→ Carboxylic acids:→

– Introduction:→

– Carboxylic acids are organic compounds having a carboxyl group (–COOH) attached to alkyl, alkenyl, alkynyl or aryl group.

– The properties of the carboxyl group remain almost same whether it is attached to an aromatic or aliphatic, saturated or unsaturated and substituted on unsubstituted subrate.

– The carboxylic acid functional group is combination of a carbonyl and a hydroxyl group.

$$-\underset{\underset{O}{\parallel}}{C}- \; + \; -OH \; \equiv \; -\underset{\underset{O}{\parallel}}{C}-OH$$

– The joining of these two functional groups alter the chemical behaviour of both these groups.

– The long chain monocarboxylic acids are commonly called fatty acids because many of them are obtained by the hydrolysis of animal fat or vegetable oils.

→ Nomenclature:→

→ Common or trivial names:→

– Depending upon the number of carboxyl group present in the molecule, they may be named as mono, di, tri and polycarboxylic acids.

- Most of the carboxylic acids had been discovered in nature before their structure known. Their common names are derived from the source and still widely used.

Formic acid	Latin → formica → Ant (obtained by distillation of ants)
Acetic acid	Latin → acetum → Vinegar
Butyric acid	Latin → butyrum → Butter
Valeric acid	Latin → Valere → to be strong (occurs in strong smelling Valerian plant)

- The lattin word for goat is caper which provides the name for caproic, caprylic and capric acid, all of which are responsible for the unsociable odour of goats.
- The acids which are first isoloated from fats are called fatty acids.

→ Derived name:→

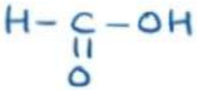
- Sometimes acids may be derived as alkyl derivatives of acetic acids.

CH_3-CH_2-COOH	$(CH_3)_2CH-COOH$	$C_6H_5-CH_2-COOH$
Methylacetic acid	Dimethylacetic acid	Phenylacetic acid

→ IUPAC system:→

$$\text{Alkane} \xrightarrow[+\text{oic acid}]{-e} \text{Alkanoic acid}$$

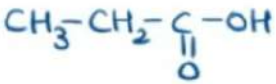
- First, longer carbon chain containing carboxylic group is selected and carbon chain is numbered to indicate the position of substituents.
- The carboxylic carbon is always given the number 1.


$H-\underset{\underset{O}{\|}}{C}-OH$

Methanoic acid
(Formic acid)


$CH_3-\underset{\underset{O}{\|}}{C}-OH$

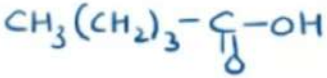
Ethanoic acid
(Acetic acid)


$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$

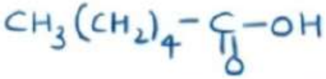
propanoic acid
(propionic acid)


$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$

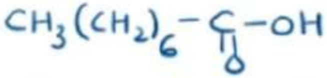
Butanoic acid
(Butyric acid)


$CH_3(CH_2)_3-\underset{\underset{O}{\|}}{C}-OH$

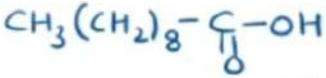
pentanoic acid
(Valeric acid)


$CH_3(CH_2)_4-\underset{\underset{O}{\|}}{C}-OH$

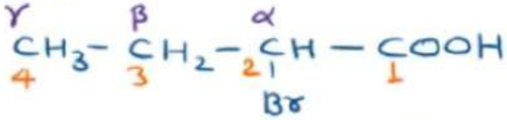
Hexanoic acid
(Caproic acid)


$CH_3(CH_2)_6-\underset{\underset{O}{\|}}{C}-OH$

Octanoic acid
(Caprylic acid)


$CH_3(CH_2)_8-\underset{\underset{O}{\|}}{C}-OH$

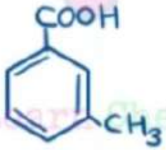
Decanoic acid
(Capric acid)

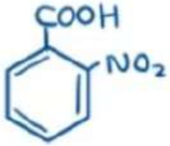

$\overset{\gamma}{\underset{4}{C}}H_3-\overset{\beta}{\underset{3}{C}}H_2-\overset{\alpha}{\underset{\underset{Br}{2|}}{C}}H-\underset{1}{C}OOH$

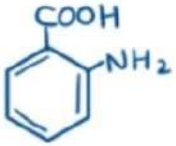
2-Bromobutanoic acid
(α- Bromobutanoic acid)

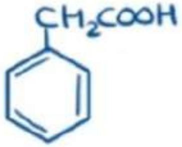
- Aromatic carboxylic acids are named as derivative of benzoic acid.
- If carboxylic group is not directly attached to aromatic ring, then the aromatic ring is named as substituent.

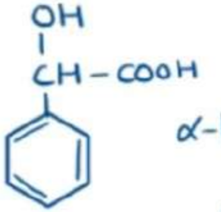

Benzoic acid


3- Methylbenzoic acid
m- Methylbenzoic acid
(m- Toluic acid)


2-Nitrobenzoic acid
o -Nitrobenzoic acid


2-Aminobenzoic acid
o- Aminobenzoic acid
(Anthranilic acid)


Phenylethanoic acid
Phenylacetic acid


α-hydroxylphenylacetic acid
(Mandelic acid)

- When a carboxylic group appears as substituent on a parent structure, it is referred to by a prefix Carboxy

2- carboxycyclohexanone

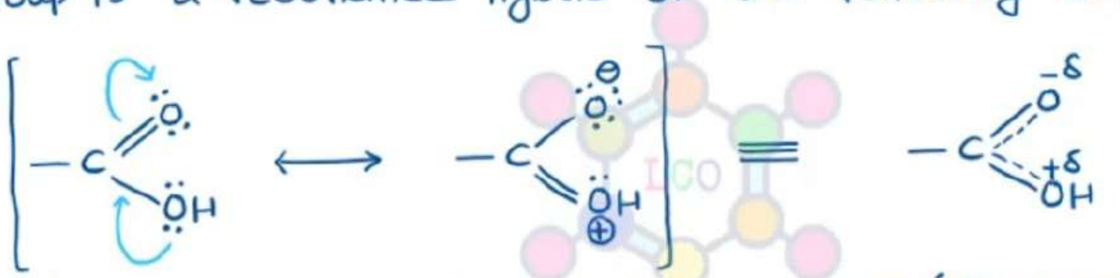
- Salts of the carboxylic acids are named by writing the name of the cation followed by the name of anion derived by replacing ending -ic acids by -ate.

$CH_3COO^-Na^+$
Sodium acetate

$CH_3COO^-NH_4^+$
Ammonium acetate

→ Structure and bonding in carboxyl group:→

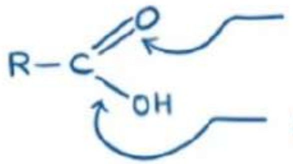
- Carboxylic group is structurally related to both carbonyl and alcoholic group.
- Carboxylic acids have some similarities to both ketones and alcohols in some of these reactions. However, they have differs from these groups.
- The carbonyl carbon of carboxylic group is sp^2 hybridised. Therefore, it is planar with C–C–O and O–C–O bond angles of 120°.
- The carboxylic group is a resonance hybrid of the following contributing forms:-



I (More stable) II (Less stable) III (Resonance hybrid)

- Form I is more stable than form II, so, form I makes more contribution in resonance hybrid. Form II is less stable is due to charge separation.
- The form III represents as average of I and II forms.
- Values of bond lengths verify the existance of resonance hybrid.

Ketone	Alcohol	Acetic acid
C=O → 122 pm	C–O → 139 pm	C=O → 125 pm C–O → 121 pm



Longer than expected (partial double bond character)

Shorter than expected (partial double bond Character)

- In case of carboxylic acid, the shape of the carbonyl π bond allow further orbital overlap. In this case, a p orbital of the hydroxyl oxygen atom interacts with π electrons of the carbonyl group to form molecular orbitals that extend over three atoms.

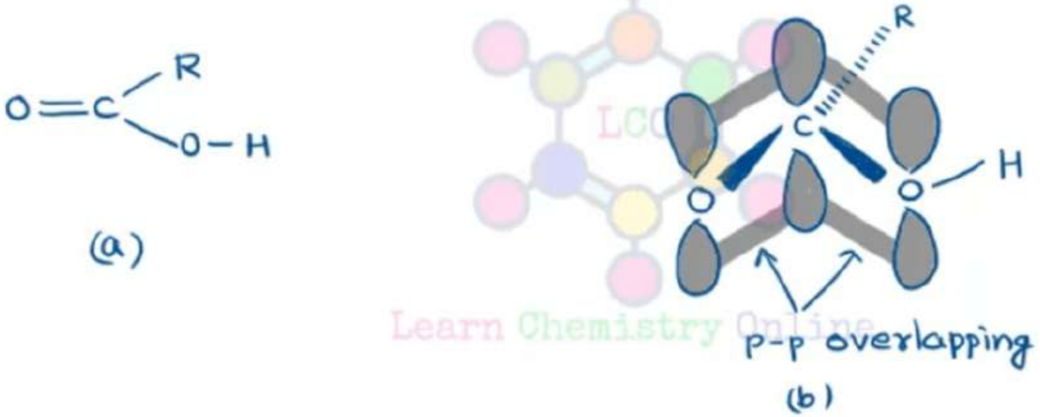


Fig:- Orbital formation of carboxylic acid

(a) σ Skeleton (b) delocalised π-bond

→ Carboxylic acids:→

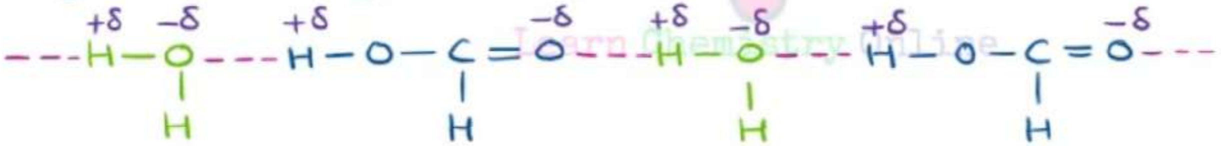
→ Physical properties:→

1 Odour:-

- Lower carboxylic acids (upto C_3) are colourless with sharp pungent smell. For example, formic and acetic acids possess sharp acid odour.
- The acids from C_4-C_8 have extraordinary unpleasent smell. Butyric acid possess the smell of rancid butter.
- These acids, formed by bacterial action, are present in traces in the skin secretions of most mammals. As metabolic processes of different persons are not exactly identical, the composition of low molecular weight carboxylic acids of skin is somewhat different and the dog is able to distinguish one person from another.

2. Solubility:→

- Water solubility of carboxylic acids is due to hydrogen bonding.



$$---\overset{+\delta}{H}-\underset{\underset{H}{|}}{\overset{-\delta}{O}}---\overset{+\delta}{H}-O-\underset{\underset{H}{|}}{C}=\overset{-\delta}{O}---\overset{+\delta}{H}-\underset{\underset{H}{|}}{\overset{-\delta}{O}}---\overset{+\delta}{H}-O-\underset{\underset{H}{|}}{C}=\overset{-\delta}{O}---$$

- Lower acids upto C_4 are fairly soluble in water in all proportions, wheras pentanoic and hexanoic acids are partially soluble in water.
- The higher acids are completely insoluble in water due to an increased proportions of the hydrocarbon moiety in the molecule.

- Benzoic acid is sparingly soluble in cold water but sufficiently soluble in hot water.
- All carboxylic acids are soluble in less polar organic solvents such as benzene, ether and alcohol.

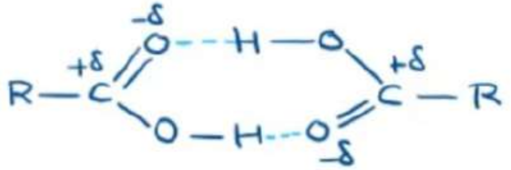
3. Boiling points:→

- The boiling points of carboxylic acids are much higher than those of hydrocarbons and higher than those of aldehydes, ketones and even alcohols of comparable molecular mass.

  e.g. b.p. of CH_3COOH (391K) is higher than n-propyl alcohol, propanal, acetone & n-butane.
- This is due to following reasons-

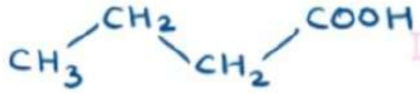
(1) O–H bond in carboxylic acid is more polarised than alcohol. It is due to electron withdrawing effect of carbonyl group.

(2) The positively polarised hydrogen atom of the O–H bond also forms H–bond with the negatively polarised oxygen atom of the carbonyl group of the other molecule. These hydrogen bonds are very strong and are not broken even in the vapour phase. In fact, in vapour phase and in aprotic solvents, most of the carboxylic acids exist as cyclic dimers in which the two molecules of the acid are held together by two strong hydroger bonds.

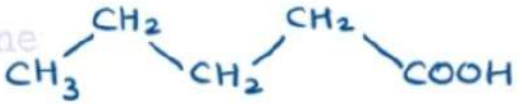


4. Melting point :→

- The melting points of aliphatic carboxylic acids do not show a regular pattern.
- The first ten members show alternation or oscillation effect, which mean that the m.p. of an acid containing even number of carbon atoms will be higher than that of the next lower and next higher homologues containing odd number of carbon atoms.
- Acid containing even number of carbon atoms have carboxyl and terminal methyl groups on the opposite side of the zig-zag carbon chain. Due to this they fit closely in the crystal lattice thereby increasing intermolecular forces of attraction resulting in higher melting points.
- Acid with odd number of carbon atoms, have the carboxyl and terminal methyl groups both on the same side of the zig-zag carbon chain due to which they cannot fit closely in the crystal lattice and have lower melting points.



acid containing even number of carbon atom



acid containing odd number of carbon atom

- The melting points of aliphatic acids having more than ten carbon atoms do not show the oscillation effect.

- The melting points and boiling points of aromatic acids are higher than those of aliphatic acids. because of planar structure of benzene ring these acids can pack closely in the crystal lattice than zig-zag structure of aliphatic acids.

→ Acidity of carboxylic acids :→

- The acidity of carboxylic acids depends upon relative ease with which it loses a proton to form the corresponding anion.
- Actually the difference in stability of the acid and its anion determines the strength of a given acid.
- Carboxylic acids ionise in aqueous solution by transferring protons to the solvent molecule. stronger acids give up most of their ionisable protons while weaker acids transfer only a smaller proportion.
- The equilibrium constant (Ka, also called dissociation constant of acid) of the process is given by the following expression.

$$R-COOH + H_2O \rightleftharpoons R-COO^{\ominus} + H_3O^{\oplus}$$

$$\boxed{K_a = \frac{[H_3O^{\oplus}][R-COO^{\ominus}]}{[R-COOH]}}$$

water is present in large excess and its concentration has been taken as constant.

$$\boxed{K_a \propto \text{degree of ionisation} \propto \text{acidic strength}}$$

→ pKa value :→

– The convenient method to express the strength of acid is pKa value which is negative logarithm of Ka.

$$\boxed{pK_a = -\log K_a}$$

Example:- Ka of acetic acid → 1.8×10^{-5}

$$pK_a = -\log(1.8 \times 10^{-5})$$
$$= -3 + 5$$
$$pK_a = 4.7$$

$$\boxed{pK_a \propto \frac{1}{\text{Acidic strength}}}$$

– pKa values of some carboxylic acids at 298 K :→

CF_3COOH = 0.2

CCl_3COOH = 0.6

$ClCH_2COOH$ = 2.8

$p-NO_2C_6H_4COOH$ = 3.4

$m-NO_2C_6H_4COOH$ = 3.5

$HCOOH$ = 3.8

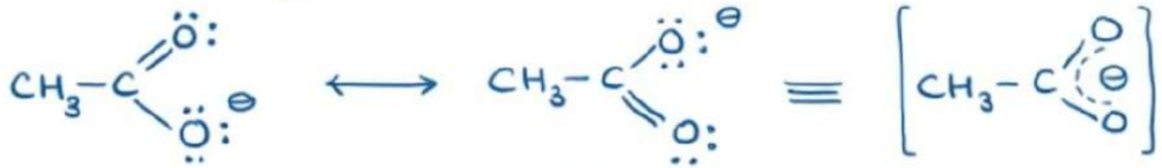
C_6H_5-COOH = 4.2

CH_3COOH = 4.7

$CH_3CH_2CH_2COOH$ = 4.9

→ Cause of Acidic nature of Carboxylic acids:→

- The acidic nature of carboxyl group can be explained on the basis of resonance stabilisation of the carboxylate anion in which two contributing forms are equivalent.



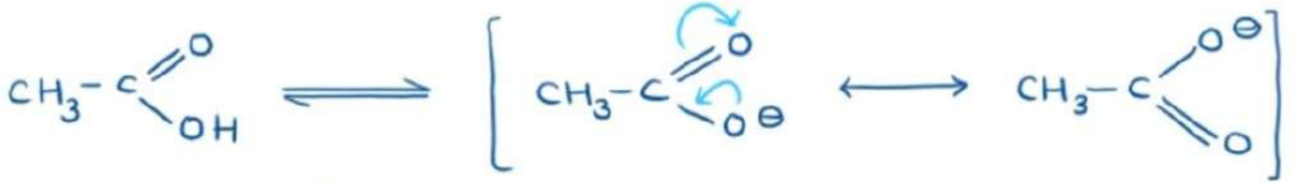
- Also, there are two contributing forms for the acid, but since the second form involves separation of charge, its contribution is minor and hence resonance in the acid is not as stabilizing as that in the anion.

- The concept of resonance is fovoured by measurments of bond lengths. There is only one bond length for both C–O bonds (128 pm) in the anion in contrast to two C–O bond lengths found in acid.

→ Comparison of Acidic character of Alcohols and carboxylic acids:→

- Carboxylic acids are more stronger acids than alcohols, although both these species dissociate by cleavage of the O–H bond.

$CH_3OH \rightleftharpoons CH_3O^{\ominus} + H^{\oplus}$ $pK_a = 15.3$



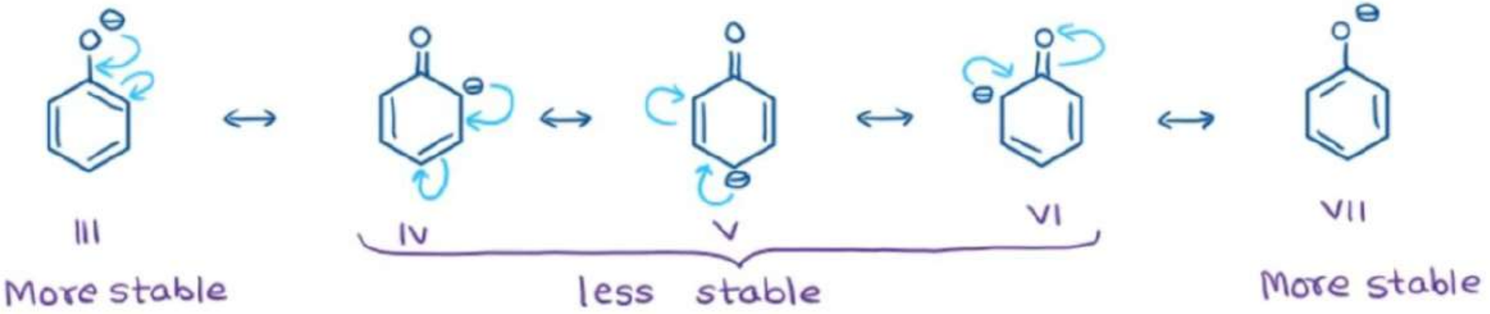
+ $H^{\oplus}$ $pK_a = 4.8$

- The is no possibility of resonance stabilisation in either alcohol and alkoxide ion while both the carboxylic acid and carboxylate ion are resonance stabilised. out of these the carboxylate anion has the greator resonance stabilisation. Therefore the dissociation equilibrium is shifed to the right to favour formation of carboxylate ion. Thus a carboxylic group is more acidic than alcohols.

→ Comparision of acidic character of phenols and carboxylic acids:→

Carboxylate ion

Phenoxide ion



- Structures I and II for the carboxylate ion and structures III and VII for the phenoxide ion have negative charge on the more electronegative oxygen atom, which contribute towards the resonance stabilization of the ions.
- In case of phenoxide ion structures IV–VI carry a negative charge on less electronegative carbon atom and hence are not important.
- In structures I and II of the carboxylate ion, the negative charge is delocalised over two oxygen atoms while for phenoxide it is localised on the same single oxygen. Therefore, carboxylate ion is much more stabilised by resonance than phenoxide ion and hence carboxylic acids are stronger acids than phenols.

→ Preparation of carboxylic acids :→

(1) Oxidation of primary alcohols or aldehydes:→

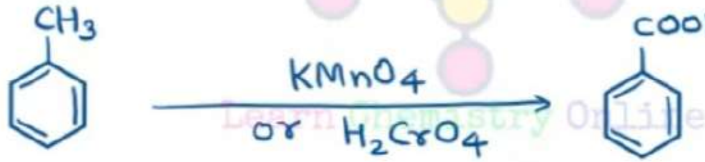
$$R-CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-COOH$$

- Mild oxidising agents such as Tollen's reagent are sufficient to oxidise an aldehyde to an acid.

$$R-CHO + 2Ag(NH_3)_2OH \longrightarrow R-COONH_4 + 2Ag + H_2O + 3NH_3$$

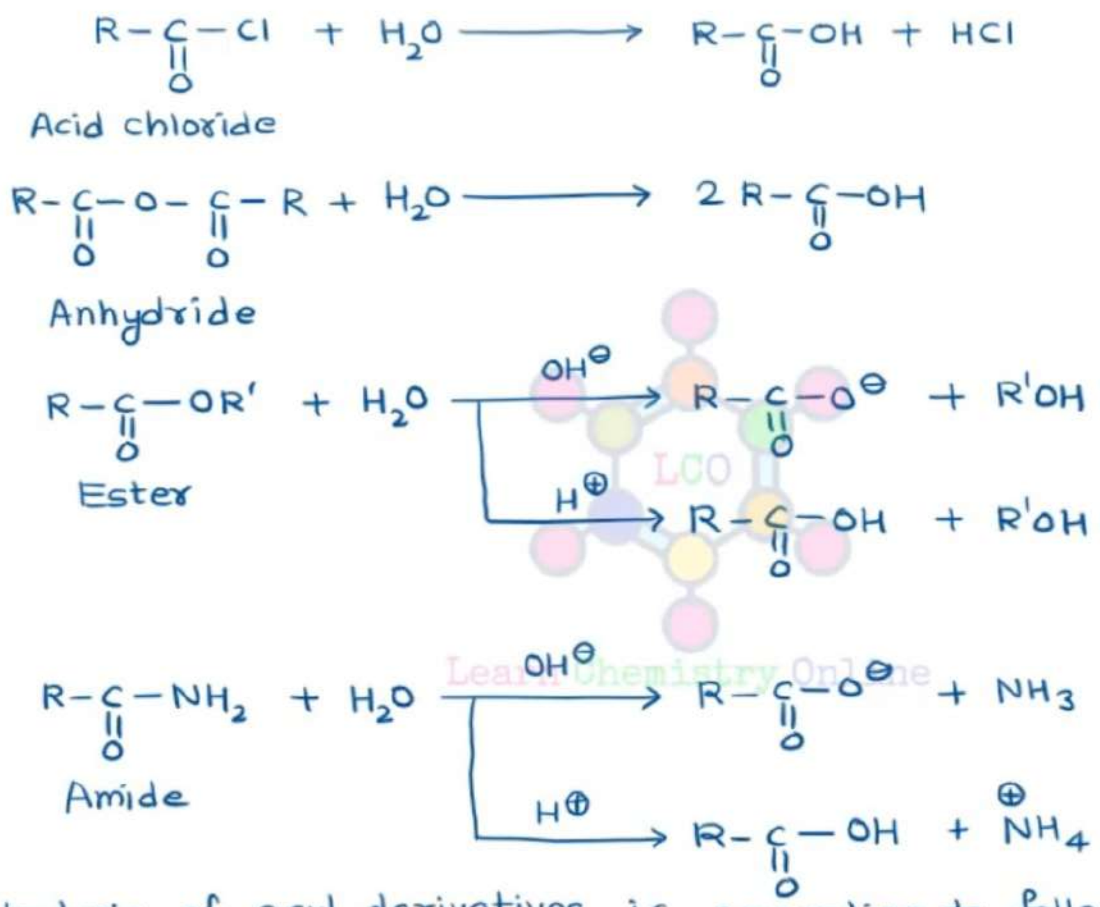
(2) Oxidation of alkylbenzenes:→

- Oxidation of side chain is used commercially to prepare aromatic carboxylic acids from alkylbenzenes.
- Since benzene ring is quite resistant to oxidation, it is possible to oxidise toluene to benzoic acid.



