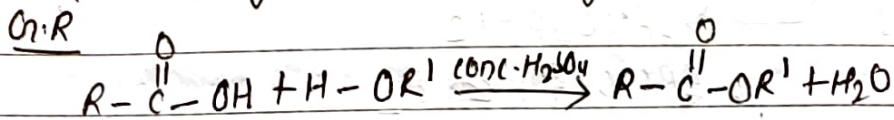
G.R



Eg:-



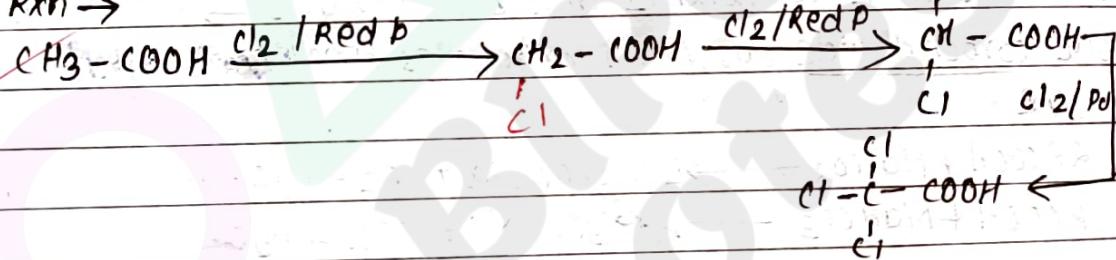
(E) Esterification reaction → Carboxylic acids reacts with alcohol in the presence of conc. H_2SO_4 to form ester.



(F) Halogenation reaction → (Hell Volnay Zelinsky reaction)
or HVZ reaction

carboxylic acids when treated with chlorine or bromine
in the presence of red phosphorus the α - H-atom are replaced by
halogens.

Rxn →



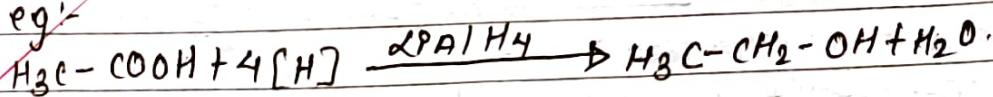
Trichloroacetic acid

(G) Reduction reaction → with $\alpha\text{PAI}/\text{H}_4$: - carboxylic acids are reduced to alcohol with $\alpha\text{PAI}/\text{H}_4$ or H_2 in presence of copper chromate (CuCr_2O_7) as catalyst.

Ch.R:-

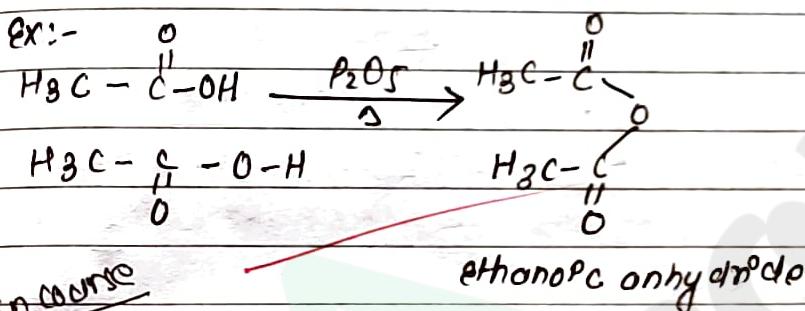
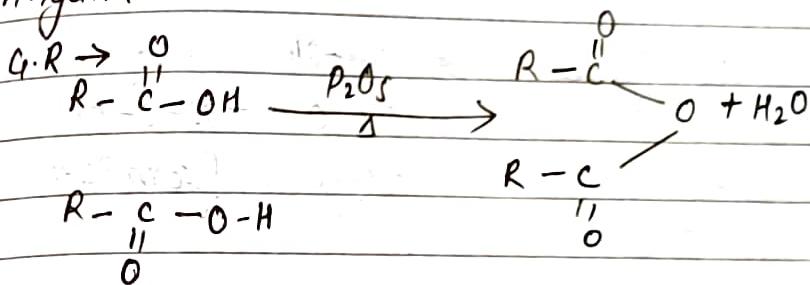


Eg:-



H. Dehydration reactions → formation of acid anhydride.

Carboxylic acids when heated with P_2O_5 gives acid anhydride.



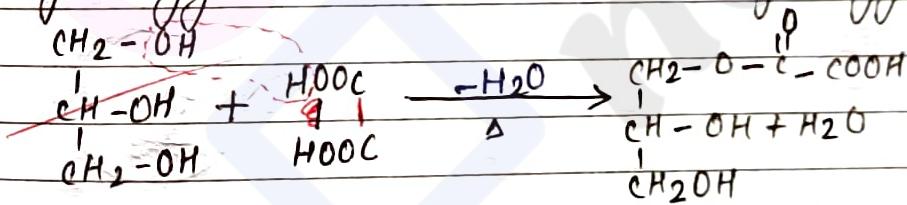
Not in course

Laboratory preparation of formic acid (methanoic acid)

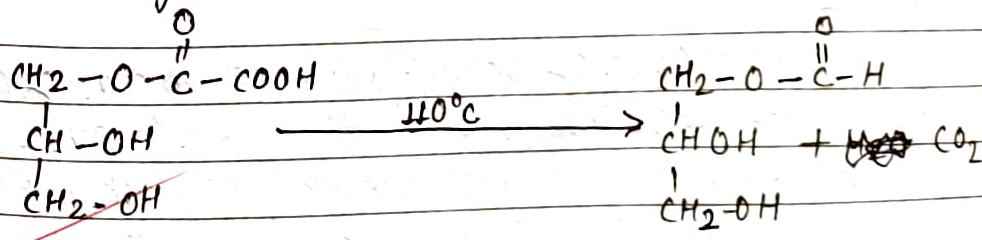
Principle:- Theory:-

It is obtained in lab by heating anhydrous glycerol with oxalic acid crystals at 110°C

I) At first, glycerol reacts with oxalic acid to form glycerol monoxalate.



II) Thus formed glycerol monoxalate decomposes at 140°C to give glycerol monoformate and CO_2 .



(iii) Finally glycerol monoformate reacts with water from oxalic acid crystals to give glycerol and formic acids.

