

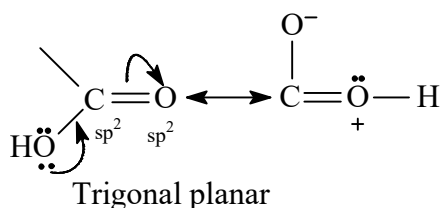
## CHAPTER - 10

# CARBOXYLIC ACIDS

- Compounds containing carboxyl functional groups are called carboxylic acids

- $\begin{array}{c} \text{O} \\ || \\ \text{—C—OH} \end{array}$  is carboxyl functional group which is a combination of carbonyl ( $>\text{C}=\text{O}$ ) and hydroxyl ( $-\text{OH}$ ) groups
- Acids containing  $\text{C}_{12}$ – $\text{C}_{18}$  carbon atoms are found in natural fats as esters of glycerol and hence are known as fatty acids.

### Structure of carboxyl functional groups



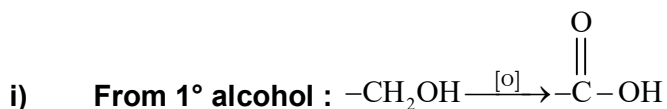
Carboxyl group undergo resonance and no free  $>\text{C}=\text{O}$  group is present in carboxylic acid and hence carboxylic acids does not known by the name “Carbonyl compounds”.

### Derivatives of CAs

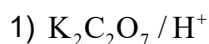
$\begin{array}{c} \text{O} \\ || \\ \text{R—C—G} \end{array}$ , where G is  $-\text{Cl}$ ,  $-\text{OR}$ ,  $-\text{OCOR}$  and  $-\text{NH}_2$  and respectively known as acid chlorides, esters, anhydrides and amides.

### Methods of preparation

#### A. OXIDATION



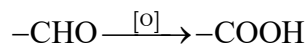
Common oxidising agents are



2)  $\text{KMnO}_4 / \text{H}^+$  OR  $\text{OH}^-$  OR  $\text{H}_2\text{O}$

3)  $\text{CrO}_3 - \text{H}_2\text{SO}_4$  (Jones reagent)

ii) **From aldehyde**

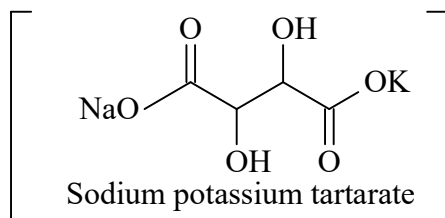


Only mild OAs are required due to high sensitivity of aldehydes towards oxidation by

Eq:

1) Tollen's reagent -  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$

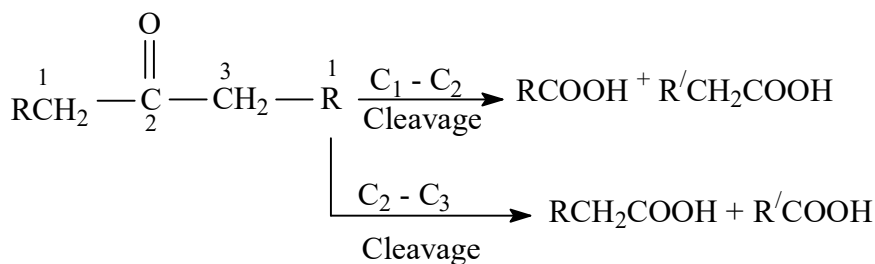
2) Fehling's solution - Ag  $\text{CuSO}_4$  + Aq. Rochelle's salt



### iii) From ketones

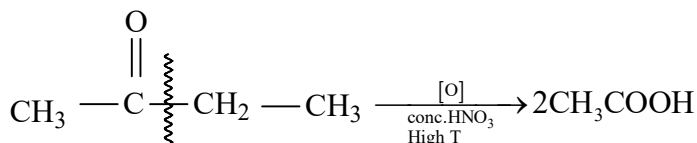
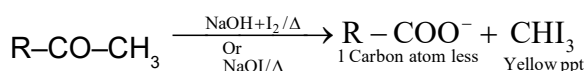
### a) Normal oxidation

Ketones are resistant towards oxidation but with strong oxidising agent under elevated temperature. But ketones give mixture of carboxylic acids



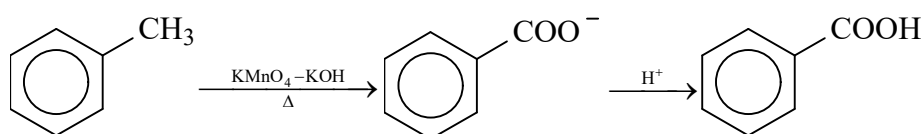
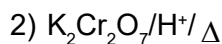
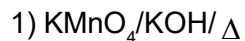
### Popoff's rule

