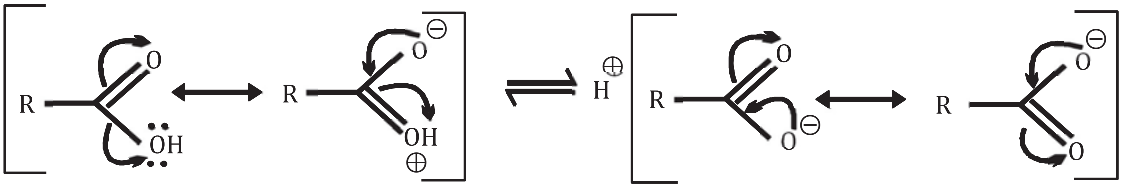
CHEMICAL PROPERTIES OF CARBOXYLIC ACID

1. Acidity of Carboxylic Acid

Acidity refers to the ease with which a substance donates a proton, resulting in the formation of an anion. The strength of an acid is determined by the disparity in stability between the acid and its corresponding anion.



Non-equivalent structures of Resonance hybrid

Equivalent structures of Resonance hybrid

Both the acid and its anion benefit from resonance stabilization, but the anion experiences significantly greater stabilization because it can generate two identical resonating structures.

2. Effect of Substituents on Acidity

Any factor that provides more stability to the anion compared to the acid will enhance the acidity, while any factor that reduces the stability of the anion will lower the acidity of the carboxylic acid.

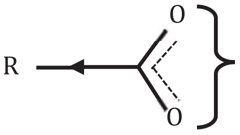
(a) Electron-withdrawing substituents enhance anion stability by dispersing the negative charge, thereby increasing the acidity of the carboxylic acid.

(b) Electron-releasing substituents increase the negative charge on the anion, reducing the stability of the carboxylate anion, and consequently decreasing the acidity of the acid.

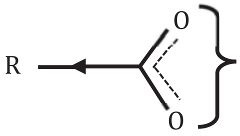
Carboxylic acids are considered weak acids, and their carboxylate ions are strong conjugate bases. They exhibit slight alkalinity due to the hydrolysis of the carboxylate anion in comparison to other species. The order of acidity and basicity of their corresponding conjugate bases is as follows.

$$\text{Acidity} -\!\!- RCOOH > HOH > ROH > CH \equiv CH > NH_3 > RH$$

$$\text{Basicity} -\!\!- RCOO^- < OH^- < HC \equiv C^- < NH_2{}^- < R^-$$



Acidity increase



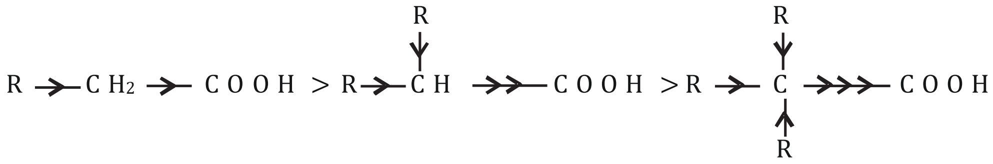
Acidity decrease

The impact of different numbers of substituents and their distances from the carboxyl group is demonstrated through the following examples.

(i) The influence of the number of substituents is evident in chloro-substituted acetic acids, where the acid strength follows the order provided below.

$$ClCH_2 -\!\!- COOH < Cl_2CHCOOH < Cl_3CCOOH$$

An increase in the number of chlorine substituents on the α-carbon atom of acetic acid intensifies the electron-withdrawing effect, leading to greater stability of the carboxylate ion. Conversely, when electron-releasing substituents are connected to the carboxylic group, the acid strength diminishes as the strength of electron release increases.