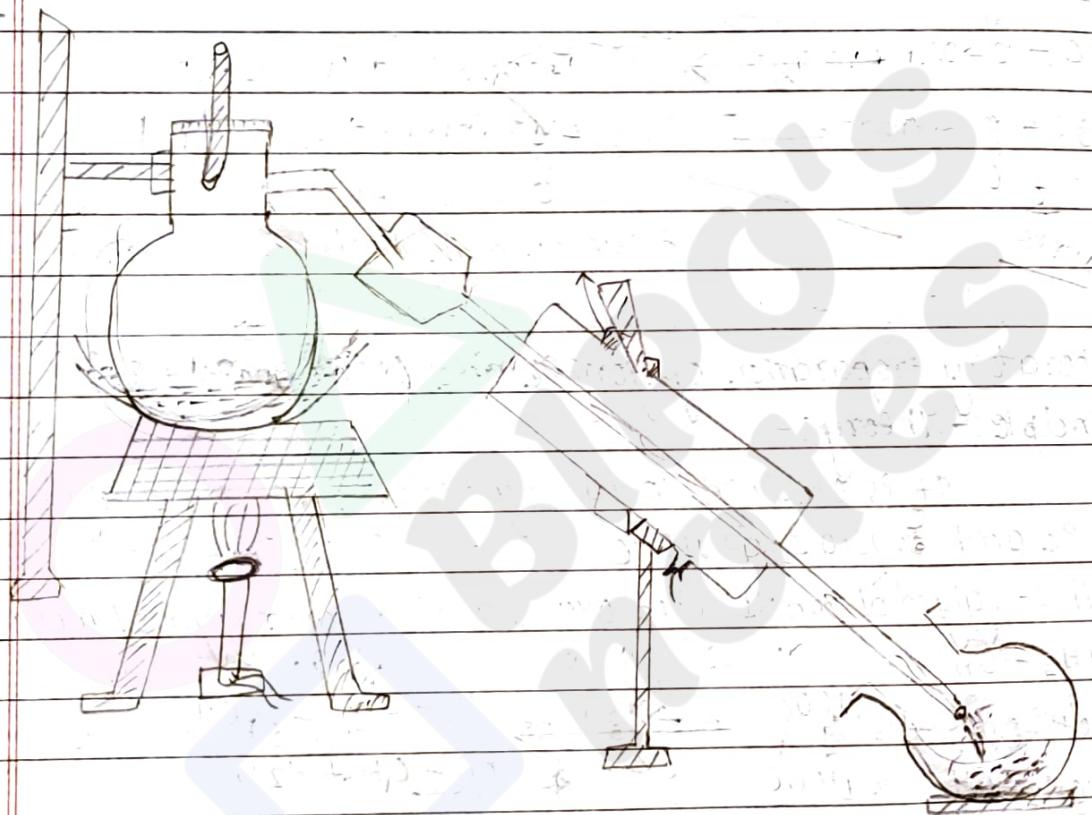
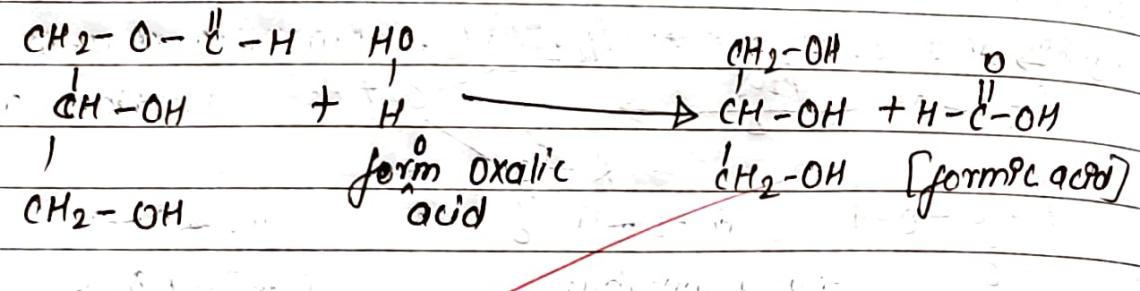


fig:- Lab preparation of formic acid

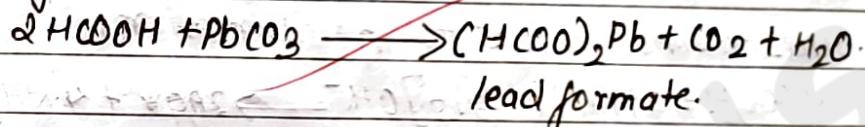
Procedure:-

About 50 ml of anhyd. Glycerol and 40 gm of oxalic acid crystals are taken into a distillation flask which is fitted with a thermometer and water condenser. The flask is heated over a sand bath at 110°C . till the evolution of CO_2 . Then the flask is cooled and 40 gm of oxalic acid crystal are

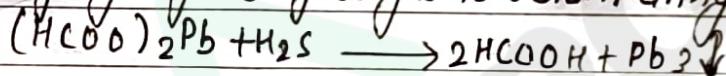
again added and heated at 110°C . The formic acid distills over and is collected in a receiver in the form of its aqueous solution.

Aqueous formic acid cannot be fractionated to get anhydrous formic acid. It is because the bpt of formic acid is nearly same to that of water (100.5°C). Hence anhydrous formic acid is obtained as follows:-

The aqueous formic acid is neutralized with PbCO_3 soln. The solution is then evaporated (concentrated) to obtain the crystals of lead formate.



→ The crystal of lead formate are separated, dried and heated in a current of hydrogen sulfide gas to obtain anhydrous formic acid.



Anhy. formic acid,

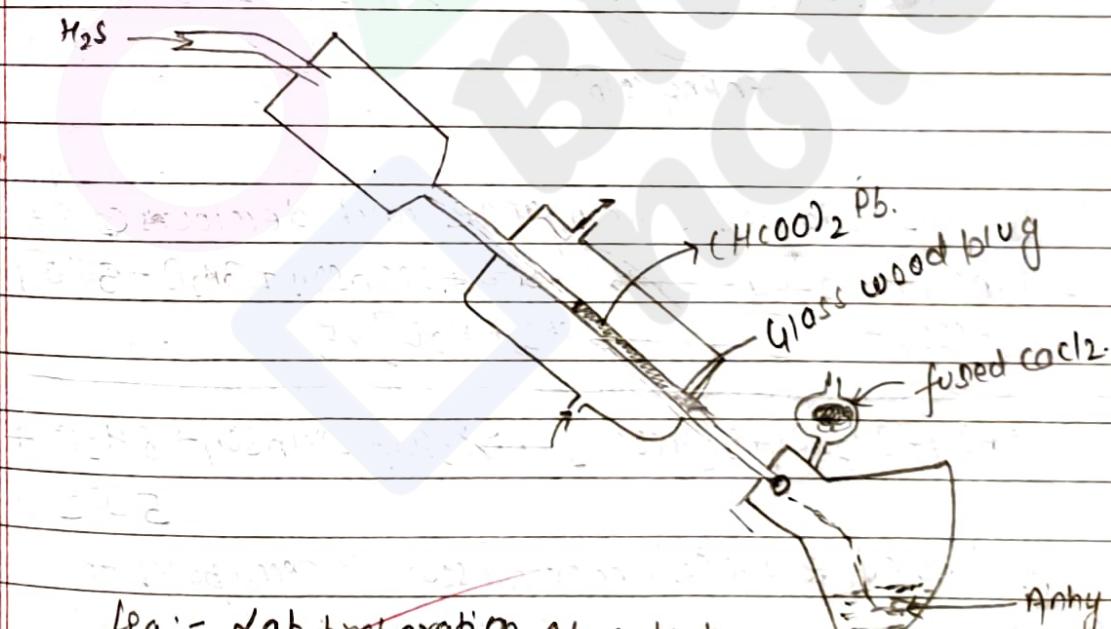


fig:- Lab preparation of anhydrous formic acid.

Abnormal behaviour of methanone acetic acid \rightarrow

Formic acid contains both carboxyl group and aldehydic group as functional group. Hence it gives some of the reactions of aldehydes.



Carboxyl group Aldehyde group.

(1) It reduces Tollens reagent to the silver mirror



Fehling soln'

(2) It reduces Fehling solution to the cuprous oxide



(3) It reduces oxidized permanganate and devolours eg Pt
 $\text{2MnO}_4^- + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5[\text{O}]$
 $\text{HCOOH} + [\text{O}] \longrightarrow \text{CO}_2 + \text{H}_2\text{O}] \times 5$

$$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5[\text{HCOOH}] \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{CO}_2$$

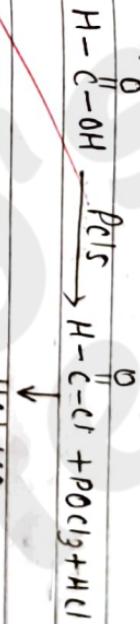
(4) When heated to 160°C under pressure it decomposes to give CO_2 and H_2 .



When heated with conc. H_2SO_4 it undergoes dehydrations to form carbon monoxide.



It reacts with PCl_5 to give formyl chloride which decomposes to give carbon monoxide.



