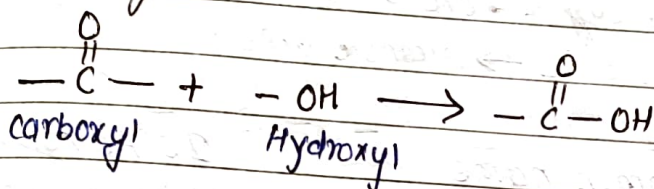


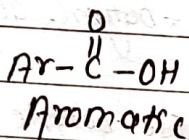
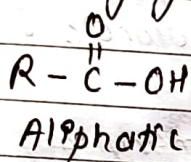
## # Carboxylic acids #

DATE

Introduction → Organic compounds having one or more carboxyl group  $(-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH})$  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 up on 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.

1# Nomenclature →

↓ Common System →

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

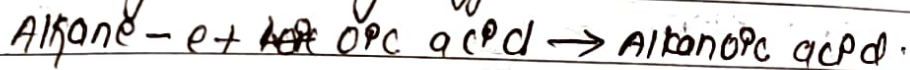
•  $\text{HCOOH}$  :- Named as formic acid, because it was first obtained by the distillation of formica (ants)

•  $\text{CH}_3\text{COOH}$  :- Named as acetic acid because it was obtained from aceto m (vinegar)

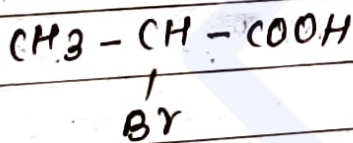
•  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  → Named as butyric acid because it was obtained from butyrum (butter).

2) IUPAC system →

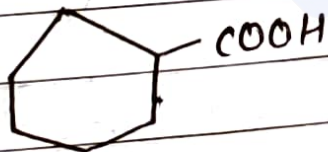
In this system carboxylic acids are known as alkan-  
oic acid. The name is obtained by replacing terminal 'e' of the  
corresponding alkane by suffix 'oic acid'.



| Formula  | Common name      | IUPAC name              |
|--|------------------|-------------------------|
| $\text{HCOOH}$   | Formic acid      | Methanoic acid          |
| $\text{CH}_3\text{COOH}$   | Acetic acid      | Ethanoic acid           |
| $\text{CH}_3\text{CH}_2\text{COOH}$  | Propionic acid   | Propanoic acid          |
| $\text{CH}_3\text{CH}_2\text{COOH}$  | n-butyric acid   | Butanoic acid           |
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{CH} - \text{COOH} \end{array}$ | ISO-butyric acid | d-methyl propanoic acid |
| $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$                    | n-valeric acid   | pentanoic acid          |

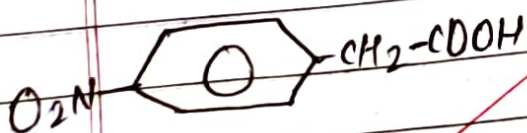


$\alpha$ -Bromo propanoic acid.



cyclohexane

carboxylic acid.

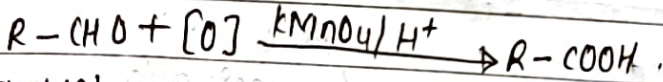


p-nitro benzoic acid.

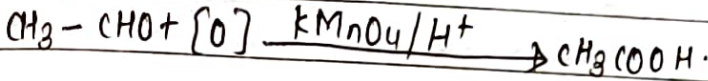
# General Methods of monocarboxylic acids.

1. From aldehydes → By this oxidation of aldehydes with acidified  $KMnO_4$  or  $K_2Cr_2O_7$ .

General reaction:-

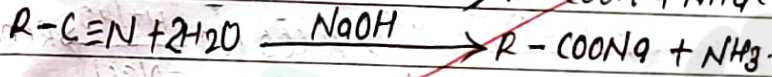
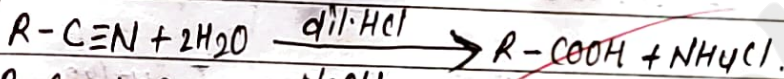


Example:-

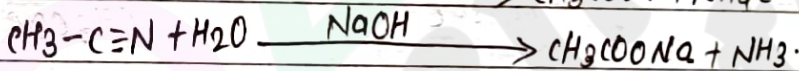
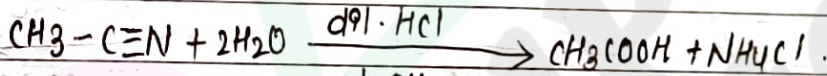


2. From nitriles → By the hydrolysis of alkyl cyanides with dilute acid or alkali gives carboxylic acids.

G.R

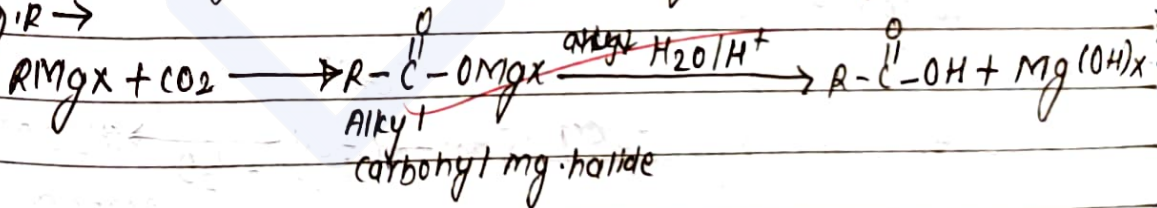


Example

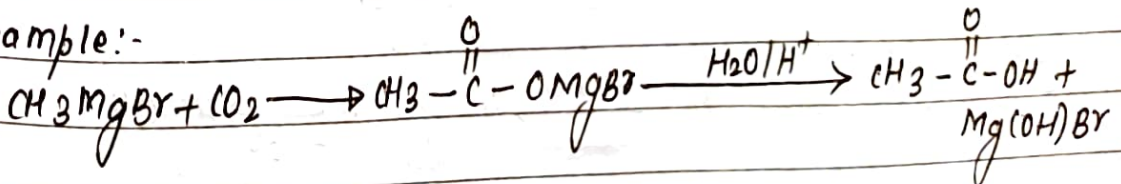


3. From Grignard reagents → By carbonation of Grignard reagent - when  $CO_2$  is passed through ethereal solution of Grignard reagent an addition compound is formed which on hydrolysis gives carboxylic acids.

G.R →



Example:-



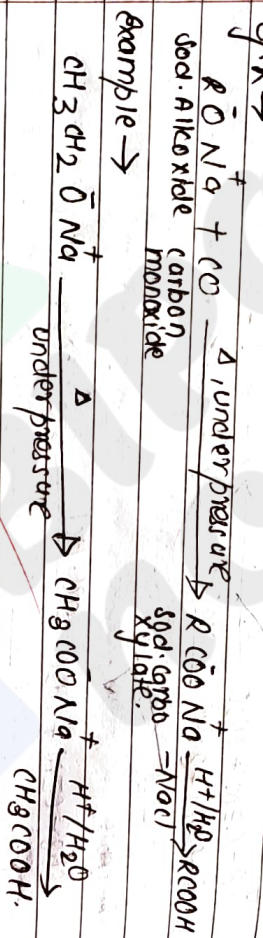
4.

From dicarboxylic acids  $\rightarrow$  By heating dicarboxylic acid in which both carboxyl group is linked to the same carbon atom.



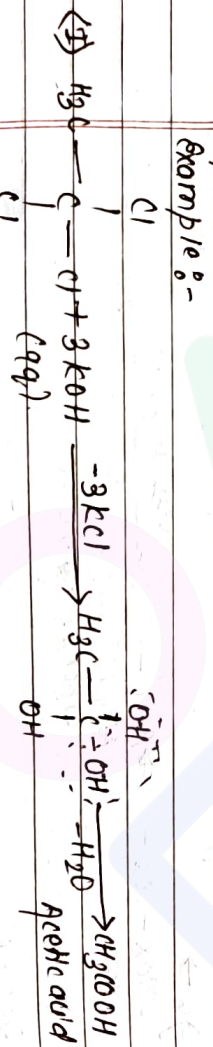
5.

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

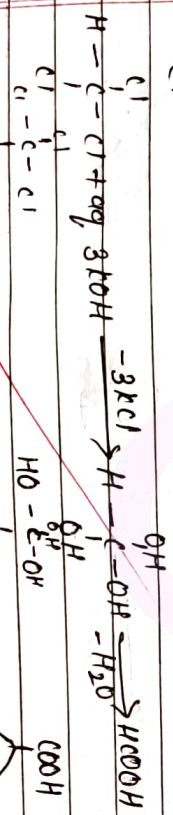


6.

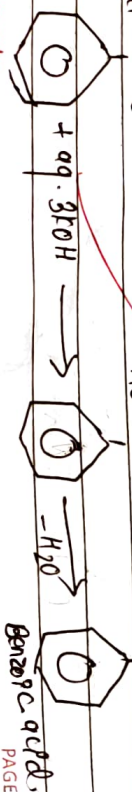
From trihaloalkane  $\rightarrow$  By hydrolysis of trihaloalkane in which all halogen atoms are linked to the same carbon with aqueous alkalis.



(II)



(III)



classmate

# Physical properties  $\rightarrow$ 1. Physical state  $\rightarrow$ 

1st three members  $\rightarrow$  colorless pungent smelling liquid  
 4th - 6 members  $\rightarrow$  oily liquid with pleasant odour.  
 The rest are colorless and odourless waxy solids.

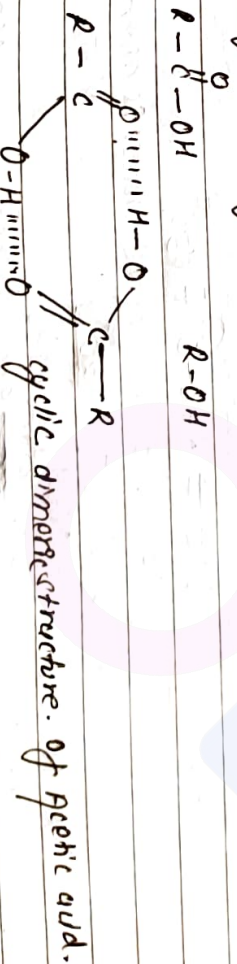
u. mp

g. Boiling point  $\rightarrow$  Carboxylic acids have higher boiling point than that of alcohols of comparable molecular mass. For ex. Acetic acid at  $118^\circ\text{C}$  and propanol boils at  $97^\circ\text{C}$  although they have same molecular mass.  
 60. The reasons are  $\rightarrow$

$\rightarrow$  The -OH bond of carboxylic acids is more strongly polarised than that of alcohol due to presence of carbonyl group adjacent to it. Hence carboxylic acids form stronger H-bond compared to alcohols.