- This oxidation proceeds through benzyl radical intermediate. Ethylbenzene and isopropylbenzene also converted into benzoic acid. but t-butylbenzene does not possess a hydrogen on the benzyl carbon, it is unable to lose a hydrogen atom to yield a stable benzyl radical. It is, therefore, not oxidised to benzoic acid.

(3) Hydrolysis of acid chlorides, anhydrides, esters and amides :→



$$R-\underset{\underset{O}{\|}}{C}-Cl + H_2O \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + HCl$$

Acid chloride

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R + H_2O \longrightarrow 2\,R-\underset{\underset{O}{\|}}{C}-OH$$

Anhydride

$$R-\underset{\underset{O}{\|}}{C}-OR' + H_2O \xrightarrow{OH^{\ominus}} R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + R'OH$$

$$R-\underset{\underset{O}{\|}}{C}-OR' + H_2O \xrightarrow{H^{\oplus}} R-\underset{\underset{O}{\|}}{C}-OH + R'OH$$

Ester

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{OH^{\ominus}} R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + NH_3$$

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{H^{\oplus}} R-\underset{\underset{O}{\|}}{C}-OH + \overset{\oplus}{N}H_4$$

Amide

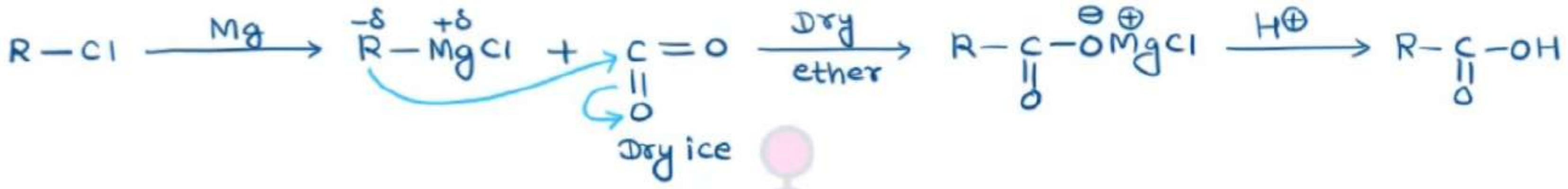
- The ease of hydrolysis of acyl derivatives is according to following order -

Acid chloride > Anhydride > Ester > Amide

(4) Hydrolysis of nitriles:→

$$R-C\equiv N + 2H_2O \xrightarrow[\Delta]{H^{\oplus} \text{ or } OH^{\ominus}} R-COOH + NH_3$$

(5) Carbonation of organometallic reagents:→

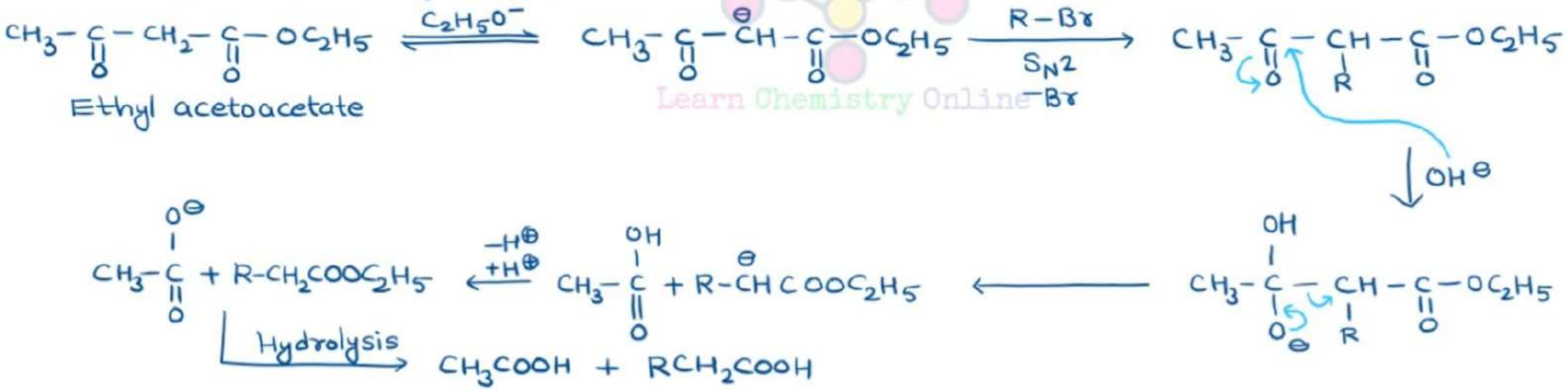


$$R-Cl \xrightarrow{Mg} \overset{-\delta}{R}-\overset{+\delta}{Mg}Cl + C(=O)=O \xrightarrow{\text{Dry ether}} R-C(=O)-\overset{\ominus}{O}\overset{\oplus}{Mg}Cl \xrightarrow{H^{\oplus}} R-C(=O)-OH$$

- Organolithium compounds can be carbonated in a similar fashion.

(6) Acetoacetic, malonic and cyanoacetic ester synthesis:→

- Acetoacetic ester synthesis



$$CH_3-C(=O)-CH_2-C(=O)-OC_2H_5 \underset{}{\overset{C_2H_5O^-}{\rightleftharpoons}} CH_3-C(=O)-\overset{\ominus}{C}H-C(=O)-OC_2H_5 \xrightarrow[S_N2,\ -Br]{R-Br} CH_3-C(=O)-CH(R)-C(=O)-OC_2H_5$$

$$\xrightarrow{OH^{\ominus}} CH_3-C(OH)(O^{\ominus})-CH(R)-C(=O)-OC_2H_5 \longrightarrow CH_3-C(=O)-OH + R-\overset{\ominus}{C}HCOOC_2H_5 \xrightarrow[+H^{\oplus}]{-H^{\oplus}} CH_3-C(=O)-O^{\ominus} + R-CH_2COOC_2H_5$$

$$\xrightarrow{\text{Hydrolysis}} CH_3COOH + RCH_2COOH$$

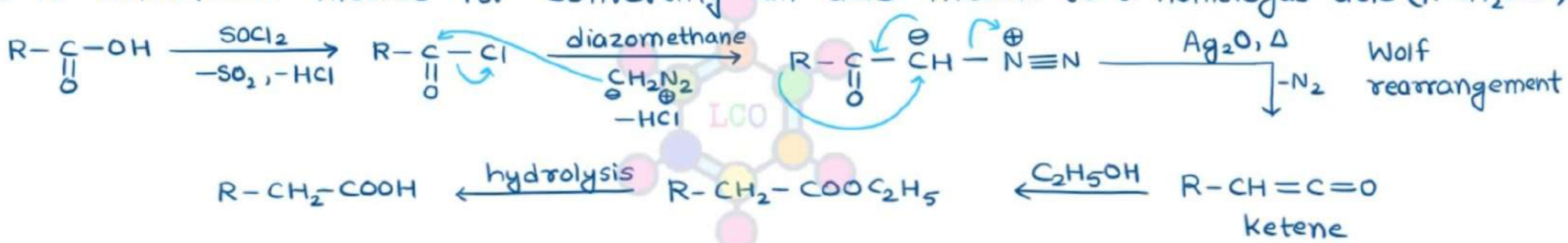
- The objective of the malonic ester synthesis is to convert a primary or secondary alkyl halide into an acid having two carbon atoms more than the starting compound.

$$R-X + NaCH(COOC_2H_5)_2 \longrightarrow R-CH(COOC_2H_5)_2 \xrightarrow{KOH} R-CH(COOH)_2 \xrightarrow[-CO_2]{\Delta} R-CH_2COOH$$

- Cyanoacetic ester can also be used in same way.

(7) Arndt - Eistert homologation:→

- This is convenient method for converting an acid R-COOH to a homologus acid $(R-CH_2COOH)$



$$R-\underset{\overset{||}{O}}{C}-OH \xrightarrow[-SO_2,\,-HCl]{SOCl_2} R-\underset{\overset{||}{O}}{C}-Cl \xrightarrow[\overset{\ominus}{C}H_2\overset{\oplus}{N}_2,\ -HCl]{\text{diazomethane}} R-\underset{\overset{||}{O}}{C}-\overset{\ominus}{C}H-\overset{\oplus}{N}\equiv N \xrightarrow[-N_2]{Ag_2O,\,\Delta} R-CH=C=O \xrightarrow{C_2H_5OH} R-CH_2-COOC_2H_5 \xrightarrow{\text{hydrolysis}} R-CH_2-COOH$$

(8) Hydrolysis of 1,1,1-trihalo derivatives of alkanes:→

$$R-CCl_3 \xrightarrow{KOH} R-\underset{\overset{||}{O}}{C}-OH$$

1,1,1-trihaloalkane

$$H-CCl_3 \xrightarrow{KOH} H-COOH$$

$$CH_3-CCl_3 \xrightarrow{KOH} CH_3-COOH$$

(9) Haloform reaction:→

- The carboxylic acid formed contains one carbon atom less than the corresponding parent ketone and haloform.

$$\mathrm{R-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOCl} R-\underset{\underset{O}{\|}}{C}-CCl_3 \xrightarrow[-CHCl_3]{NaOH} R-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Na} \xrightarrow{H^{\oplus}} R-\underset{\underset{O}{\|}}{C}-OH}$$

(10) Baeyer - villiger oxidation:→

$$\mathrm{R-\underset{\underset{O}{\|}}{C}-R' + C_6H_5COOOH \xrightarrow[-C_6H_5COOH]{} R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow{Hydrolysis} R-\underset{\underset{O}{\|}}{C}-OH + R'OH}$$

(11) Carboxylation of alkenes:→

$$\mathrm{CH_2{=}CH_2 + CO + \underset{Steam}{H_2O} \xrightarrow[673\,K]{H_3PO_4} CH_3CH_2COOH}$$

(12) From sodium alkoxide and carbon monoxide:→

$$\mathrm{R-\overset{\ominus}{O}\overset{\oplus}{Na} + CO \xrightarrow[\Delta]{Pressure} R-COO\overset{\ominus\oplus}{Na} \xrightarrow{H^+/H_2O} R-COOH + HCl}$$

→ Reactions of carboxylic acids :→

- Except formic acid, all the carboxylic acids consist of two parts i.e.

(i) An alkyl or an aryl group

(ii) A carboxyl group

- The carboxyl group is made up of a carbonyl group and a hydroxyl group. Therefore, carboxylic acids are expected to show the reactions of both these groups. However, due to proximity, these groups may interact with each other and therefore, the reactions expected for these groups are somewhat different.

Further due to resonance, the partial positive charge on carbonyl group is decreased and hence it would be attacked by the nucleophiles less readily. It is therefore, carboxylic acids do not undergo nucleophilic addition reactions of aldehydes and ketones. Viewing alternatively, bonding between the carbonyl carbon of an acid and a nucleophile would destroy the conjugate stabilisation of the system and hence this addition is not favoured.

- Some of the more important reaction of carboxylic acids are discussed below –

(I) Reactions due to H- atom of the carboxyl group : Acidic behaviour

(i) Reaction with metals :→ metals → Na, K, Ca, Mg, Zn etc.

$$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$$

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$

$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2$$

(ii) Reaction with carbonates and bicarbonates:-

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

- The carbon of CO_2 comes from Na_2CO_3 or $NaHCO_3$. The mechanism of the reaction is as follows-

- This reaction is used to detect the presence of a carboxyl group in an organic compound.

(iii) Reaction with alkalies:→

- Carboxylic acids react with hydroxides and metallic oxides to form salts.

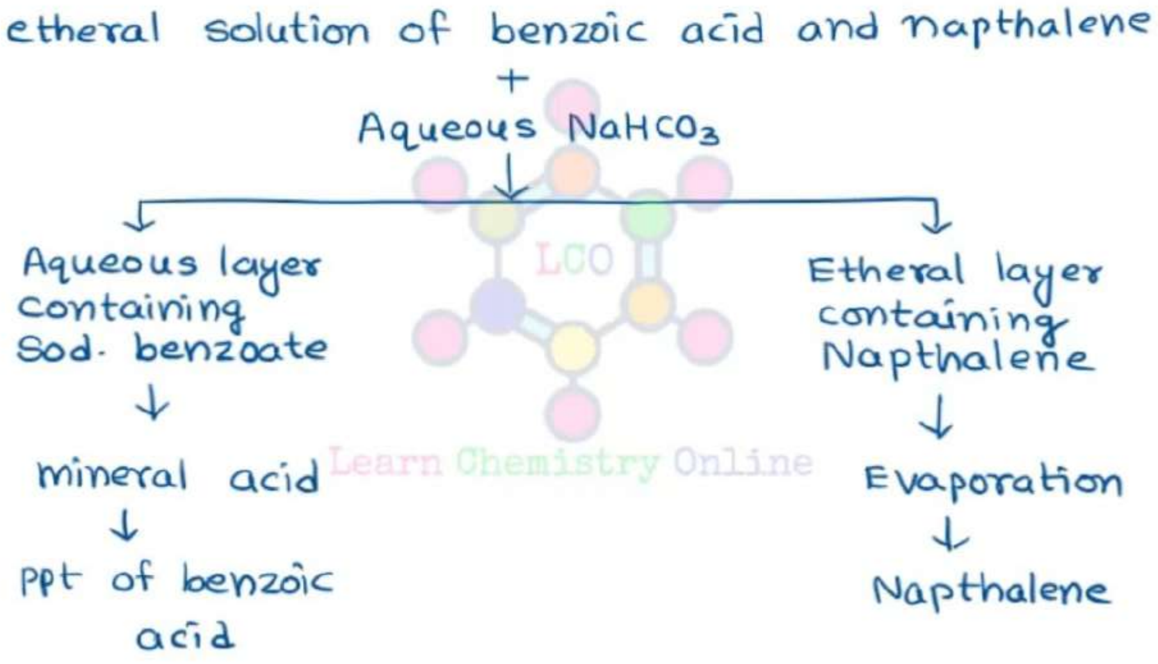
$$RCOOH + NaOH \longrightarrow \underset{\text{Sod. Carboxylate}}{RCOONa} + H_2O$$

$$RCOOH + NH_4OH \longrightarrow \underset{\text{Ammo. Carboxylate}}{RCOONH_4} + H_2O$$

$$2\,RCOOH + HgO \longrightarrow \underset{\text{Mercuric Carboxylate}}{(RCOO)_2Hg} + H_2O$$

- Carboxylic acids are much weaker than mineral acids such as HCl, H_2SO_4 and HNO_3. Therefore, salts of carboxylic acids are readily decomposed by these mineral acids to regenerate carboxylic acids.

– Example :- separation of benzoic acid from ethereal solution of benzoic acid and napthalene



→ Reactions of carboxylic acids:→ (Part-2)

II - Reactions due to –OH group of carboxylic acids: synthesis of acid chlorides, esters and amides :→

(i) Synthesis of acid chlorides:→

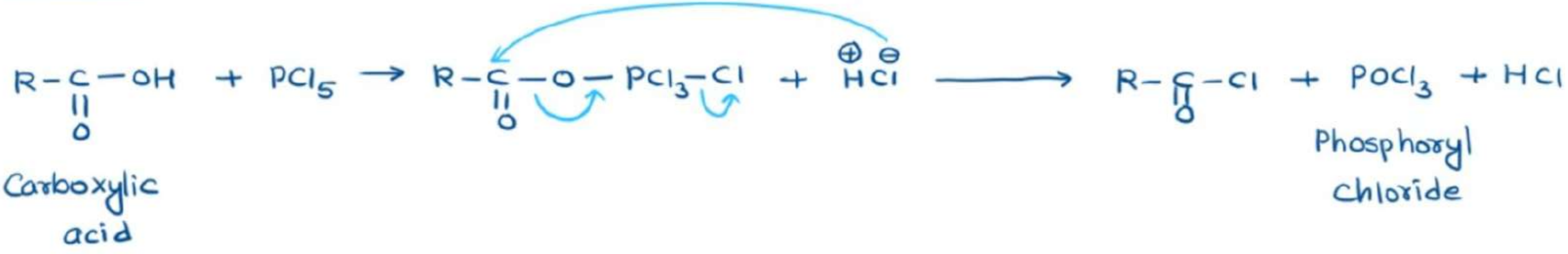
- The acid chlorides may be obtained in good yields by refluxing carboxylic acids with $SOCl_2$ or PCl_5.

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + POCl_3 + HCl$$

- Mechanism:→

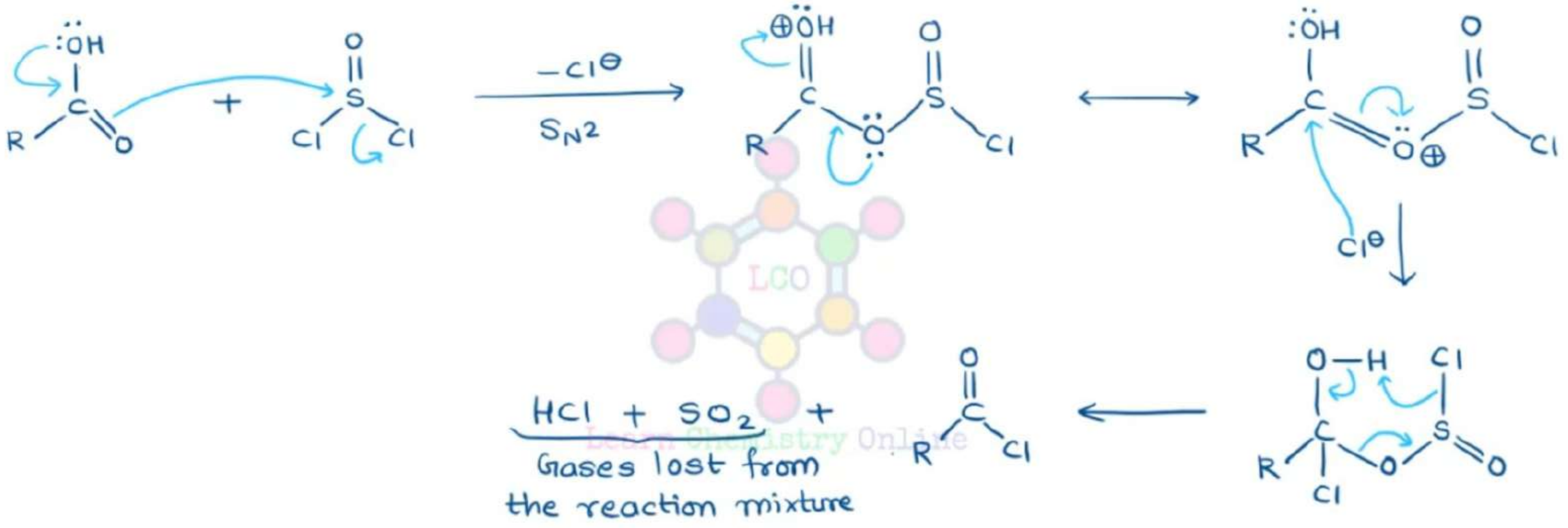


$$\underset{\text{Carboxylic acid}}{R-\underset{\underset{O}{\|}}{C}-OH} + PCl_5 \rightarrow R-\underset{\underset{O}{\|}}{C}-O-PCl_3-Cl + \overset{\oplus\ \ominus}{HCl} \longrightarrow R-\underset{\underset{O}{\|}}{C}-Cl + \underset{\text{Phosphoryl chloride}}{POCl_3} + HCl$$

$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$

→ Mechanism:→

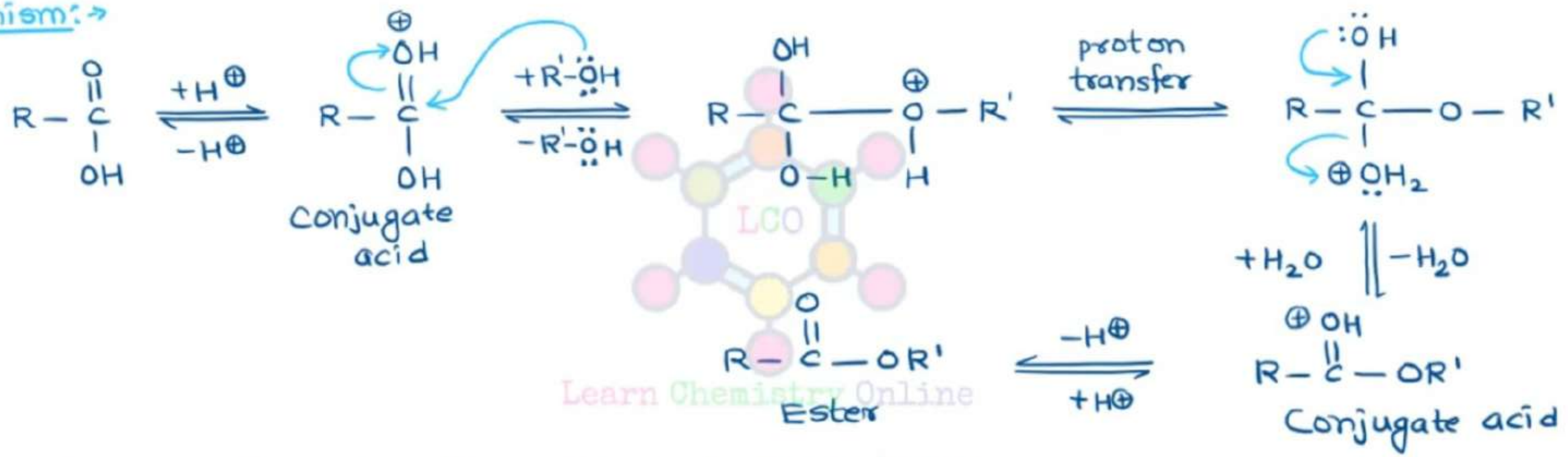


(ii) Synthesis of esters :→

(a) Fisher estrification :→

$$CH_3COOH + C_2H_5OH \xrightarrow[\text{Reflux}]{H^{\oplus}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

- Mechanism :→



(b) From sod. salt of carboxylic acids and alkyl halide:–

$$CH_3COONa + CH_3CH_2Br \xrightarrow{C_2H_5OH} CH_3COOCH_2CH_3 + NaBr$$

(c) From diazomethane:–

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

(iii) Synthesis of amides (Reaction with NH_3):→

$$R-COOH + NH_3 \longrightarrow \underset{\text{Ammo. salt}}{RCO\overset{\ominus}{O}\overset{\oplus}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Amide}}{RCONH_2}$$

$\oplus$

→ Reactions of carboxylic acids :→ (Part - 3)

III - Reactions involving whole –COOH group : Reduction of carboxylic acids :→

- Carboxylic acids are reduced to primary alcohols by reaction with $LiAlH_4$ in ether.

$$4\,RCOOH + LiAlH_4 \longrightarrow 4H_2 + (RCH_2O)_4AlLi \xrightarrow{H^+} 4\,RCH_2\text{-}OH$$

- Diborane reacts rapidly with carboxylic acids and reducing them to corresponding primary alcohols.

$$3RCOOH + B_2H_6 \longrightarrow (RCH_2O)_3B \xrightarrow{H^{\oplus}} 3RCH_2OH$$

- Primary alcohol can also be obtained by following method.

$$RCOOH \xrightarrow[\text{Estrification}]{R'\text{-}OH/H^{\oplus}} RCOOR' \xrightarrow[\text{Beauveault Blanc Reduction}]{Na/C_2H_5OH} RCH_2OH + R'OH$$

- The industrial process for the reduction of carboxylic acids to primary alcohols involves high pressure of hydrogen in presence of catalyst.

$$RCOOH + 2H_2 \xrightarrow[680\text{ atm}]{Ru} RCH_2OH + H_2O$$

- Carboxylic acids, on reduction with hydroiodic acid and red phosphorus at 473K, gives alkanes.

$$RCOOH + 6HI \xrightarrow[473\ K]{Red\ P} R-CH_3 + 2H_2O + 3I_2$$

$$CH_3COOH + 6HI \xrightarrow[473\ K]{Red\ P} CH_3-CH_3 + 2H_2O + 3I_2$$

In the above reactions, the $-COOH$ group is reduced to a $-CH_3$ group

- Mild reducing agents such as sodium borohydride, do not reduce carboxylate anion. If a molecule contains carboxylic acid as well as a ketone or an aldehyde, sodium borohydride reduced simple carbonyl group without reducing the acid function.