Uses of some carboxylic acids →

Formic acid →

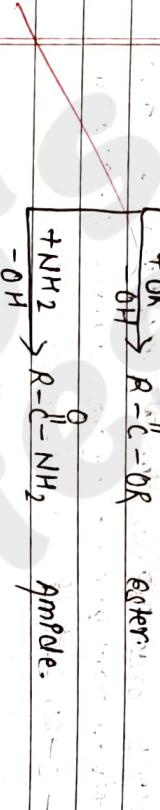
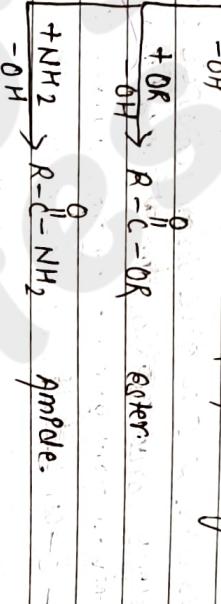
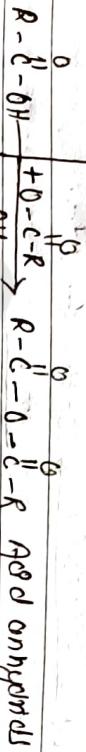
- In the lab preparation of carbon monoxide.
- In medicine.
- As salts are used in the hydrogenation of vegetable oil.
- As coagulating agent for latex.

Acetic acid →

- In the manufacture of dyes, rayons (fibres) and perfumes.
- As solvent.
- As vinegar for the preparation of pickles.
- For coagulation of latex.

Derivatives of Monocarboxylic acids →

Compounds formed by replacement of -OH group of carboxylic acid by $-X$, $-O-C(=O)-R$, $-OR$ and $-NH_2$ are called also esters of carboxylic acids.



[1] Acyl halides $\rightarrow R-\overset{O}{C}-X$ $R =$ Alkyl / Aryl

Among the acyl halide alkyl chlorides are most much
ve and common compounds.

Nomenclature: \rightarrow -OR replaced by -Cl halide.

Formula common name IUPAC name

$H-\overset{O}{C}-Cl$ Formyl chloride

$H_2C-\overset{O}{C}-Cl$ Acetyl chloride

$CH_3-(CH_2-\overset{O}{C}-Cl)$ Propenyl chloride

$CH_3-\overset{O}{C}-CH-\overset{O}{C}-Cl$ α -Chloro-propionyl

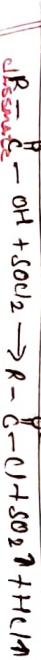
$\begin{matrix} 2 & | \\ & \backslash \end{matrix}$ chloride

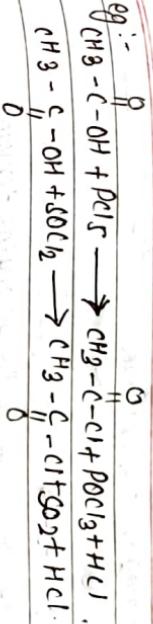
$^0\underset{\text{Benzene}}{C}_6H_5-C-\overset{O}{C}-Cl$ Benzoyl chloride

Preparation \rightarrow

1. Acyl chlorides are obtained by treating carboxylic acid with

PCl_3 , PCl_5 or $SOCl_2$. [Good chlorinating group]





In industrial scale aryl-chloride are obtained by distilling Na- or Ca-salts of carboxylic acids with phosphoryl chloride (POCl_3) or sulphuryl chloride.

Ex:-



Sod. metaphosphate



3. Benzyl chloride is obtained by heating benzene with carbonyl chloride in the presence of anhydrous aluminium chloride.



* physical properties →

1. physical states → lower aryl chlorides are colourless liquid whereas the higher aryl chlorides are colourless solids with pungent smell both.

d. solubility → Aryl chlorides

↳ dissolves slowly in water due to hydrophilic.

All aryl chlorides are readily soluble in organic solvents.

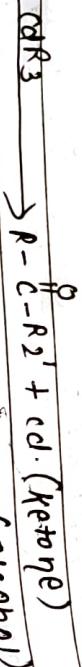
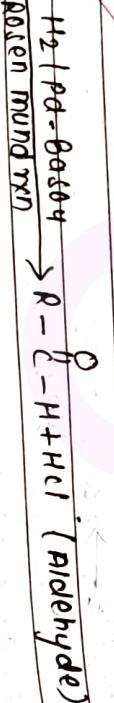
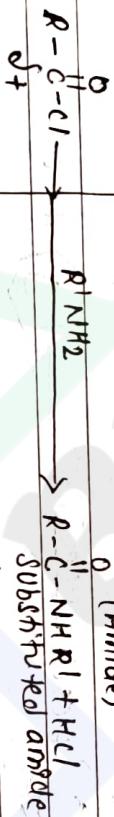
4. boiling points → Aryl chlorides have lower boiling points than their corresponding carboxylic acid. It is due to absence of permanent

Effect of H-bonding on acyl chlorides

Chemical properties →

Acy chlorides are most reactive among the derivatives of carbonyl compounds. In acyl chlorides the highly electronegative chlorine atom is linked to the carbonyl group. It makes the carbonyl carbon electrophilic. Hence they undergo nucleophilic substitution easily.

The chemical properties of acyl chloride are summarized below:-



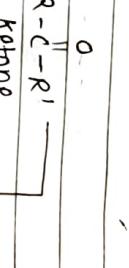
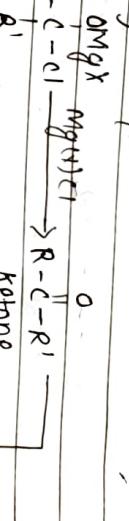
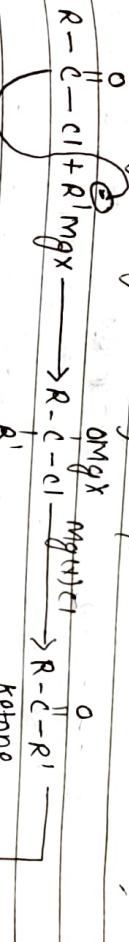
(R-C(=O)-)

classmate

② Reaction with Grignard reagent

With Grignard reagent ketone is formed, which further reacts with

Grignard reagent to give tertiary alcohol.



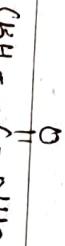
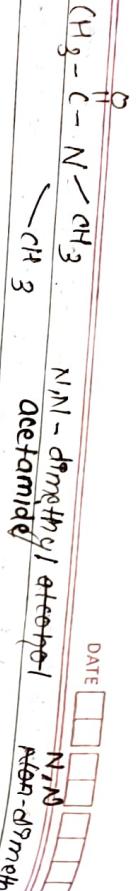
(3° alcohol)

* Uses of acyl halides:-

- They are used as acylating agent.
- They are used for preparation of several derivatives, dyes, shampoos and pharmaceuticals.

* Acid anhydrides → Anhydrides are named by replacing the suffix 'oic' or 'oic acid' of common name and 'oic' acids as IUPAC, name of the corresponding carboxylic acid with 'oate'.

Formula	Common name	IUPAC name
$\text{H} - \overset{\text{O}}{\underset{\text{C}}{\text{N}}\text{H}_2}$	Formamide	Methanamide
$\text{CH}_3 - \overset{\text{O}}{\underset{\text{C}}{\text{N}}\text{H}_2}$	Acetamide	Ethanamide
$\text{CH}_3 - \overset{\text{O}}{\underset{\text{C}}{\text{N}}\text{H}_2}$	Propionic acid	Propanamide
$\text{CH}_3 - \overset{\text{H}}{\underset{\text{C}}{\text{N}}\text{H}_2}$	Propanamide	Propanamide
$\text{CH}_3 - \overset{\text{H}}{\underset{\text{C}}{\text{N}}\text{H}} - \text{CH}_3$	N-methyl acetamide	N-methyl propanamide



Benzamide

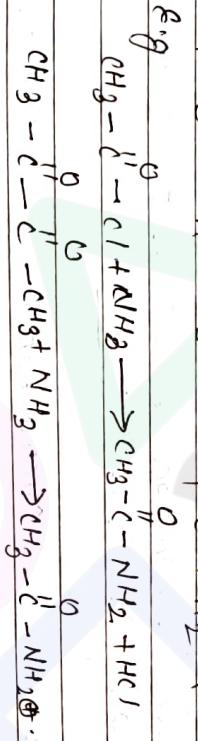
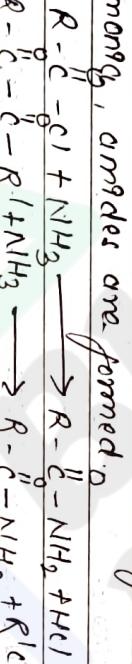
Benzamide.