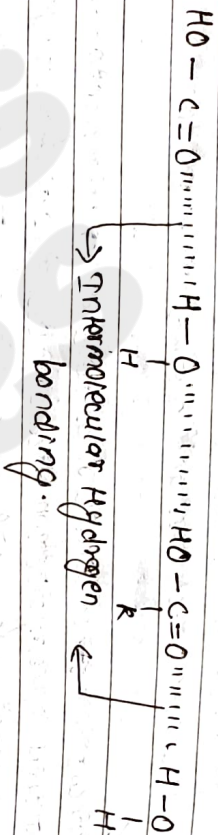


$\rightarrow$  The alcohol can form H-bonding only through -OH group but carboxylic acids can form H-bondings through -OH group and carbonyl group leading to the dimeric structure. Hence the observed molecular mass being double the actual molecular mass. Hence it makes carboxylic acid higher boiling than alcohol.



$\rightarrow$  The boiling point of high aliphatic and aromatic carboxylic acid increases with increase in molecular size due to a corresponding increase in Vander waals force of attraction.

3. Solubility: 1st 4-member are soluble in water due to formation of intermolecular H-bonding with water molecules.

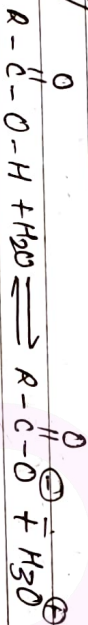


→ The solubility in water decrease with increase in the size of alkyl groups. All carboxylic acid are soluble in organic solvents.

## # Chemical properties →

1. Acidic nature → reactions due to H-atoms of the -OH group 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 acid is dissolved in water it ionizes to give carboxylate anion and hydrogen ions. These ions are in dynamic equilibrium with the carboxylic acid molecules.



The equilibrium constant for the process is given by

$$K_{eq} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

Water is present in large excess therefore it's concentration is taken as constant.

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



where  $K_e$  = Ionization constant or acid dissociation constant.

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

or  $pK_a = -\log K_a$ .

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

⑧ Resonance stabilization → In aqueous solution the ions are in equilibrium with the undissociated acid molecule.



The carboxylic acids are stabilized by resonance as follows:-



The positive charge on the oxygen of the -OH group of acids makes the release of H-atoms as hydrogen ion easier. Hence, carboxylic acids are acidic in nature.

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



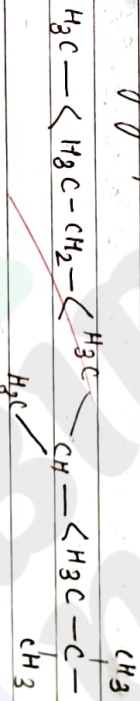


use e-density & height of O-atom of -OH group and cannot built the bond electron pair strength and H<sup>+</sup> cannot be release.



∴ Hence formate or formic acid is more stronger acid than are the acid.

→ The electron releasing effect of alkyl group is described as +I effect. The effect alkyl group increase in this order:-



Therefore, the acid strength carboxylic acids increase in the

Order:-



∴ 2,2-dimethyl propanoic acid.

→ The electron withdrawing group such as Halogen, -NO<sub>2</sub>, -CN etc increase the acid strength of the carboxylic acid. It decreases electron density at the O-atom of -OH group and more release of H<sup>+</sup> ion easier.

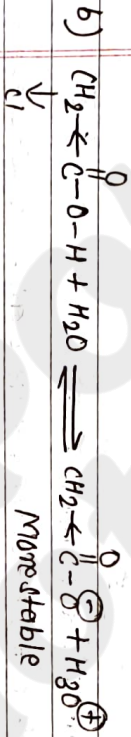
It stabilizes the carboxylate anion by the dispersal of neg<sup>ve</sup>

five change.  
For eg:-

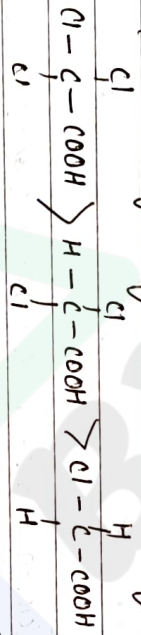
Consider acetic acid and monochloro-acetic acid.



These -Cl atom makes the release of H<sup>+</sup> ion easier.

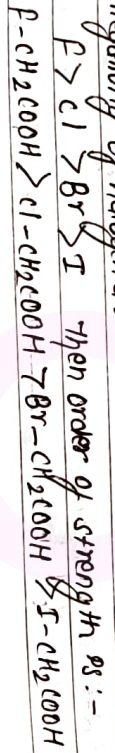


9) The acid strength of carboxylic acids increases with increase in the number of halogen atoms. That's why

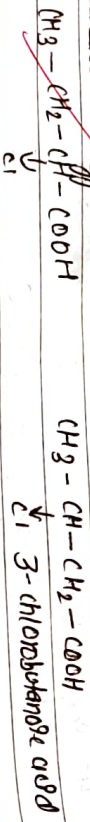


$\text{p}^{\text{p}}$ -chloroacetic acid       $\text{d}^{\text{I}}$ -chloroacetic acid      Mono-chloroacetic acid.

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

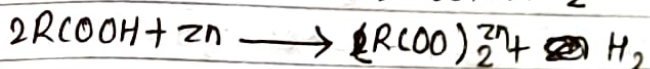
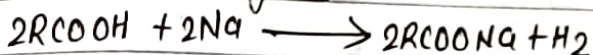


11) The acid strength of carboxylic acid decreases with increase in distance of the electron withdrawing group from -COOH group due to decrease in  $\text{p}^{\text{p}}$  effect.

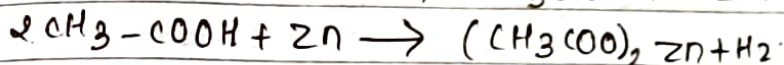
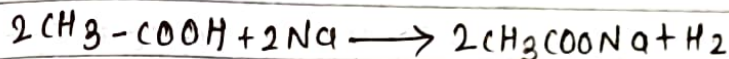


$\text{p}^{\text{p}}$ -chlorobutanoic acid       $\text{m}$ -chlorobutanoic acid  
 $\text{m}$ -chlorobutanoic acid       $\text{p}$ -chlorobutanoic acid  
 $\text{Cl}$        $\text{Cl}$        $\text{Cl}$        $\text{Cl}$

(A) Reaction with Metals  $\rightarrow$  Carboxylic acids reacts with metals Zn, Na, K etc to liberate  $H_2$  gas.



Example-

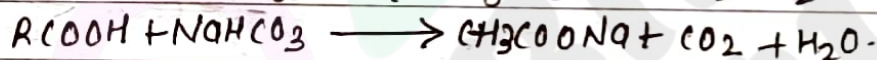
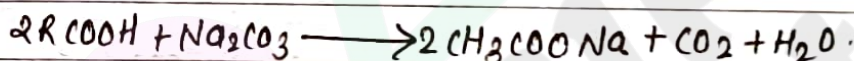


(B) Reaction with alkali  $\rightarrow$  Carboxylic acids reacts with alkali to give salt and water.



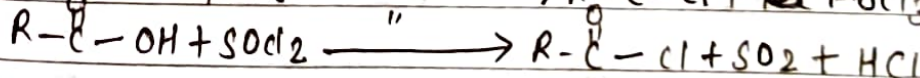
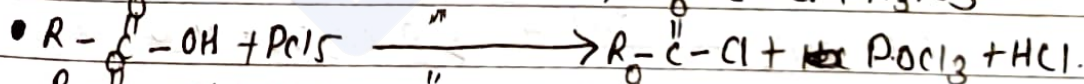
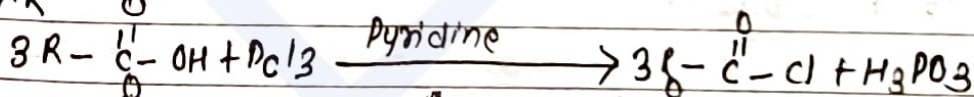
(C) Reaction with carbonates and bicarbonates  $\rightarrow$  carboxylic acids give carbon dioxide gas from carbonates and bicarbonates.

G.R

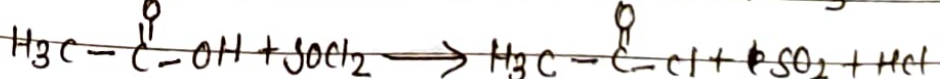
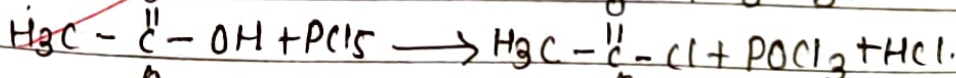
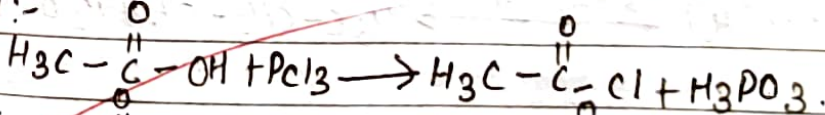


(D) Reaction with  $PCl_3$ ,  $PCl_5$  or  $SOCl_2$   $\rightarrow$  Carboxylic acid reacts with  $PCl_3$ ,  $PCl_5$ ,  $SOCl_2$  to give acid chloride.

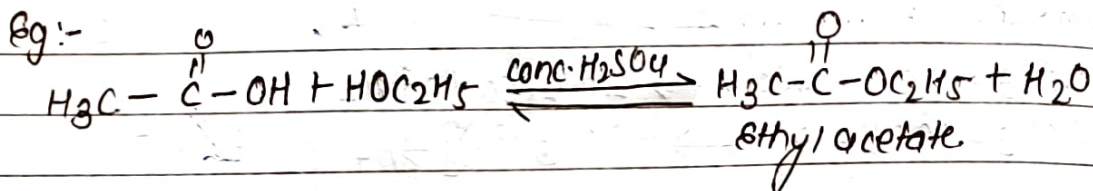
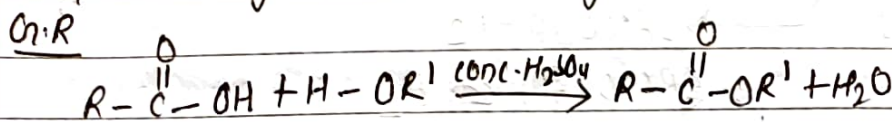
G.R



eg:-

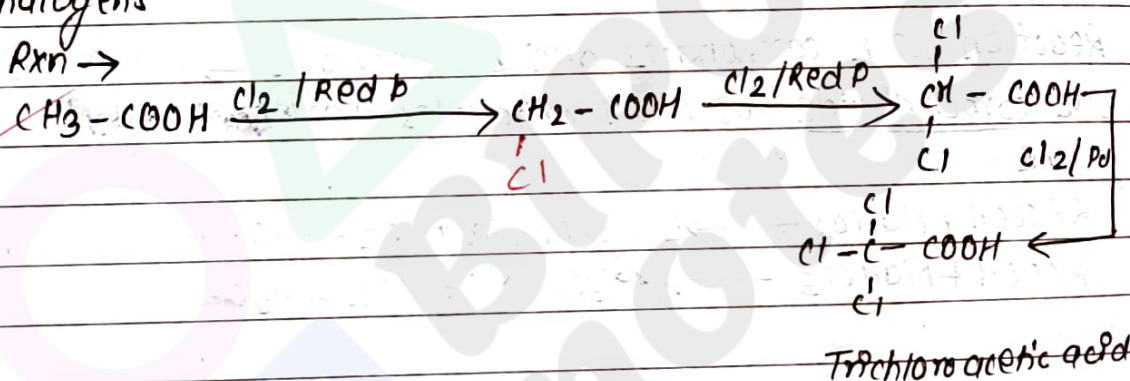


(E) Esterification reaction  $\rightarrow$  Carboxylic acids reacts with alcohol in the presence of conc.  $H_2SO_4$  to form ester.