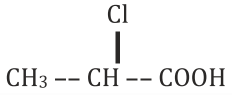
$$R \rightarrow CH_2 \rightarrow COOH > R \rightarrow \underset{}{\overset{R \downarrow}{CH}} \twoheadrightarrow COOH > R \rightarrow \underset{R \uparrow}{\overset{R \downarrow}{C}} \rightarrow\!\!\rightarrow\!\!\rightarrow COOH$$

(ii) The impact of the substituent's nature is exemplified by a range of halo acetic acids, and their acid strength can be ranked as follows.

$$ICH_2-COOH < BrCH_2COOH < ClCH_2COOH < F\,CH_2COOH$$

$$CH_3-CH_2-CH_2-COOH < CH_2 = \underset{(sp^2)}{\underset{\uparrow}{CH}}-CH_2-COOH < N{\equiv}\underset{(sp)}{\underset{\uparrow}{C}}-CH_2-COOH$$

(iii) Effect of the position of the substituent: The effect of the substituent decreases as its distance from —COOH group increases.



$$CH_3-\overset{Cl}{\overset{|}{CH}}-COOH$$

α-chloro propanoic acid
electron withdrawing
effect more

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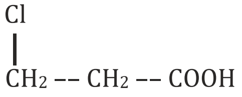
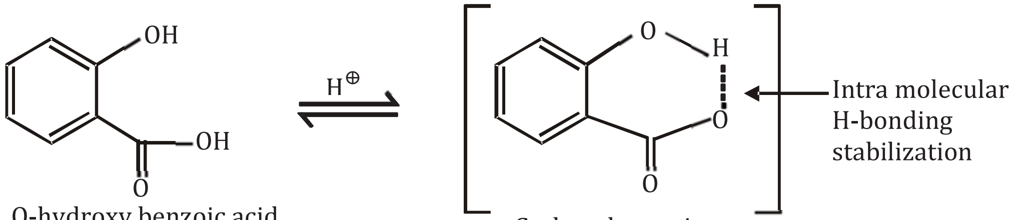


$$\overset{Cl}{\overset{|}{CH_2}}-CH_2-COOH$$

β-chloro propanoic acid
electron withdrawing
effect less

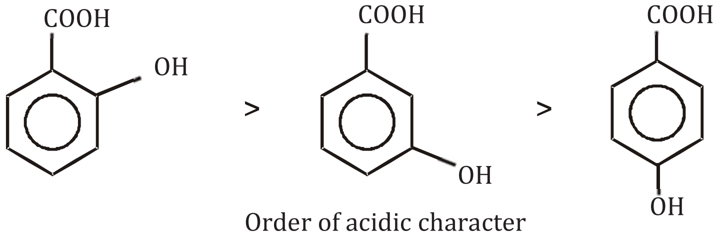
3. Ortho Effect

The Ortho-substituted benzoic acid, regardless of whether the substituent is electron-withdrawing or electron-releasing, exhibits higher acidity compared to its para and meta isomers. This phenomenon is referred to as the ortho effect, and it arises from the combined effects of steric hindrance and intramolecular hydrogen bonding. This effect occurs whenever the opportunity arises to stabilize the carboxylate anion due to the proximity of the substituent. Groups such as -OH, -Cl, and -NO_2 provide even greater stabilization to the anion through direct interaction via intramolecular hydrogen bonding.



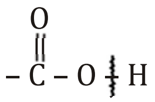
O-hydroxy benzoic acid
(Salicylic acid)

Carboxylate aninon



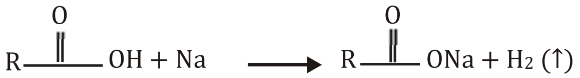
Order of acidic character

Reaction due to cleavage of ––O––H bond as acid



$$-\overset{O}{\overset{\|}{C}}-O \,\vdots\, H$$

(i) Reaction with active metals [alkali and alkaline metal]



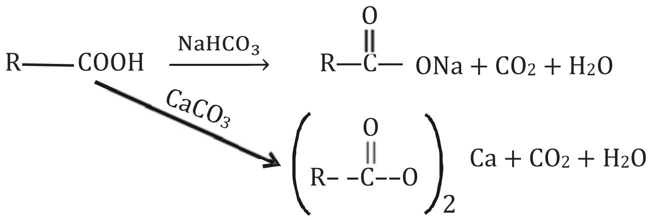
$$R-\overset{\overset{O}{\|}}{C}-OH + Na \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + H_2\,(\uparrow)$$