Preparations:-

1. When ammonium salts of carbonylic acids are heated amide are formed.



2. When acids chlorides or acid anhydride react with ammonium salts of carboxylic acids are formed.



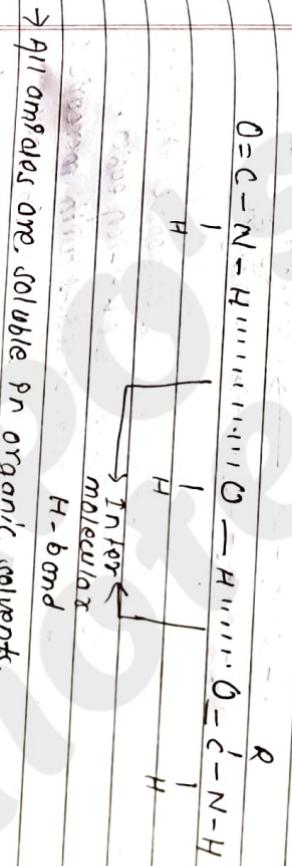
3. By the partial hydrolysis of alkyl nitrile (alkyne nitrite) with conc. HCl



Physical properties:-

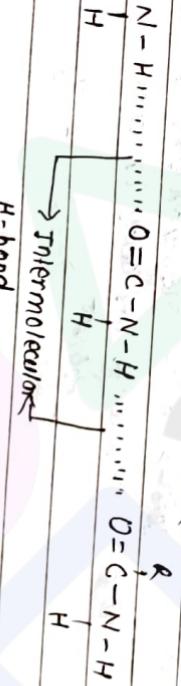
1) Physical state:- Except formamide all other amides are colorless crystalline solids.

2) Solubility:- Amides up to 5 carbon atoms are soluble in water due to formation of intermolecular H-bonds between amides and water molecules.



→ All amides are soluble in organic solvents.

3) M.p and B.pt → The melting point & boiling point of amide are higher than those expected from their molecular masses. It is due to formation of intermolecular H-bonds between the own molecule.

Chemical properties

→ Amides are least reactive among derivatives of carboxylic acid.

It is due to lower p.e.t. of C=NH₂ bond.

C.O.F. Resonance stabilisation of molecule.



1. Amphoteric nature

(Q)

~~as weak bases~~. Hence they are amphoteric in nature.

~~Suspension~~: Due to presence of lone pair of electron on the nitrogen atom amides act as bases but they are less basic than amides amuges, because according to structure (II) the lone pair is not easily available for protonation. Hence it reacts with strong acids to form salts.



(B)

Acidic nature: → The positive charge develops on the N-atom (structure-II) makes the release of H-atom easier. Hence amides act as weak acid. It reacts with mercuric oxide to form salt and with sodium to evolve H_2 gas.

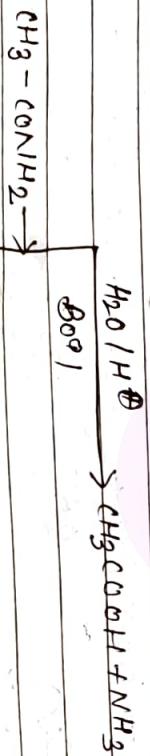
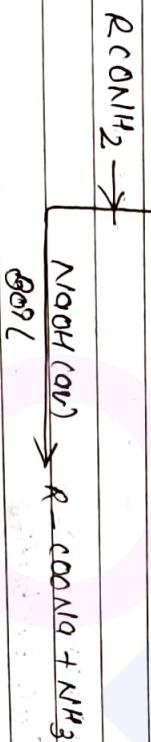
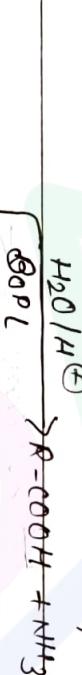


Mercuric ethylamido



Sodium acetate

Hydrolysis: → Amides are hydrolysed to carboxylic acid when boiled with dil. acids or alkali.



8. Dehydration → when amides are heated with P_2O_5 phosphorous pice) penitrode gets dehydrated to form alkyl cyanide (alkyne)



4. Reduction → when amides are reduced in the presence of LiAlH_4 primary amines are formed. Ex:



Reaction

5. Reduction w/ H_2 nitrous acid → when amide reacts w/ H_2 nitrous acid carboxylic acids and nitrogen gas are formed.



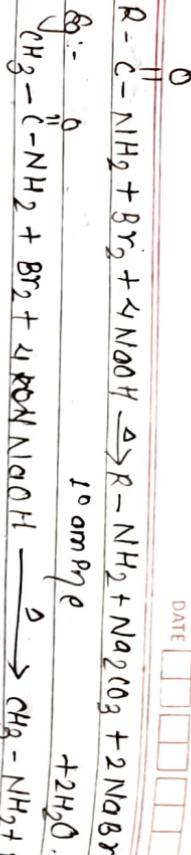
eg:-



~~v. note~~

6. Reaction w/ Pb(OAc)_4 and $\text{AlCl}_3 \rightarrow$ (Hoffmann's bromamide or hypobromamide):-

when amides are heated with bromine and AlCl_3 , primary amines are formed having one carbon atom less than that of parent amine. This reaction is called decarboxylation reaction.



Closes 0 -

1

\Rightarrow Preparation of primary amine.

$$(3) \text{ Acid anhydride} \rightarrow R-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-R$$

-reved from carboxylic acid by the loss of water molecule

$$R - \overset{\text{OH}}{\underset{\text{O}}{\text{C}}} - OH \rightarrow R - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} -$$

$$R - C - O + H \xrightarrow{\Delta} R - C = O + HO$$

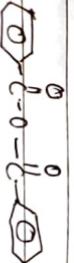
acid anhydride

Nomenklatur

Hormula	common name	Diac Name
$\text{CH}_3 - \overset{\text{O}}{\underset{\text{C}}{\text{O}}} - \text{O} - \overset{\text{C}}{\underset{\text{H}_3}{\text{C}}} - \text{CH}_3$	Acetic anhydride	Ethanac anhydride

$\text{C}_2\text{H}_5 - \text{C} = \text{O} - \text{C}(\text{O})\text{C}_2\text{H}_5$ propionic anhydride

$\text{CH}_3 - \overset{\text{H}}{\underset{\text{C}}{\text{C}}} - \overset{\text{O}}{\underset{\text{C}}{\text{C}}} - \text{C}_2\text{H}_5$	Acetic propanone anhydride	ethano propano anhydride
--	-------------------------------	-----------------------------



classmate

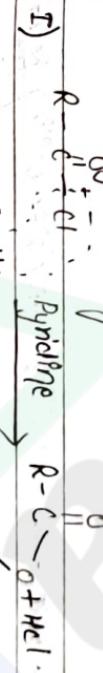
Preparations →

1. When carboxylic acids are heated in the presence of PbO_2 , anhydrides are formed.

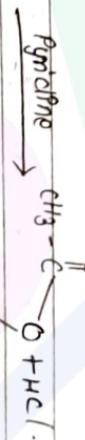


$$\begin{array}{ccc}
 & \text{O} & \\
 & || & \\
 \text{CH}_3 - \text{C} & \xrightarrow{\Delta} & \text{CH}_3 - \text{C} \\
 & \backslash & / \\
 & \text{O} & \text{H} \\
 & \text{O} & \\
 & \text{O} & \\
 \text{CH}_3 - \text{C} & \xrightarrow{\text{PDS}} & \text{CH}_3 - \text{C} + \text{H}_2\text{O} \\
 & \backslash & / \\
 & \text{O} & \text{H} \\
 & \text{O} & \\
 & \text{O} & \\
 \end{array}$$