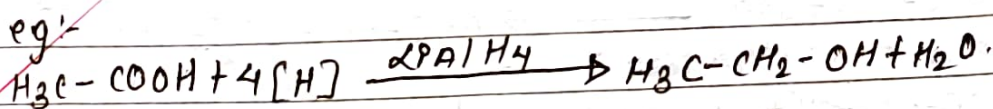
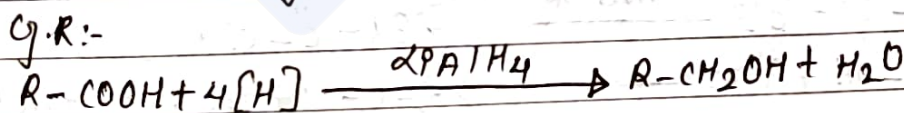


(F) Halogenation reaction  $\rightarrow$  (Hell Volhard Zepinsky reaction) or HVZ reaction

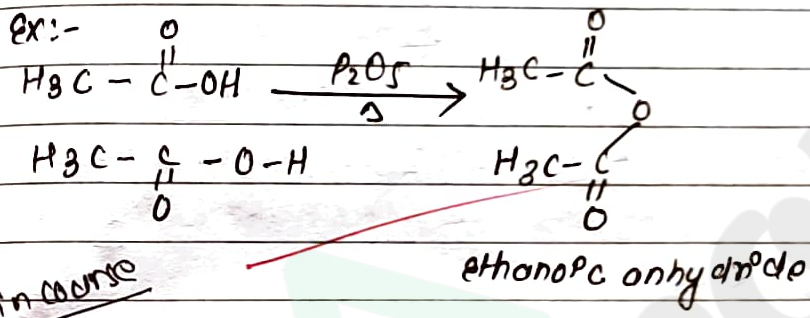
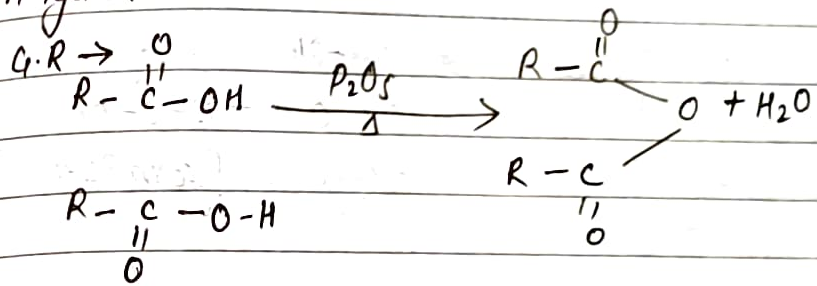
carboxylic acids when treated with chlorine or bromine in the presence of red phosphorus the  $\alpha$ -H atoms are replaced by halogens.



(G) Reduction reaction  $\rightarrow$  with  $\alpha$ -AlH<sub>4</sub>:- Carboxylic acids are reduced to alcohol with  $\alpha$ -AlH<sub>4</sub> or H<sub>2</sub> in presence of copper chromate ( $CuCr_2O_7$ ) as catalyst.



H. Dehydration reactions → formation of acid anhydride.  
 Carboxylic acids when heated with  $P_2O_5$  gives acid anhydride.

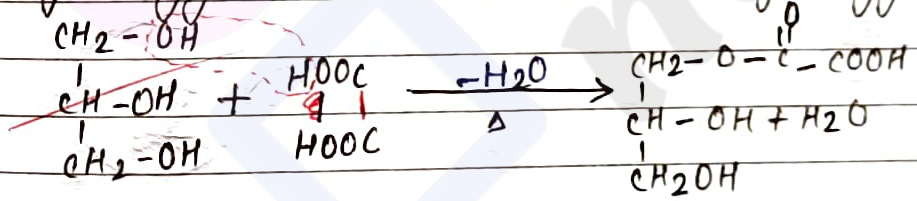


Not in course

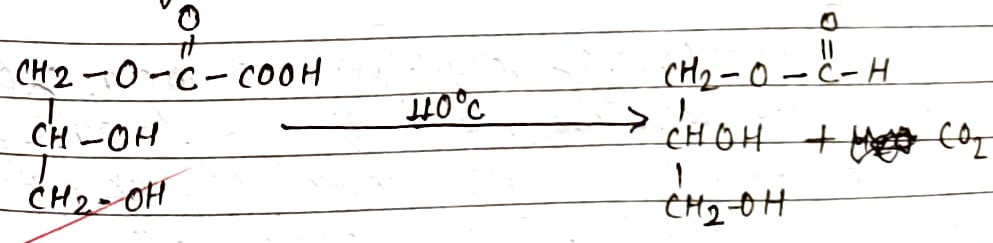
# laboratory preparation of formic acid (methanoic acid)  
 Principle:- theory:-

It is obtained in lab by heating anhydrous glycerol with oxalic acid crystals at  $110^\circ\text{C}$

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



II) Thus formed glycerol monooxalate decomposes at  $110^\circ\text{C}$  to give glycol monoformate and  $\text{CO}_2$ .



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

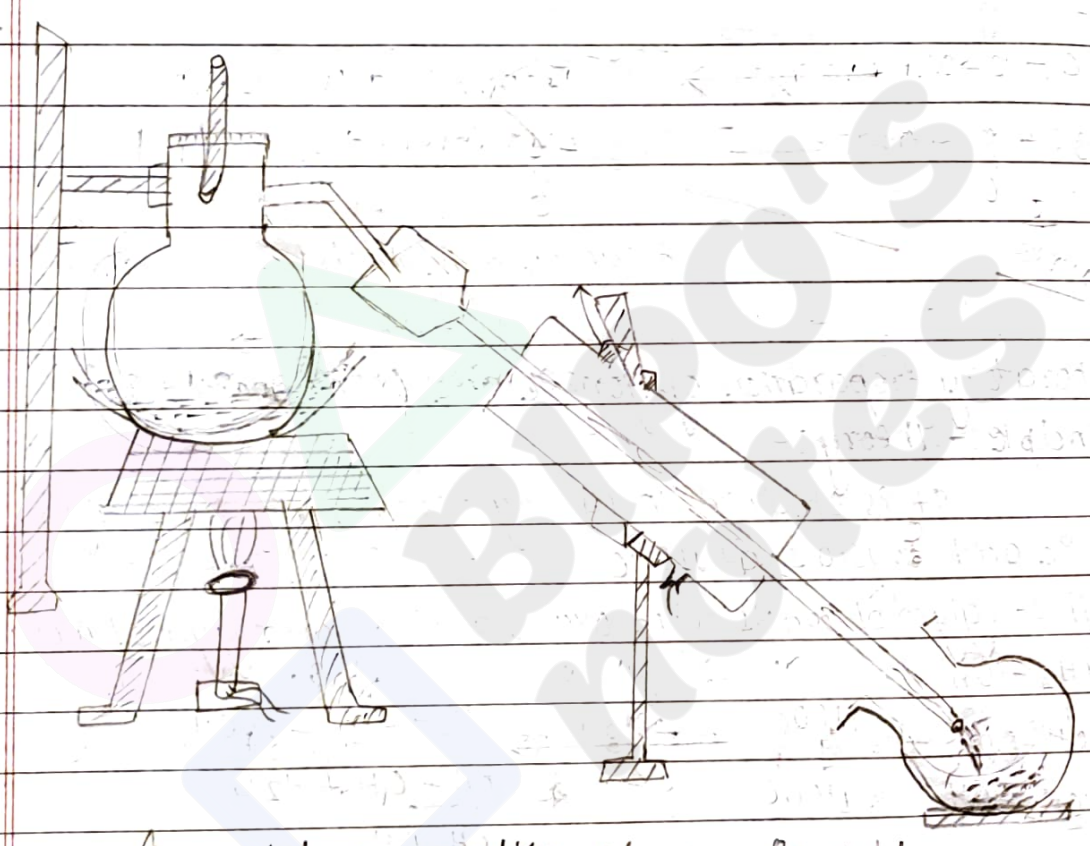
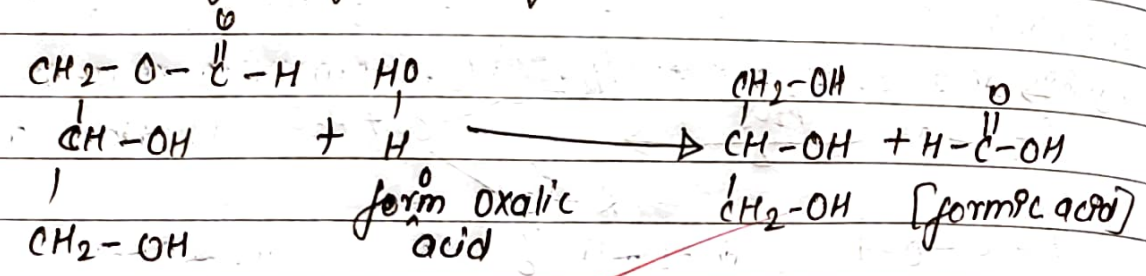


fig:- Lab preparation of formic acid

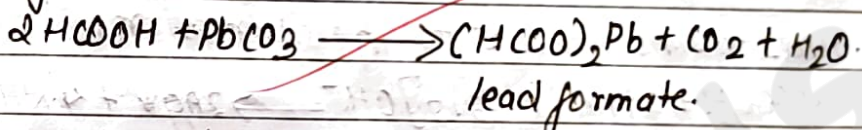
Procedure:-

About 50 ml of anhy. 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<sub>2</sub>. Then the flask is cooled and 40 gm of oxalic acid crystal are

again added and heated at  $110^{\circ}\text{C}$ . The formic acid distill 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 ( $100.5^{\circ}\text{C}$ ). Hence anhydrous formic acid is obtained as follows:-

The aqueous formic acid is neutralized with  $\text{PbCO}_3$  soap; the solution is then evaporated (concentrated) to obtain the crystals of lead formate.