(ii) Reaction with CaO

$$2R-COOH + CaO \longrightarrow (RCOO)_2Ca + H_2O$$

(iii) Reaction with Bicarbonates and Carbonates

Carboxylic acid reacts with carbonates and bicarbonates to liberate CO_2 gas



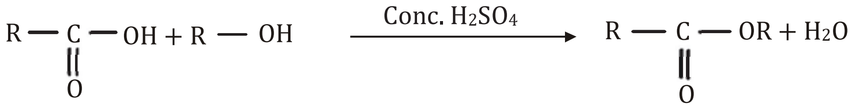
$$R-COOH \xrightarrow{NaHCO_3} R-\overset{\overset{O}{\|}}{C}-ONa + CO_2 + H_2O$$

$$R-COOH \xrightarrow{CaCO_3} \left(R-\overset{\overset{O}{\|}}{C}-O\right)_2 Ca + CO_2 + H_2O$$

Reaction Involving Cleavage of –Oh Group

Esterification

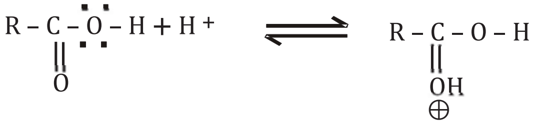
When carboxylic acid reacts with alcohol in the presence of conc. H_2SO_4 to form ester, it is known as esterification



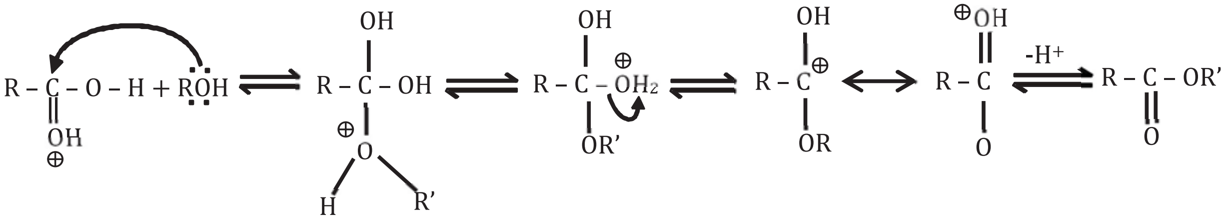
$$R-\underset{\underset{O}{\|}}{C}-OH + R-OH \xrightarrow{\text{Conc. } H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O$$

Mechanism

$$H_2SO_4 \longrightarrow H^+ +$$



$$R-\underset{\underset{O}{\|}}{C}-\ddot{O}-H + H^+ \rightleftharpoons R-\underset{\underset{\overset{\oplus}{OH}}{\|}}{C}-O-H$$

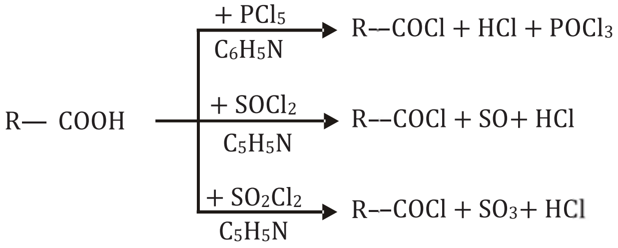


The reactivity of alcohols in the formation of esters is significantly influenced by their structure. When there are bulkier substituents near the -OH group, the reaction proceeds more slowly. This observation holds true for acid-catalyzed reactions as well.

$$CH_3OH > CH_3CH_2OH > (CH_3)_2\,CHOH > (CH_3)_3\,COH$$

$$H{-}{-}COOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$$

Formation of Acid Chloride



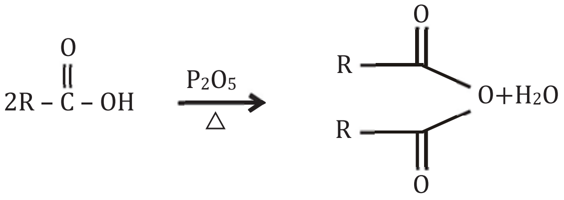
$$R\text{—}COOH \xrightarrow[C_6H_5N]{+\ PCl_5} R\text{—}COCl + HCl + POCl_3$$

$$R\text{—}COOH \xrightarrow[C_5H_5N]{+\ SOCl_2} R\text{—}COCl + SO + HCl$$

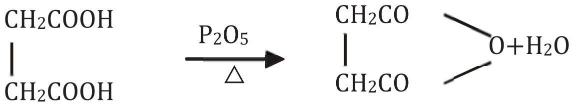
$$R\text{—}COOH \xrightarrow[C_5H_5N]{+\ SO_2Cl_2} R\text{—}COCl + SO_3 + HCl$$