Q: When acid chloride is treated with carboxylic acid or $\text{P}_t\text{S}_\text{O}_\text{C}_\text{l}_\text{O}_\text{C}_\text{H}_\text{C}_\text{H}_\text{O}$ um so I_r , anhydride is formed.



$$\begin{array}{c}
 \text{CH}_3-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}=\text{Cl} \\
 | \\
 \text{Pyridine} \rightarrow \text{CH}_3-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\text{O} + \text{HCl} \\
 | \\
 \text{CH}_3-\overset{\text{C}}{\underset{\text{H}}{\text{C}}}-\text{O} \\
 | \\
 \text{O}
 \end{array}$$



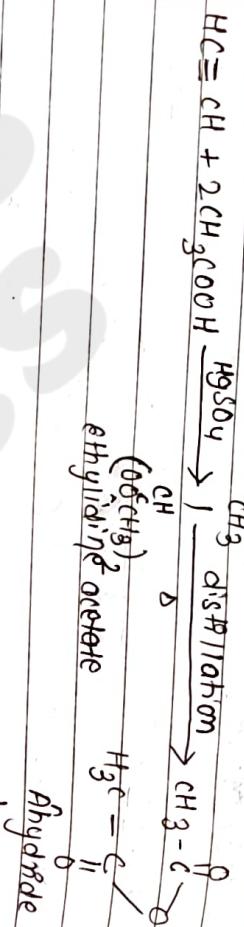
$R-C=O-Na$ $R-C_6H_5$



classmate

When acetylene is treated with acetic acid in the presence of mercury sulphate anhydride is formed.

Rxn:-



Physical properties:-

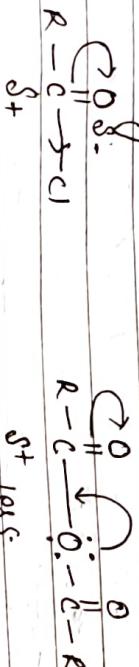
1. physical states :- lower aliphatic acid anhydride are colorless buttgent smelling liquids whereas the higher members aromatic acid anhydrides are colorless compd.

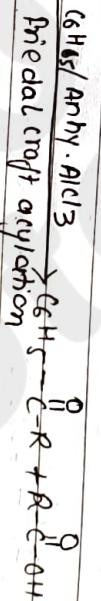
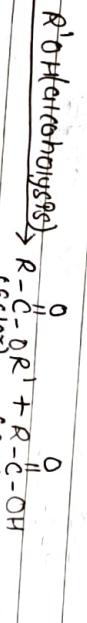
2. Solubility :- Acid anhydride are sparingly (slightly) soluble in water but readily soluble in organic solvents.

3. Boiling point :- Acid anhydride have higher boiling point than that of corresponding acids due to bigger molecular size and molecular mass.

Chemical properties :-

1. Acid anhydrides are less reactive than acid chlorides towards nucleophilic substitution reaction. It is because the +ve char ge on the acyl carbon of acid anhydride is decreased by resonance as follows:-

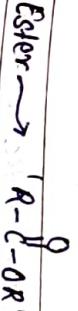




Uses :-

1. Acryl anhydrides are used as acylating agent. They are better acylating agents than acyl chloride because the reactions are not vigorous and can be easily controlled.

[R]



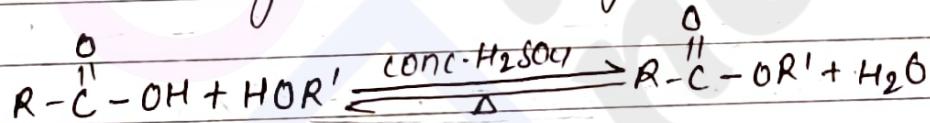
Nomenclature:-

Ester's are named by replacing suffix -oic acid of the common name by ester. carboxylic acids with 'ate' and adding the name of acyl before it.

Formula	Common name	IUPAC name
$\text{H}-\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_2\text{H}_5$	Ethyl formate	Ethyl methanoate
$\text{CH}_3-\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_2\text{H}_5$	Ethyl acetate	Ethyl ethanoate
$\text{CH}_3-\text{CH}_2-\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_2\text{H}_5$	Ethyl propionate	Ethyl propanoate
$\text{CH}_3-\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OCH}_3$	Methyl acetate	Methyl ethanote
$\begin{matrix} \beta & \text{CH}_3 & \text{O} \\ & & \\ \text{CH}_3 & -\text{CH} & -\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_2\text{H}_5 \\ & 2 & 1 \end{matrix}$	Ethyl α -methyl propionate	Ethyl -2-methyl propanoate
$\text{C}_6\text{H}_5-\overset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OC}_6\text{H}_5$	phenyl benzoate	phenyl benzoate

Preparation:-

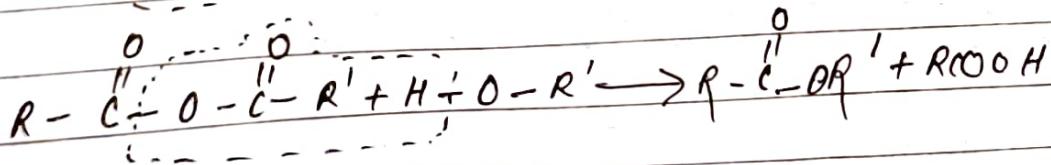
1. When carboxylic acid is heated with alcohol in the presence of conc. H_2SO_4 gives ester (esterification)

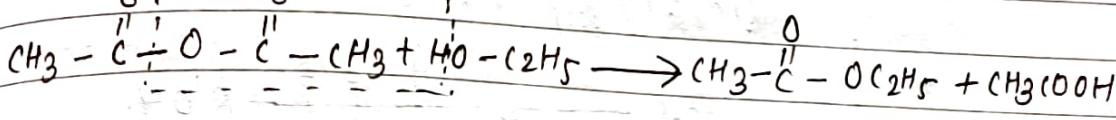
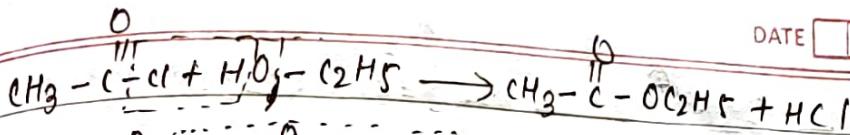


e.g.

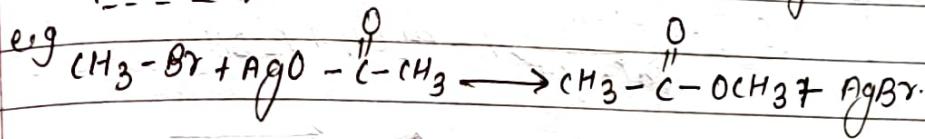
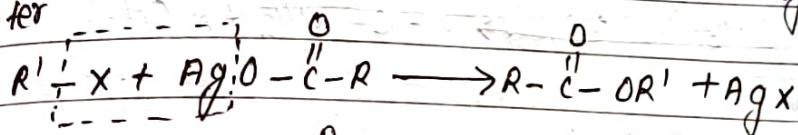


2. When acid chlorides or acid anhydrides are treated with alcohol gives ester.





3. When haloalkane is heated with silver salts of carboxylic acid gives ester



Properties:-

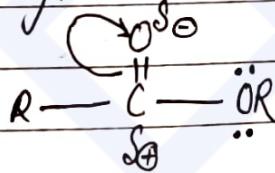
1. Physical state :- Esters are colorless liquids or solids with characteristic pleasant fruity smell.

Ethyl butanoate \rightarrow Pineapple.

Octyl ethanate \rightarrow Orange.