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

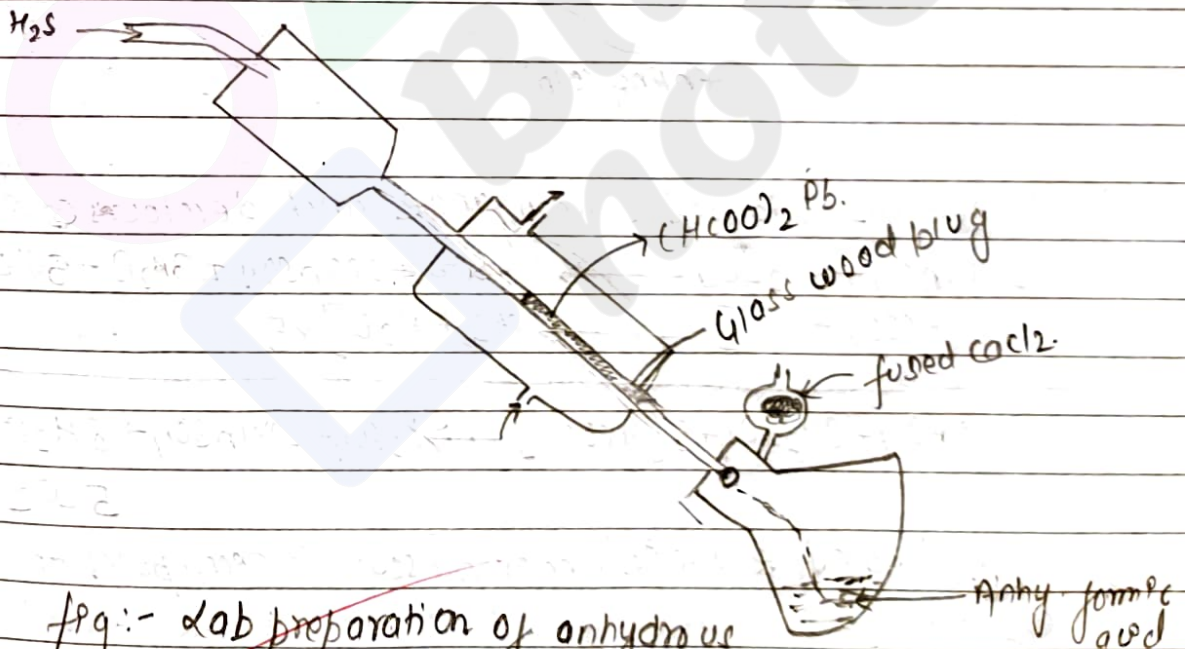
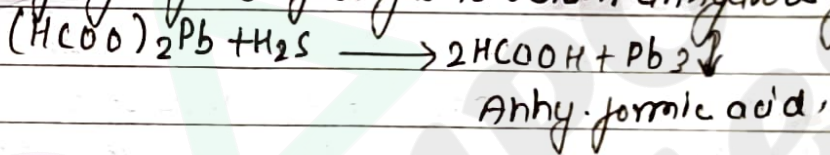


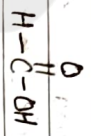
fig:- Lab preparation of anhydrous formic acid.

# Abnormal behaviour of methanoic acids  $\rightarrow$

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



Carboxyl group

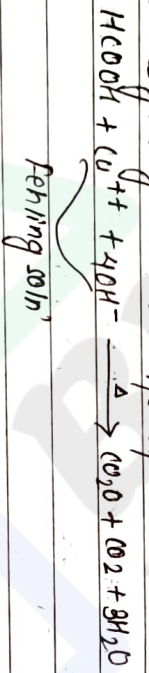


Aldehyde group.

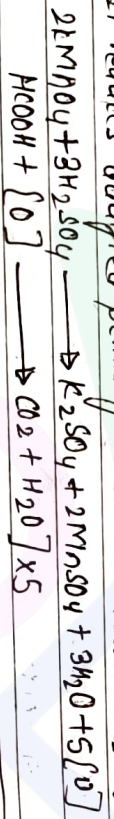
(1) It reduces Tollens reagents to the silver mirror



(2) It reduces Fehling solution to the cuprous oxide



(3) It reduces acidified permanganate and dichromate of



(4) When heated to 160°C under pressure it decomposes to give  $\text{CO}_2$  and  $\text{H}_2$ .

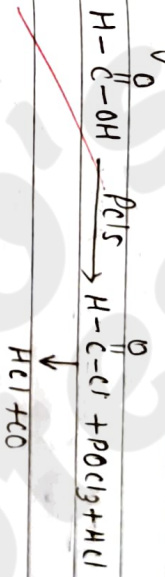




When heated with conc.  $H_2SO_4$  it undergoes dehydration to form carbon monoxide.



It reacts with  $PCl_5$  to give phosgene which decomposes to give carbon monoxide.



### Uses of some carboxylic acids $\rightarrow$

#### Formic acid $\rightarrow$

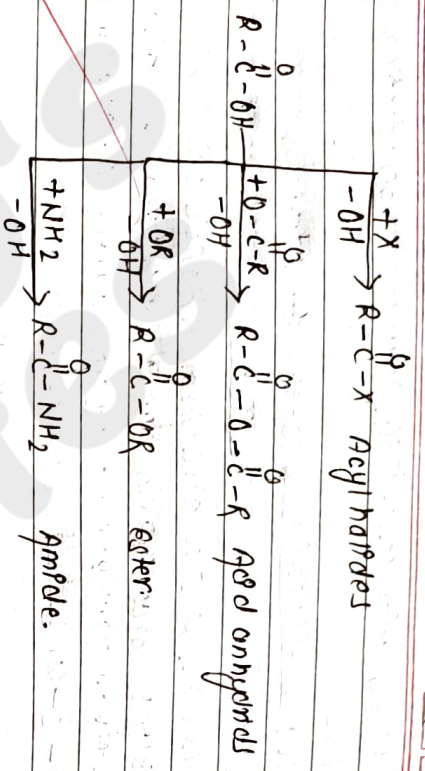
- In the lab preparation of carbon monoxide.
- In medicine.
- $NaO_2$ -salts are used in the hydrogenation of vegetable oil.
- As coagulating agent for latex.

#### Acetic acid $\rightarrow$

- 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 $\rightarrow$

Compounds formed by replacement of -OH group of carboxylic acid by -X, -O-C-R, -OR and -NH<sub>2</sub> are called derivatives of carboxylic acids.



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

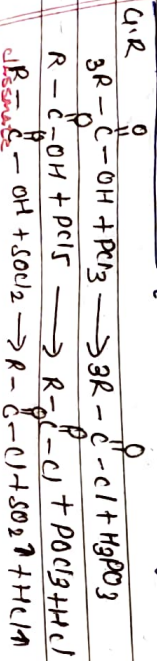
Among the acyl halide acyl chlorides are most reactive and common compounds.

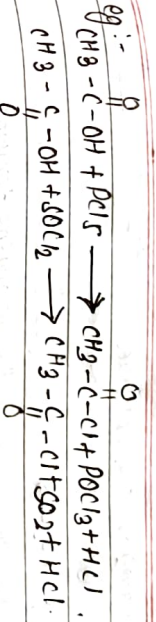
Nomenclature  $\rightarrow$  -e acid replaced by -yl halide.

|   |                                     |                                     |
|---|-------------------------------------|-------------------------------------|
| Formula   | Common name                         | IUPAC name                          |
| $H-\overset{O}{\parallel}{C}-Cl$  | Formyl chloride                     | Methanoyl chloride                  |
| $H_2C-\overset{O}{\parallel}{C}-Cl$   | Acetyl chloride                     | Ethanoyl chloride                   |
| $CH_3-CH_2-\overset{O}{\parallel}{C}-Cl$  | Propionyl chloride                  | Propanoyl chloride                  |
| $\begin{matrix} Cl \\   \\ CH_3-CH-CH_2 \\   \\ Cl \end{matrix} - \overset{O}{\parallel}{C}-Cl$ | $\alpha$ -chloro-propionyl chloride | $\alpha$ -chloro propanoyl chloride |
| $C_6H_5-\overset{O}{\parallel}{C}-Cl$   | Benzoyl chloride                    | Benzoyl chloride                    |

# Preparation  $\rightarrow$

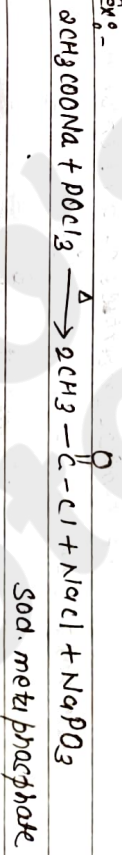
1. Acyl chlorides are obtained by treating carboxylic acids with  $PCl_5, PCl_3$  or  $SOCl_2$ . [good chloro releasing group]



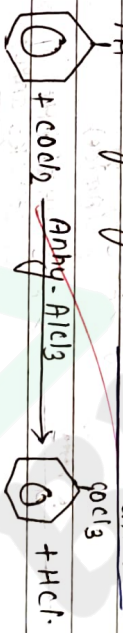


In industrial scale acyl-chloride are obtained by distilling Na- or Ca-salts of carboxylic acids with phosphorus (chloride)  $\text{POCl}_3$  or sulphuryl chloride.

Ex:-



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



**Physical properties** →

1. Physical states → Lower acyl chlorides are colourless liquid whereas as the higher acyl chlorides are colourless solids with pungent smell both.

2. Solubility → Acyl chlorides

↳ dissolves slowly in water due to hydrolysis.  
 → All acyl chlorides are readily soluble in organic solvents.

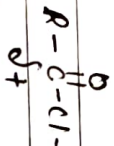
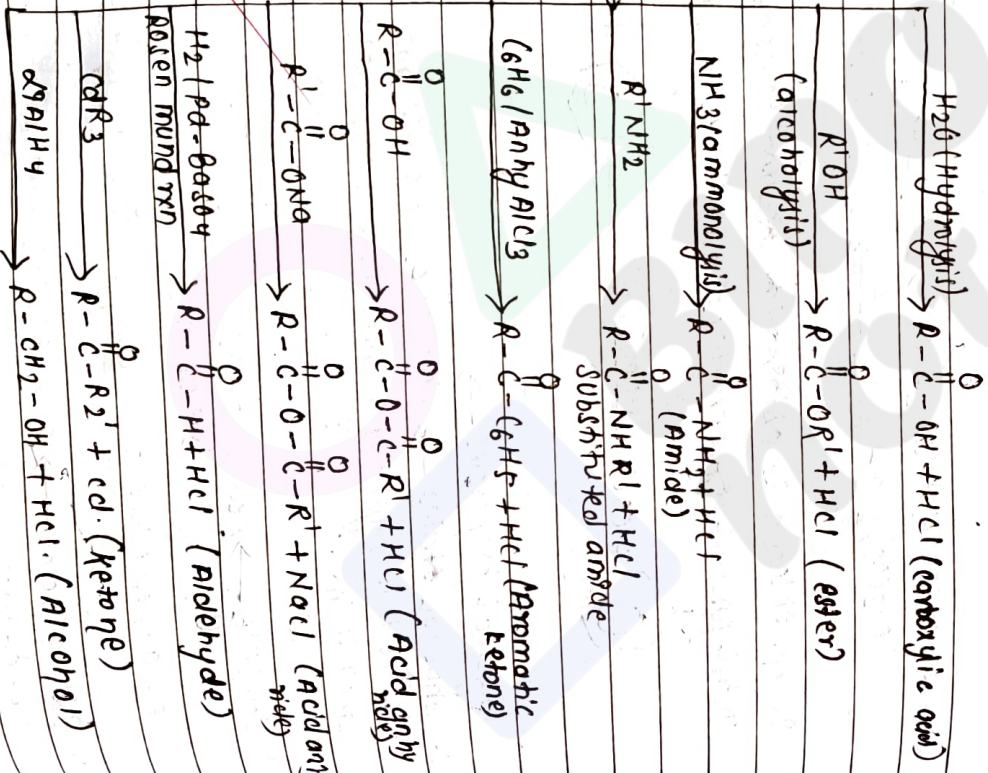
3. Boiling points → Acyl chlorides have lower boiling points than their that of corresponding carboxylic acid. It is due to absence of hydrogen

color H-bonding on acyl chlorides.