Formation of Acid Anhydride

When carboxylic acids are subjected to a dehydrating agent such as P_2O_5, they undergo a reaction that leads to the formation of an anhydride through the elimination of a water molecule.

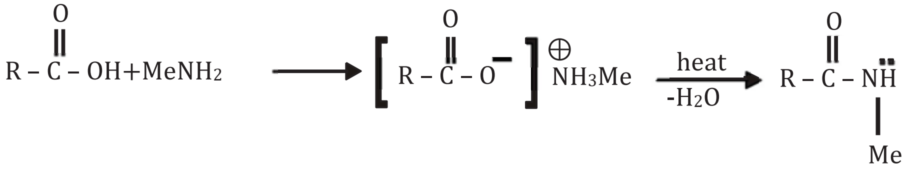


$$2R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\triangle]{P_2O_5} (RCO)_2O + H_2O$$



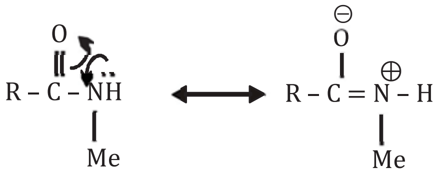
Succinic acid → Succinic anhydride

Formation of Amides



$$R-\overset{\overset{O}{\|}}{C}-OH + MeNH_2 \longrightarrow \left[R-\overset{\overset{O}{\|}}{C}-O^{-}\right]\overset{\oplus}{N}H_3Me \xrightarrow[-H_2O]{heat} R-\overset{\overset{O}{\|}}{C}-\ddot{N}H-Me$$

The lone pair of electrons on the nitrogen atom participates in resonance, resulting in the presence of a partial positive charge on the nitrogen atom.



$$R-\overset{\overset{O}{\|}}{C}-\ddot{N}H(Me) \longleftrightarrow R-\overset{\overset{\ominus}{O}}{C}=\overset{\oplus}{N}(Me)-H$$

As a result, the degree of hydrogen bonding increases, leading to higher boiling and melting points for amides compared to other types of acid derivatives.

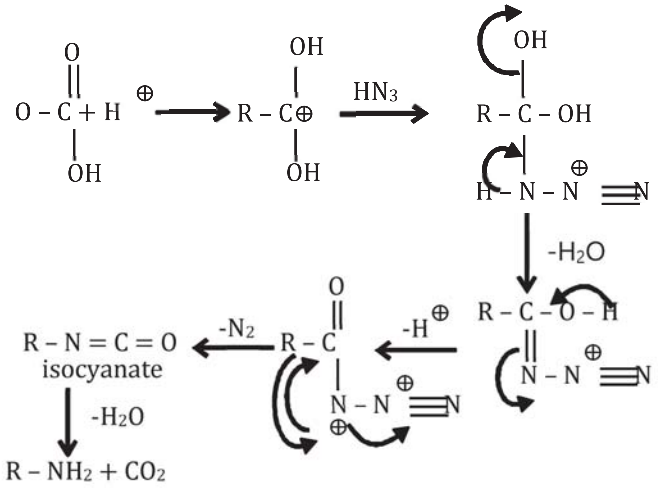
4. Reactions Involving – COOH Group

Schmidt Reaction

Carboxylic acids, when combined with hydrazoic acid in the presence of concentrated H_2SO_4 at 90°C, result in the production of primary amines.