“During oxidation of unsymmetrical ketones,  $>\text{C}=\text{O}$  group lies with smaller alkyl groups”

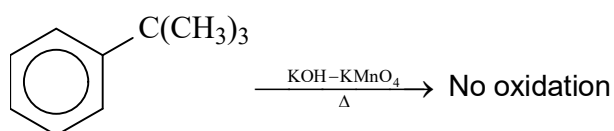
iv) **Oxidation of methyl ketones - Haloform reactions**

**iv. From alkyl benzenes - for benzoic acids**

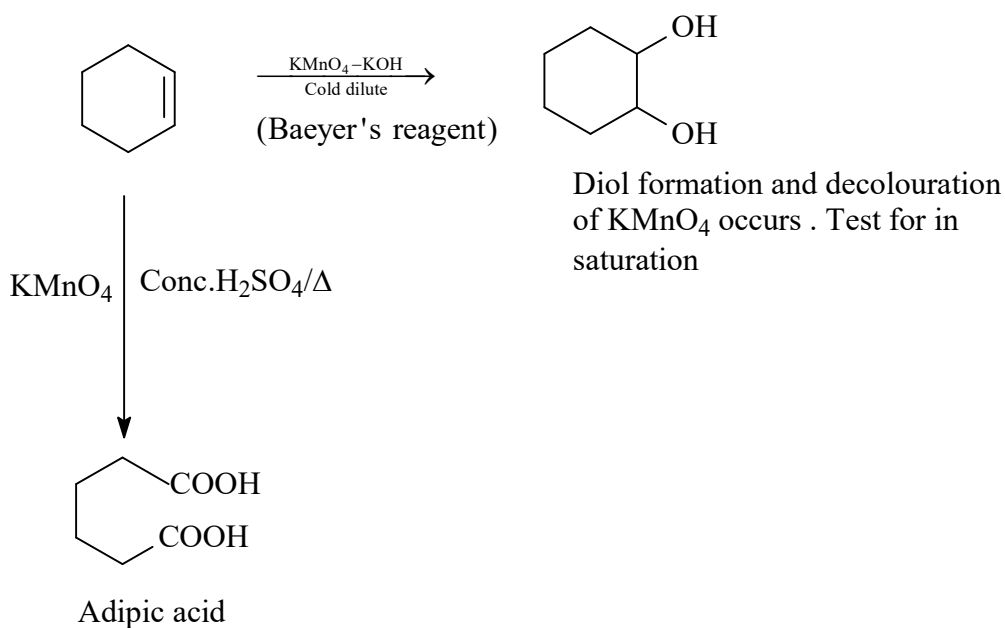
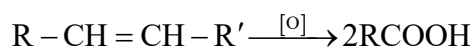
Common oxidising agents are

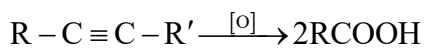


$\text{KMnO}_4\text{-KOH}$  can oxidise any side chain irrespective of chain length except  $3^\circ$  alkyl groups. Necessary condition for this oxidation is the presence of benzylic H, which is absent when the side chain is  $3^\circ$  alkyl group.



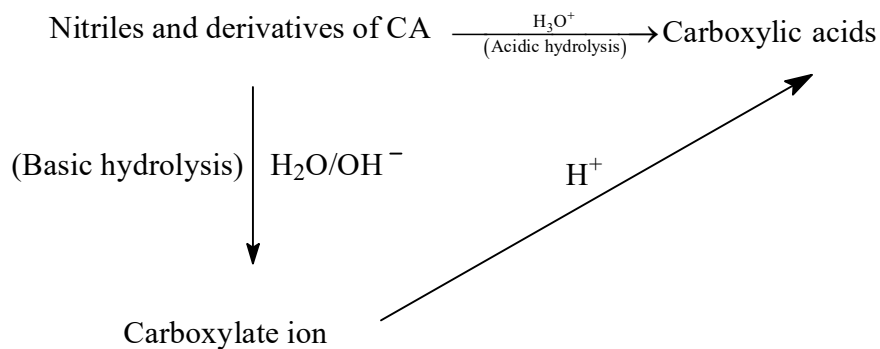
**Note:**

**V. From alkenes****vi) From alkynes**

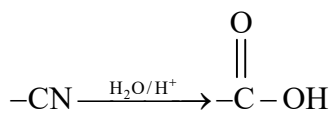


## B. HYDROLYSIS

## Generally



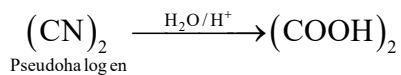
### i) From nitriles



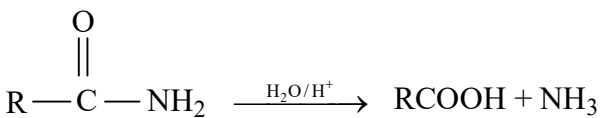
But  $-\text{CN}$  on partial hydrolysis gives amides