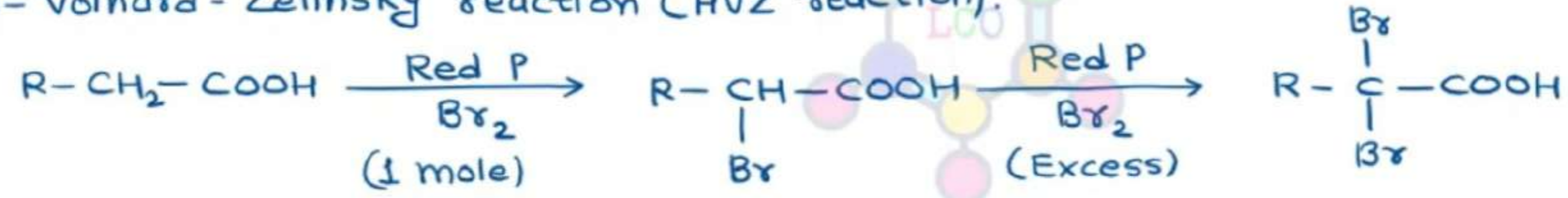
$$H-\underset{\underset{O}{||}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-ONa \xrightarrow{NaBH_4} HOCH_2CH_2CH_2CH_2-\overset{\overset{O}{||}}{C}-ONa$$

→ Reactions of carboxylic acids :→ (Part - 4)

IV - Reaction of alkyl group :→

→ Hell-Volhard-Zelinsky reaction : Halogenation :→

- The extent of enolisation of carboxylic acids as compared to ketone is negligibly small and carboxylic acids do not undergo halogenation even in the presence of acids. That is why, acetic acid is used as a solvent in most of the bromination reactions.
- However when a carboxylic acid is treated with halogen in the presence of red phosphorus, it results in the formation of an α-haloacid. This reaction is known as Hell-Volhard-Zelinsky reaction (HVZ reaction).

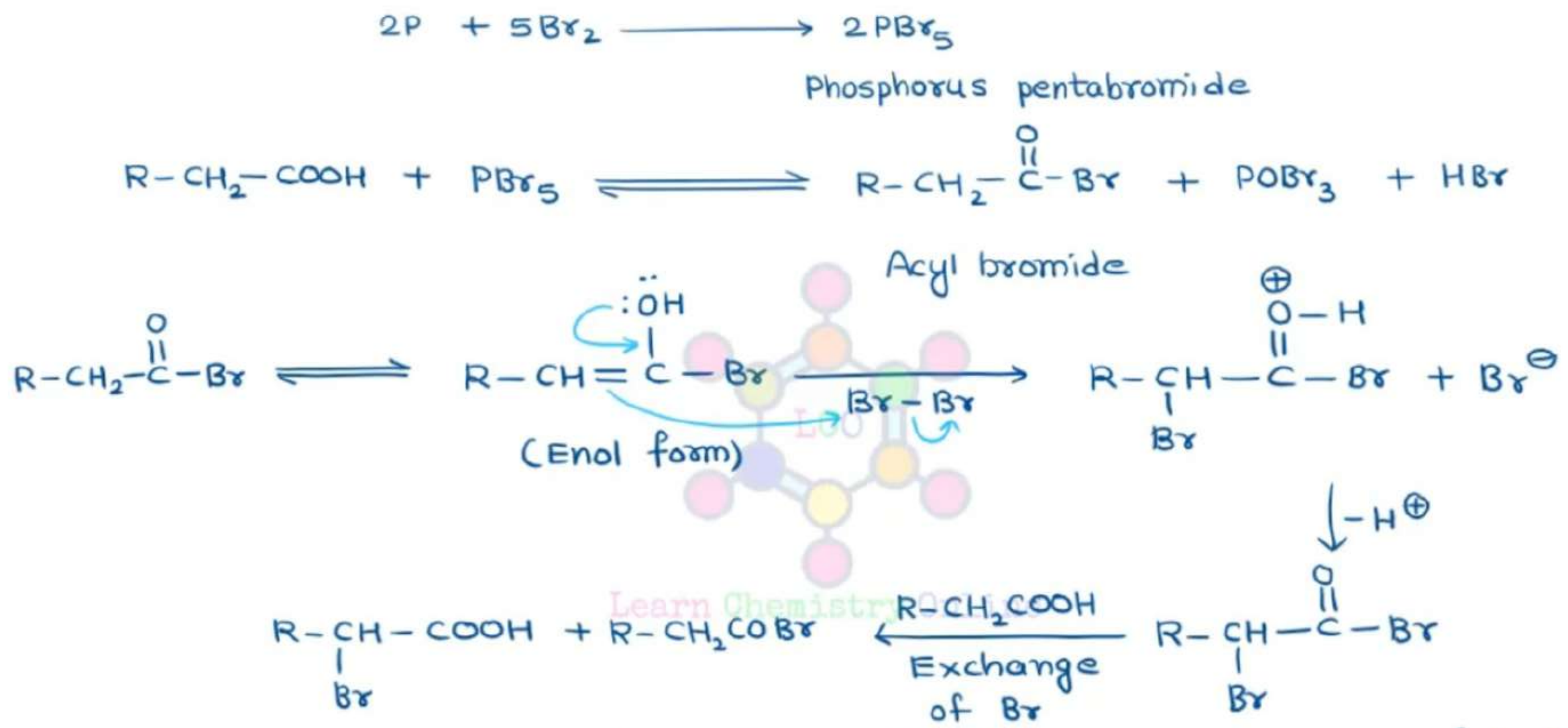


$$R-CH_2-COOH \xrightarrow[\text{Br}_2\ (1\text{ mole})]{\text{Red P}} R-\underset{\underset{Br}{|}}{CH}-COOH \xrightarrow[\text{Br}_2\ (\text{Excess})]{\text{Red P}} R-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-COOH$$

- Role of Red P :→

- The catalytic effect of red phosphorus has been explained on the basis of the fact that carboxylic acid is first converted into the acyl halide and then the acyl halide undergoes substitution by halogen at α-position. Acyl halide are known to undergo halogenation much more rapidly than acids.

- Mechanism :→



$$2P + 5Br_2 \longrightarrow 2PBr_5$$

$$R-CH_2-COOH + PBr_5 \rightleftharpoons R-CH_2-\overset{O}{\overset{\|}{C}}-Br + POBr_3 + HBr$$

$$R-CH_2-\overset{O}{\overset{\|}{C}}-Br \rightleftharpoons R-CH=\overset{\ddot{O}H}{\overset{|}{C}}-Br \xrightarrow[Br-Br]{} R-\underset{Br}{\underset{|}{CH}}-\overset{\overset{\oplus}{O}-H}{\overset{\|}{C}}-Br + Br^{\ominus}$$

$$\xrightarrow{-H^{\oplus}} R-\underset{Br}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-Br \xrightarrow[\text{Exchange of Br}]{R-CH_2COOH} R-\underset{Br}{\underset{|}{CH}}-COOH + R-CH_2COBr$$

- All the α-hydrogens can successively be replaced using an excess of halogen. The reaction can, however, be stopped at mono-, di- or trisubstitution stage using appropriate amount of halogen

- Bromine and chlorine are equally useful.

$$CH_3-COOH \xrightarrow[Cl_2]{\text{Red P}} ClCH_2-COOH \xrightarrow[Cl_2]{\text{Red P}} Cl_2CH-COOH \xrightarrow[Cl_2]{\text{Red P}} Cl_3C-COOH$$

- Bromination stops after all the α-hydrogn atoms are displaced whereas chlorination continous farther in the chain.
- HVZ reaction has considerable synthetic utility since the α-halogenated carboxylic acids can be easily converted into a number of α-substituted carboxylic acids by nucleophilic displacement reactions.

→ Reactions of carboxylic acids :→ (Part-5)

V - Decarboxylation :→

(a) Chemical decarboxylation :→

- On heating carboxylic acid with sodalime ($NaOH + CaO$), decarboxylation of carboxylic acid takes place and corresponding alkane is formed.

$$\underset{}{RCOONa} + NaOH \xrightarrow[630\,K]{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

$$\underset{\text{Sod. propionate}}{CH_3CH_2COONa} + NaOH \xrightarrow[630\,K]{CaO} \underset{\text{Ethane}}{CH_3-CH_3} + Na_2CO_3$$

- Mechanism:→

$$R-\overset{}{\underset{\overset{\|}{O}}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} \xrightarrow{\Delta} \underset{\text{Carbanion}}{\overset{\ominus}{R}\overset{\oplus}{Na}} + O=C=O$$

$$\overset{\ominus}{R}\overset{\oplus}{Na} \xrightarrow[(H_2O)]{+H^{\oplus}} \underset{\text{Alkane}}{R-H} + NaOH$$

- Effect of substituents on decarboxylation :→

- Any factor which increases the stability of carbanion, formed during the process, should increase the rate of decarboxylation.

(b) Electrolytic decarboxylation (Kolbe's electrolytic reaction):-

- Electrolysis of aq. solution of sodium or potassium salts of fatty acids gives alkanes.

$$2\,RCOONa \longrightarrow \underset{\text{At anode}}{2RCOO^-} + \underset{\text{At cathode}}{2Na^+} \quad \text{(Ionisotion)}$$

$$2H_2O \rightleftharpoons \underset{\text{At anode}}{2\overset{\ominus}{O}H} + \underset{\text{At cathode}}{2H^{\oplus}} \quad \text{(Ionisation)}$$

$$\text{At anode} \quad 2RCOO^{\ominus} \xrightarrow[-e^-]{} \underset{\text{(unstable)}}{2RCOO^{\bullet}} \xrightarrow[-2CO_2]{} 2R^{\bullet} \xrightarrow{\text{Coupling}} \underset{\text{Alkane}}{R-R}$$

- Both Na^+ (from salt) and H^+ (from H_2O) are present at cathode, but H^+ ions are preferentially discharged due to their lower discharge potential compared to Na^+ ions and thus hydrogen gas is evolved at the cathode.

$$\text{At cathode} \quad 2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$$

- The overall Kolbe's reaction may be represented as

$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} R-R + CO_2 + H_2 + 2NaOH$$

- Electrolysis of sodium formate, however, yields only H_2 and not an alkane.

(c) Hundsdiecker reaction : Decarboxylation of silver salts of carboxylic acids in presence of bromine.

- Aryl / alkyl bromides containing one carbon atom less than the parent acid are obtained

$$\underset{\text{Silver acetate}}{CH_3COOAg} + Br_2 \xrightarrow{CCl_4,\ Reflux} \underset{\text{Methyl bromide}}{CH_3-Br} + CO_2 + AgBr$$

— Mechanism:→

Step - I Formation of acyl hypobromite

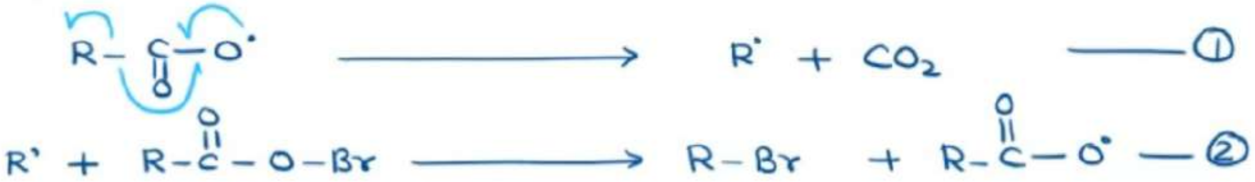
$$R-\underset{\underset{O}{\|}}{C}-OAg + Br_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-O-Br + AgBr$$

Step-II Chain initiation

$$R-\underset{\underset{O}{\|}}{C}-O-Br \longrightarrow R-\underset{\underset{O}{\|}}{C}-O^{\cdot} + Br^{\cdot}$$

Acyloxy radical

Step-III chain propagation



$$R-\underset{\underset{O}{\|}}{C}-O^{\cdot} \longrightarrow R^{\cdot} + CO_2 \quad \text{—— ①}$$

$$R^{\cdot} + R-\overset{\overset{O}{\|}}{C}-O-Br \longrightarrow R-Br + R-\overset{\overset{O}{\|}}{C}-O^{\cdot} \quad \text{—— ②}$$

- Reactions ① and ② are repeated again and again until the reaction is complete.

→ Effects of substituents on acid-strength:→

(a) Aliphatic acids:→

- The carboxylic acids ionises as per following expression—

$$\underset{}{R-COOH} \rightleftharpoons \underset{\text{Carboxylate ion}}{R-COO^{\ominus}} + \underset{\text{proton}}{H^{\oplus}}$$

$$\text{stability of carboxylate ion} \propto \frac{1}{\text{-ve charge of carboxylate ion}}$$

$$\text{stability of carboxylate ion} \propto \text{acidic strength}$$

(i) Effect of electron-donating group (+I effect):→

- Electron-donating group (+I effect) increases the negative charge on the anion and hence destabilising the carboxylate anion and consequently decreases the strength of the acid.

+I effect → $-CH_3 < -C_2H_5 < -CH(CH_3)_2 < -C(CH_3)_3$

Acidic strength → $CH_3COOH > C_2H_5COOH < (CH_3)_2CH-COOH > (CH_3)_3CCOOH$

(ii) Effect of electron-attrating groups (-I effect):→

- Electron-attracting group (-I effect) decreases the negative charge on the anion and hence stabilising the carboxylate anion and consequently increases the strength of the acid.

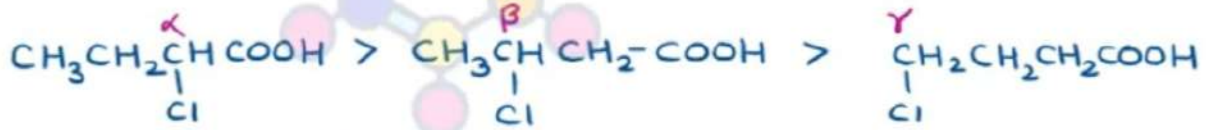
Acidic strength $CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$

- Fluoroacetic acid is more stronger than chloroacetic acid. because fluorine is most electron attracting halogen.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

- The inductive effect decreases with increasing distance of electron-attracting group from the carboxyl group.

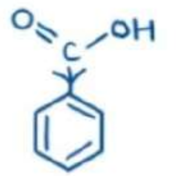
Acid strength



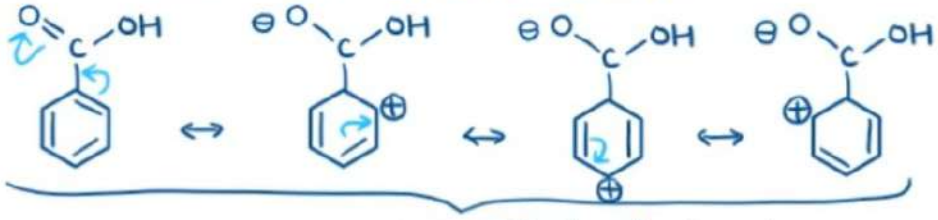
$CH_3CH_2\underset{Cl}{\overset{\alpha}{C}}HCOOH > CH_3\underset{Cl}{\overset{\beta}{C}}HCH_2-COOH > \underset{Cl}{\overset{\gamma}{C}}H_2CH_2CH_2COOH$

(b) Aromatic acids:→

- In aromatic acids the carboxylic group is directly attached to the aromatic ring which exerts -I effect as well as +R effect as shown below-



-I effect
of phenyl group



+R effect of phenyl group

- The overall electron-donating effect (−I effect and +R effect) of phenyl group (C_6H_5-) is weaker than +I effect of any alkyl group. As a result, unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aromatic acids.

Acidic order $HCOOH > C_6H_5COOH > CH_3COOH$

→ Effect of substituent on acidic strength of aromatic acids :→

- Electron-withdrawing groups (−I effect) tend to stabilise the carboxylate anion by decreasing −ve charge on anion and hence increases the acidic strength.

- Electron- donating groups (+I effect) tend to destabilise the carboxyate anion by increasing −ve charge on anion and hence decreases the acidic strength.

→ Effect of substituents on m- and p- positions :→

Electron withdrawing group -

- p-isomer is stronger acid than m-isomer
- In case of p-isomer electron withrawing group withdraws electrons both by −R effect and −I effect while in case of m-isomer, only the −I effect works.

Electron donating group -

- p-isomer is weaker acid than m-isomer
- In case of p-isomer both +R and −I effect works but +R effect predominates, hence acidic strength decreases due to destabilisation of anion. While in case of m-isomer only the −I effect works and there is no +R effect. Since +R effect outweights the −I effect, therefore p-isomer is weaker acid than m-isomer.

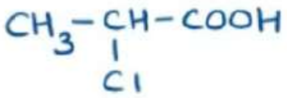
→ Ortho effect :→

- Ortho isomers (containing EDG or EWG) are stronger than m- and p-isomers. This effect is called ortho effect. This effect is due to a combination of both steric and electronic factors.

Example:- O-Toluic acid > Benzoic acid > m-Toluic acid > P-Toluic acid

→ Halo acids:→

- Halo acids are the substituted acids obtained by the replacement of one or more hydrogen atoms of the alkyl group of the parent acid by halogen atom(s)

$ClCH_2COOH$	Chloroacetic acid
$Cl_2CH\ COOH$	Dichloroacetic acid
$Cl_3CH\ COOH$	Trichloroacetic acid
 $CH_3-\underset{\displaystyle Cl}{\underset{\mid}{C}H}-COOH$	α-chloropropionic acid

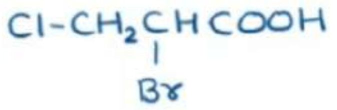
→ Nomenclature:→

(i) Common system:→

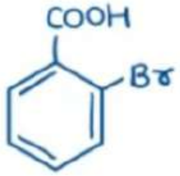
- In this system, they are assigned trivial names and the position of halogen atom(s) is indicated by Greek letters α, β, γ, δ etc.

(ii) IUPAC system:→

- In this system, the position of the halogen denoted by the number of carbon atom bearing the halogen.
- The carbon of the carboxyl group being always numbered as 1

	Common	IUPAC
$ClCH_2COOH$	Chloroacetic acid	Chloroethanoic acid
$Br\,CH_2CH_2COOH$	β- Bromopropionic acid	3-Bromopropanoic acid
 $Cl-CH_2\underset{\underset{Br}{\vert}}{C}HCOOH$	α-Bromo-β-Chloropropionic acid	2-Bromo-3-Chloropropanoic acid

- Aromatic acids are named by indicating the position of halogen atom with respect to carboxylic group using the symbols o, m, p or numbers 1,2,3 etc.



2-Bromobenzoic acid
o-Bromobenzoic acid

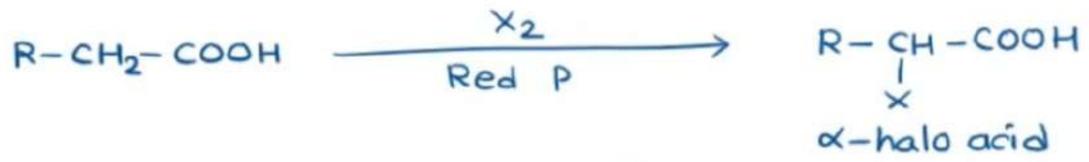
3-Bromobenzoic acid
m-Bromobenzoic acid

4-Bromobenzoic acid
p-Bromobenzoic acid

→ Methods of formation of halo acids:→

(a) Preparation of α-haloacids:→

(1) Hell-Volhard-Zelinsky reaction (HVZ reaction):→



$$R-CH_2-COOH \xrightarrow[\text{Red P}]{X_2} R-\underset{\underset{X}{|}}{CH}-COOH$$

α-halo acid

$$\underset{\text{Butyric acid}}{CH_3-CH_2-CH_2-COOH} \xrightarrow[\text{Red P}]{Br_2} CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-COOH$$

- In presence of excess of halogen, the products obtained are α,α-dihalo acids or α,α,α-trihalo acids.

$$\underset{\text{Chloroacetic acid}}{ClCH_2COOH} \xrightarrow[\text{Red P}]{Cl_2} \underset{\text{dichloroacetic acid}}{Cl_2CHCOOH} \xrightarrow[\text{Red P}]{Cl_2} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH}$$

- Bromination occurs exclusively at α-position while chlorination first occurs at the α-position and when all the α-hydrogens have been replaced, it occurs further at β-and γ-positions along the chain.
- α-haloacids can also be obtained by passing Cl_2 or Br_2 through the boiling carboxylic acid in presence of sunlight and halogen carrier (I, P, S, Fe etc.)

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[I_2/P/S/Fe]{Br_2,\ h\nu} \underset{\text{Monobromoacetic acid}}{BrCH_2COOH} \xrightarrow[I_2/P/S/Fe]{Br_2,\ h\nu} \underset{\text{dibromoacetic acid}}{Br_2CHCOOH} \xrightarrow[I_2/P/S/Fe]{Br_2,\ h\nu} \underset{\text{tribromoacetic acid}}{Br_3CCOOH}$$

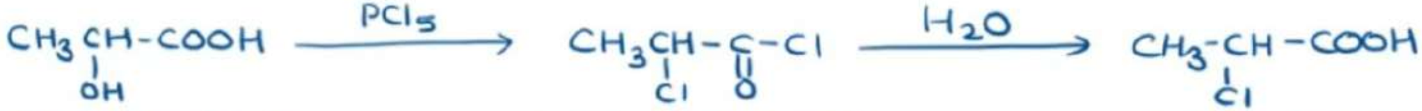
2. Finkelstein reaction:→

– synthesis of α-Iodoacids.

$$\underset{\alpha\text{-Bromopropionic acid}}{CH_3CHBrCOOH} + KI \longrightarrow \underset{\alpha\text{-Iodopropionic acid}}{CH_3CHICOOH} + KBr$$

3. Halogenation of alkylmalonic acid followed by decarboxylation.

4. From hydroxy acids by the action of hydrogen halide or phosphorous halides:→



$$\underset{\substack{|\\OH}}{CH_3CH}\text{-}COOH \xrightarrow{PCl_5} CH_3\underset{\substack{|\\Cl}}{CH}\text{-}\underset{\substack{\|\\O}}{C}\text{-}Cl \xrightarrow{H_2O} CH_3\text{-}\underset{\substack{|\\Cl}}{CH}\text{-}COOH$$

α-Hydroxypropionic acid (Lactic acid)

α-chloropropionyl chloride

α-Chloropropionic acid

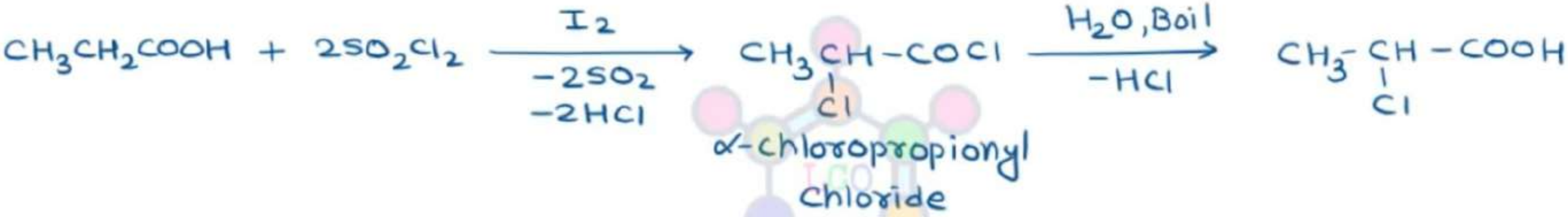
5. From amino acid:-

$$R\text{-}\underset{NH_2}{\underset{|}{CH}}-COOH + NOCl \longrightarrow R\text{-}\underset{Cl}{\underset{|}{CH}}\text{-}COOH + N_2 + H_2O$$

Nitrosyl Chloride

α-halo acid

6. From carboxylic acid and sulphonyl chloride:→



$$CH_3CH_2COOH + 2SO_2Cl_2 \xrightarrow[-2SO_2,\ -2HCl]{I_2} CH_3\underset{Cl}{\underset{|}{CH}}-COCl \xrightarrow[-HCl]{H_2O,\ Boil} CH_3-\underset{Cl}{\underset{|}{CH}}-COOH$$

α-chloropropionyl Chloride

(b) Preparation of β-haloacids:→

1. From α, β-unsaturated acids:→

$$CH_2{=}CHCOOH + HBr \longrightarrow BrCH_2CH_2COOH$$

Acrylic acid β- Bromopropionic acid

- This reaction is an example of anti-Markownikoff addition → This is due to −I effect of carboxylic acid.