$$R—COOH + N_3H \xrightarrow{Conc.H_2SO_4} R—NH_2 + N_2 + CO_2$$

Mechanism



5. Soda lime Decarboxylation

When carboxylic acids are subjected to heating with soda lime (a mixture of NaOH and CaO), they undergo a transformation, resulting in the formation of an alkane with one fewer carbon atom than the original acid.

$$R---COOH \xrightarrow[\Delta]{Soda\ lime} R--H + CO_2$$

Hunsdicker Reaction:

$$R--COOH \xrightarrow{Ag_2O} R--COO^- Ag^+ \xrightarrow[in\ CCl_4]{Br_2} R--Br + AgBr + CO_2$$

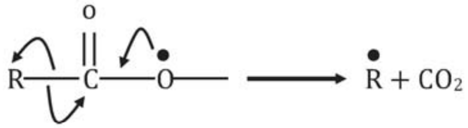
Mechanism

Reaction proceeds through free radical mechanism in various steps.

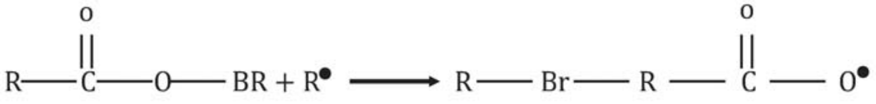
(i) Chain initiation

$$R-\overset{O}{\overset{||}{C}}-O-BR \longrightarrow R-\overset{O}{\overset{||}{C}}-\dot{O}-\dot{Br}$$

(ii) Chain propagation step



$$R-\overset{O}{\overset{||}{C}}-\dot{O}- \longrightarrow \dot{R} + CO_2$$



$$R-\overset{O}{\overset{||}{C}}-O-BR + R^{\bullet} \longrightarrow R-Br-R-\overset{O}{\overset{||}{C}}-O^{\bullet}$$

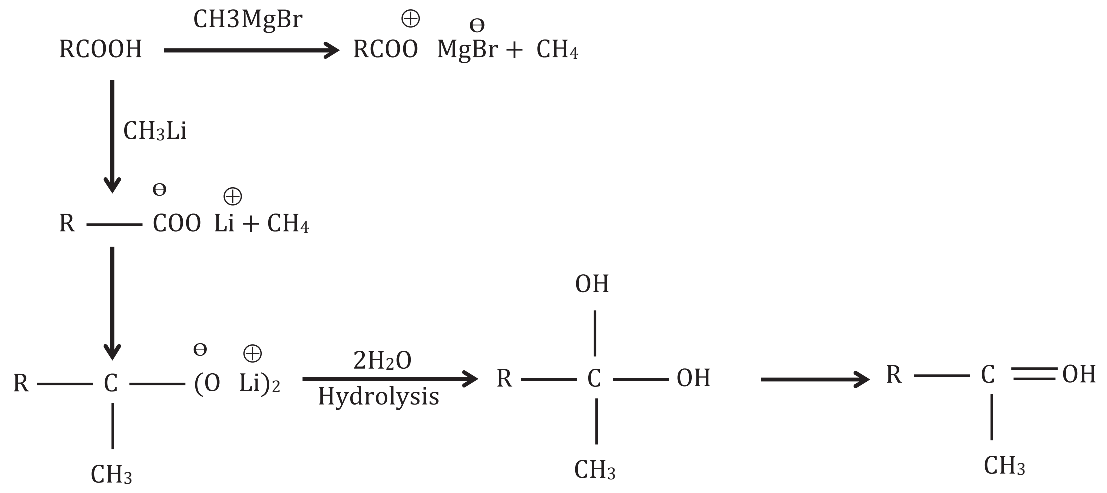
(iii) Chain termination

$$\dot{R} + \dot{R} \longrightarrow R-R$$

$$R-\overset{\overset{O}{\|}}{C}-\dot{O} + \dot{R} \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-R$$

$$\dot{Br} + \dot{Br} \longrightarrow Br_2$$

With excess of organometallic compounds

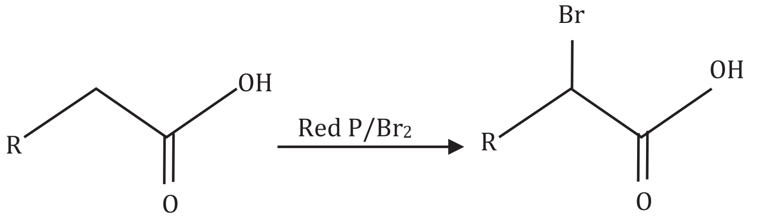


Acetone

2 moles of organometallic compounds are needed to form ketone.