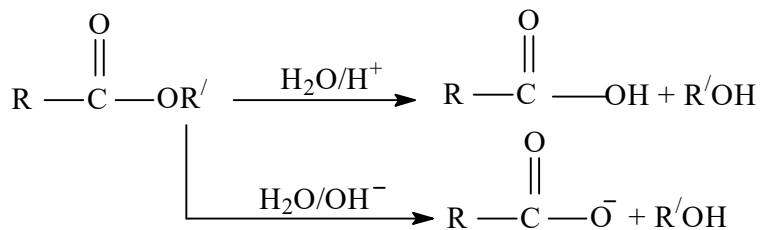
Oxalic acid is prepared from cyanogen  $(\text{CN})_2$

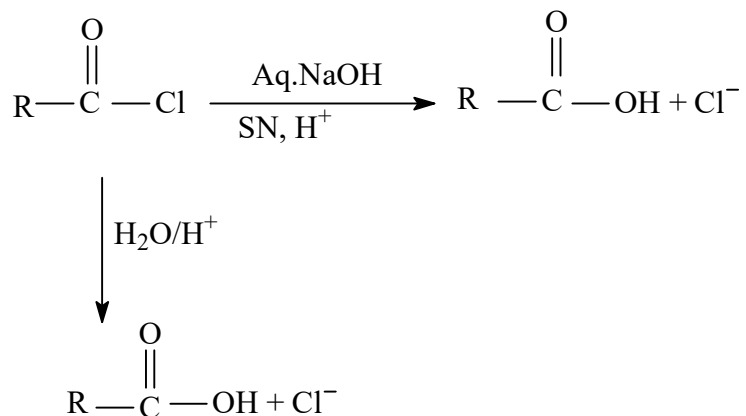
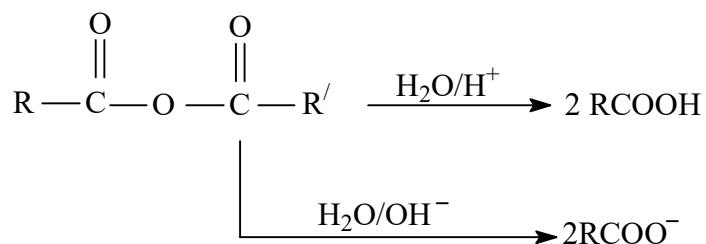
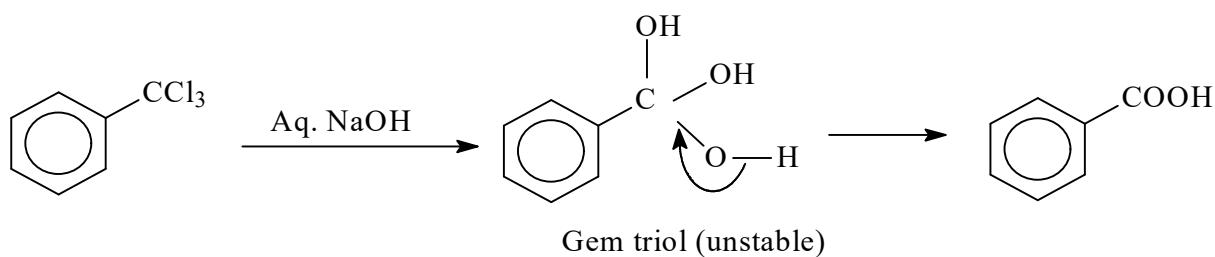
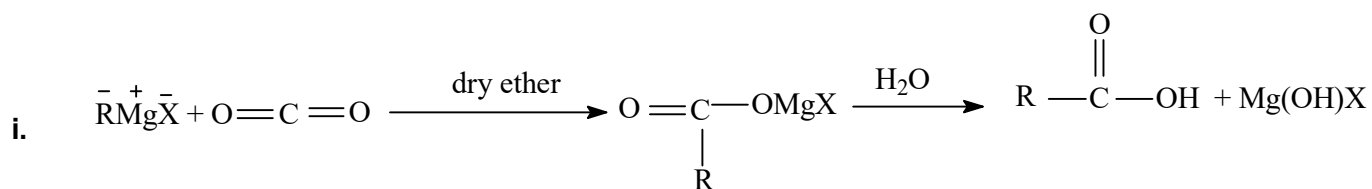