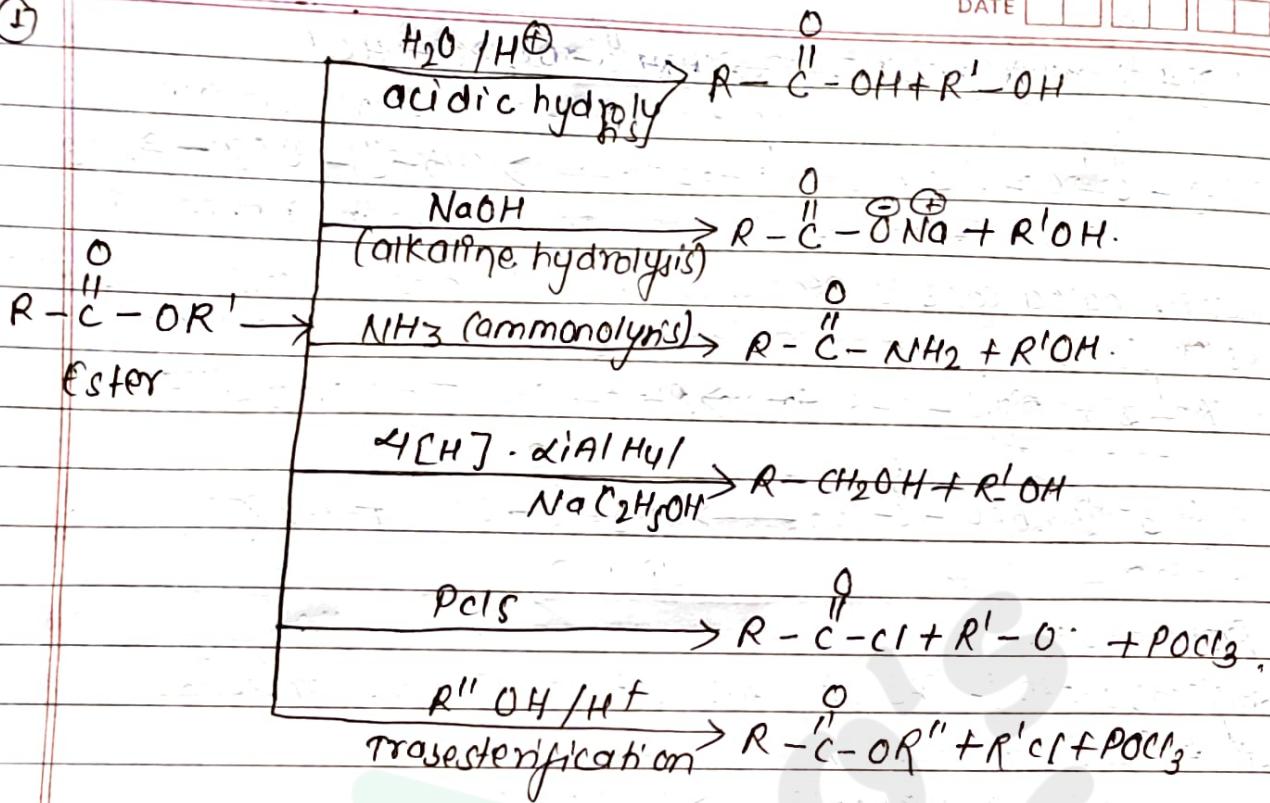
2. Solubility :- Esters are sparingly soluble in water but readily soluble in organic solvent.

3. Bpt :- They have lower boiling point as compare to that of corresponding carboxylic acids i.e due to absence of intermolecular bond.

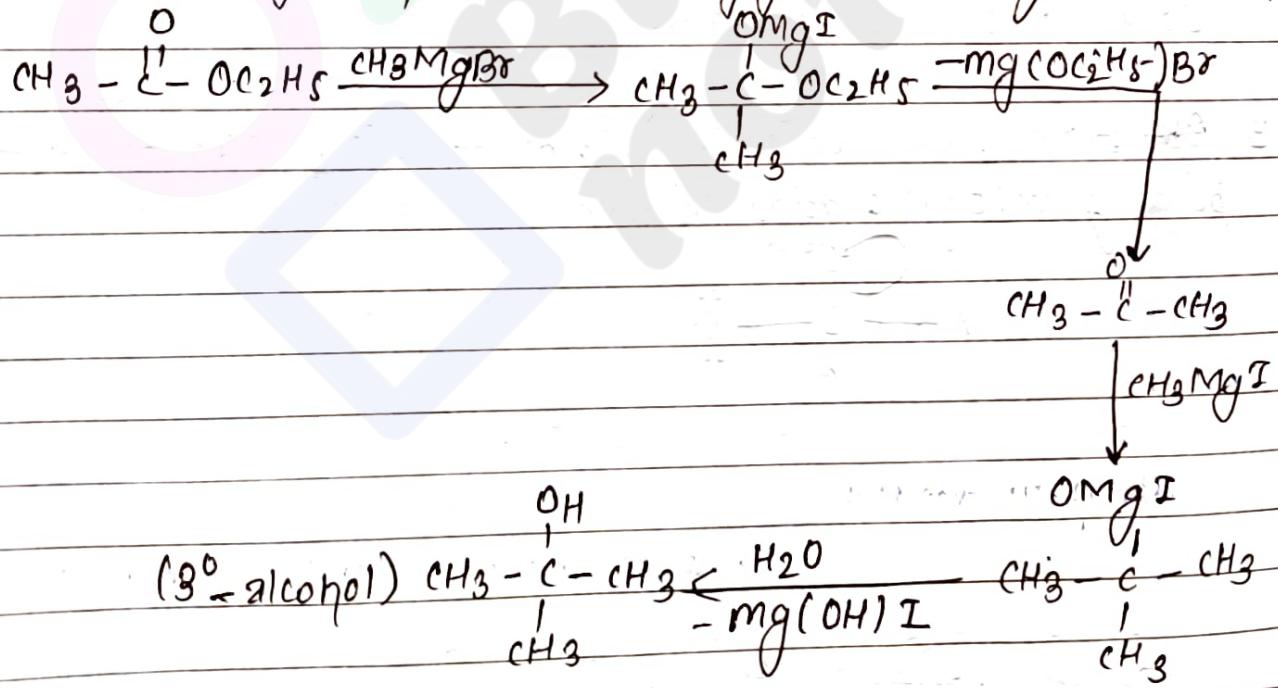


P.T.O.

(1)

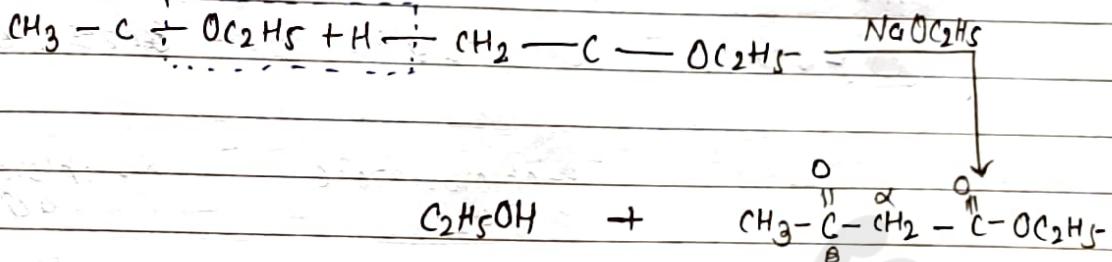


(2) Reaction with Grignard's reagent → when esters except ester of formic acid reacts with Grignard reagent to give tertiary alcohol as final product. Esters of formic acid gives 2° alcohol.



③ Claisen's condensation → when ester's ha

When ester's having α -hydrogen atom undergoes self condensation in the presence of strong base sodium ethoxide gives β keto ester. This reaction is known as Claisen's condensation.



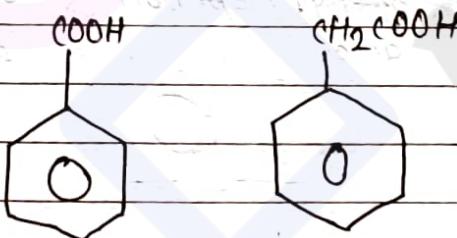
Ethyl acetoacetate (β -ketoester)

Uses:-

- 1) As industrial solvents for paints, OPIs, jet resins etc.
- 2) In the preparation of artificial flavours & essences.