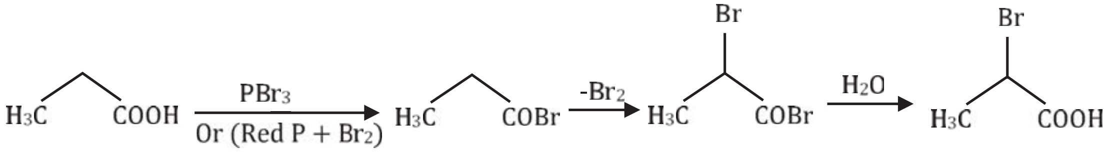
6. Hell-Volhard-Zelinsky Reaction

This is α-halogenation of a carboxylic acid.

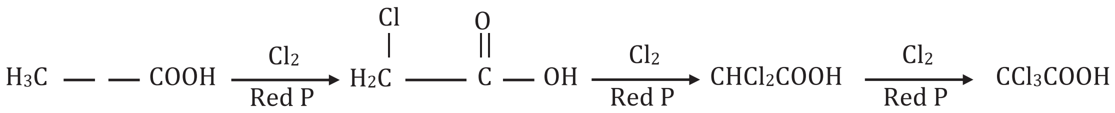


α - bromo acid

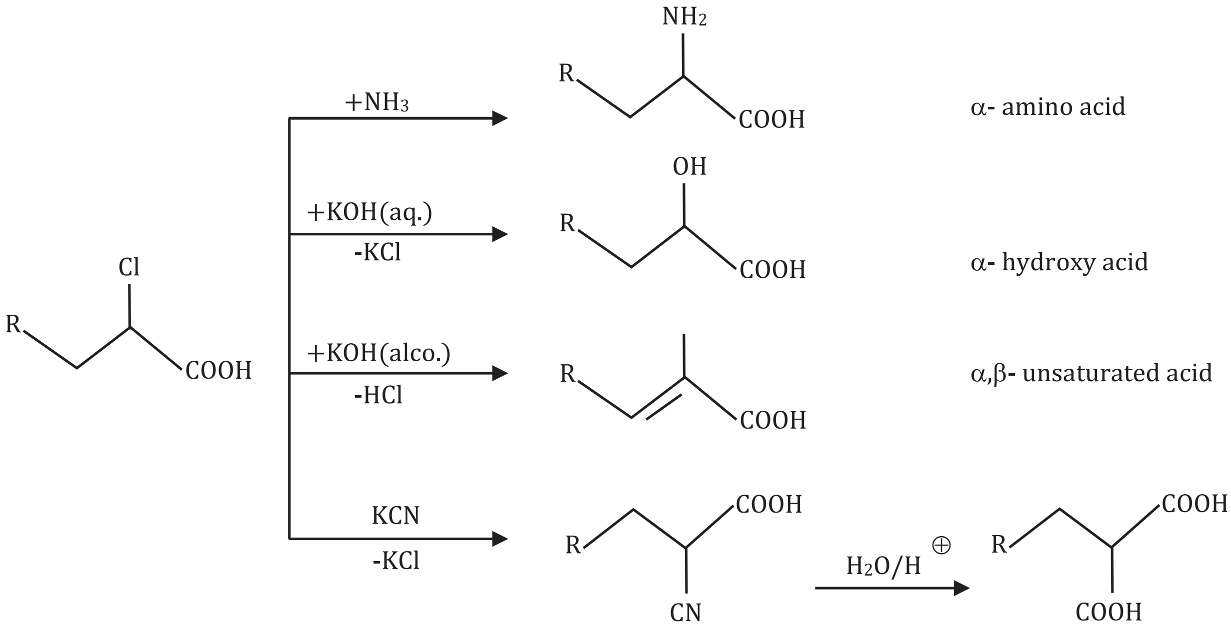
Possible Mechanism for the reaction is



PBr_3 is employed with the aim of converting -OH groups into -Br groups, enhancing the acidity of the alpha-hydrogen atoms, which are then substituted with bromine atoms from Br_2.