## ii. From amides



### iii. From esters



**iv. From acid chloride****v. From anhydrides****vi. From Gem-trihalides****C. GRIGNARD REAGENT - DRY ICE METHOD****Physical properties**

1. Physical appearance and order

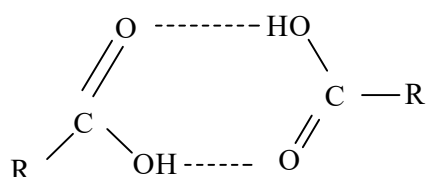
Upto 9 carbon atoms, CAs are volatile liquids and they have characteristic odour but after 9 carbon atoms they are non-volatile wax like solids and do not have odour

## 2. Solubility in water

Upto 4 carbon atoms, they are readily soluble in water due to hydrogen bond formation with  $H_2O$  but as number of carbon atoms increases solubility decreases due to increase hydrophobic part.

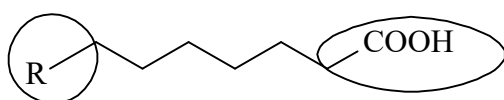
## Boiling point (BP)

CAs have highest BP among aldehydes, ketones, even alcohols of comparable molar mass due to extensive hydrogen bonding. Even in the vapour phase, CAs exist as dimer due to H-bond formation.

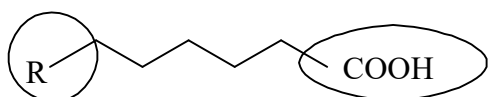


## Melting point (MP)

There is no regular trend is observed for mp of carboxylic acids but CAs with even number of carbon atoms have high MP, than that with odd number of carbon atoms.



Symmetric and fits to crystal lattice

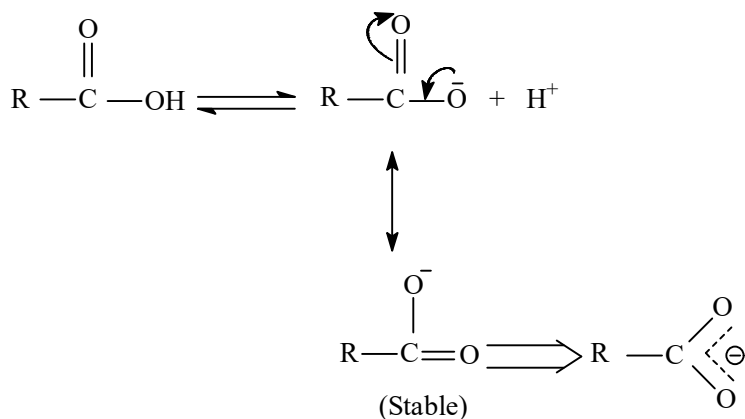


## CHEMICAL PROPERTIES

### A. Reactions involving cleavage of O-H bonds

#### 1) Acidity

Acidity of CA is due to the following reaction



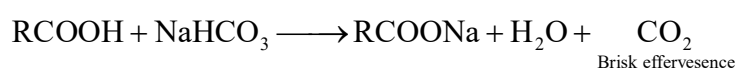
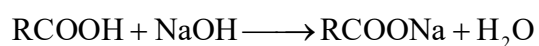
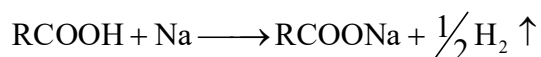
$$\text{Dissociation constant } K_a = \frac{[\text{RCOO}^-][\text{H}^+]}{[\text{ROOH}]}$$

As  $K_a \uparrow$   $[\text{H}^+] \uparrow$  acidity also increases

Since  $\text{p}K_a = -\log K_a$ ,

As  $K_a \uparrow$   $\text{p}K_a \downarrow$  acidity  $\uparrow$

Due to the high acidic nature of CAs, it can even react with weak base  $\text{NaHCO}_3$  unlike phenol

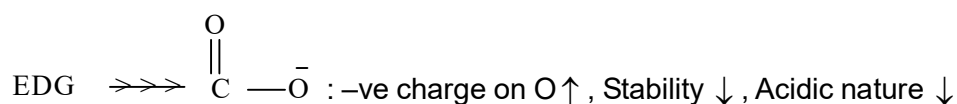
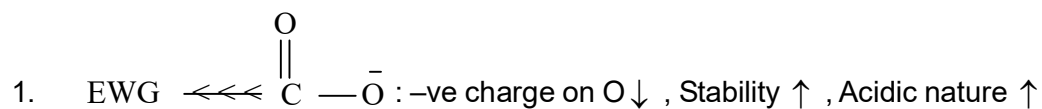


$\text{NaHCO}_3$  test is used to distinguish  $\text{RCOOH}$  from other acidic compounds

### Reason for high acidic nature

Stability of carboxylate ion due to resonance which is more stable than phenoxide which in turn more stable than alkoxide ion.