Chemical properties →

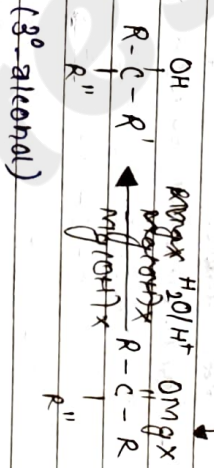
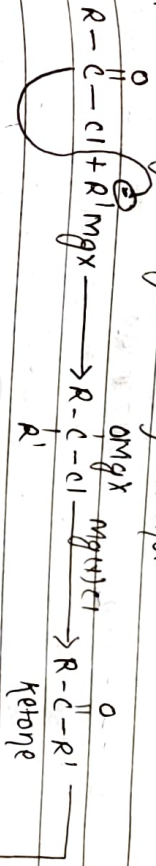
Acyl chlorides are most reactive among the derivatives of carboxylic acids. In acyl chlorides the highly electronegative chlorine atoms are linked to the carbonyl groups. It makes the carbonyl carbon electron deficient. Hence they undergo nucleophilic substitution easily.

The chemical properties of acyl chloride are summarized below:-



~~Answer~~  
classmate

④ Reaction with Grignard reagent → when acid chlorides reacts with Grignard reagent ketone is formed, which further reacts with Grignard reagent to give tertiary alcohol.

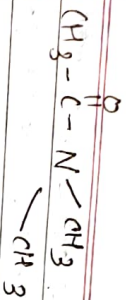


\* Uses of acylhalides:-

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

\* Acid amides → Amides are named by replacing the suffix (o) acid of common name and (o) acids as IUPAC, name of the corresponding carboxylic acid with 'amide'.

| Formula  | Common name       | IUPAC name          |
|--|-------------------|---------------------|
| $H-\overset{\overset{O}{\parallel}}{C}-NH_2$         | Formamide         | Methanamide         |
| $CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2$      | Acetamide         | Ethanamide          |
| $CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-NH_2$ | Propionamide      | Propanamide         |
| $CH_3-\overset{\overset{O}{\parallel}}{C}-NH-CH_3$   | N-methylacetamide | N-methyl ethanamide |



N,N-dimethyl acetamide

N,N-dimethylethanamide



Benzamide

Benzamide

### Preparations:-

1. When ammonium salts of carboxylic acids are heated amides are formed.



e.g.:-

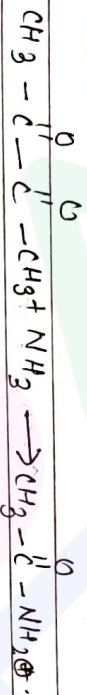
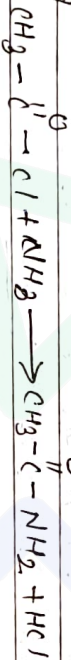


C<sub>6</sub>H<sub>5</sub>.

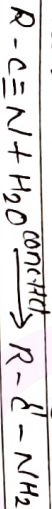
2. When acid chlorides or acid anhydride reacts with ammonia, amides are formed.



e.g.



3. By the partial hydrolysis of alkyl cyanide (alkane nitrile) with conc. HCl



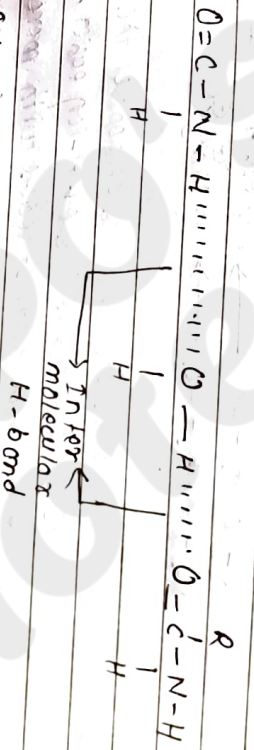
e.g.



### physical properties-

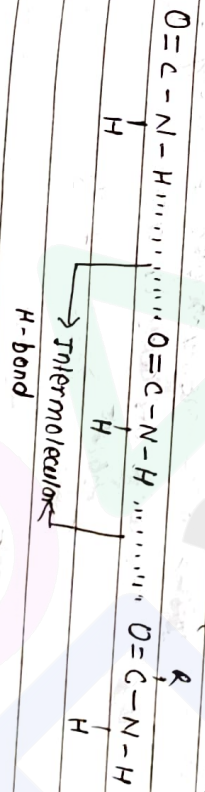
1) physical state- Except formamide all other amides are color less crystalline solids.

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.

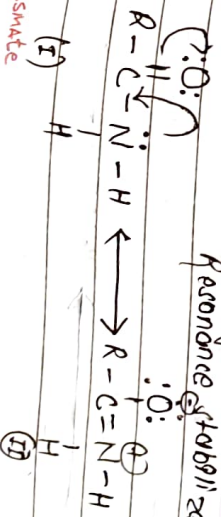
3) Mpt and Bpt → The melting point and boiling point of amide are higher than those expected from their molecular masses. It is due to formation of intermolecular H-bonds between its own molecule



### Chemical properties

→ Amides are least reactive among derivatives of carboxylic acid. It is due to lower pKa of  $\alpha$ -NH<sub>2</sub> bond.

Resonance stabilization of molecule.



classmate

1.

Amphoteric nature  $\rightarrow$  Amides act as weak acids as well as weak bases. Hence they are amphoteric in nature.

DATE

(a) Basic nature: Due to presence of lone pair of electron on the nitrogen atom amide act as bases but they are less basic than amines amines, because according to structure (I) the lone pair is not easily available for protonation. Hence it reacts with strong acids to form salts.



(b)

Acidic nature:  $\rightarrow$  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 ethoxide



Sodium acetamide

(c) Hydrolysis:  $\rightarrow$  Amides are hydrolysed to carboxylic acid when boiled with dil acids or alkalis.



classmate

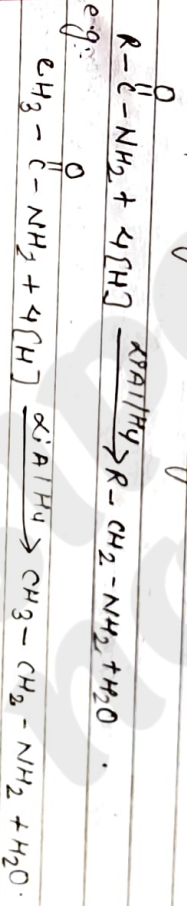
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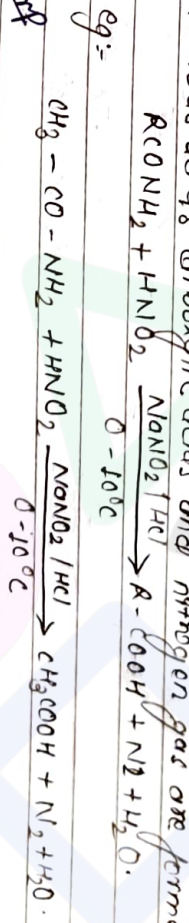
8. Dehydration → when amides are heated with  $P_2O_5$  phosphorus pentoxide gets dehydrated to form alkyl cyanide (alkyl nitrile).



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

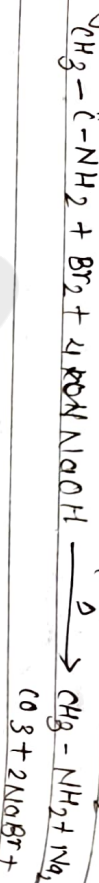
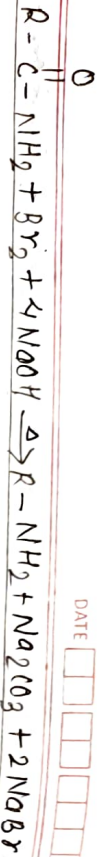


5. Reduction with nitrous acid → when amide reacts with nitrous acid or carboxylic acids and nitrogen gas are formed.



6. Reaction with  $Br_2$  and alkalis → (Hoffmann's bromamide reaction or hypobromamide):-

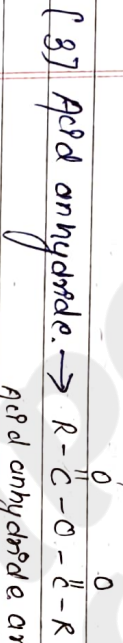
When amides are heated with bromine and alkalis, primary amines are formed having one carbon atom less than that of parent amide. This reaction is called decarboxylation reaction.



Uses:-

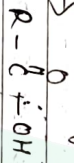
⊕ In the preparation of 1<sup>o</sup> amine.

→ Dimethyl formamide (DMF) and dimethyl acetamide (DMAc) are used as solvent.



-formed from carboxylic acid by the loss of water molecule

Ex:  $R-C(=O)-OH$



+ H<sub>2</sub>O



acid anhydride

Nonperoxide:

Formula common name IUPAC Name

CH<sub>3</sub>-C(=O)-O-C(=O)-CH<sub>3</sub> Acetic anhydride Ethanoic anhydride

C<sub>6</sub>H<sub>5</sub>-C(=O)-O-C(=O)-C<sub>6</sub>H<sub>5</sub> Propanoic anhydride Propanoic anhydride

CH<sub>3</sub>-C(=O)-O-C(=O)-C<sub>2</sub>H<sub>5</sub> Acetic propanoic anhydride Ethanoic propanoic anhydride



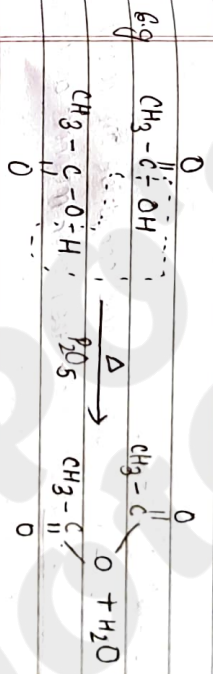
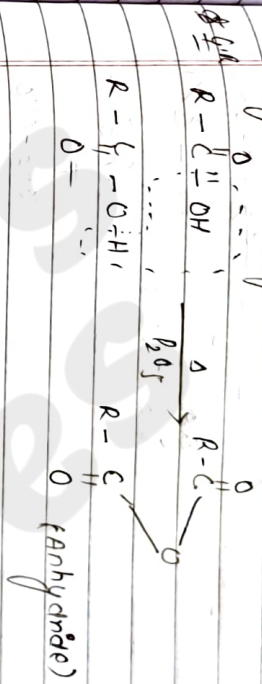
classmate

benzoic anhydride

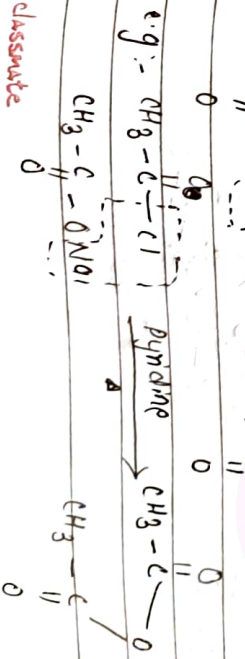
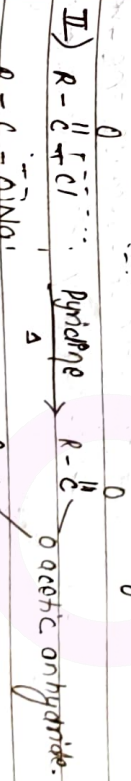
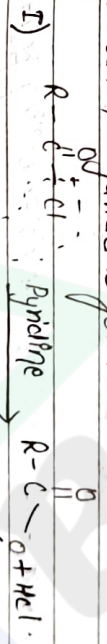
benzoic anhydride

Preparations :->

1. when carboxylic acids are heated in the presence of P<sub>2</sub>O<sub>5</sub>, anhydrides are formed.