2. From β-hydroxyacids:→

$$HOCH_2-CH_2-COOH \xrightarrow{HBr} BrCH_2CH_2COOH$$

β-hydroxypropionic acid

3. From olefin cyanohydrin:→

$$\underset{\text{Ethylene cyanohydrin}}{HO-CH_2-CH_2-CN} + 2HBr + H_2O \longrightarrow BrCH_2CH_2COOH + NH_4Br$$

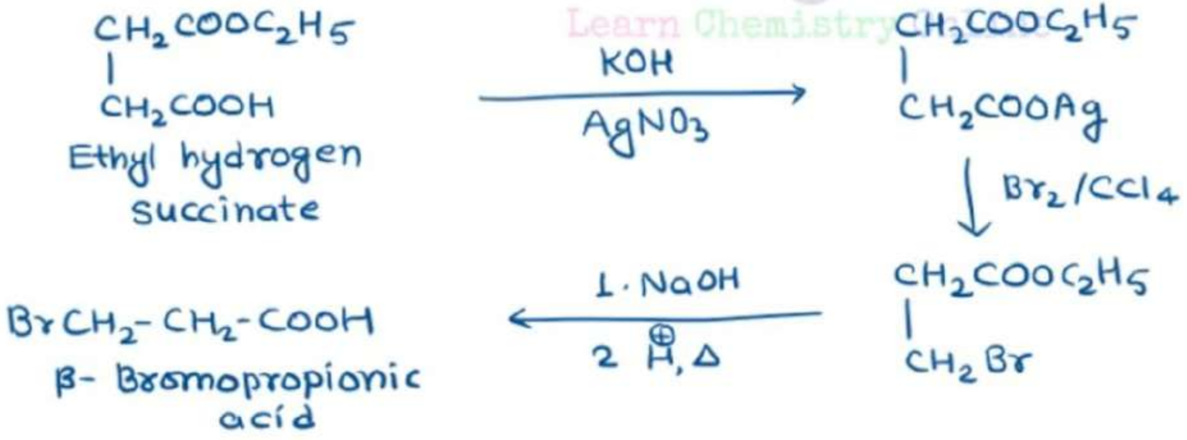
4. By oxidation of alkene halohydrins:→

$$\underset{\text{Ethylene chlorohydrin}}{Cl-CH_2-CH_2-OH} \xrightarrow[HNO_3]{[O]} \underset{\beta\text{-chloropropionic acid}}{Cl-CH_2-CH_2-COOH}$$

5. From unsaturated aldehydes:→

$$CH_2=CH-CHO \xrightarrow{HCl} Cl-CH_2-CH_2-CHO \xrightarrow{[O]} Cl-CH_2-CH_2-COOH$$

6. Hunsdieker reaction:→



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOH \end{array} \xrightarrow[AgNO_3]{KOH} \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOAg \end{array} \xrightarrow{Br_2/CCl_4} \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2Br \end{array} \xrightarrow[2.\ \overset{\oplus}{H},\Delta]{1.\ NaOH} BrCH_2-CH_2-COOH$$

Ethyl hydrogen succinate

β- Bromopropionic acid

(c) Preparation of γ-haloacids:→

1. From β,γ-unsaturated acids:→

$$CH_3CH = CHCH_2COOH + HBr \longrightarrow CH_3CHBrCH_2CH_2COOH$$

β-γ-unsaturated acid γ-Haloacid

2. From γ-hydroxy acids:→

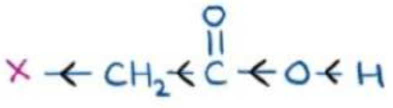
$$HOCH_2-CH_2CH_2-COOH \xrightarrow[-H_2O]{HCl} ClCH_2CH_2CH_2COOH$$

γ-hydroxybutyric acid γ-Chlorobutyric acid

→ Halo acids :-

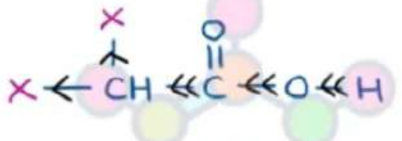
→ Physical properties :->

- The lower haloacids are colourless liquids while the higher ones are solid.
- The haloacids show acidic character when dissolved in water. The strength of the acid depends upon the nature, number and the position of the halogen atom in the chain.
- This acidic character is due to electron withdrawing inductive effect (−I effect) of the halogen atom.



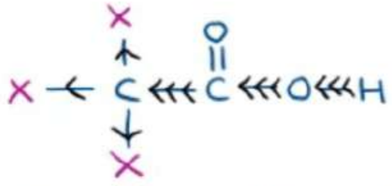
$X \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow O \leftarrow H$

Monohaloacetic acid



$X \leftarrow \overset{X}{\overset{\uparrow}{C}}H \twoheadleftarrow \overset{O}{\overset{\|}{C}} \twoheadleftarrow O \twoheadleftarrow H$

Dihaloacetic acid



$X \leftarrow \underset{X}{\underset{\downarrow}{\overset{X}{\overset{\uparrow}{C}}}} \lll \overset{O}{\overset{\|}{C}} \lll O \lll H$

Trihaloacetic acid

- For the same halogen atom, more is the number of halogen atom attached to α-carbon, the stronger is its inductive effect and thus stronger is the acid. Trifluoroacetic acid is the strongest organic acid.
- If the distance of the halogen atom increases from the carboxyl group, acid strength decreases. because with increasing distance −I effect of halogen atom decreases. Thus the order of decreasing acid strength is as follows –

α-haloacids > β-haloacids > γ-haloacids

- The strength of acid decreases with a decrease in the electronegativity of the halogen atom

Example:- Decreasing order of strength of halocarboxylic acid is as follows:-

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$$

→ Chemical reactions of halo acids:→

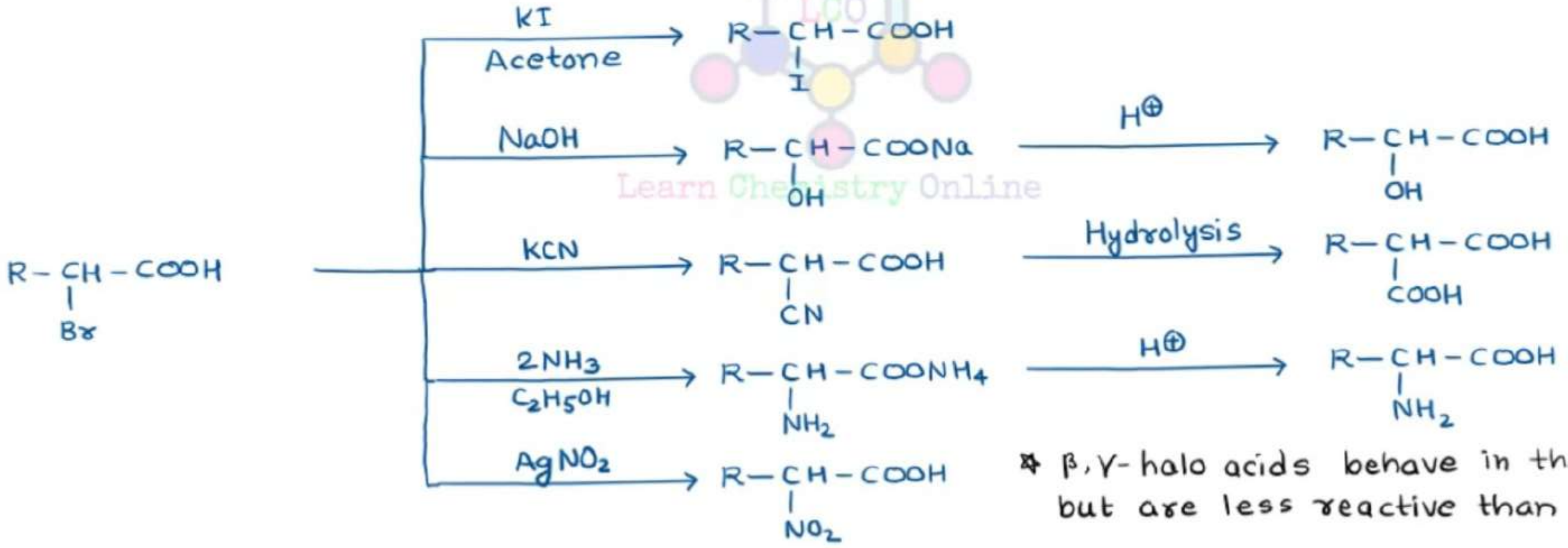
- Halo acids have two sites of activity, so they undergo reactions of both alkyl halide and carboxylic acids.

1. Reactions of the halogen atom:→

- The reactions of halogen attached to α- carbon is similar to alkyl halides. The reactivity of halogen in carboxylic acid is more than in alkyl halide.

(a) Bimolecular nucleophilic substitution reactions (S_N2):→

- The halogen atoms of α-haloacids are more reactive (due to -I effect of -COOH group) and undergo a variety of S_N2 reactions.



$$R-\underset{Br}{\underset{|}{C}}H-COOH \xrightarrow[Acetone]{KI} R-\underset{I}{\underset{|}{C}}H-COOH$$

$$R-\underset{Br}{\underset{|}{C}}H-COOH \xrightarrow{NaOH} R-\underset{OH}{\underset{|}{C}}H-COONa \xrightarrow{H^{\oplus}} R-\underset{OH}{\underset{|}{C}}H-COOH$$

$$R-\underset{Br}{\underset{|}{C}}H-COOH \xrightarrow{KCN} R-\underset{CN}{\underset{|}{C}}H-COOH \xrightarrow{Hydrolysis} R-\underset{COOH}{\underset{|}{C}}H-COOH$$

$$R-\underset{Br}{\underset{|}{C}}H-COOH \xrightarrow[C_2H_5OH]{2NH_3} R-\underset{NH_2}{\underset{|}{C}}H-COONH_4 \xrightarrow{H^{\oplus}} R-\underset{NH_2}{\underset{|}{C}}H-COOH$$

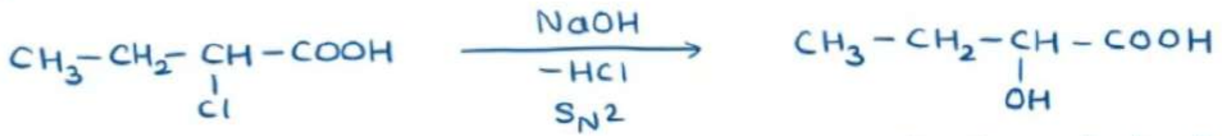
$$R-\underset{Br}{\underset{|}{C}}H-COOH \xrightarrow{AgNO_2} R-\underset{NO_2}{\underset{|}{C}}H-COOH$$

✲ β, γ- halo acids behave in the same way but are less reactive than α-halo acids.

(b) Action of alkali:→

- Depending upon the position of halogen atom relative to carboxylic group, the action of alkali with different haloacids give different products.

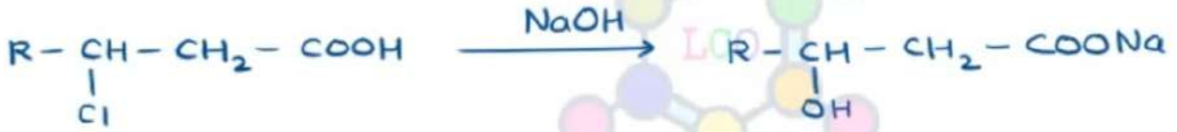
(i) α-haloacids :→



$$CH_3-CH_2-\underset{Cl}{\underset{|}{CH}}-COOH \xrightarrow[\substack{-HCl \\ S_N2}]{NaOH} CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-COOH$$

α-chlorobutyric acid α-hydroxybutyric acid

(ii) β-haloacids:→

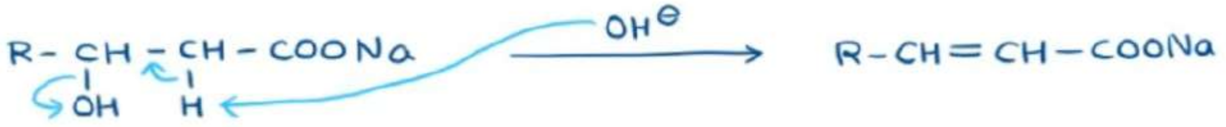


$$R-\underset{Cl}{\underset{|}{CH}}-CH_2-COOH \xrightarrow{NaOH} R-\underset{OH}{\underset{|}{CH}}-CH_2-COONa$$

(substitution reaction)

β-hydroxy acid

- prolonged heating of β-hydroxy acid with aq. alkali give α,β- unsaturated acids by base catalysed elimination of water.



$$R-\underset{OH}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH}}-COONa \xrightarrow{OH^{\ominus}} R-CH=CH-COONa$$

(Elimination reaction)

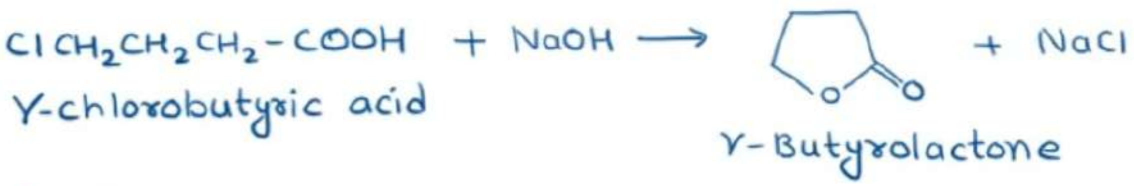
- Example:-

$$CH_3CHClCH_2COOH \xrightarrow[(ii)\ H^{\oplus}]{(i)\ KOH} CH_3CHOHCH_2COOH \xrightarrow[\substack{(ii)\ H^{\oplus} \\ -H_2O}]{(i)\ KOH} CH_3CH=CHCOOH$$

β-Chlorobutyric acid β-hydroxy butyric acid Crotonic acid

(iii) γ-and δ- halo acids :-

- These form lactones (cyclic Ketones) on treatment with alkali.



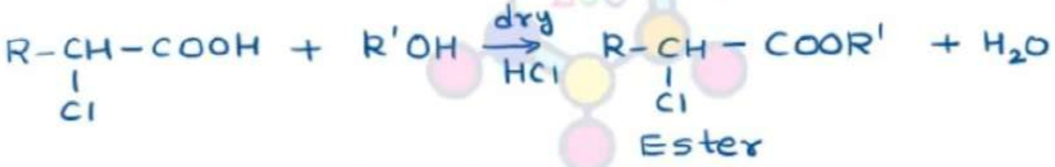
$ClCH_2CH_2CH_2-COOH + NaOH \longrightarrow$ γ-Butyrolactone $+ NaCl$

γ-chlorobutyric acid

2. Reactions of carboxylic group:→

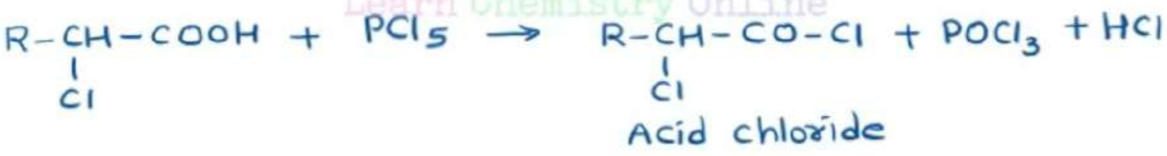
$$R-\underset{Cl}{\underset{|}{C}H}-COOH + NaOH \longrightarrow R-\underset{Cl}{\underset{|}{C}H}-COONa + H_2O$$

Salt



$$R-\underset{Cl}{\underset{|}{C}H}-COOH + R'OH \xrightarrow[HCl]{dry} R-\underset{Cl}{\underset{|}{C}H}-COOR' + H_2O$$

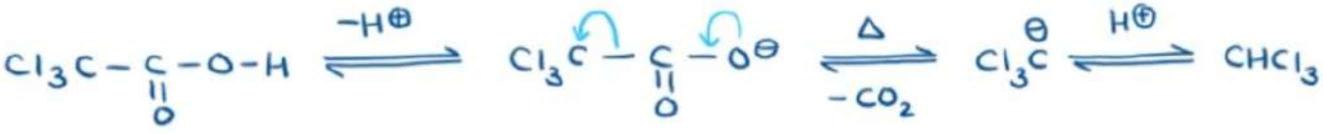
Ester



$$R-\underset{Cl}{\underset{|}{C}H}-COOH + PCl_5 \longrightarrow R-\underset{Cl}{\underset{|}{C}H}-CO-Cl + POCl_3 + HCl$$

Acid chloride

3. Decarboxylation:→



$$Cl_3C-\underset{O}{\underset{||}{C}}-O-H \xrightleftharpoons{-H^{\oplus}} Cl_3C-\underset{O}{\underset{||}{C}}-O^{\ominus} \xrightleftharpoons[-CO_2]{\Delta} Cl_3\overset{\ominus}{C} \xrightleftharpoons{H^{\oplus}} CHCl_3$$

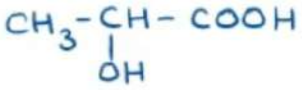
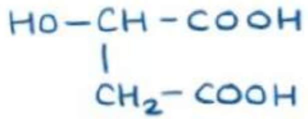
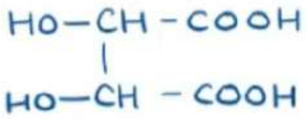
→ Hydroxy acids :→

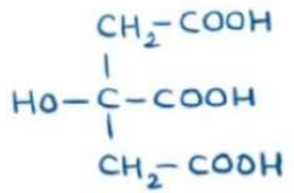
- Hydroxy acids are polyfunctional compounds having hydroxyl group (–OH) as well as carboxyl group (–COOH).
- Many of the hydroxy acids occur in nature.

Example – Tartaric acid occurs in tamarind.
Citric acid occurs in citrus fruits.
Malic acid occurs unripe apple.

→ Nomenclature :→

- In common system, hydroxy acids are named as derivatives of the parent acid, where the position of hydroxy group is denoted by greek letters α, β, γ etc.
- In IUPAC system, the position of hydroxy group is indicated by numbers.

Hydroxy acid	Common name	IUPAC name
$HO-CH_2-COOH$	Hydroxyacetic acid (Glycollic acid)	Hydroxyethanoic acid
 $CH_3-\underset{\overset{\mid}{OH}}{CH}-COOH$	α-Hydroxypropionic acid (Lactic acid)	2-Hydroxypropanoic acid
 $\begin{array}{l}HO-CH-COOH\\ \qquad\mid\\ \qquad CH_2-COOH\end{array}$	Monohydroxysuccinic acid (Malic acid)	2-Hydroxybutanedioic acid
 $\begin{array}{l}HO-CH-COOH\\ \qquad\mid\\ HO-CH-COOH\end{array}$	Dihydroxysuccinic acid (Tartaric acid)	2,3-Dihydroxybutanedioic acid



$$HO-\underset{CH_2-COOH}{\overset{CH_2-COOH}{C}}-COOH$$

β-Hydroxytricarballylic acid
(citric acid)

2-Hydroxy-1,2,3-propane-tricarboxylic acid

→ Methods of formation:→

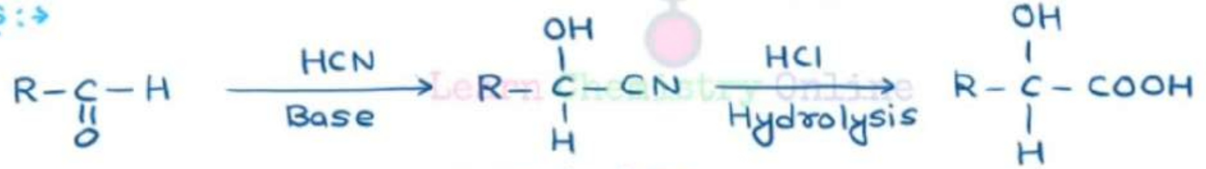
1. From α-halocarboxylic acid:→

$$Cl-CH_2-COOH \xrightarrow[\text{(Moist } Ag_2O)]{AgOH} HO-CH_2-COOH$$

Chloroacetic acid   Glycollic acid

$$Cl-CH_2-COOH \xrightarrow[\Delta]{\overset{\ominus}{O}H} HO-CH_2-COOH$$

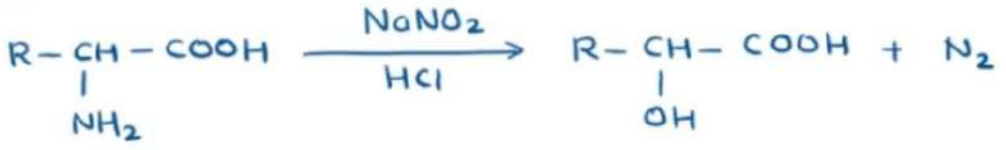
2. From aldehydes:→



$$R-\underset{O}{\overset{}{\underset{\|}{C}}}-H \xrightarrow[\text{Base}]{HCN} R-\underset{H}{\overset{OH}{C}}-CN \xrightarrow[\text{Hydrolysis}]{HCl} R-\underset{H}{\overset{OH}{C}}-COOH$$

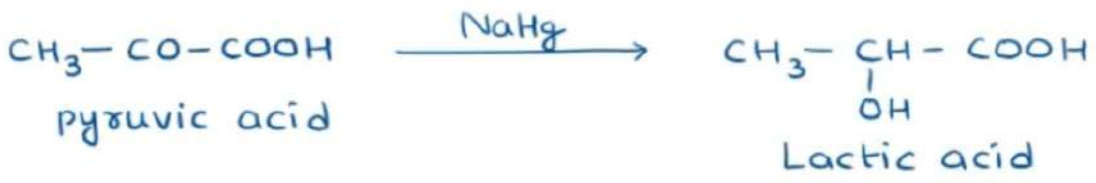
Cyanohydrin

3. From amino acids:→



$$R-\underset{NH_2}{CH}-COOH \xrightarrow[HCl]{NaNO_2} R-\underset{OH}{CH}-COOH + N_2$$

4. From aldehydic and ketonic acids:→



$$\underset{\text{pyruvic acid}}{CH_3-CO-COOH} \xrightarrow{NaHg} \underset{\text{Lactic acid}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH}$$

5. From ketoesters:→

$$CH_3COCH_2COOC_2H_5 \xrightarrow[423\,K]{Ni/H_2} CH_3CHOHCH_2COOC_2H_5 \xrightarrow[(ii)\ H^{\oplus}]{(i)\ KOH} CH_3CHOHCH_2COOH$$

β-hydroxybutyric acid

6. Reformatsky reaction:→

$$R-\overset{\displaystyle O}{\overset{||}{C}}-H \xrightarrow{Zn/BrCH_2COOEt} R-\overset{\displaystyle \overset{\ominus}{O}\overset{\oplus}{Zn}Br}{\overset{|}{CH}}-CH_2COOEt \xrightarrow{H_3O^{\oplus}} R-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2COOH$$

7. From polyhydric alcohols and hydroxy aldehydes:→

$$HO-CH_2-CH_2-OH \xrightarrow{dil.\ HNO_3} HOCH_2COOH$$

$$HO-CH_2-CH_2-CHO \xrightarrow{Ag_2O} HOCH_2CH_2COOH$$

→ Physical properties:→

(i) Physical state :- Hydroxy acids are colourless crystalline solids or syrupy liquids.

(ii) Solubility:- They are readily soluble in water because both the functional groups (–OH and –COOH) can form hydrogen bond with water. They are less soluble in ether.

(iii) m.p. and b.p. :→ Due to formation of hydrogen bonds they have higher m.p. and b.p. as compared to the corresponding fotty acids.

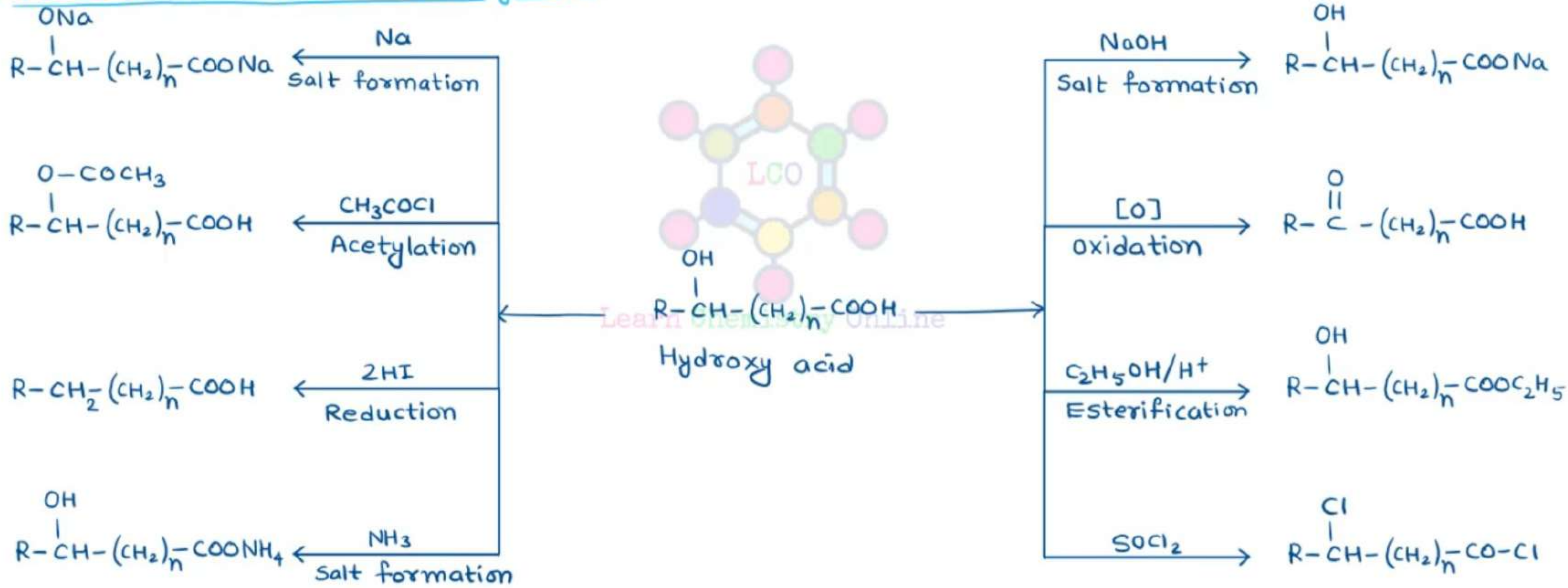
(iv) Acidic character:→ Due to electron withdrawing effect of OH group they are stronger acids than corresponding unsubstituted acids.