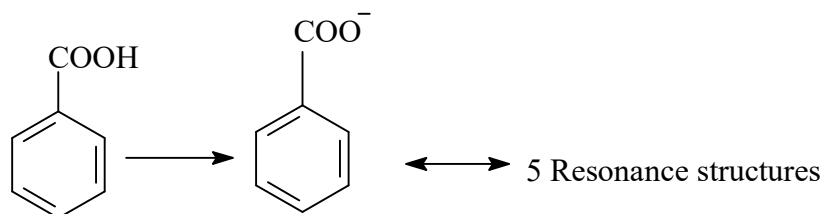
### Acidity of aliphatic carboxylic acids



2. Distance between EWG and  $-\text{COOH}$  group  $\downarrow$  acidity  $\uparrow$  and so on.

3. As the number of EWG  $\uparrow$  acidity  $\uparrow$  and so on

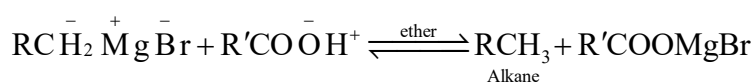
### Acidity of benzoic acid and substituted benzoic acid



Also  $-\text{COOH}$  group is coplanar with ring (an essential requirement of effective overlap of orbitals)

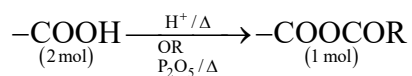
Due to highly stable benzoate ion, it is more acidic than aliphatic CA except  $\text{HCOOH}$ .

## II. Reaction with Grignard reagent

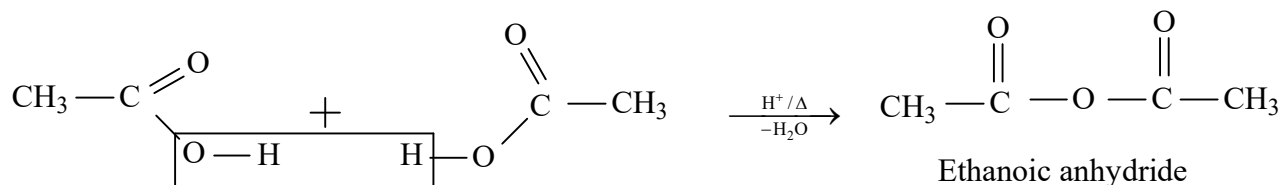


## B. Reactions involving cleavage of C–OH bond

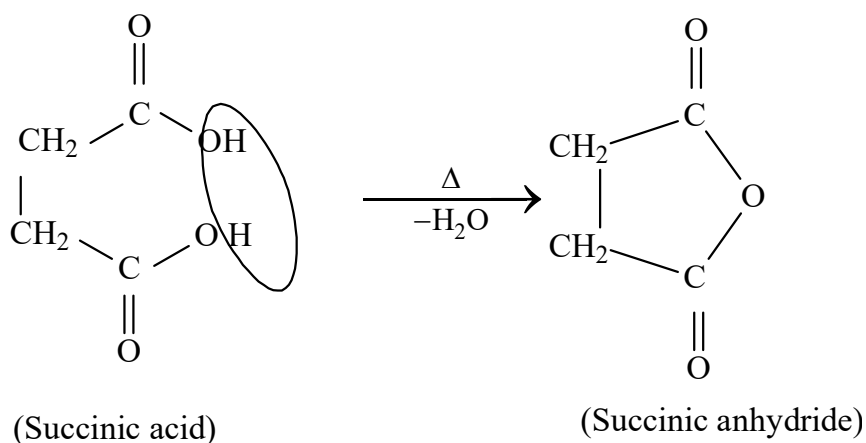
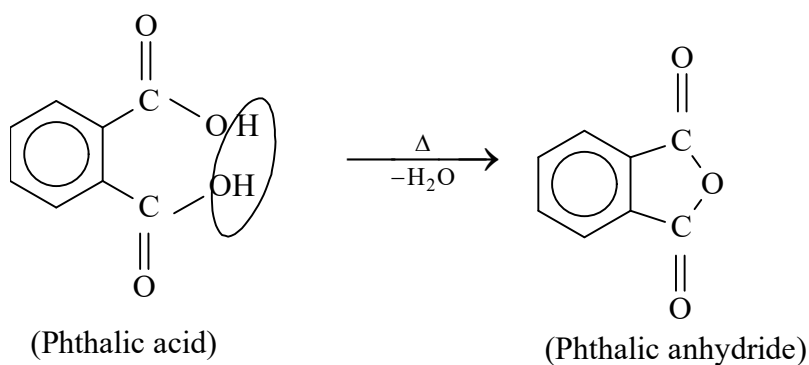
### I. Formation of anhydrides