Aromatic carboxylic acid

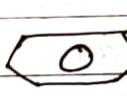
In aromatic carboxylic acids the COOH group is either linked to benzene ring or to the side chain of the benzene ring.



Nomenclature:-

Aromatic carboxylic acids in which the $-\text{COOH}$ groups are directly linked to benzene ring or to the side chain are named as derivatives of Benzoic acids, both in common and IUPAC system.

Some carboxylic acids may have their special common name also, but aromatic carboxylic acids in which the -COOH group are present on the side chain are known as phenyl derivatives of aliphatic acids.

Formula	Common Name	IUPAC Name
	Benzoic acid	Benzoic acid
c1 	p-chlorobenzoic acid	4-chlorobenzoic acid
	o-hydroxybenzoic acid (Salicylic acid)	o-hydroxybenzoic acid
	o-methylbenzoic acid	o-methylbenzoic acid
	Phenyl acetic acid	phenylethanolic acid
	β -phenylpropanoic acid	β -phenylpropanoic acids

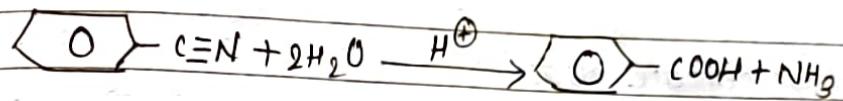
Benzoyl Benzoic acid

* Preparation of Benzoyl acids (C_6H_5COOH)

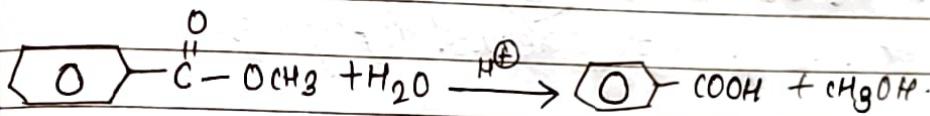
- When benzyl alcohol or benzaldehyde react with acidic potassium permanganate ($KMnO_4$, benzoyl acid is formed)



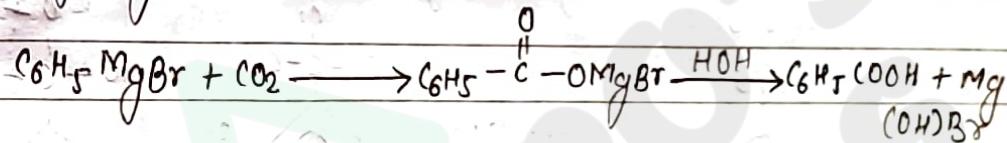
2. When benzonitrile (phenyl cyanide) undergoes hydrolysis with HCl gives benzoic acid.



3. When methyl benzoate undergoes acidic hydrolysis gives benzoic acid.

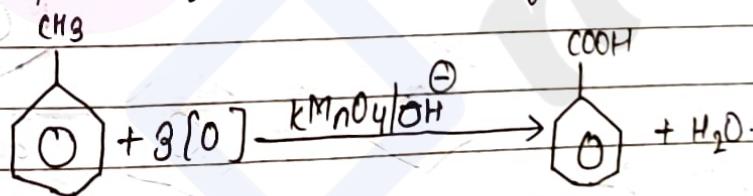


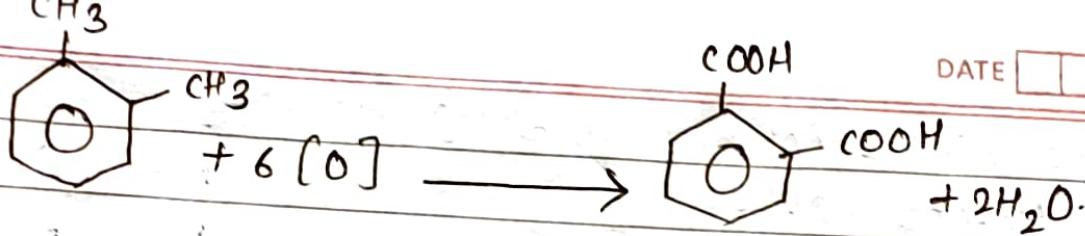
4. When phenyl magnesium bromide reacts with carbondioxide followed by hydrolysis gives benzoic acid.



5. When alkyl benzene reacts with alk. KMnO_4 benzoic acid is formed.

In this process the alkyl group is oxidised to $-\text{COOH}$ irrespective of the nature & length of the alkyl group.



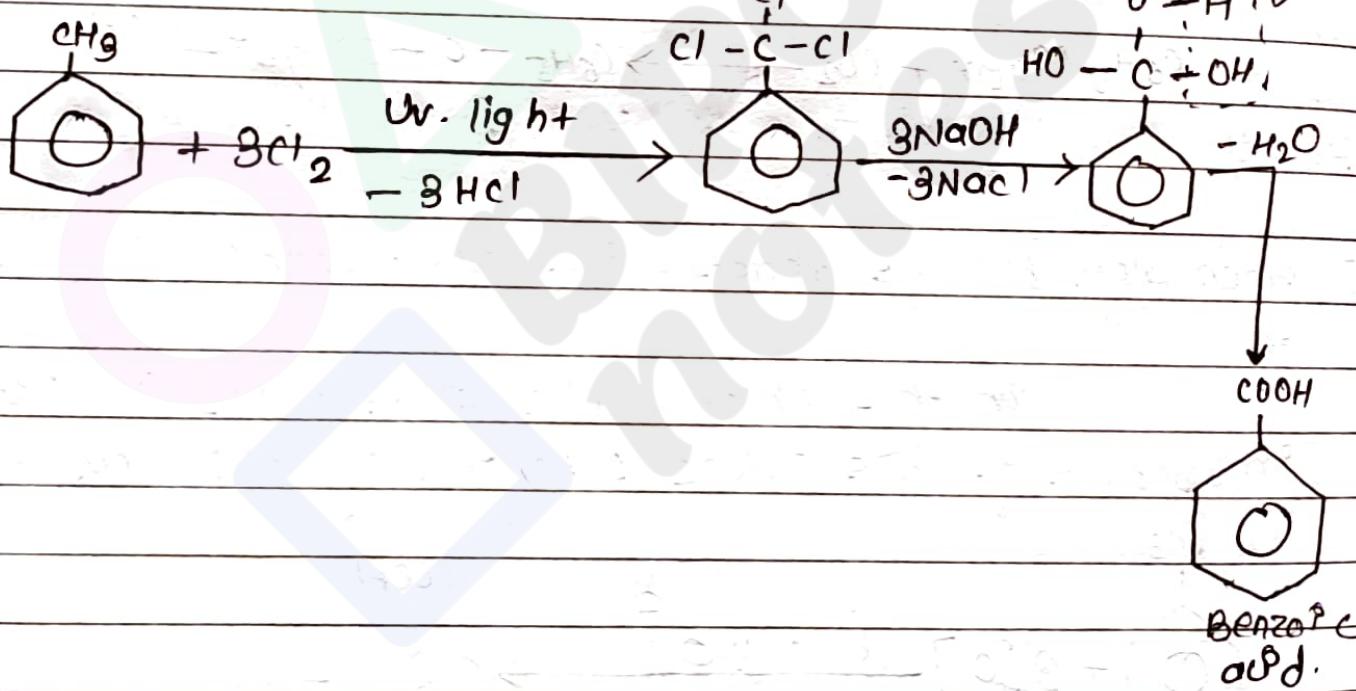


Uses of benzoic acid:-

- 1) As food preservative
- 2) Lab reagent.
- 3) In the manufacture of dyes, drugs etc.
- 4) Methyl & ethyl benzoates are used as perfumes.

Industrial preparations:-

When toluene is boiled with bubbling Cl gas in the presence of UV light and alkaline hydrolysis give benzoic acid.