→ Hydroxy acids :→

→ Chemical reactions:→

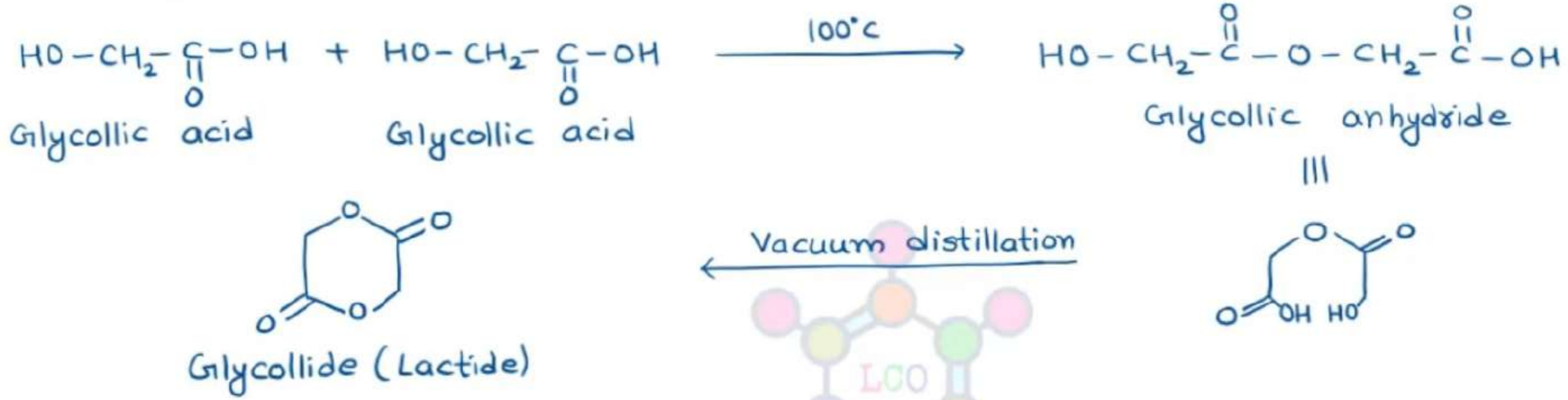
– The molecule of hydroxy acid contains a carboxyl group and a alcoholic group due to which they undergo reactions characteristic of both carboxyl and hydroxyl group. However because of presence of these two groups together, they undergo some additional reactions also.

1. Reactions of –OH and –COOH groups:→

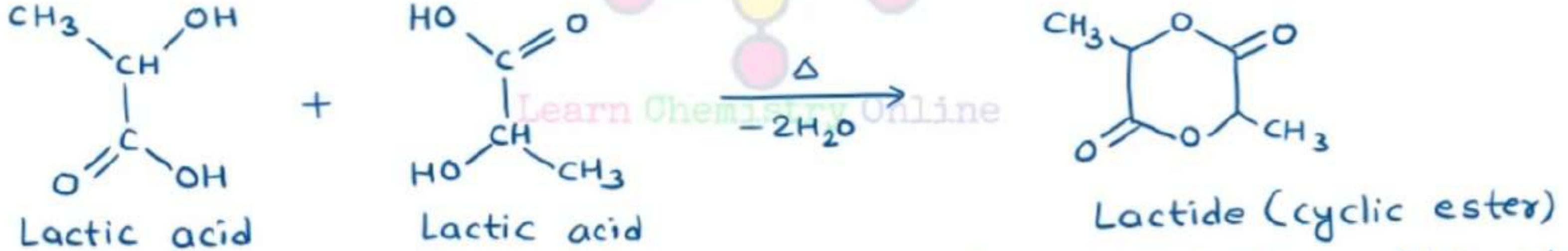


2 Action of heat :→

(i) α-hydroxy acids :→



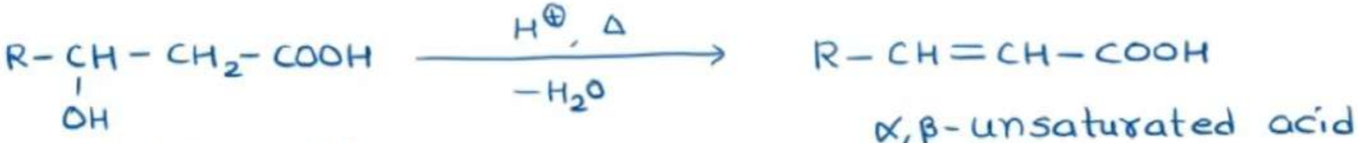
$$HO-CH_2-\overset{O}{\underset{}{C}}-OH + HO-CH_2-\overset{O}{\underset{}{C}}-OH \xrightarrow{100^\circ C} HO-CH_2-\overset{O}{C}-O-CH_2-\overset{O}{C}-OH$$



- However, in presence of a trace of Lewis acid such as anhydrous $AlCl_3$, glycollic acid yields a linear polyester.

$$\left.\begin{matrix}\text{Glycollic acid}\\ \text{OR}\\ \text{Glycollide}\end{matrix}\right\} \xrightarrow{AlCl_3} HO\left(CH_2-\overset{O}{C}-O\right)_n CH_2COOH$$

(ii) β-hydroxy acids:-



$$R-\underset{OH}{\underset{|}{CH}}-CH_2-COOH \xrightarrow[-H_2O]{H^{\oplus},\ \Delta} R-CH=CH-COOH$$

β-hydroxy acid

α,β-unsaturated acid

(iii) γ- and δ- hydroxy acids :-

$$\underset{OH}{\underset{|}{CH_2}}-CH_2-CH_2-COOH \rightleftharpoons \text{Lactone} + H_2O$$

γ-hydroxy acid

Lactone

(iv) Epsilon and longer hydroxy acids:-

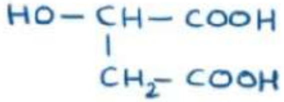
- Undergo intermolecular estrification to give linear polymer.

$$HO-CH_2-CH_2-CH_2-CH_2-CH_2-COOH \xrightarrow{\Delta} \left[O-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n + nH_2O$$

ε-hydroxy acid

A linear polymer

→ Malic acid :→

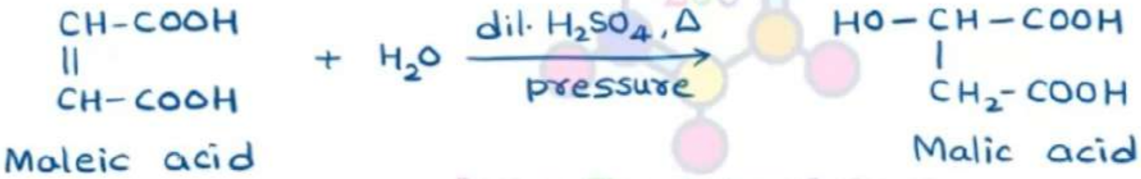
- Malic acid (Latin Malum = apple)
- 

$$\mathrm{HO-\underset{\displaystyle CH_2-COOH}{\underset{|}{C}H}-COOH}$$

- It is also called 2-hydroxybutane-1,4-dioic acid or monohydroxy succinic acid and occurs in unripe apples, berries and and grapes.
- It is used in beverages and as a purgative.

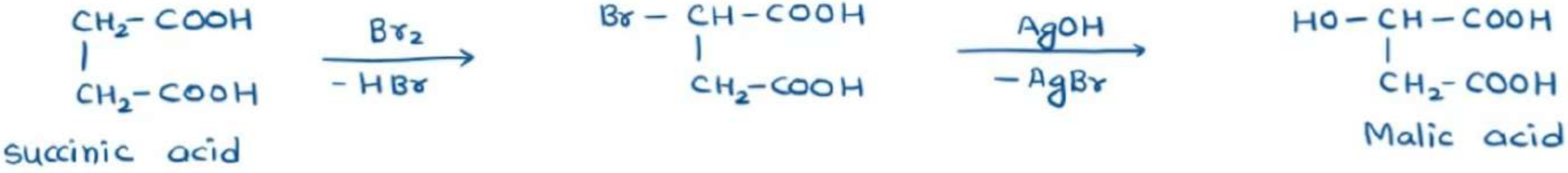
→ Methods of formation :→

(i) From maleic acid :→



$$\underset{\text{Maleic acid}}{\mathrm{CH-COOH \atop \| \atop CH-COOH}} + H_2O \xrightarrow[\text{pressure}]{\text{dil. } H_2SO_4,\ \Delta} \underset{\text{Malic acid}}{\mathrm{HO-CH-COOH \atop | \atop CH_2-COOH}}$$

(ii) From succinic acid :→



$$\underset{\text{succinic acid}}{\mathrm{CH_2-COOH \atop | \atop CH_2-COOH}} \xrightarrow[-HBr]{Br_2} \mathrm{Br-CH-COOH \atop | \atop CH_2-COOH} \xrightarrow[-AgBr]{AgOH} \underset{\text{Malic acid}}{\mathrm{HO-CH-COOH \atop | \atop CH_2-COOH}}$$

(iii) From tartaric acid :→

$$\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ HO-CH-COOH \end{array} + 2HI \longrightarrow \begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ \quad\;\; CH_2-COOH \end{array} + I_2 + H_2O$$

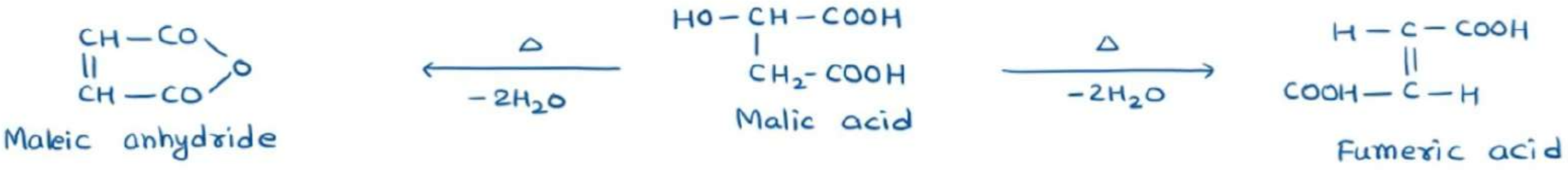
→ Physical properties :→

- Malic acid is a colourless, crystalline deliquesent solid.
- Readily soluble in water.
- Shows optical isomerism due to presence of one chiral center.

→ Chemical reaction :→

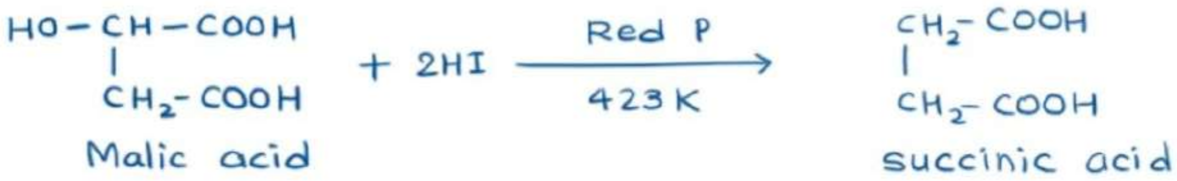
- Due to presence of the presence of $-OH$ and $-COOH$ groups, malic acid exhibits reactions of a secondary alcohol and a dicarboxylic acid.

(i) Dehydration :→



$$\begin{array}{l} CH-CO \\ \| \qquad\quad \rangle O \\ CH-CO \end{array} \xleftarrow[-2H_2O]{\Delta} \begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ \quad\;\; CH_2-COOH \end{array} \xrightarrow[-2H_2O]{\Delta} \begin{array}{l} H-C-COOH \\ \quad\;\; \| \\ COOH-C-H \end{array}$$

(ii) Reduction:→

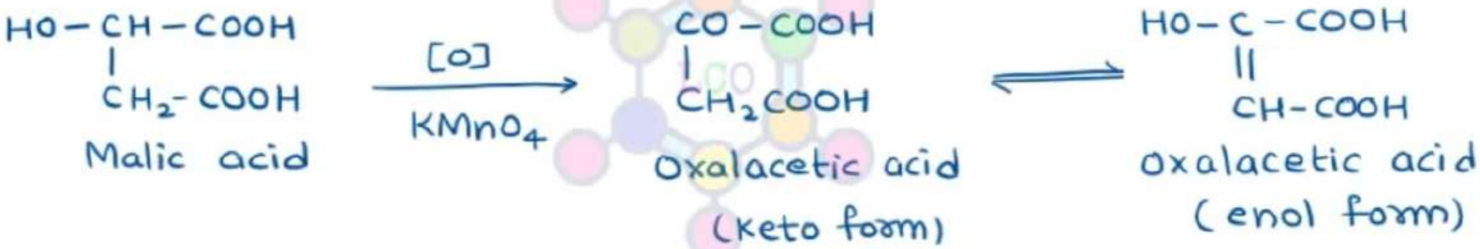


$$\underset{\text{Malic acid}}{\begin{array}{l}HO-CH-COOH\\ \quad\;\; |\\ \quad\;\; CH_2-COOH\end{array}} + 2HI \xrightarrow[423\,K]{\text{Red P}} \underset{\text{succinic acid}}{\begin{array}{l}CH_2-COOH\\ |\\ CH_2-COOH\end{array}}$$

(iii) Oxidation:→

– Different products are obtained under different conditions.

(a) Oxidation with $KMnO_4$:–

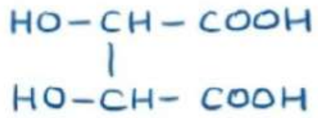


$$\underset{\text{Malic acid}}{\begin{array}{l}HO-CH-COOH\\ \quad\;\; |\\ \quad\;\; CH_2-COOH\end{array}} \xrightarrow[KMnO_4]{[O]} \underset{\substack{\text{Oxalacetic acid}\\ \text{(Keto form)}}}{\begin{array}{l}CO-COOH\\ |\\ CH_2COOH\end{array}} \rightleftharpoons \underset{\substack{\text{oxalacetic acid}\\ \text{(enol form)}}}{\begin{array}{l}HO-C-COOH\\ \quad\;\; \|\\ \quad\;\; CH-COOH\end{array}}$$

(b) Oxidation with chromic acid :-

$$\underset{\text{Malic acid}}{\begin{array}{l}HO-CH-COOH\\ \quad\;\; |\\ \quad\;\; CH_2-COOH\end{array}} \xrightarrow[CrO_3]{[o]} \underset{\text{Malonic acid}}{CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}} + CO_2 + H_2O$$

→ Tartaric acid: →

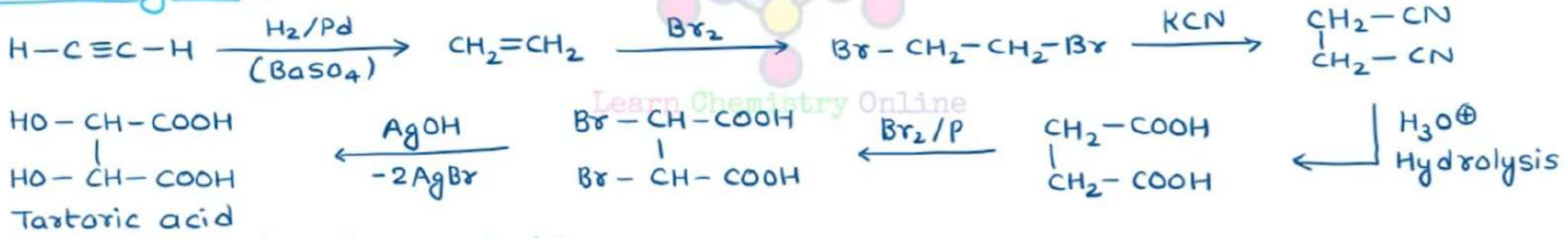


$$\begin{array}{l} HO-CH-COOH \\ \quad\ | \\ HO-CH-COOH \end{array}$$

- Common name → α, α' – dihydroxy succinic acid
- IUPAC name → 2,3- dihydroxybutan-1,4- dioic acid
- Tartaric acid contains two similar chiral carbon atoms. It may exist as dextro, laevo, meso and racemic mixture.
- It occurs as its potassium salt in grapes, tamarind and berries.
- Some derivatives of tartaric acid are used in laboratory, medicine and industry.

→ Methods of formation: →

(i) From acetylene: →

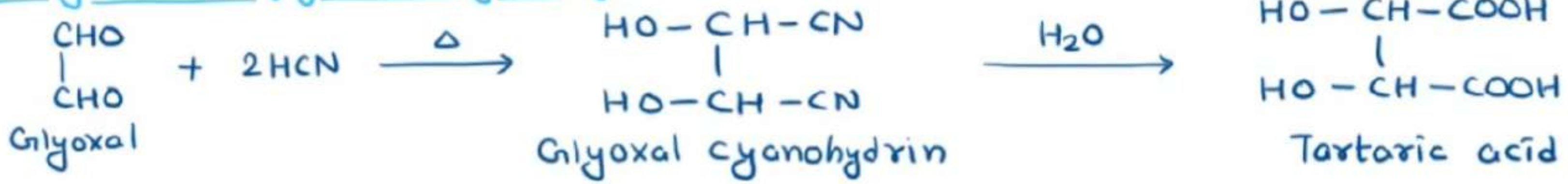


$$H-C\equiv C-H \xrightarrow[(BaSO_4)]{H_2/Pd} CH_2=CH_2 \xrightarrow{Br_2} Br-CH_2-CH_2-Br \xrightarrow{KCN} \begin{array}{l} CH_2-CN \\ | \\ CH_2-CN \end{array}$$

$$\begin{array}{l} CH_2-CN \\ | \\ CH_2-CN \end{array} \xrightarrow[\text{Hydrolysis}]{H_3O^{\oplus}} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array} \xrightarrow{Br_2/P} \begin{array}{l} Br-CH-COOH \\ \quad\ | \\ Br-CH-COOH \end{array} \xrightarrow[-2AgBr]{AgOH} \begin{array}{l} HO-CH-COOH \\ \quad\ | \\ HO-CH-COOH \end{array}$$

Tartaric acid

(ii) Hydrolysis of glyoxal cyanohydrin: →

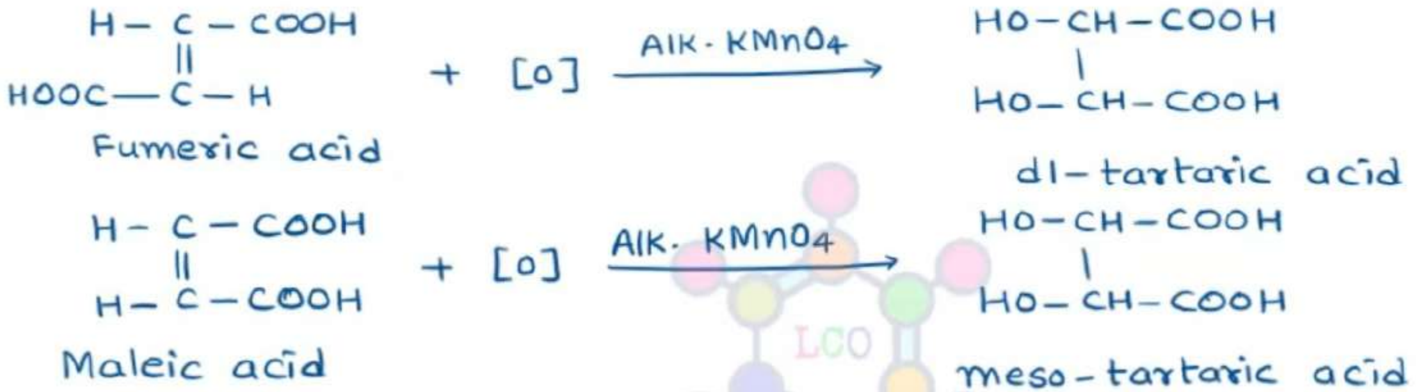


$$\begin{array}{l} CHO \\ | \\ CHO \end{array} + 2HCN \xrightarrow{\Delta} \begin{array}{l} HO-CH-CN \\ \quad\ | \\ HO-CH-CN \end{array} \xrightarrow{H_2O} \begin{array}{l} HO-CH-COOH \\ \quad\ | \\ HO-CH-COOH \end{array}$$

Glyoxal　　Glyoxal cyanohydrin　　Tartaric acid

(iii) Hydroxylation of fumeric acid and maleic acid :→

- dl-tartaric acid is obtained when fumeric acid is treated with dilute alkaline $KMnO_4$, whereas the same reaction with maleic acid produces meso-tartaric acid.



$$\begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array} + [O] \xrightarrow{Alk.\,KMnO_4} \begin{array}{c}HO-CH-COOH\\ |\\ HO-CH-COOH\end{array}$$

Fumeric acid

dl-tartaric acid

$$\begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array} + [O] \xrightarrow{Alk.\,KMnO_4} \begin{array}{c}HO-CH-COOH\\ |\\ HO-CH-COOH\end{array}$$

Maleic acid

meso-tartaric acid

(iv) From α-α'-dibromosuccinic acid :→

$$\begin{array}{c}Br-CH-COOH\\ |\\ Br-CH-COOH\end{array} + 2AgOH \longrightarrow \begin{array}{c}HO-CH-COOH\\ |\\ HO-CH-COOH\end{array} + 2AgBr$$

dl-tartaric acid

(v) (–) tartaric acid does not occur in nature and is obtained by resolution of dl-tartaric acid.

→ Physical properties :→

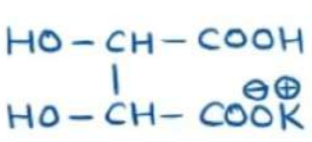
- Tartaric acid is a colourless crystalline solid.
- It is readily soluble in water and alcohol but insoluble in ether and other organic solvents.

→ chemical reactions :→

- A molecule of tartaric acid contains two secondary alcoholic groups and two carboxyl groups and hence they show the properties of both groups.

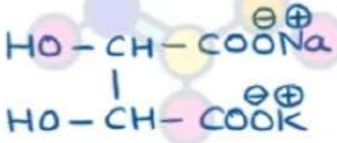
(i) Formation of salts :→

- Being a dibasic acid, tartaric acid form varius salts when treated with alkalis, carbonates and bicarbonates.