Eg:



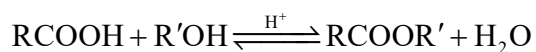
Cyclic anhydrides are prepared by simply heating the suitable dicarboxylic acid



This method is suitable for preparing a five or six membered ring.

### II. Esterification

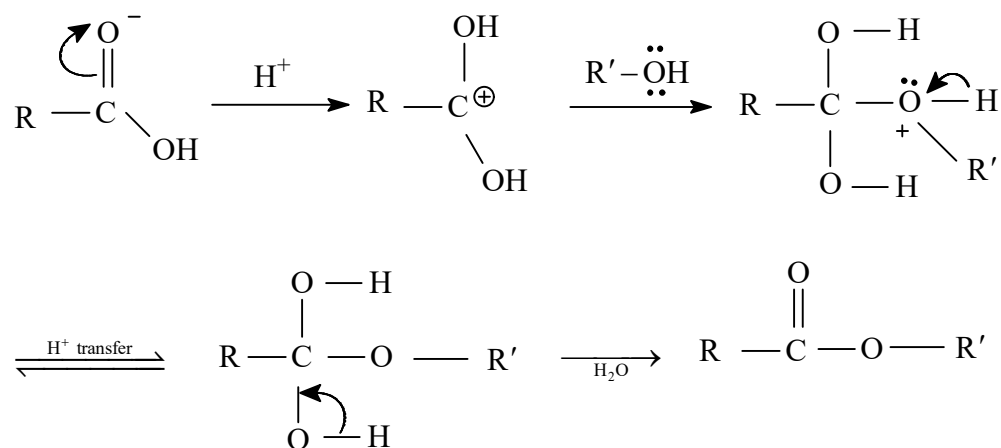
CAs are esterified with alcohols or phenols in the presence of a mineral acid such as conc.  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas as a catalyst.





**Mechanism, Acid catalysed esterification**

The mechanism is a type of nucleophilic acyl substitution, in which a nucleophile such as alcohol displaces the leaving group of an acyl derivative, here ester.



The reverse of this mechanism is the mechanism of acid catalysed hydrolysis of ester.

**Reactivity**

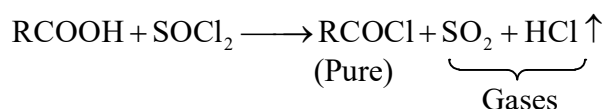
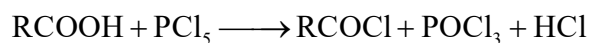
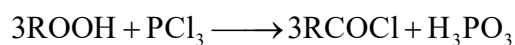
$$\text{Reactivity} \propto \frac{1}{\text{Steric hindrance on RCOOH/ROH}}$$

Eg: CAs;  $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{RCH}_2\text{COOH} > \text{R}_2\text{CHCOOH} > \text{R}_3\text{COOH}$