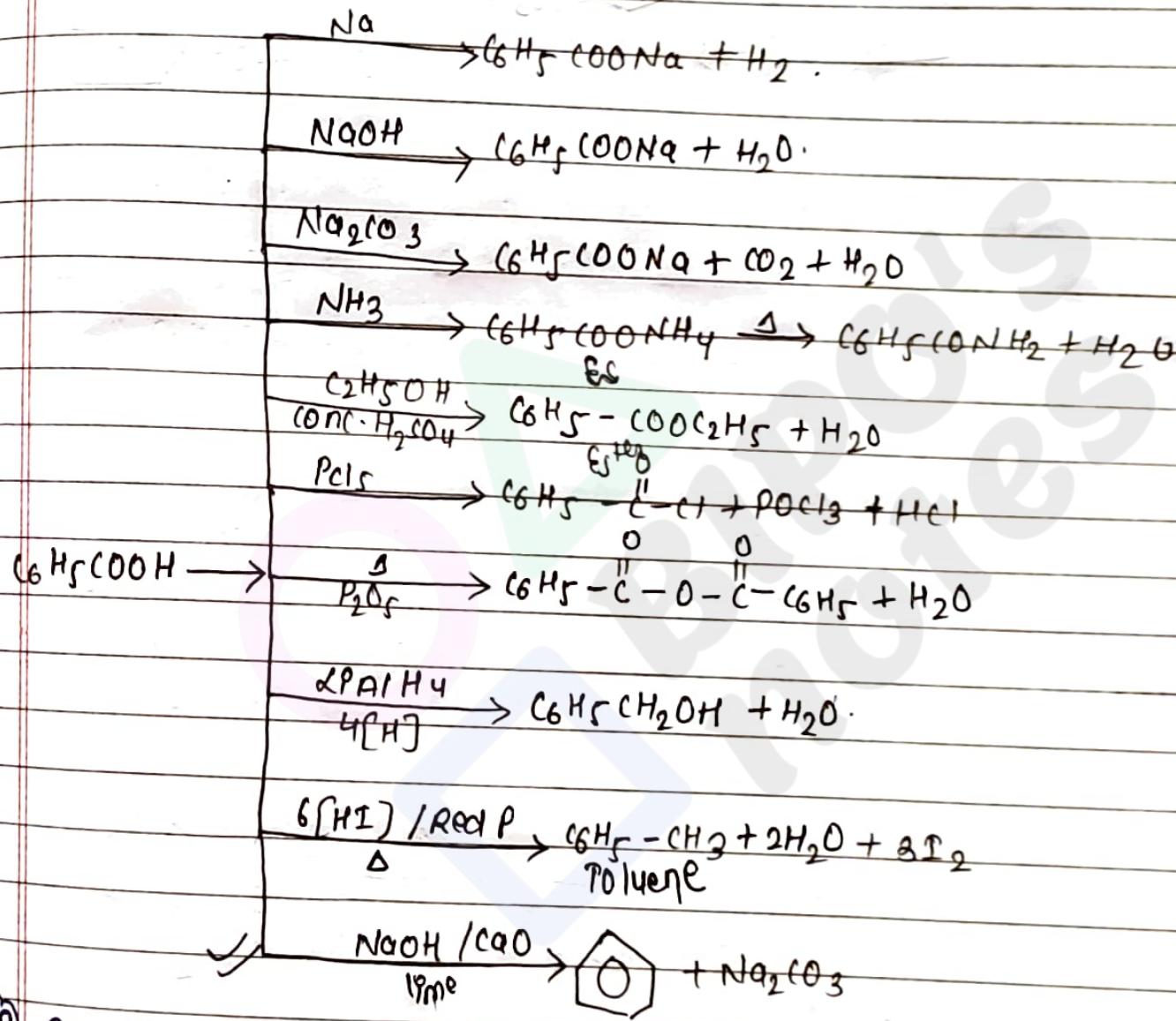
Physical properties:-

1. colourless crystalline solid.
2. It is slightly soluble in water but readily soluble in organic solvent.
3. It sublimes on heating.

chemical properties

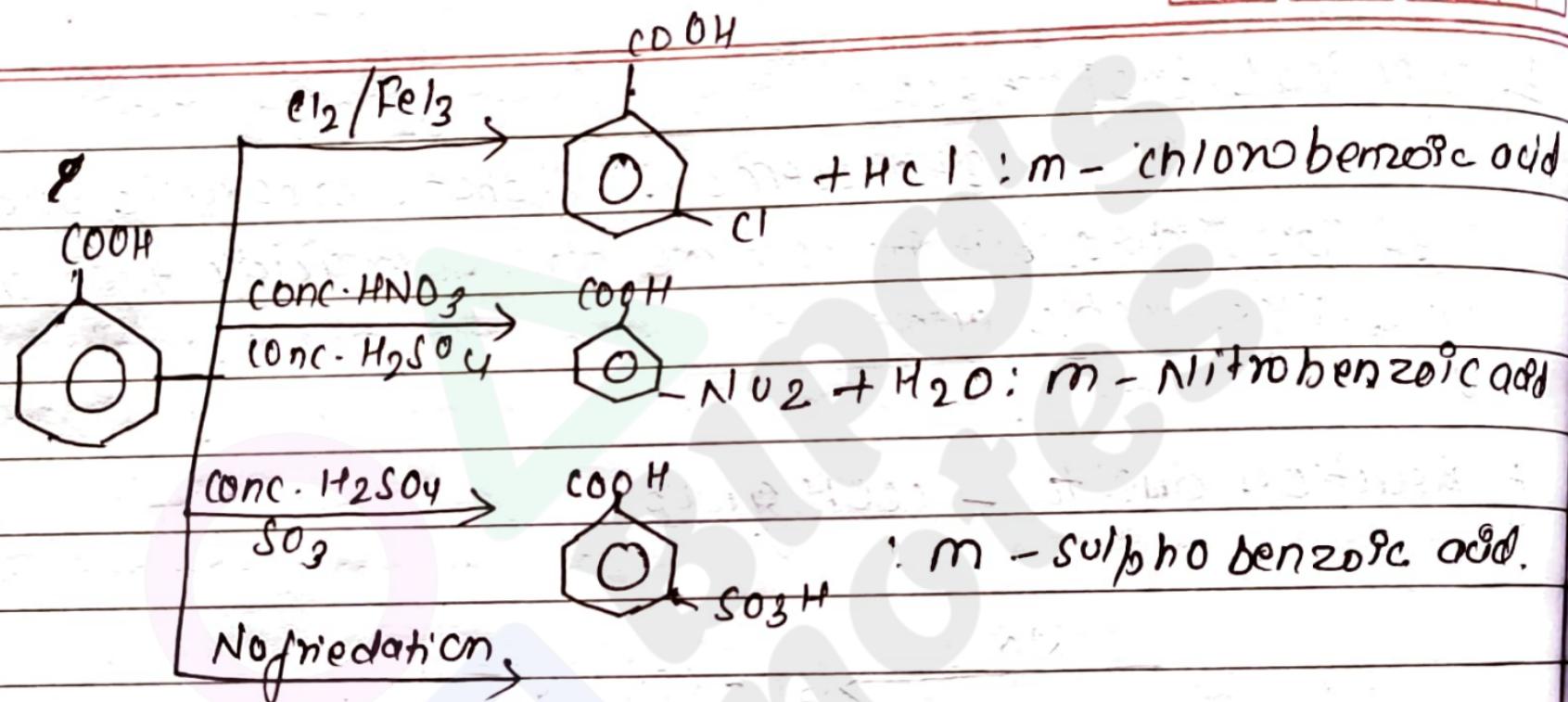
It resembles aliphatic carboxylic acids in its chemical properties but it is more stronger acid than aliphatic carboxylic like acetic acids.

(A) Reaction due to -COOH group.



(B) Reaction due to benzene ring \rightarrow The -COOH group is an electron withdrawing group, hence it deactivates the benzene ring and gives meta-products during electrophilic substitution rxn.

fig of R-S & R-HS (Resonance hybrid structure)



Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.

Folders

Name ↑

 Biology	 chemistry
 English	 maths
 Nepali	 Physics



Feedbacks:

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