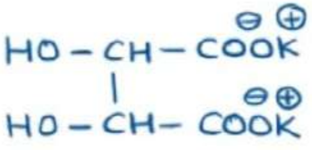
$$\begin{array}{l} HO-CH-COOH \\ \qquad | \\ HO-CH-COO^{\ominus}K^{\oplus} \end{array}$$

Potassium hydrogen tartarate (acid salt)



$$\begin{array}{l} HO-CH-COO^{\ominus}Na^{\oplus} \\ \qquad | \\ HO-CH-COO^{\ominus}K^{\oplus} \end{array}$$

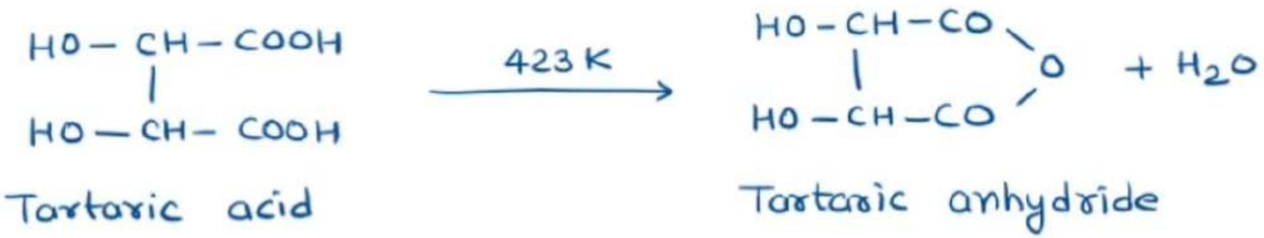
Sodium potassium tartarate (Normal mixed salt)



$$\begin{array}{l} HO-CH-COO^{\ominus}K^{\oplus} \\ \qquad | \\ HO-CH-COO^{\ominus}K^{\oplus} \end{array}$$

Potassium tartarate (Normal salt)

(ii) Action of heat :→

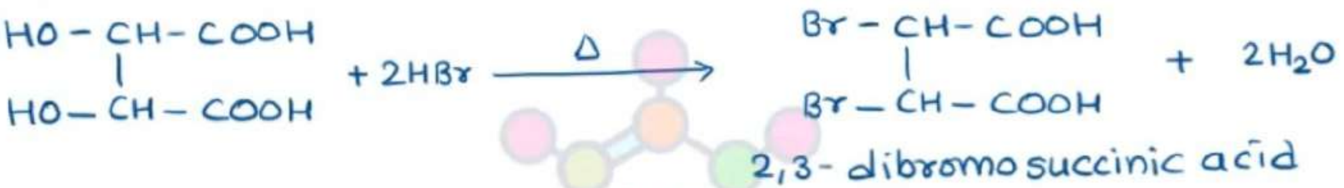


$$\begin{array}{l} HO-CH-COOH \\ \qquad | \\ HO-CH-COOH \end{array} \xrightarrow{423\,K} \begin{array}{l} HO-CH-CO \\ \qquad | \qquad\qquad \rangle O \\ HO-CH-CO \end{array} + H_2O$$

– on heating strongly, it chars with smell of burning sugar to give pyruvic acid.

$$\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ HO-CH-COOH \end{array} \xrightarrow[\text{heating}]{\text{Strong}} \underset{\text{pyruvic acid}}{CH_3COCOOH} + CO_2 + H_2O$$

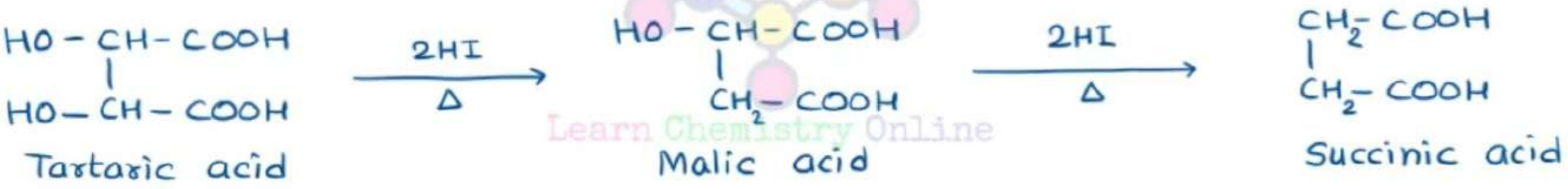
(iii) Reaction with HBr :→



$$\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ HO-CH-COOH \end{array} + 2HBr \xrightarrow{\Delta} \begin{array}{l} Br-CH-COOH \\ \quad\;\; | \\ Br-CH-COOH \end{array} + 2H_2O$$

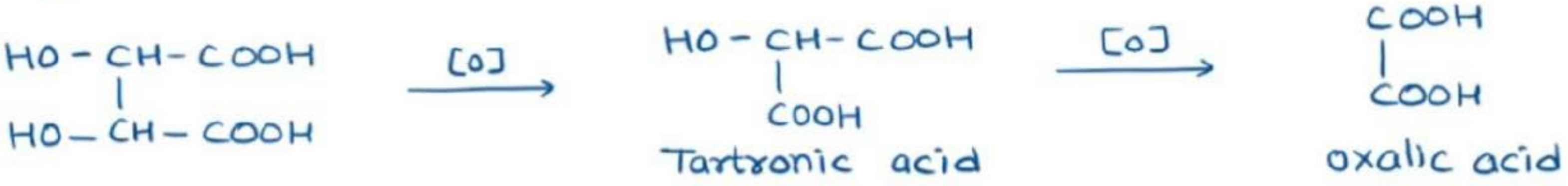
2,3-dibromosuccinic acid

(iv) Reduction :→



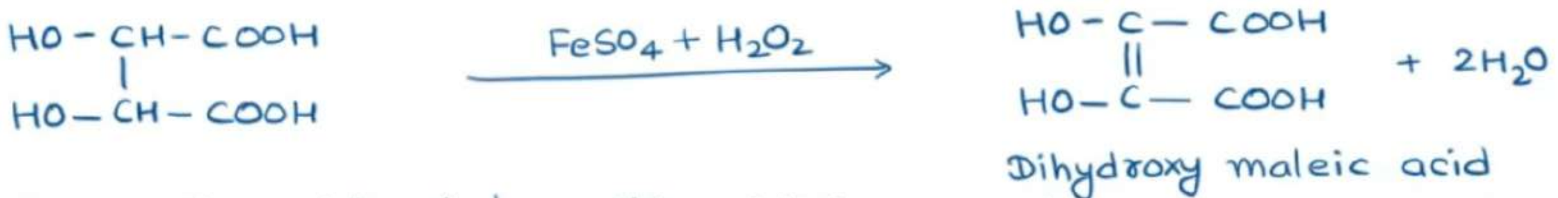
$$\underset{\text{Tartaric acid}}{\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ HO-CH-COOH \end{array}} \xrightarrow[\Delta]{2HI} \underset{\text{Malic acid}}{\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ \quad\; CH_2-COOH \end{array}} \xrightarrow[\Delta]{2HI} \underset{\text{Succinic acid}}{\begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}}$$

(v) Oxidation :→ Mild oxidising agents oxidises it to tartronic acid. However with strong oxidising agents, it forms oxalic acid.



$$\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ HO-CH-COOH \end{array} \xrightarrow{[O]} \underset{\text{Tartronic acid}}{\begin{array}{l} HO-CH-COOH \\ \quad\;\; | \\ \quad COOH \end{array}} \xrightarrow{[O]} \underset{\text{oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}}$$

- With Fenton's reagent (alkaline $H_2O_2 + FeSO_4$) it is oxidised to dihydroxy maleic acid.



$$\begin{matrix} HO-CH-COOH \\ | \\ HO-CH-COOH \end{matrix} \xrightarrow{FeSO_4 + H_2O_2} \begin{matrix} HO-C-COOH \\ \| \\ HO-C-COOH \end{matrix} + 2H_2O$$

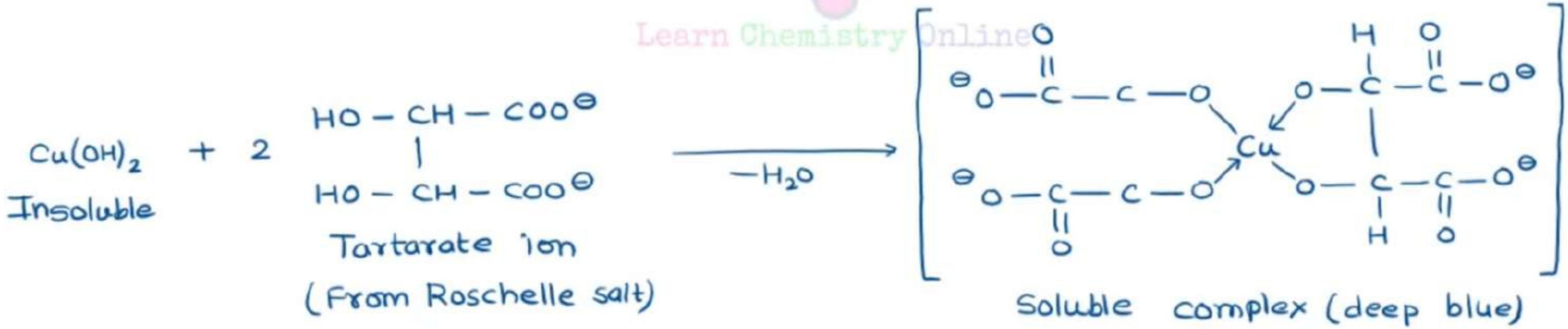
Dihydroxy maleic acid

- Tartaric acid is easily oxidised by mild oxidising agents. It reduces Tollen's reagent to silver mirror.

$$\text{Tartaric acid} \xrightarrow[\text{Tollen's reagent}]{Ag(NH_3)_2OH} \text{Tartronic acid} + Ag\downarrow + CO_2 + H_2O$$

(vi) Formation of complexes:→

- In Fehling's solution, the insoluble copper hydroxide $Cu(OH)_2$, first formed, get dissolved due to formation of a soluble complex between Cu^{+2} and tartarate ion as shown below-



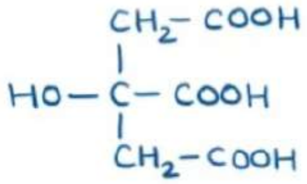
$$Cu(OH)_2 + 2\begin{matrix} HO-CH-COO^{\ominus} \\ | \\ HO-CH-COO^{\ominus} \end{matrix} \xrightarrow{-H_2O}$$

Insoluble

Tartarate ion
(From Roschelle salt)

Soluble complex (deep blue)

→ ~~C~~itric acid:→



$$HO-\overset{\overset{\large CH_2-COOH}{|}}{\underset{\underset{\large CH_2-COOH}{|}}{C}}-COOH$$

2-Hydroxypropane-1,2,3-tricarboxylic acid

- Citric acid is a monohydroxy tribasic acid occuring naturally in many fruits especially in unripe fruits of citrus family such as lemon, orange, keenus etc.
- Lemon juice contains about 6-10%. citric acid.

→ Methods of formation:→

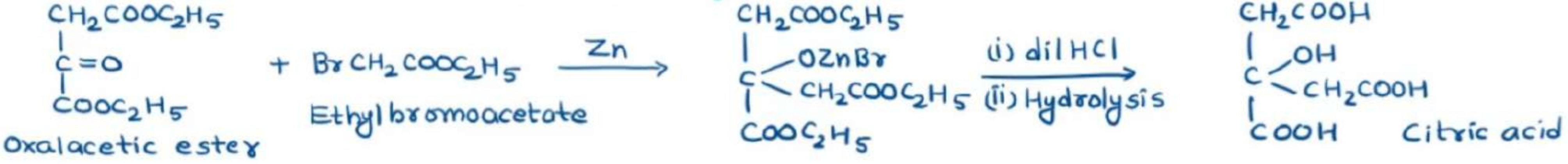
1. Isolation of citric acid from lemon juice:→

lemon juice boiled and filtered ⟶ Filtrate is neutrilised with $CaCO_3$ → Calcium citrate is precipitated

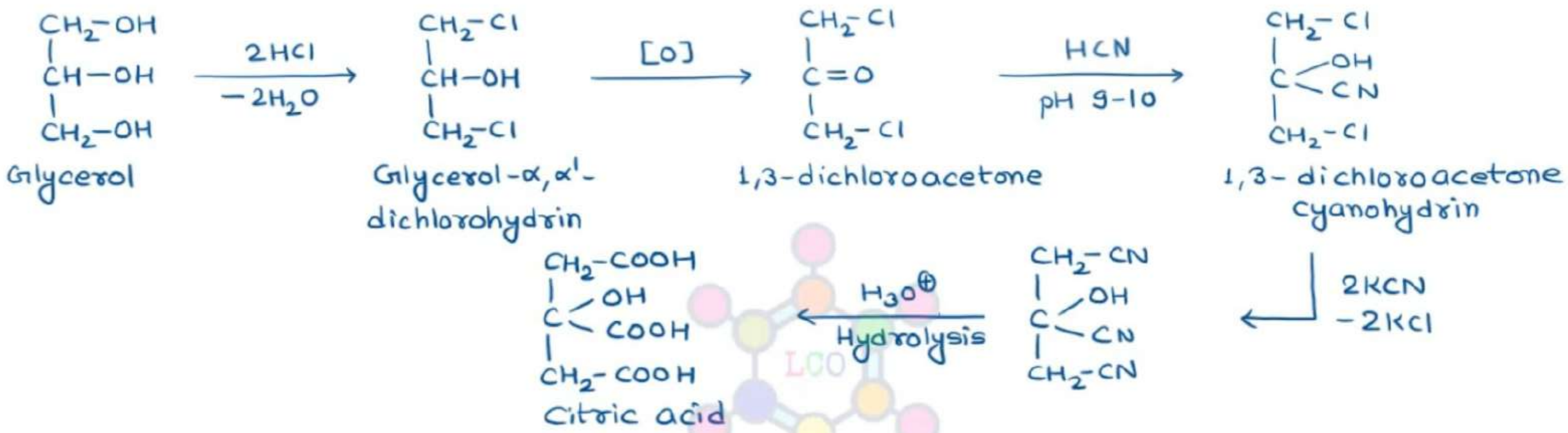
Calcium citrate is treated with dil. H_2SO_4 ← Calcium citrate is precipitated

→ Calcium sulphate is separated as solid and filtrate is concentrated to give crystals of citric acid mono hydrate.

2. From oxalacetic acid ester (Reformatsky reaction):→



(iii) From glycerol:→



(iv) Manufacture of citric acid from molasses:→

- Citric acid is manfactured by fermenting 10-12 % solution of purified molasses at 30°C in presence of certain inorganic salts such as calcium carbonate.

→ Physical properties:→

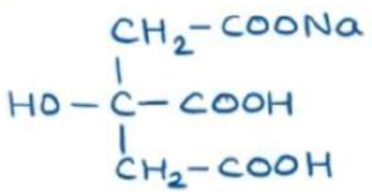
- Citric acid is a Colourless crystalline solid.
- It is readily soluble in water and alcohol but not in ether.
- The crystalline acid melts at 374 K and on heating to 403 K, it lose water of crystallisation.
- The anhydrous acid melts at 426 K.

→ Chemical properties:→

- It ungergoes reactions of both α- and β-hydroxy acids since the $-OH$ group is α-to one carboxyl group and β-to the other two.

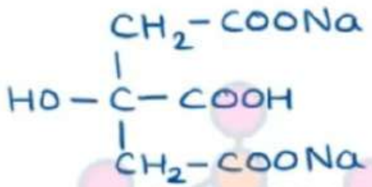
1. Salt formation:→

- Being tribasic acid, citric acid forms three series of salts.



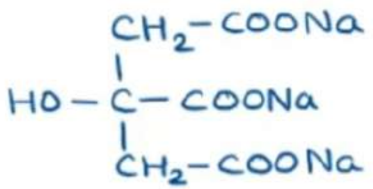
$$\begin{array}{l} \quad\; CH_2-COONa \\ \quad\;\; | \\ HO-C-COOH \\ \quad\;\; | \\ \quad\; CH_2-COOH \end{array}$$

Monosodium dihydrogen citrate



$$\begin{array}{l} \quad\; CH_2-COONa \\ \quad\;\; | \\ HO-C-COOH \\ \quad\;\; | \\ \quad\; CH_2-COONa \end{array}$$

Disodium monohydrogen citrate



$$\begin{array}{l} \quad\; CH_2-COONa \\ \quad\;\; | \\ HO-C-COONa \\ \quad\;\; | \\ \quad\; CH_2-COONa \end{array}$$

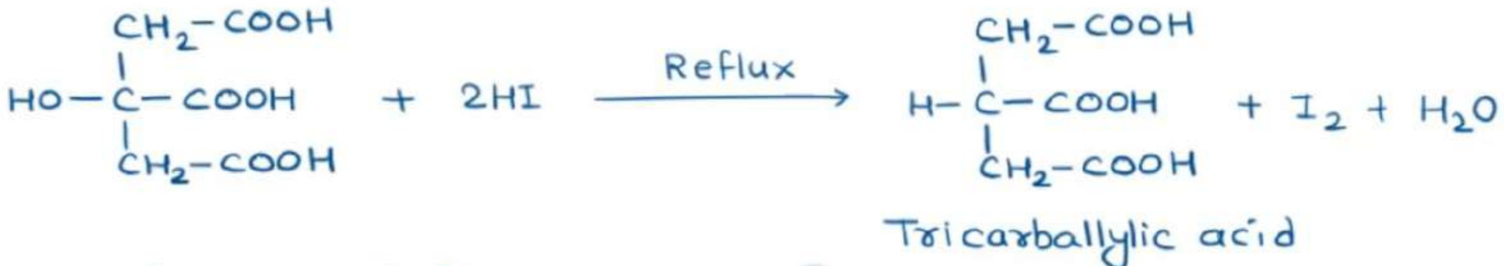
Trisodium citrate

2. Acetylation:→

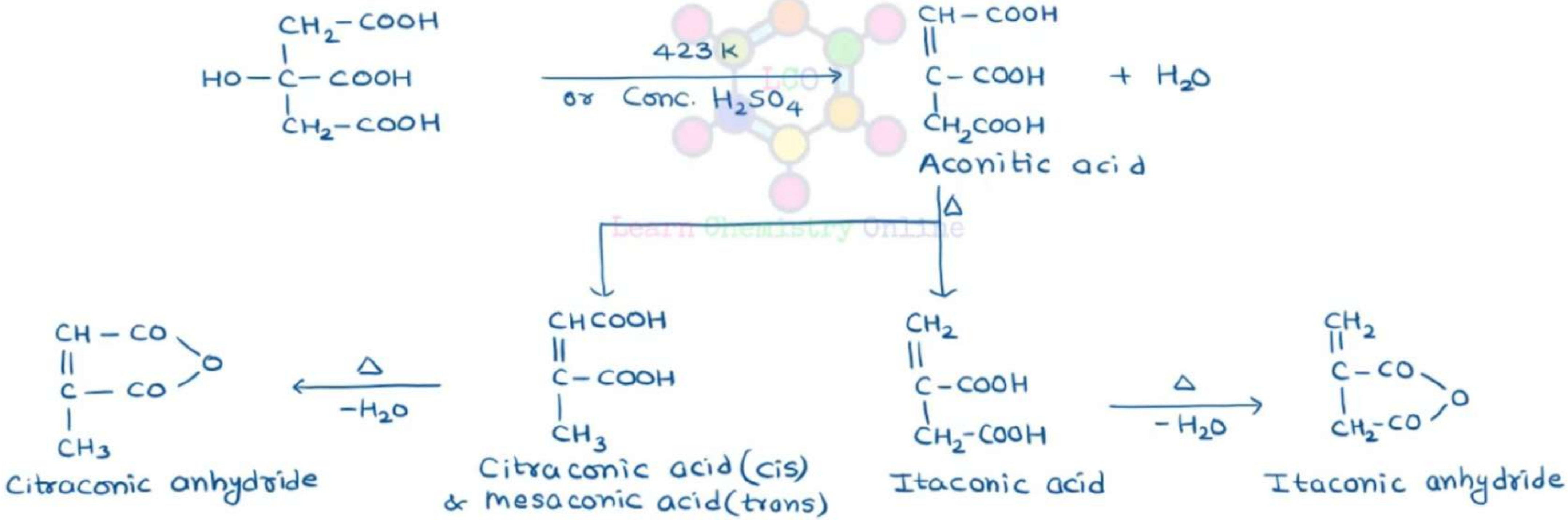
$$\begin{array}{l} \quad\; CH_2-COOH \\ \quad\;\; | \\ HO-C-COOH \\ \quad\;\; | \\ \quad\; CH_2-COOH \end{array} + \begin{array}{c} (CH_3CO)_2O \\ OR \\ CH_3COCl \end{array} \longrightarrow \begin{array}{l} \qquad\qquad\quad CH_2-COOH \\ \qquad\qquad\quad\; | \\ CH_3COO-C-COOH \\ \qquad\qquad\quad\; | \\ \qquad\qquad\quad CH_2-COOH \end{array}$$

Monoacetyl citric acid

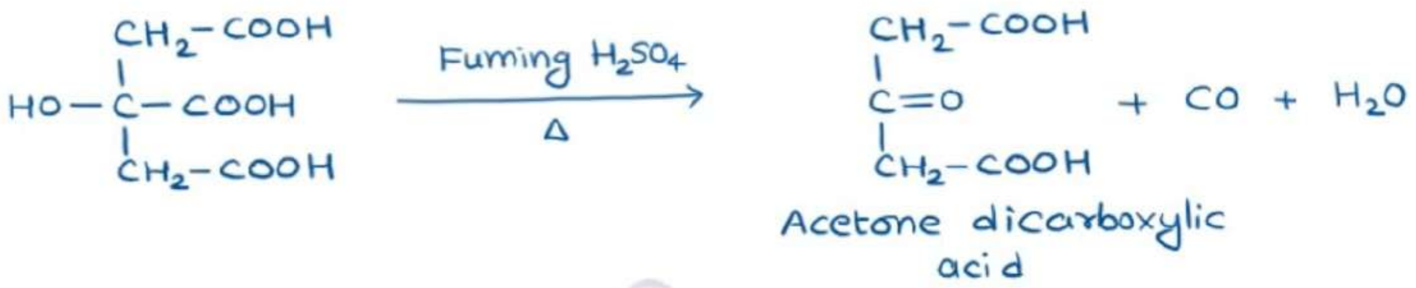
3. Reduction with HI :→



4. Action of heat (dehydration):→



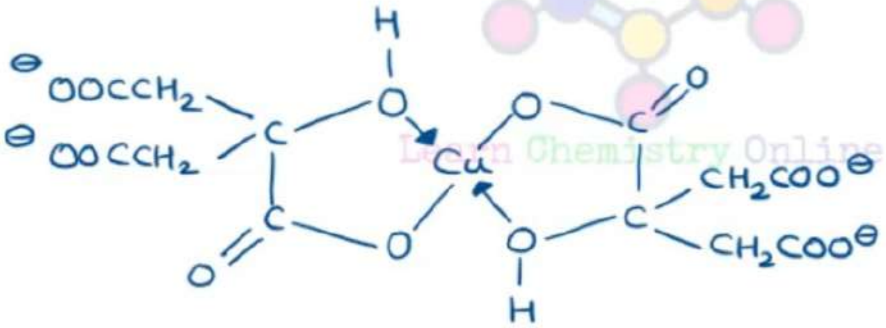
5. Reaction with fuming H_2SO_4:→



$$HO-C(CH_2-COOH)_2-COOH \xrightarrow[\Delta]{\text{Fuming } H_2SO_4} (CH_2-COOH)_2C=O + CO + H_2O$$

6. Complex formation:→

- Like tartaric acid, citric acid is also forms soluble complex salts with Benedict solution which contains copper sulphate, sodium carbonate and sodium citrate.



→ Unsaturated monocarboxylic acids :→

- Carboxylic acids containing carbon-carbon double bond or triple bond are known as unsaturated monocarboxylic acids.
- General formula $C_nH_{2n-1}-COOH$.
- Naturally occuring compound is oleic acid [$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$]. which is present in olive oil.
- These acids may be considered as the derivatives of alkenes or alkynes obtained by replacing a hydrogen atom by a carboxyl group.

→ Nomenclature :→

- Common names are assigned on the basis of source or history of discovery.
- IUPAC names are assigned on the basis of following guidelines-

(i) Select the longest carbon chain containing double or triple bond and the carboxyl group.

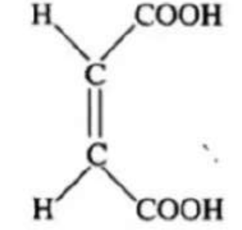
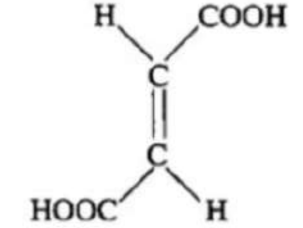
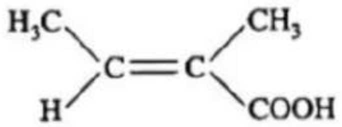
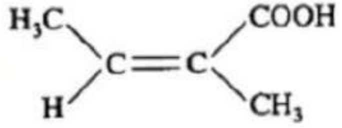
(ii)

$$\text{Alkene} \xrightarrow[+\text{oic acid}]{-e} \text{Alkenoic acid}$$

$$\text{Alkyne} \xrightarrow[+\text{oic acid}]{-e} \text{Alkynoic acid}$$

(iii) The position of double or triple bond with respect to the carboxyl group is indicated by a number.