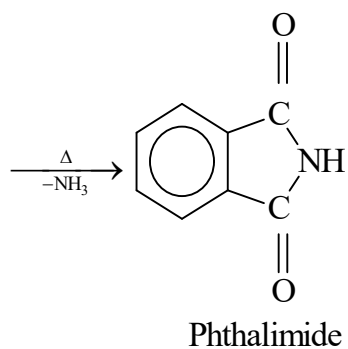
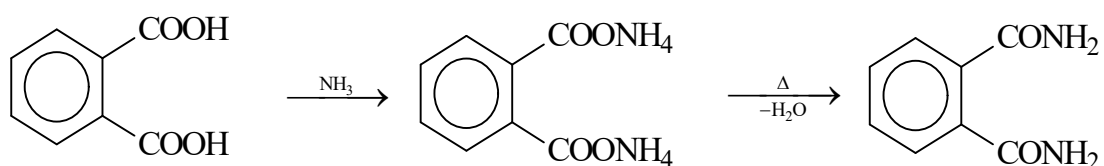
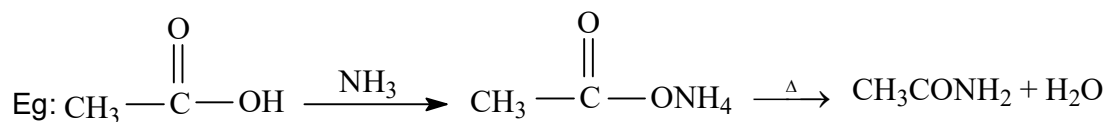
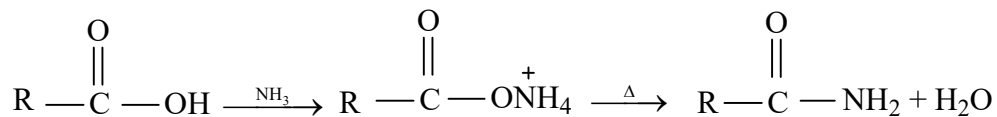
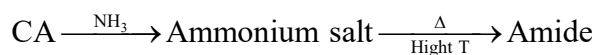
Alcohol:  $\text{CH}_3\text{OH} > \text{RCH}_2\text{OH} > \text{R}_2\text{CHOH} > \text{R}_3\text{COH}$   
(1°) (2°) (3°)

**III. Reactions with  $\text{PCl}_3$ ,  $\text{PCl}_5$  and  $\text{SOCl}_2$** 

–OH group of carboxylic acid behaves like that of alcohol and is easily replaced by Cl atom on treating with  $\text{PCl}_3$ ,  $\text{PCl}_5$  or  $\text{SOCl}_2$  (preferred)

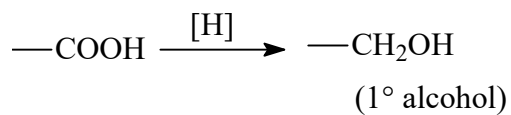


#### IV. Reaction with $\text{NH}_3$



#### C. Reactions involving $-\text{COOH}$ group

##### I. Reduction



Reducing agents are:

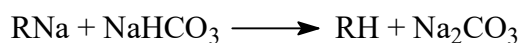
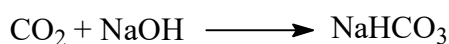
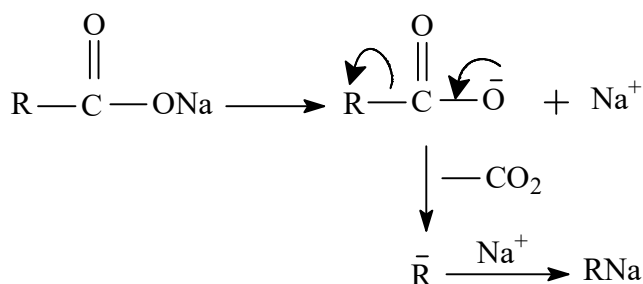
- 1)  $\text{LiAlH}_4$  / Ether
- 2)  $\text{B}_2\text{H}_6$  or  $\text{BH}_3$  / THF

Most of the RAs are selective that is they will not disturb multiple bonds

## II. Decarboxylation

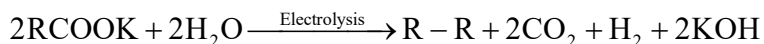
i) Soda-lime decarboxylation ( $\text{NaOH} + \text{CaO} = 3 : 1$ )

For relatively fast decarboxylation, we prefer sodium salts of carboxylic acids.



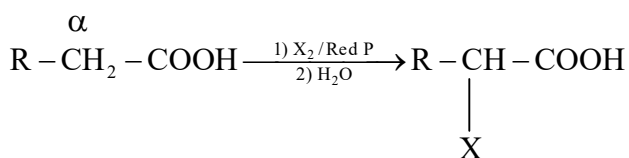
## iii. Kolbe's Electrolysis

Alkali metal salts of CA also undergo decarboxylation on electrolysis of their aqueous solution and form a hydrocarbon having twice the number of carbon atoms.