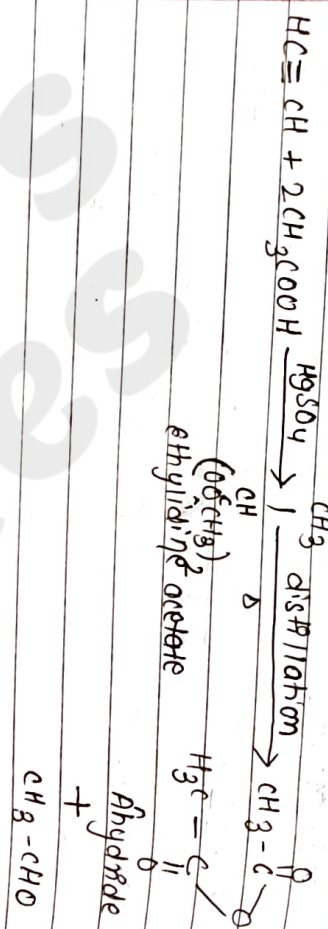


2. When acid chloride is treated with carboxylic acid or its salt, um salt, anhydride is formed.



3) When acyl chloride is treated with acetic acid in the presence of mercury sulfate anhydride is formed.

$R^1R^2$ :-



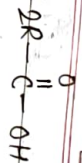
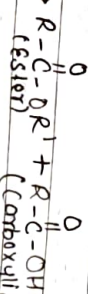
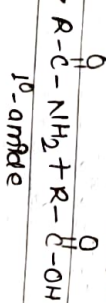
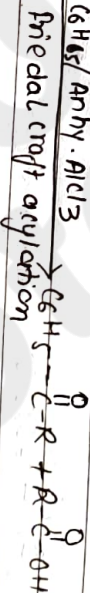
Physical properties:-

1. Physical states:- Lower aliphatic acid anhydride are colorless pungent smelling liquids where as the higher members aromatic acid anhydrides are colorless solids.
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.

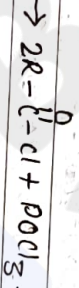
Chemical properties:-

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



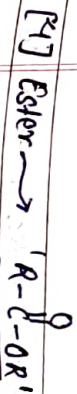
$H_2O$  (Hydrolysis) $R^1O$  (hydrolysis) $NH_3$  (ammonolysis) $R^1-NH_2$  $CH_3Mg/Anhy. AlCl_3$  $PCl_5/H_4$  $P[OH]$ 

Pcls.



Uses:-

1. Acid 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.



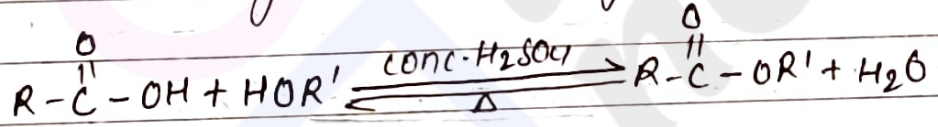
Nomenclature:-

Esters are named by replacing suffix -ic acid of the common and IUPAC name of corresponding carboxylic acids with 'ate' and adding the name of alkyl before it.

| Formula   | Common name                       | IUPAC name                 |
|---|-----------------------------------|----------------------------|
| $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$  | ethyl formate                     | ethyl methanoate           |
| $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$   | ethyl acetate                     | ethyl ethanoate            |
| $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$   | ethyl propionate                  | ethyl propanoate           |
| $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$  | methyl acetate                    | methyl ethanoate           |
| $  \begin{array}{cccc}  & & \text{CH}_3 & \text{O} \\  & &   &    \\  \beta & \alpha & & \\  \text{CH}_3 & -\text{CH} & -\text{C} & -\text{OC}_2\text{H}_5 \\  3 & 2 & 1 & \\  \end{array}  $ | ethyl $\alpha$ -methyl propionate | ethyl -2-methyl propionate |
| $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_6\text{H}_5$  | phenyl benzoate                   | phenyl benzoate            |

Preparations: -

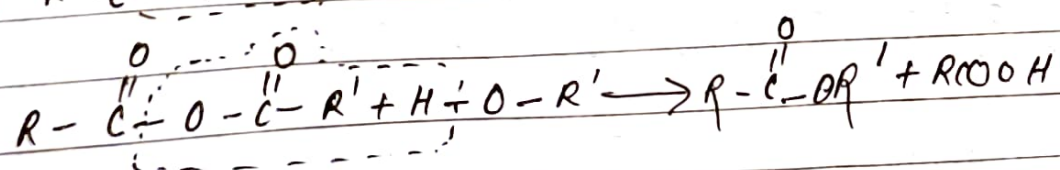
1. When carboxylic acid is heated with alcohol in the presence of conc.  $\text{H}_2\text{SO}_4$  gives ester (esterification)

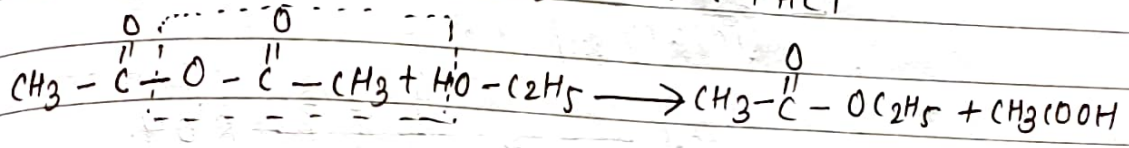
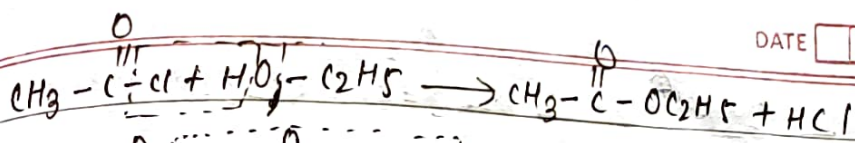


e.g

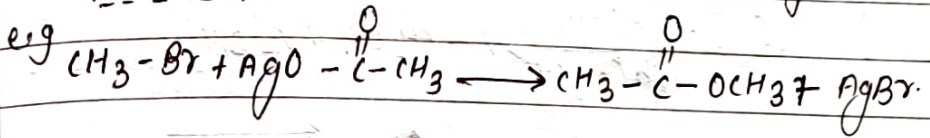
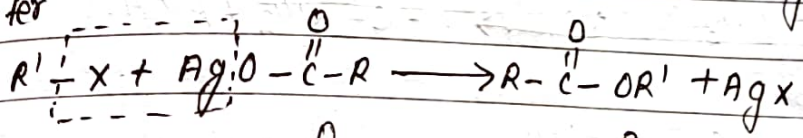


2. When acid chlorides or acid anhydrides are treated with alcohol gives ester.





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



### # Properties :-

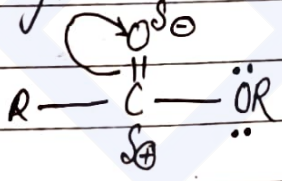
1. Physical state :- Esters are colorless liquids or solids with characteristic pleasant fruity smell.

ethyl butanoate  $\rightarrow$  pineapple.

Octyl ethanoate  $\rightarrow$  Orange.

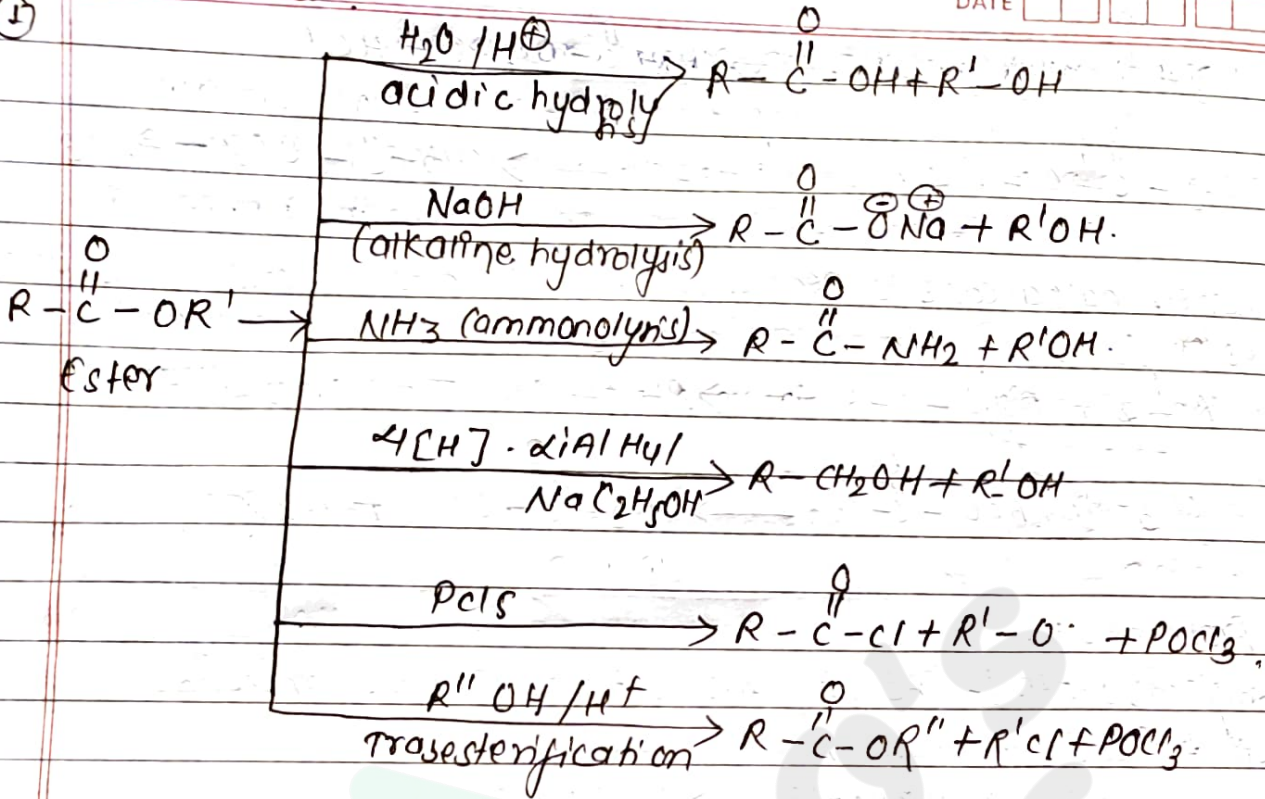
2. Solubility :- Esters are sparingly soluble in water but readily soluble in organic solvent.