→ Examples

Acid	Common names	IUPAC names
$CH_2{=}CHCOOH$	Acrylic acid	Propenoic acid
$CH_3CH{=}CHCOOH$	Crotonic acid	But-2-enoic acid
$C_6H_5CH{=}CHCOOH$	Cinnamic acid	3-Phenylpropenoic acid
	Maleic acid	*cis*-Butenedioic acid (Z-Butenedioic acid)
	Fumaric acid	*trans*-Butenedioic acid (E-Butenedioic acid)
	Tiglic acid	Z-2-Methylbut-2-enoic acid
	Angelic acid	E-2-Methylbut-2-enoic acid
$HC{\equiv}C{-}COOH$	Propiolic acid	Prop-2-ynoic acid

→ Unsaturated monocarboxylic acids:→

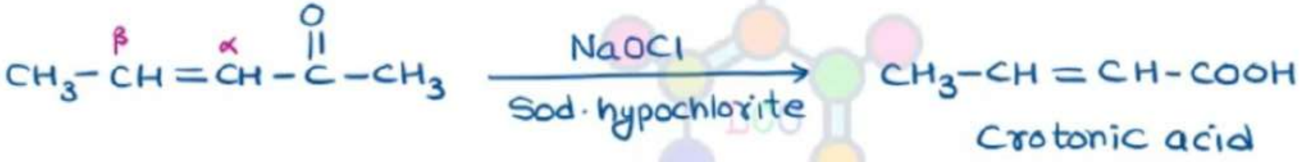
→ Methods of formation:→

1. From α, β- unsaturated aldehydes:→

$$\overset{\beta}{CH_2}=\overset{\alpha}{CH}-CHO \xrightarrow{[O]} CH_2=CH-COOH$$

Acrolein → Acrylic acid

2. From α, β- unsaturated methyl Ketones:→ (haloform reaction)



$$CH_3-\overset{\beta}{CH}=\overset{\alpha}{CH}-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Sod. hypochlorite}]{NaOCl} CH_3-CH=CH-COOH$$

Crotonic acid

3. From β-haloacids:→

$$Cl-\overset{\beta}{CH_2}-\underset{\underset{H}{|}}{\overset{\alpha}{CH}}-COO^{\ominus} \xrightarrow[\overset{\ominus}{O}H]{\text{dehydrohalogenation}} CH_2=CH-COO^{\ominus} + H_2O + Cl^{\ominus}$$

4. From β-hydroxy acids:→

$$HO\overset{\beta}{CH_2}\overset{\alpha}{CH_2}COOH \xrightarrow{\Delta} CH_2=CH-COOH$$

5. From acetylene:→

$$\underset{\text{Acetylene}}{CH\equiv CH} + HCN \longrightarrow \underset{\text{Vinyl cyanide}}{CH_2=CH-CN} \xrightarrow{H_3O^{\oplus}} \underset{\text{Acrylic acid}}{CH_2=CH-COOH}$$

6. Grignard reaction:→

$$\underset{\text{Vinyl halide}}{CH_2=CH-X} + Mg \xrightarrow{THF} \underset{\text{Vinyl magnesium halide}}{CH_2=CHMgX} \xrightarrow{CO_2} CH_2=CH-\underset{\underset{O}{\|}}{C}-OMgX \xrightarrow{H_3O^{\oplus}} CH_2=CH-COOH$$

7. Hydrolysis of unsaturated nitriles :→

$$\underset{\text{Allyl chloride}}{CH_2=CH-CH_2-Cl} \xrightarrow[C_2H_5OH,\ \Delta]{CN^{\ominus}} \underset{\text{Allyl cyanide}}{CH_2=CH-CH_2-CN} \xrightarrow{H_3O^{\oplus}} \underset{\text{Vinyl acetic acid}}{CH_2=CH-CH_2-COOH}$$

8. Perkin reaction:→

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + (CH_3CO)_2O \xrightarrow[\substack{\Delta \\ -CH_3COOH}]{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5-CH=CH-COOH}$$

9. Knoevenagel condensation:→

$$CH_3CHO + CH_2(COOC_2H_5)_2 \xrightarrow[\Delta(-H_2O)]{Pyridine} CH_3CH=C(COOC_2H_5)_2 \xrightarrow{H_3O^{\oplus}} CH_3CH=C(COOH)_2 \xrightarrow[-CO_2]{\Delta} \underset{\text{Crotonic acid}}{CH_3CH=CHCOOH}$$

* Aromatic unsaturated acid can also be prepared by this reaction.

→ Unsaturated monocarboxylic acids:→

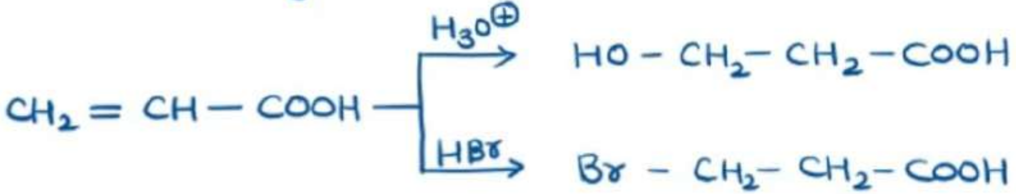
→ Chemical reaction:→

- Unsaturated acids having the double bond away from the carboxylic group [$R-CH=CH-(CH_2)_n-COOH$] behave like simple olefins and simple monocarboxylic acids.
- In case of α,β- unsaturated acids, the chemical reactivity of the double bond and the carboxylic group is affected due to conjugation. This conjugation not only affects the reactivity of the two groups but also reverses the orientation of addition.
- Like other bifunctional compounds these compounds exhibit reactions due to double bond, the carboxylic group and both.

A. Reactions due to C=C double bond.

(i) Addition of halogens, water and halogen acids:→

- In general, olefinic double bond undergoes halogenation, hydration and hydrohalogenation etc. but the rates of these reactions are relatively slow due to conjugation of the C=C group with the carboxylic group.
- Addition of water and halogen acids takes place opposite to Markownikoff's rule.

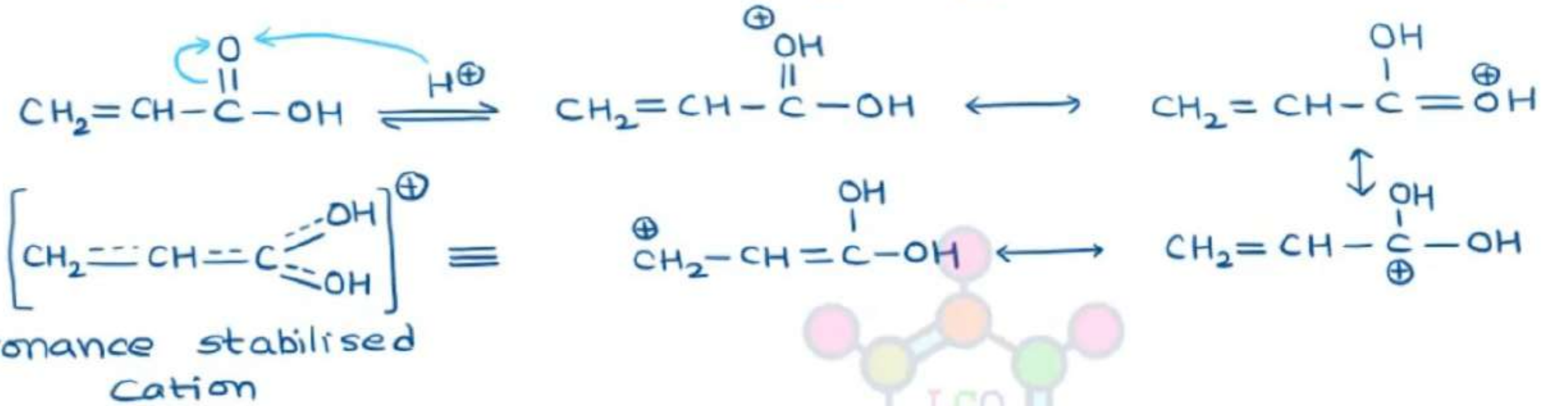


$$CH_2=CH-COOH \xrightarrow{H_3O^{\oplus}} HO-CH_2-CH_2-COOH$$

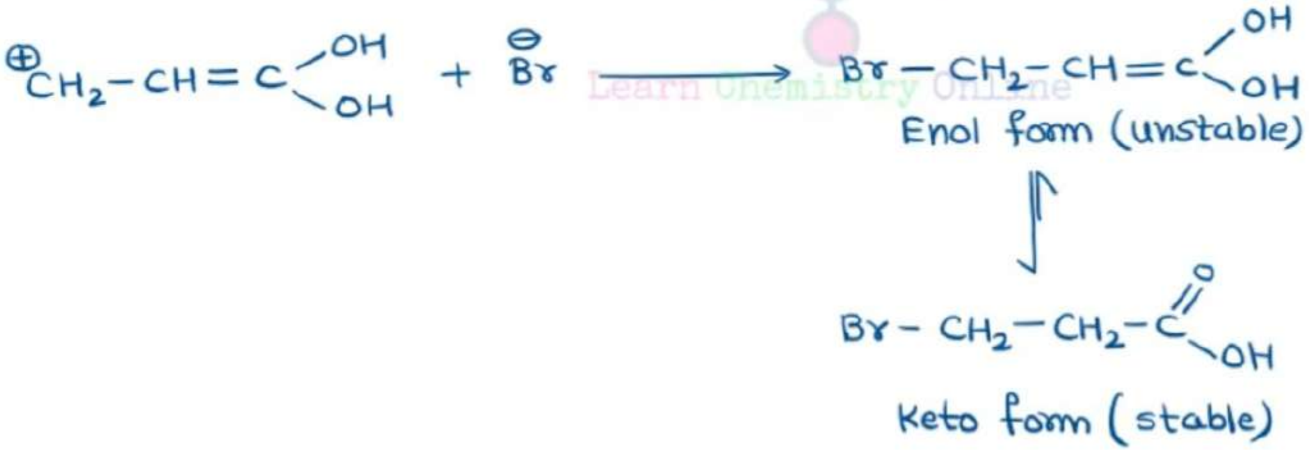
$$CH_2=CH-COOH \xrightarrow{HBr} Br-CH_2-CH_2-COOH$$

- Like conjugated dienes, 1,4 addition also takes place in two steps.

Step-I Addition of proton to carbonyl oxygen of -COOH group.



Step-II Attack of nucleophile on positively charged carbon.



(ii) Double bond migration:→

- When a α, β- or β, γ- unsaturated acid is boiled with strong alkali solution it changes into an equilibrium mixture of both - by a double bond shifting.
- The resulting reaction mixture upon acidification gives a mixture in which α, β-unsaturated acid predominates.

$$R-\overset{\gamma}{C}H=\overset{\beta}{C}H-\overset{\alpha}{C}H_2-COOH \xrightleftharpoons{NaOH} R-\overset{\gamma}{C}H_2-\overset{\beta}{C}H=\overset{\alpha}{C}H-COOH$$

(iii) Reduction:→

$$CH_2=CHCOOH \xrightarrow{Na + C_2H_5OH} CH_3CH_2COOH$$

propanoic acid

$$CH_2=CHCOOH \xrightarrow[ether]{LiAlH_4} CH_2=CHCH_2OH$$

Allyl alcohol (unsaturated primary alcohol)

(iv) Reaction with dil KMnO₄:→

$$CH_2=CHCOOH + H_2O + [O] \xrightarrow[KMnO_4]{Cold} \underset{}{\overset{OH}{\overset{|}{C}}}H_2-\overset{OH}{\overset{|}{C}}HCOOH$$

Glyceric acid

B. Reactions of -COOH group:→

(i) Salt formation:→

$$\underset{\text{Acrylic acid}}{CH_2=CH-COOH} + NaOH \xrightarrow[-H_2O]{} \underset{\text{Sod. acrylate}}{CH_2=CH-CO\overset{\ominus}{O}\overset{\oplus}{Na}}$$

$$2\underset{\text{Crotonic acid}}{CH_3-CH=CH-COOH} + Na_2CO_3 \xrightarrow[-H_2O]{} \underset{\text{Sod. crotonate}}{2CH_3-CH=CH-CO\overset{\ominus}{O}\overset{\oplus}{Na}}$$

(ii) Formation of esters:→

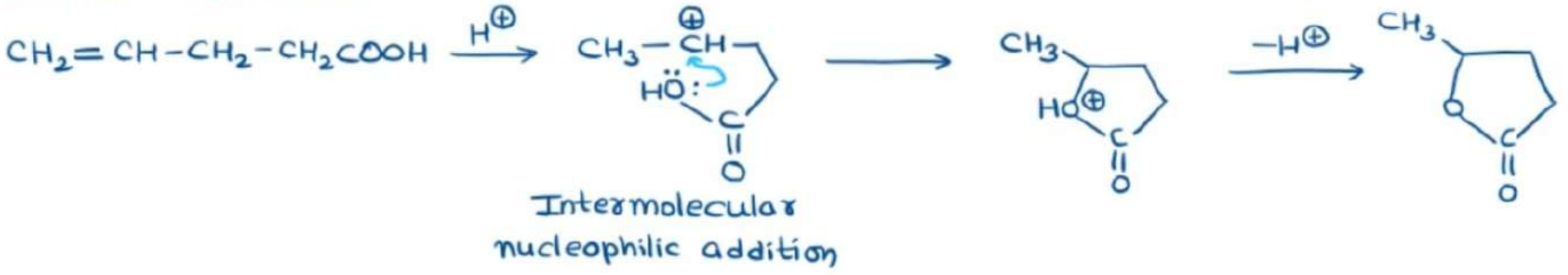
$$CH_3CH=CH-COOH + C_2H_5OH \xrightarrow[\Delta]{H^{\oplus}} \underset{\text{Ethyl crotonate}}{CH_3CH=CHCOOC_2H_5}$$

(iii) Reaction with PCl_5:→

$$CH_3CH=CH-COOH + PCl_5 \longrightarrow \underset{\text{Crotonyl Chloride}}{CH_3-CH=CH-COCl} + POCl_3 + HCl$$

C. Reactions due to both groups:→

(i) Lactone formation:→

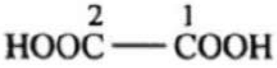


→ Dicarboxylic acids:→

- Compounds containing two carboxylic groups are called dicarboxylic acids.
- Examples:- Malic and tartaric acid (Naturally occurring)
  Adipic acid (a monomer of nylon)
  Phthalic acid (a starting compound for the preparation of dyestuffs)
  Terephthalic acid (a monomer of terelyne)

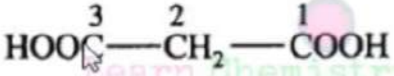
→ Nomenclature:→

- Most of common names of dicarboxylic acids are based on their source.
  Example:- Oxalic acid, $(COOH)_2$, obtained from the plants of oxalis family.
- In IUPAC system, they are named as dioic acids.
- The positions of two carboxyl groups are indicated by arabic numerals.
- Example



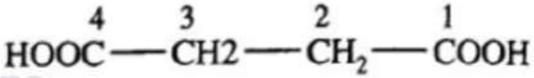
$\overset{2}{HOOC}—\overset{1}{COOH}$

Ethane-1,2-dioic acid
(Oxalic acid)



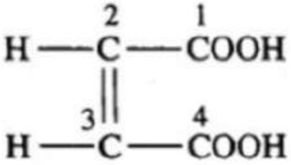
$\overset{3}{HOOC}—\overset{2}{CH_2}—\overset{1}{COOH}$

Propane-1,3-dioic acid
(Malonic acid)

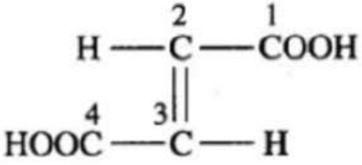


$\overset{4}{HOOC}—\overset{3}{CH2}—\overset{2}{CH_2}—\overset{1}{COOH}$

Butane-1,4-dioic acid
(Succinic acid)



Cis 2-butene-1,4-dioic acid
(Maleic acid)



Trans 2-butene-1,4-dioic acid
(Fumaric acid)

$HOOC—(CH_2)_4—COOH$

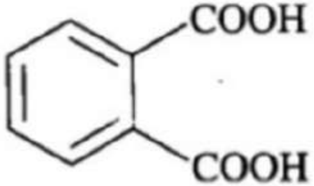
Hexane-1,6-dioic acid
(Adipic acid)

$$HOO\overset{5}{C}—\overset{4}{C}H_2—\overset{3}{C}H_2—\overset{2}{C}H_2—\overset{1}{C}OOH$$

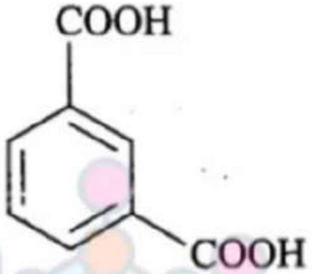
Pentane-1,5-dioic acid
(Glutaric acid)

$$HOOC—(CH_2)_5—COOH$$

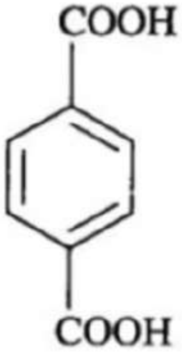
Heptane-1,7-dioic acid
(Pimelic acid)



Benzene-1,2-dicarboxylic acid
(Phthalic acid)



Benzene-1,3-dicarboxylic acid
(Isophthalic acid)



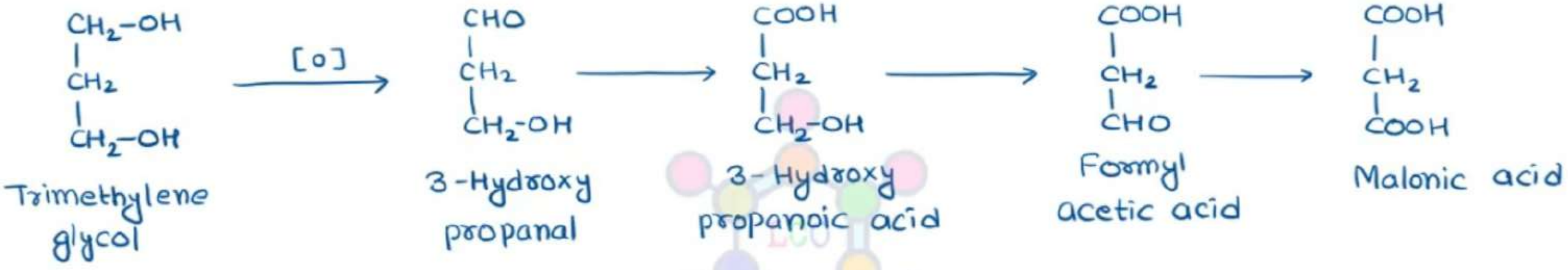
Benzene-1,4-dicarboxylic acid
(Terephthalic acid)

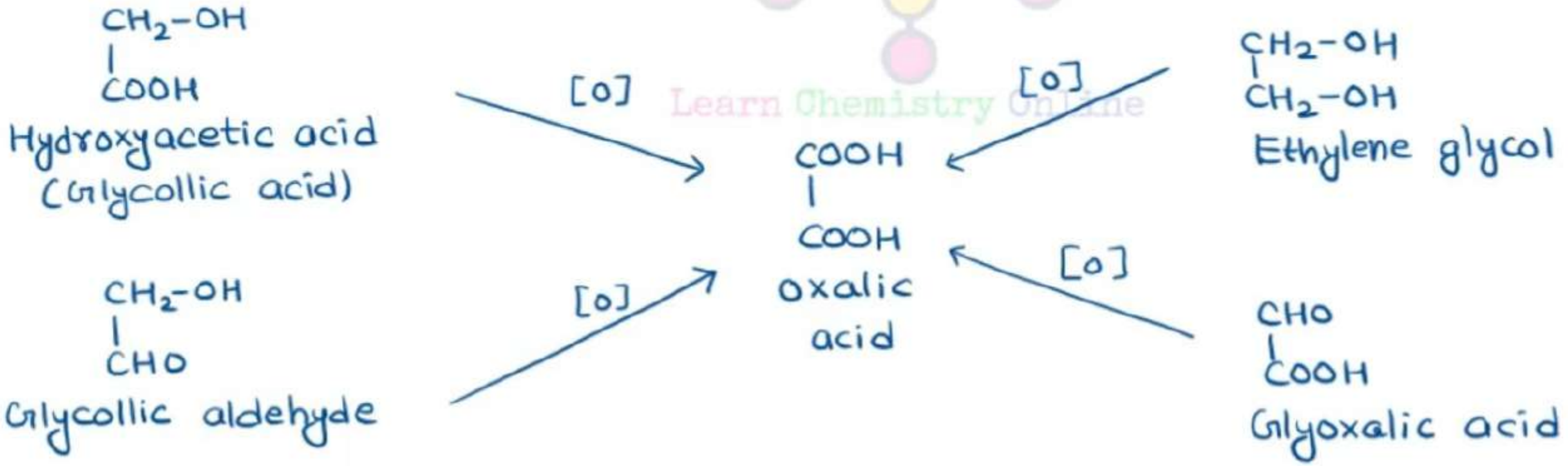
→ Dicarboxylic acids :→

→ Methods of formation :→

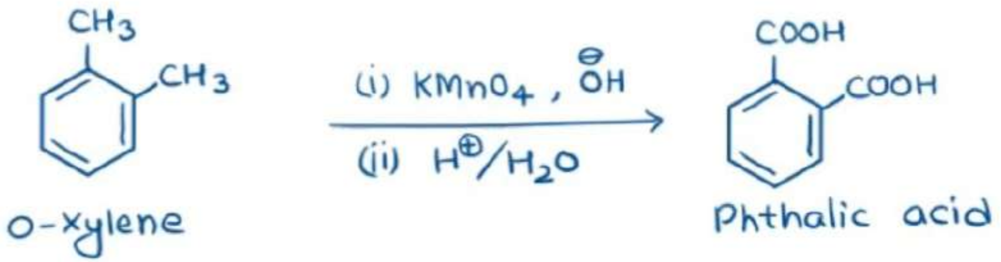
(i) Oxidative methods :→

(a) oxidation of glycols, hydroxy acids, hydroxy aldehydes, aldehydic acids :→





(b) oxidation of dialkylbenzene:→



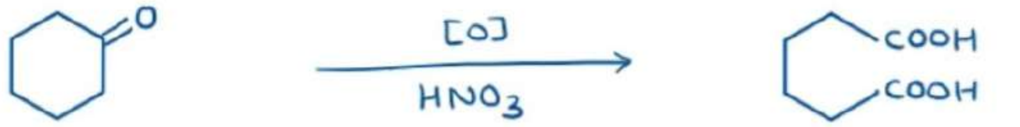
o-xylene

Phthalic acid

(c) Oxidation of unsaturated acids:→

$$\underset{\text{oleic acid}}{CH_3(CH_2)_7-CH=CH-(CH_2)_7-COOH} \xrightarrow[\text{HNO}_3 \text{ Cleavage of } C=C \text{ bond}]{[O]} \underset{\text{Nonanoic acid}}{CH_3-(CH_2)_7-COOH} + \underset{\text{Nonane-1,9-dioic acid (Azelaic acid)}}{HOOC-(CH_2)_7-COOH}$$

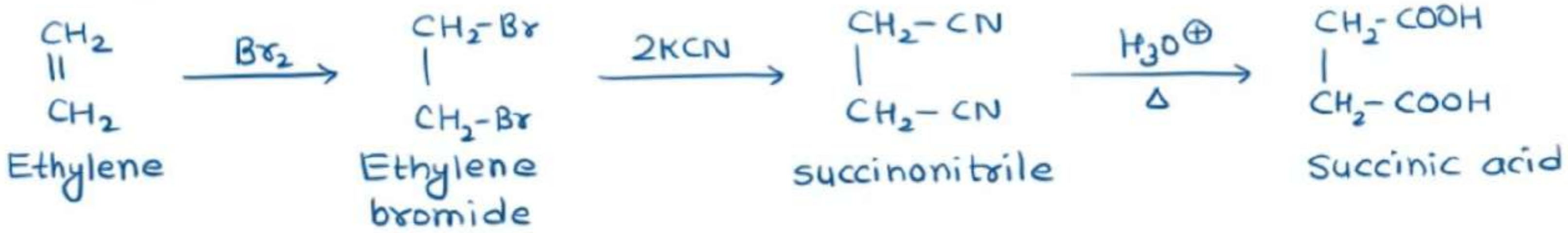
(d) oxidation of cyclic ketones:→



cyclohexanone

Hexane-1,6-dioic acid
(Adipic acid)