## D. Substitution Reactions in the hydrocarbon part

## I. Halogenation - HVZ Reaction



(X = Cl, Br)

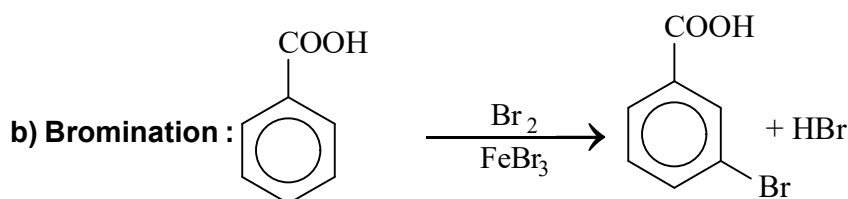
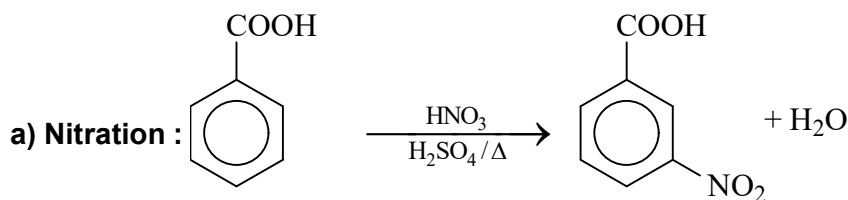
$\alpha$ -Halocarboxylic acid

If more than one molar equivalent of  $\text{X}_2$  is used, the product obtained are  $\alpha$ ,  $\alpha$ -dihalo and  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trihalo acids respectively.

If more than one molar equivalent of  $\text{X}_2$  is used, the product obtained are  $\alpha$ ,  $\alpha$ -dihalo and  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trihalo acids respectively.

## II. Ring substitution (SE)

–COOH  $\longrightarrow$  Ring deactivator , Meta director } Both –R and –I



Aromatic carboxylic acids do not undergo Friedel-Craft reactions due to

- 1) Strong deactivating nature of –COOH group
- 2)  $\text{AlCl}_3$  (Lewis acid) gets bonded to the carboxyl group, through the lone pair on oxygen.

### Uses of CAs

- $\text{HCOOH}$  - In rubber, textile, dyeing, leather and electroplating industries
- $\text{CH}_3\text{COOH}$  - As a solvent and as vinegar in food industry
- Adipic acid - Manufacture of nylon-6, 6
- Higher fatty acid - For the manufacture of soaps and detergents
- Esters of benzoic acid - In perfumes
- Sodium benzoate and Benzoic acid - Food preservatives

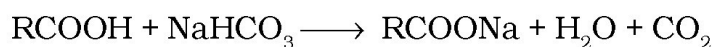
## Carboxyl Group

### Theory

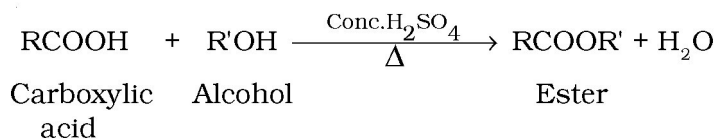
Organic compounds containing carboxyl functional groups are called carboxylic acids.

The term carboxyl, derives its name from the combination of words carbonyl and hydroxyl because carboxylic functional group

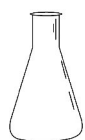
contains both of these groups ( $\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$ ). These acids turn blue litmus red and react with sodium hydrogencarbonate solution to produce effervescence due to the formation of carbon dioxide. This is a test that distinguishes carboxylic acids from phenols.



These react with alcohols in the acidic medium to produce esters.



### Material Required



- Test tube holder : One
- Glass rod : One
- Test tubes : As per need



- Blue litmus paper /solution : As per need
- Ethyl alcohol : As per need
- Sodium hydrogencarbonate solution : As per need

### Procedure

### Procedure

#### A. Litmus test

Ethyl alcohol



Put a drop of the liquid compound or a drop of the solution of the compound with the help of a glass rod on a moist blue litmus paper. If the blue colour of the litmus paper changes to red, the presence of either a carboxylic group or a phenolic group is indicated.

#### B. Sodium hydrogencarbonate test

Take 2 mL of saturated aqueous solution of sodium hydrogencarbonate in a clean test tube. Add a few drops of the liquid compound or a few crystals of solid compound to it. The evolution of brisk effervescence of  $\text{CO}_2$  indicates the presence of carboxyl group.

#### C. Ester test

Take about 0.1 g compound in a test tube, add 1 mL ethanol or methanol and 2-3 drops of concentrated sulphuric acid. Heat the reaction mixture for 10-15 minutes in a hot water bath at about  $50^\circ\text{C}$ . Pour the reaction mixture in a beaker containing aqueous sodium carbonate solution to neutralise excess sulphuric acid and excess carboxylic acid. Sweet smell of the substance formed indicates the presence of carboxyl function in the compound.

### Precaution

Add the compound in sodium hydrogencarbonate solution slowly so that effervescence is visible clearly.