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

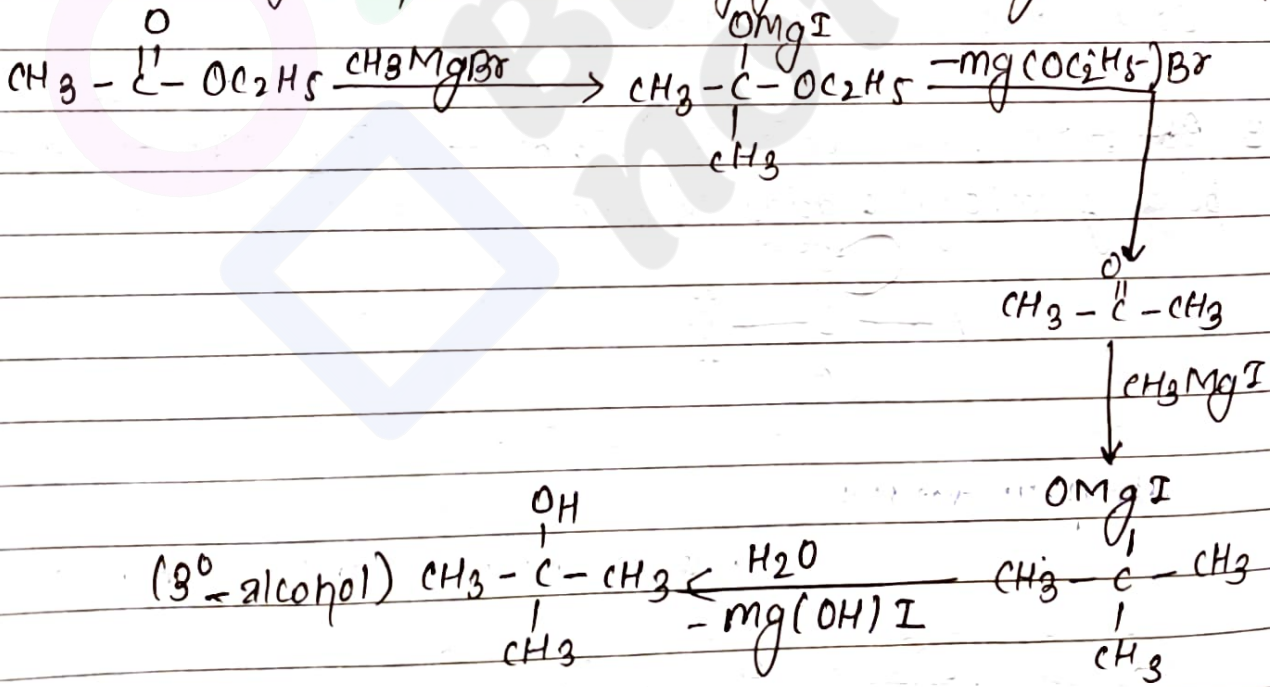


P.T.O.

①

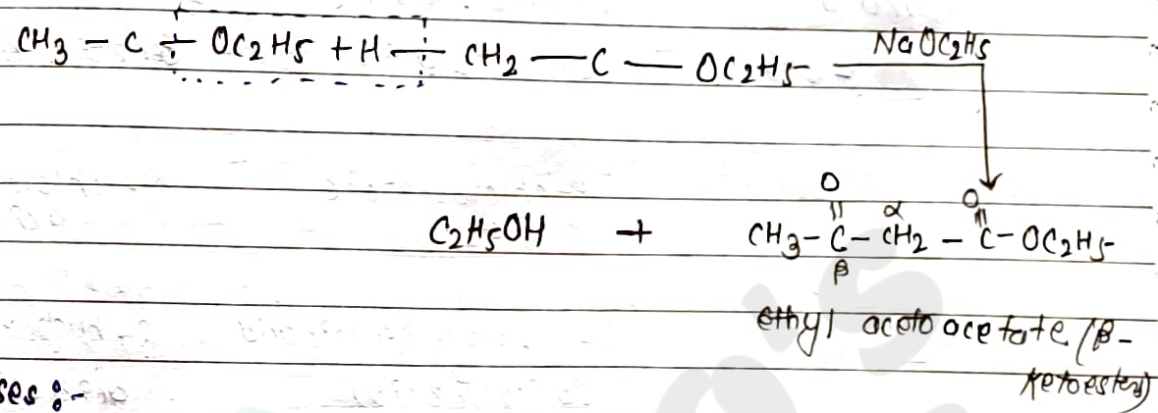


② Reaction with Grignard's reagent  $\rightarrow$  when esters except ester of formic acid reacts with Grignard reagent to give tertiary alcohol as final product. Ester of formic acid gives 2° alcohol.





③ Claisen's condensation → When ester's having  $\alpha$ -hydrogen atom undergoes self condensation in the presence of strong base sodium ethoxide gives  $\beta$  keto ester. This reaction is known as Claisen's condensation.

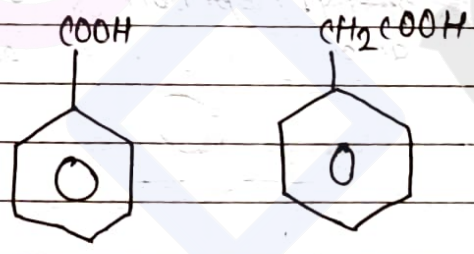


Uses :-

- 1) It is industrial solvents for paints, oils, varnishes etc.
- 2) In the preparation of artificial flavours & essences.

Aromatic carboxylic acid

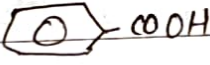

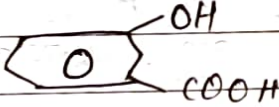


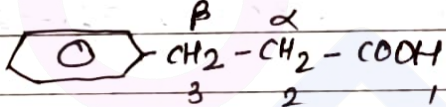
In aromatic carboxylic acids the COOH group is either linked to benzene ring or to the side chain of the benzene ring



Nomenclature :-

Aromatic carboxylic acids in which the -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 in the side chain are known as phenyl derivatives of aliphatic acids.

| Formula  | Common Name                                | IUPAC Name                      |
|--|--|---------------------------------|
|     | Benzoic acid                               | benzoic acid.                   |
| c)  | p-chlorobenzoic acid                       | 4-chlorobenzoic acid.           |
|     | o-hydroxy benzoic acid<br>(Salicylic acid) | 2-hydroxy benzoic acid.         |
|    | o-methyl benzoic acid                      | 2-methyl benzoic acid           |
|   | Phenyl acetic acid                         | phenyl ethanoic acid.           |
|   | $\beta$ -phenyl propanoic acid             | $\beta$ -phenyl propanoic acids |

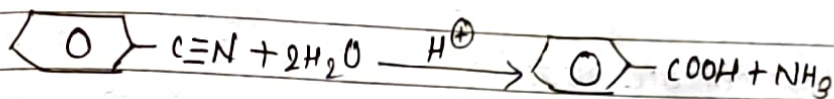
### Classes of Benzoic acid

#### \* Preparation of Benzoic acids ( $C_6H_5COOH$ )

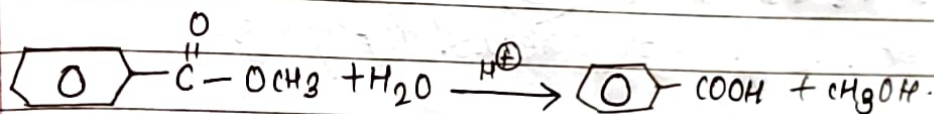
1. When benzyl alcohol or benzaldehyde react with dilute potassium permanganate ( $KMnO_4$ , benzoic acid is formed)



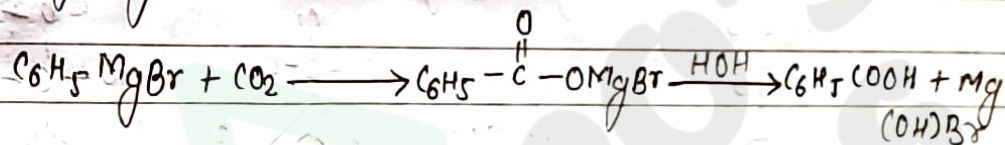
2. When benzonitrile (phenyl cyanide) undergoes hydrolysis with  $\text{HCl}$  gives benzoic acid.



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

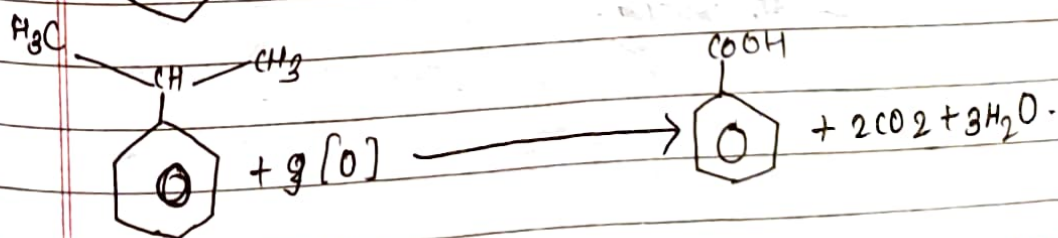
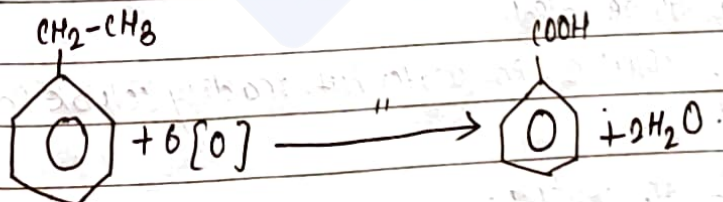
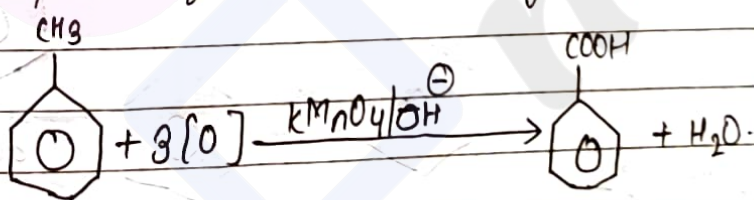


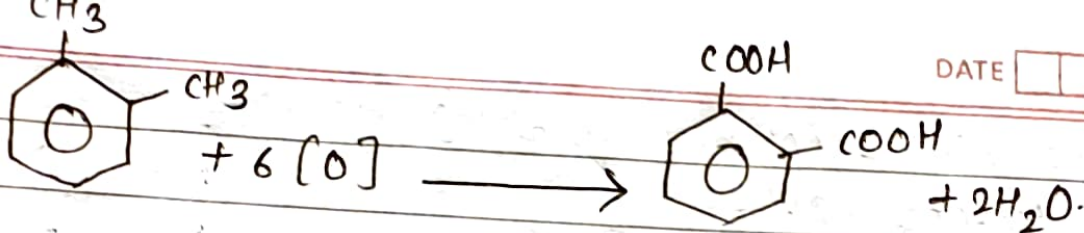
4. When phenyl magnesium bromide reacts with carbon dioxide followed by hydrolysis gives benzoic acid.