~~(ii)~~ Hydrolysis of α,β - dinitriles :→



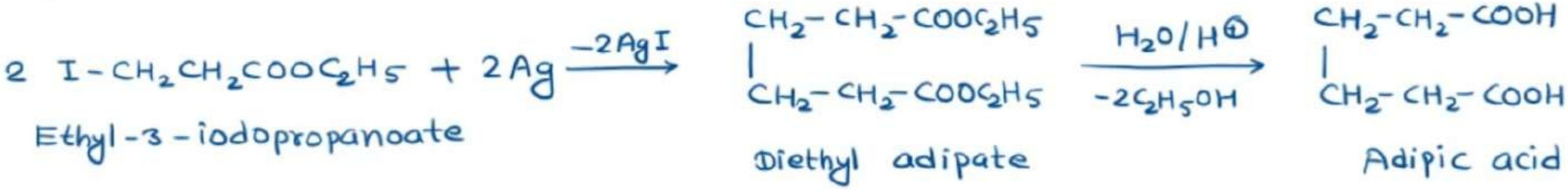
$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}} \xrightarrow{Br_2} \underset{\text{Ethylene bromide}}{\begin{matrix}CH_2-Br\\ | \\ CH_2-Br\end{matrix}} \xrightarrow{2KCN} \underset{\text{succinonitrile}}{\begin{matrix}CH_2-CN\\ | \\ CH_2-CN\end{matrix}} \xrightarrow[\Delta]{H_3O^{\oplus}} \underset{\text{Succinic acid}}{\begin{matrix}CH_2-COOH\\ | \\ CH_2-COOH\end{matrix}}$$

(iii) Hydrolysis of ω - cyano carboxylic acids :→

$$\underset{\omega\text{-cyanocarboxylic acid}}{NC-(CH_2)_n-COOH} \xrightarrow[HCl,\ \Delta]{\text{Hydrolysis}} \underset{\text{Dicarboxylic acid}}{HOOC-(CH_2)_n-COOH} + NH_4Cl$$

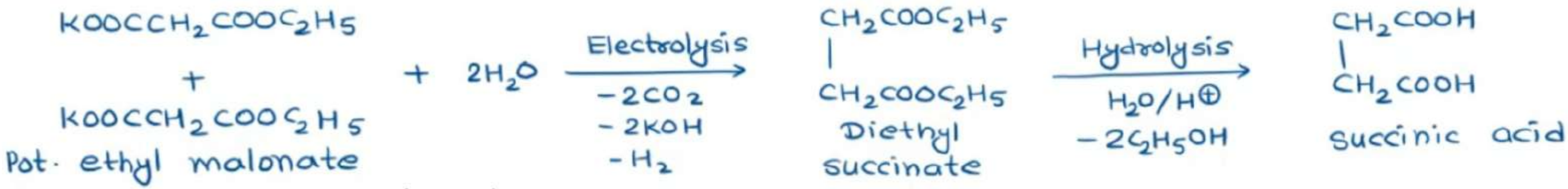
$$\underset{\text{Cyanoacetic acid}}{NC-CH_2-COOH} \xrightarrow[HCl,\ \Delta]{\text{Hydrolysis}} \underset{\text{Malonic acid}}{HOOC-CH_2-COOH} + NH_4Cl$$

(iv) From halogenated acids :→



$$\underset{\text{Ethyl-3-iodopropanoate}}{2\ I-CH_2CH_2COOC_2H_5} + 2Ag \xrightarrow{-2AgI} \underset{\text{Diethyl adipate}}{\begin{matrix}CH_2-CH_2-COOC_2H_5\\ | \\ CH_2-CH_2-COOC_2H_5\end{matrix}} \xrightarrow[-2C_2H_5OH]{H_2O/H^{\oplus}} \underset{\text{Adipic acid}}{\begin{matrix}CH_2-CH_2-COOH\\ | \\ CH_2-CH_2-COOH\end{matrix}}$$

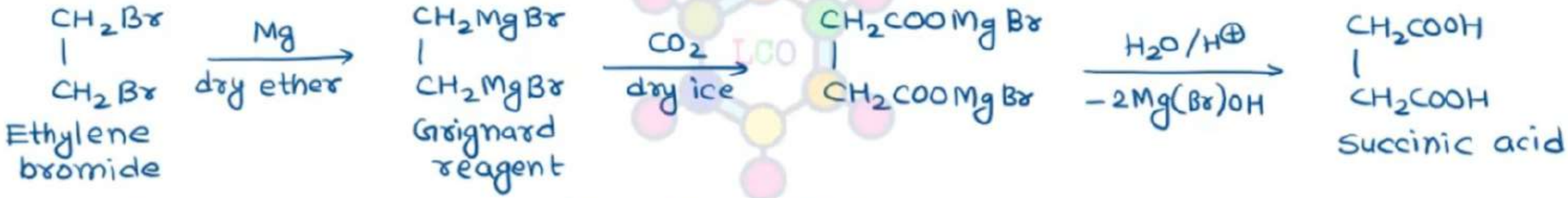
(v) Crum-Brown and Walker electrolytic method :→



$$\begin{array}{c} KOOCCH_2COOC_2H_5 \\ + \\ KOOCCH_2COOC_2H_5 \\ \text{Pot. ethyl malonate} \end{array} + 2H_2O \xrightarrow[\substack{-2CO_2 \\ -2KOH \\ -H_2}]{\text{Electrolysis}} \begin{array}{c} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \\ \text{Diethyl} \\ \text{succinate} \end{array} \xrightarrow[\substack{H_2O/H^{\oplus} \\ -2C_2H_5OH}]{\text{Hydrolysis}} \begin{array}{c} CH_2COOH \\ | \\ CH_2COOH \\ \text{Succinic acid} \end{array}$$

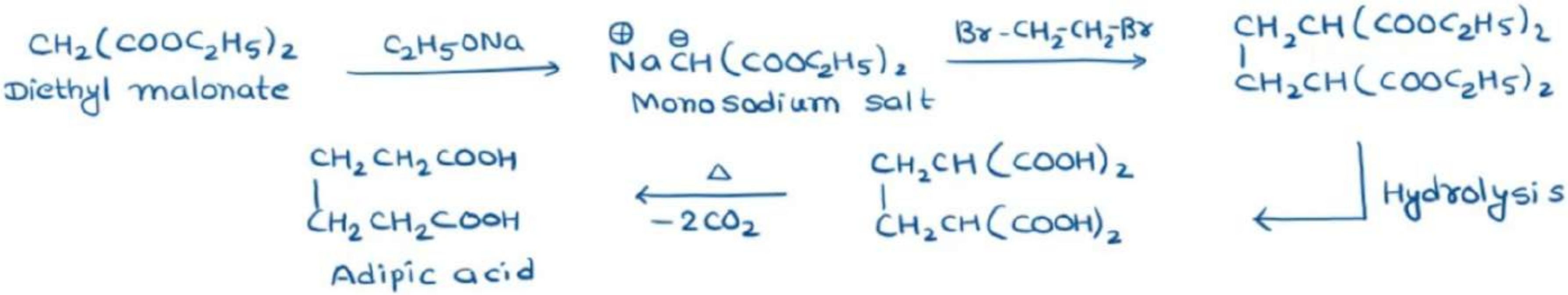
* This method is similar to Kolbe's electrolysis.

(vi) From Grignard reagents of dihaloalkanes :→



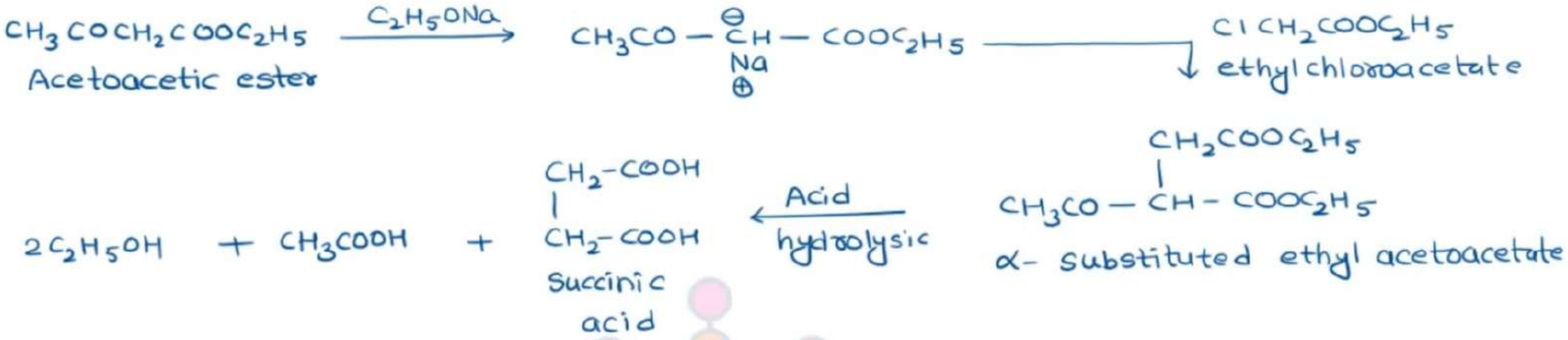
$$\begin{array}{c} CH_2Br \\ | \\ CH_2Br \\ \text{Ethylene} \\ \text{bromide} \end{array} \xrightarrow[\text{dry ether}]{Mg} \begin{array}{c} CH_2MgBr \\ | \\ CH_2MgBr \\ \text{Grignard} \\ \text{reagent} \end{array} \xrightarrow[\text{dry ice}]{CO_2} \begin{array}{c} CH_2COOMgBr \\ | \\ CH_2COOMgBr \end{array} \xrightarrow[-2Mg(Br)OH]{H_2O/H^{\oplus}} \begin{array}{c} CH_2COOH \\ | \\ CH_2COOH \\ \text{Succinic acid} \end{array}$$

(vii) From malonic ester or acetoacetic ester :→



$$\begin{array}{c} CH_2(COOC_2H_5)_2 \\ \text{Diethyl malonate} \end{array} \xrightarrow{C_2H_5ONa} \begin{array}{c} \overset{\oplus}{Na}\overset{\ominus}{C}H(COOC_2H_5)_2 \\ \text{Mono sodium salt} \end{array} \xrightarrow{Br-CH_2-CH_2-Br} \begin{array}{c} CH_2CH(COOC_2H_5)_2 \\ | \\ CH_2CH(COOC_2H_5)_2 \end{array}$$

$$\xrightarrow{\text{Hydrolysis}} \begin{array}{c} CH_2CH(COOH)_2 \\ | \\ CH_2CH(COOH)_2 \end{array} \xrightarrow[-2CO_2]{\Delta} \begin{array}{c} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \\ \text{Adipic acid} \end{array}$$



$$\underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5} \xrightarrow{C_2H_5ONa} CH_3CO-\underset{\underset{\oplus}{Na}}{\overset{\ominus}{C}H}-COOC_2H_5 \xrightarrow[\text{ethyl chloroacetate}]{ClCH_2COOC_2H_5}$$

$$2C_2H_5OH + CH_3COOH + \underset{\text{Succinic acid}}{\begin{matrix}CH_2-COOH\\ |\\ CH_2-COOH\end{matrix}} \xleftarrow[\text{hydrolysic}]{\text{Acid}} \underset{\alpha\text{- substituted ethyl acetoacetate}}{CH_3CO-\overset{\overset{CH_2COOC_2H_5}{|}}{C}H-COOC_2H_5}$$

→ Dicarboxylic acids:→

→ Physical properties:→

1. Physical state:→ All dicarboxylic acids are colourless crystalline solids.

2. Solubility:→ Lower members are soluble in water. However, with increase in molecular weigth the solubility in water decreases but in ether it increases.

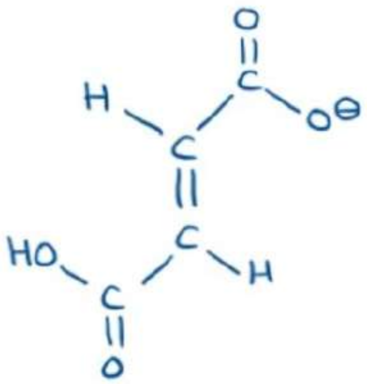
   The acids containing odd number of carbon atoms are more soluble than those containing even number of carbon atoms whether preceding or following.

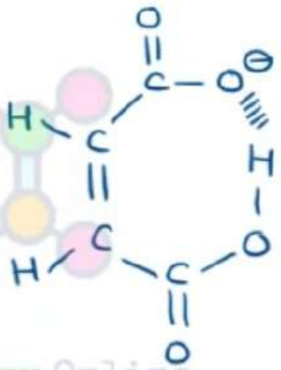
3. Melting points:→ The melting points of dicarboxylic acids follow oscillation rule; the m.p. of acid containing even number of carbon atoms are higher than those containing odd number of carbon atoms. dicarboxylic acids containing even number of carbon atoms are more closely packed in crystal lattice as compare to dicarboxylic acids containing odd number of carbon atoms.

4. Acidic character:→ The acidic strength of dicarboxylic acids decreases with increase in molecular weight. They dissociates in two steps. The value of dissociation constant (K_1) of the first carboxyl group is more than that of second one (K_2). The higher value of K_1 is due to -I effect of one carboxyl group on the other. This effect decreases as the carbon chain increases. The lower value of K_2 is due to +I effect of carboxylate anion on the second carboxylate group.

- The second ionisation of fumeric acid is 24 times less than the first ionisation, whereas, it is 24000 times less in case of maleic acid.

The reason for this is that carboxylate anion of maleic acid as compared to that of fumeric acid has a much larger attractive electrostatic effect on the proton of second carboxylic group. This is true as the carboxylate anion of the former is stabilised by intramolecular hydrogen bond.


Fumarate anion


Maleate anion

→ Dicarboxylic acids:→

→ Chemical reactions:→

1. Effect of heat and dehydroting agents:-

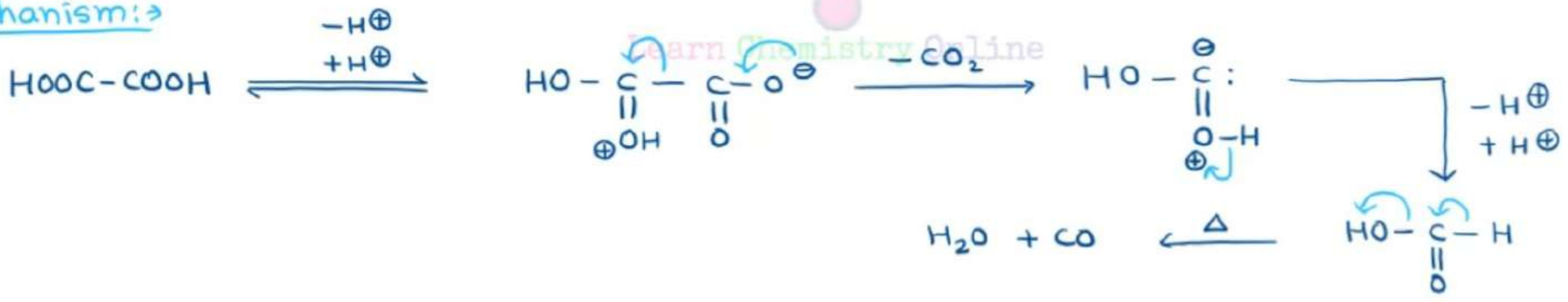
– The bevaviour of dicarboxylic acids towards heat and dehydrating agents is specific depending upon the chain length.

(i) Acids with one or no intervening carbon atom:→

$$\underset{(COOH)_2\cdot 2H_2O}{\text{Crystalline oxalic acid}} \xrightarrow[373\ K]{\Delta} \underset{(m.p.\ 472\ K)}{\text{Anhydrous oxalic acid}} \xrightarrow[\substack{473\ K \\ \text{decarboxylation} \\ (-CO_2)}]{\Delta} \text{Formic acid}$$

$$HOOC-COOH \xrightarrow{\Delta} [HCOOH + CO_2] \longrightarrow H_2O + CO + CO_2$$

→ Mechanism:→

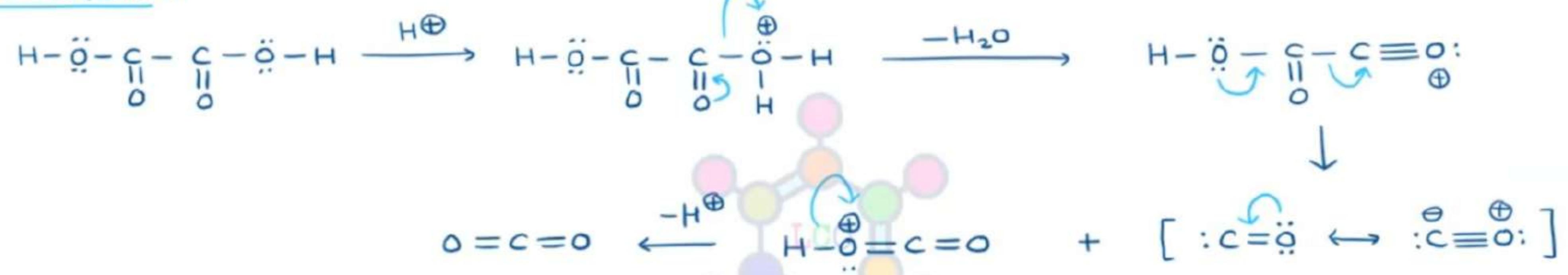


Formic acid

- when oxalic acid heated with conc. H_2SO_4, it dehydrates to form CO_2 and CO. (test of oxalate ion in inorganic mixture analysis).

$$H_2C_2O_4 \xrightarrow[373\,K]{H^{\oplus}} H_2O + CO + CO_2$$

→ Mechanism: →



- Malonic acid upon heating near melting point undergoes decarboxylation forming acetic acid.

$$HOOC-CH_2-COOH \xrightarrow{\Delta} CH_3COOH + CO_2$$

- when heated with a dehydrating agent, such as phosphorus pentaoxide, it gives carbon suboxide

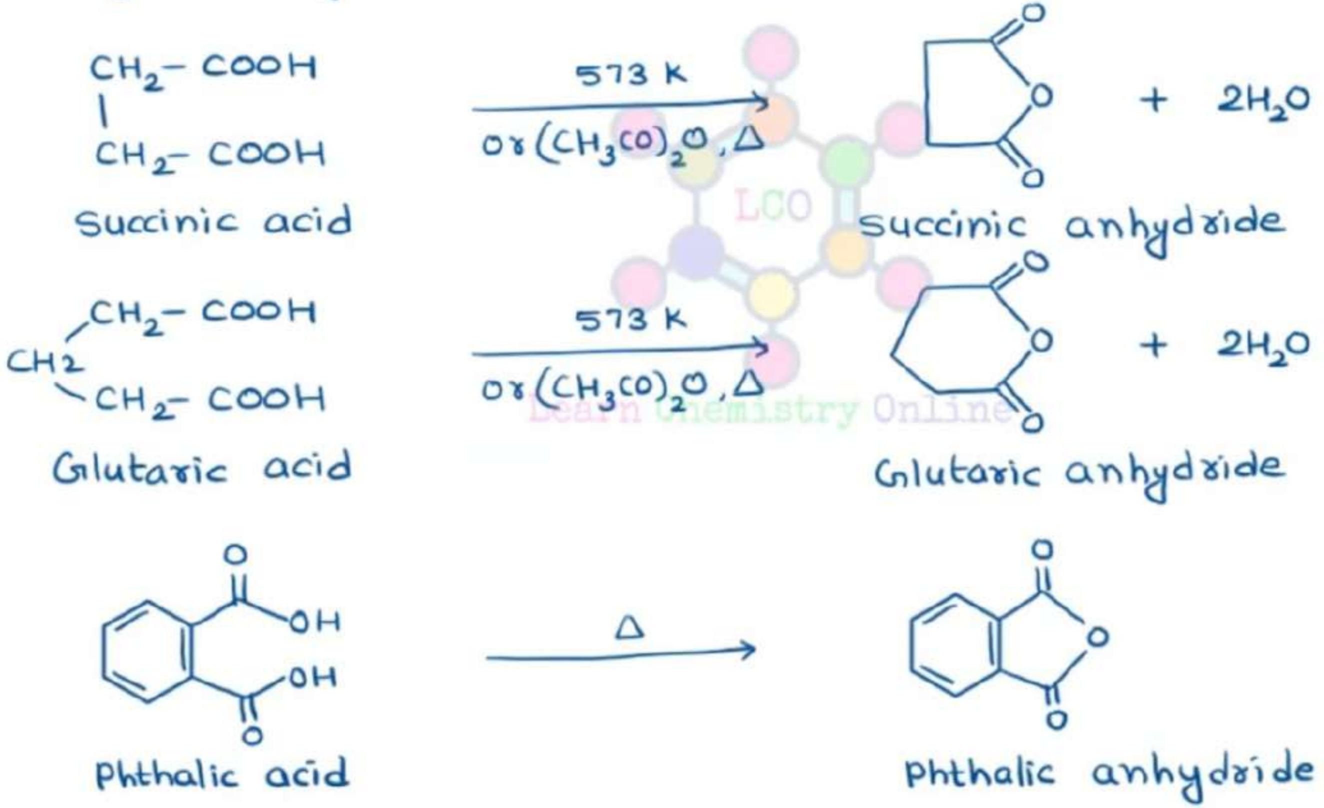
$$HOOC-CH_2-COOH \xrightarrow{P_2O_5} O=C=C=C=O$$

Carbon suboxide (behave like diketene)

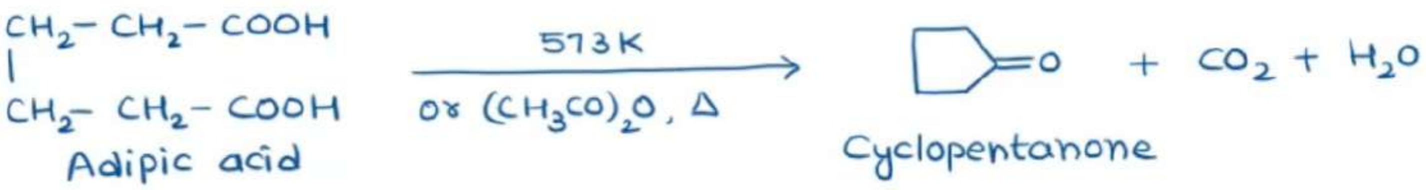
- on adding water in carbon suboxide, it converts into malonic acid.

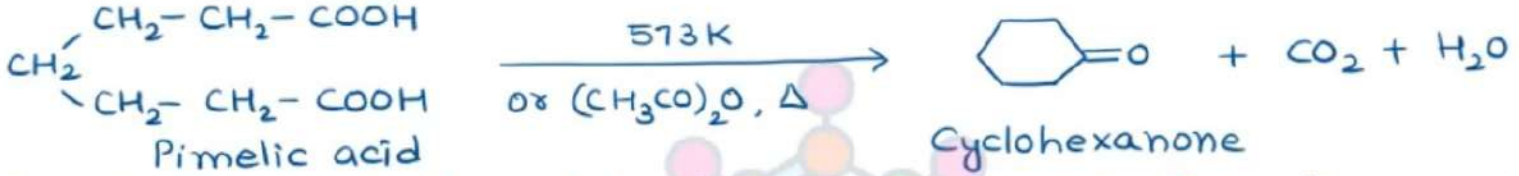
(ii) Acids with two or three intervening carbon atoms:-

- With increasing length of carbon chain in dicarboxylic acids, the electron attracting inductive effect of one carboxylic group on the other becomes weak and decarboxylation is difficult. Thus dicarboxylic acids are heated above their melting points, they sublimate. However, heating these acids with a dehydrating agent results in the formation of cyclic anhydrides.



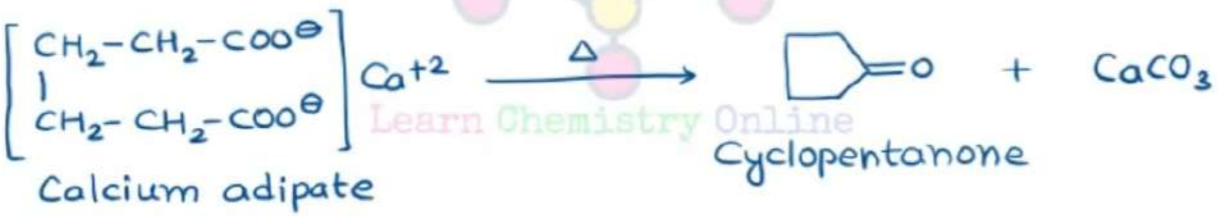
(iii) Acids with four or more intervening carbon:→





- With further increase in the chain length, the acids form linear polymeric anhydrides.

(iv) Action of heat on salts:→



- The action of heat mentioned above is governed by Blanc's Rule. According to this rule, 1,3-dicarboxylic acids on heating give monocarboxylic acids, 1,4 and 1,5-dicarboxylic acids on heating give cyclic anhydrides whereas 1,6 and 1,7-dicarboxylic acids give cyclic ketones.