5. When alkyl benzene reacts with  $\text{KMnO}_4$  benzoic acid is formed.

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



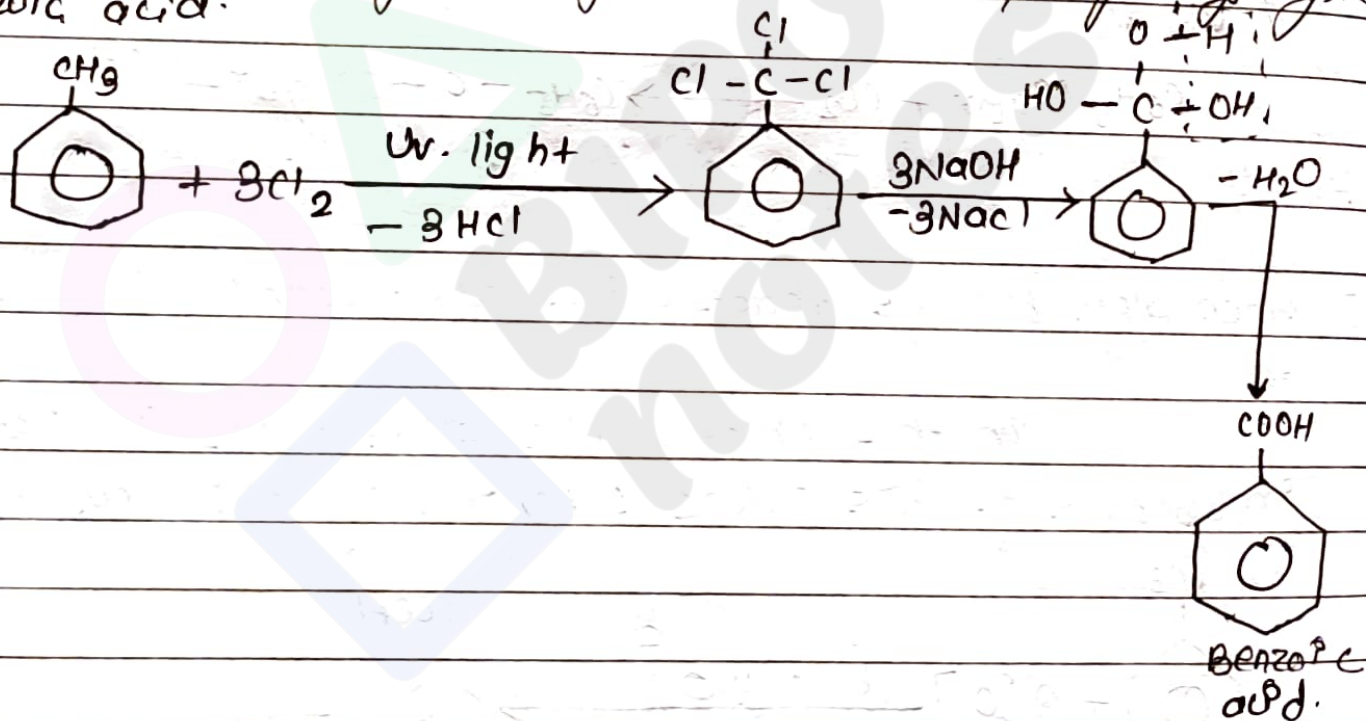


Uses of benzoic acid:-

- 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.



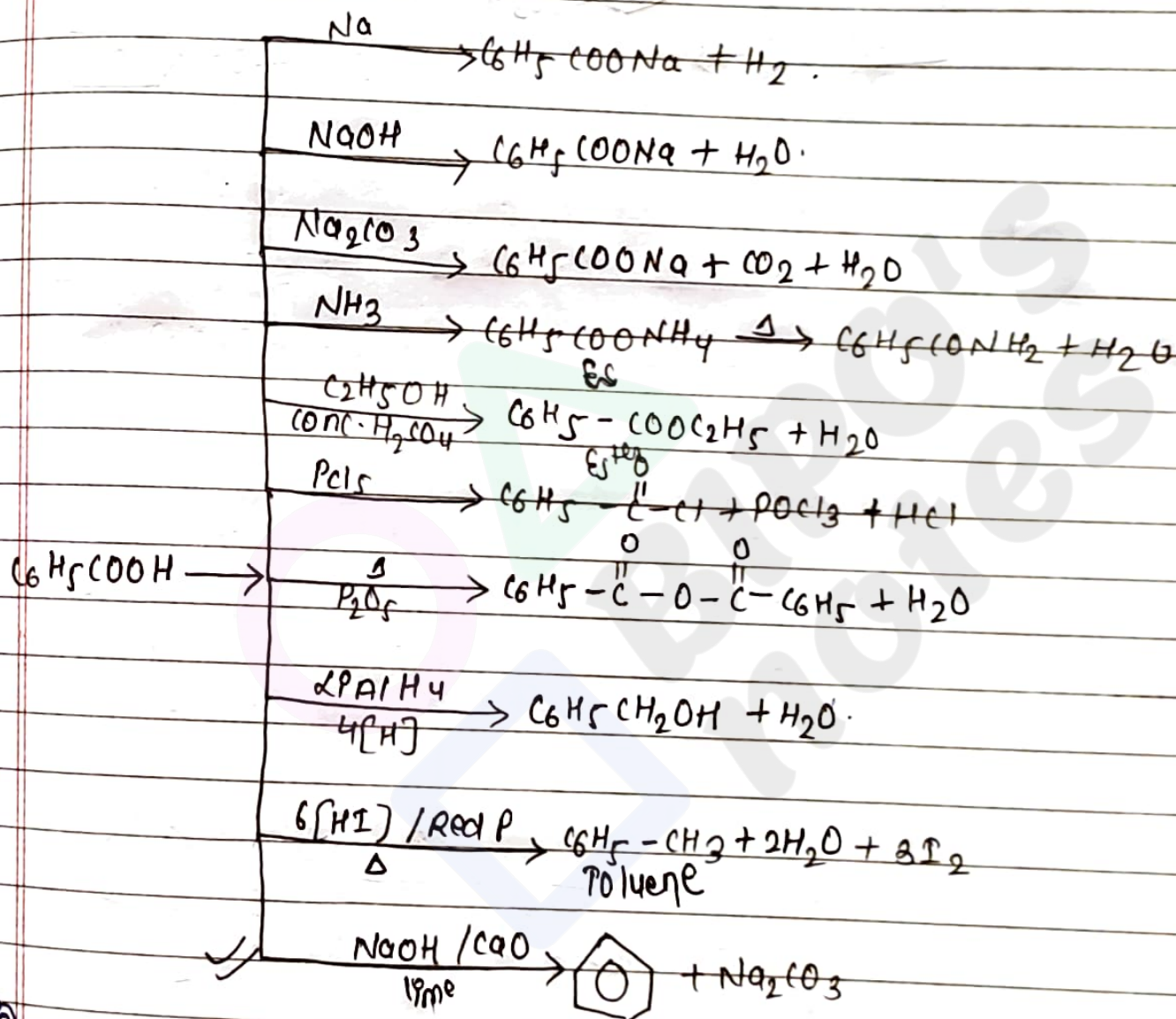
Physical properties:-

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

## # Chemical properties:-

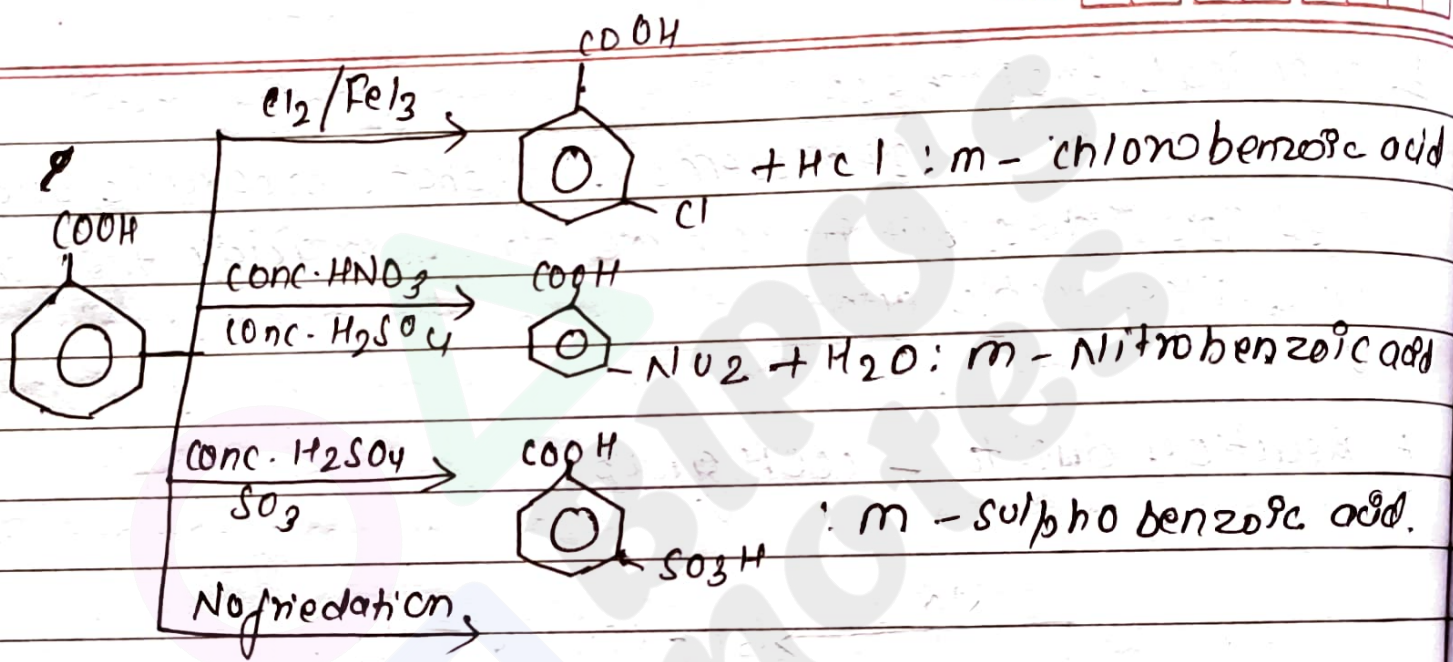
It resembles aliphatic carboxylic acids in its chemical properties but it is more stronger acids than aliphatic carboxylic like acetic acids.

### (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.H.S (Resonance Structure)









# Bipin Khatri


(Bipo)

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**Class 12** complete notes and paper collection.

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