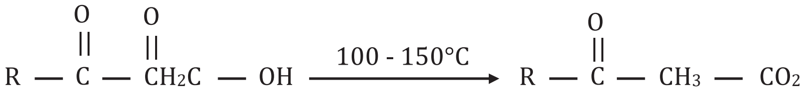


$$H_3C - COOH \xrightarrow[\text{Red P}]{Cl_2} H_2\overset{\overset{Cl}{|}}{C} - \overset{\overset{O}{\|}}{C} - OH \xrightarrow[\text{Red P}]{Cl_2} CHCl_2COOH \xrightarrow[\text{Red P}]{Cl_2} CCl_3COOH$$



This reaction progresses beyond mono-substitution and continues until all the alpha-hydrogen atoms have been replaced. The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.

7. Heating of β-keto acid

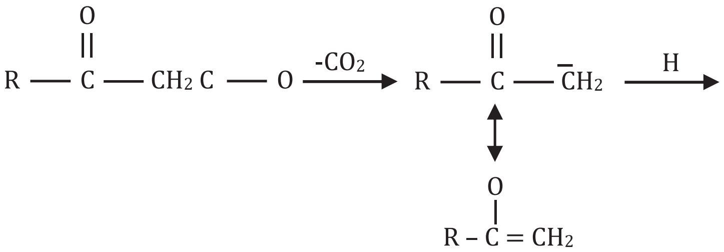


$$R - \overset{\overset{O}{||}}{C} - CH_2\overset{\overset{O}{||}}{C} - OH \xrightarrow{100 - 150°C} R - \overset{\overset{O}{||}}{C} - CH_3 - CO_2$$

β - Keto acid

There are two facts on which ease of decarboxylation depends.

(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.

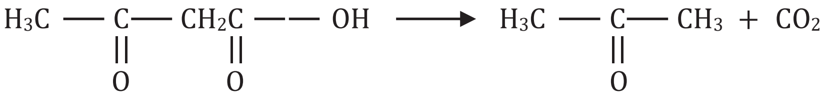


$$R - \overset{\overset{O}{||}}{C} - CH_2\,C - O \xrightarrow{-CO_2} R - \overset{\overset{O}{||}}{C} - \bar{C}H_2 \xrightarrow{H}$$
$$\updownarrow$$
$$R - \overset{\overset{O}{|}}{C} = CH_2$$

Resonance stabilized enolate anion

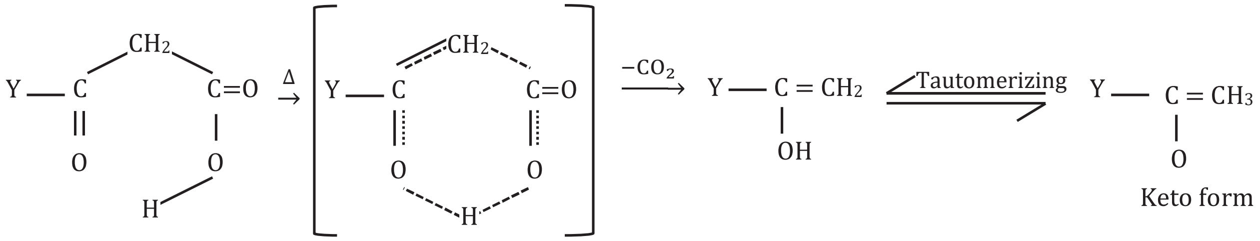
This anion is much more stable than the anion formed by decarboxylation of an ordinary carboxylic acid anion.

(ii) When the acid undergoes decarboxylation, this process can occur through a six-membered cyclic transition state. Upon heating alone or in the presence of a base, a β-keto acid experiences the swift elimination of CO_2.



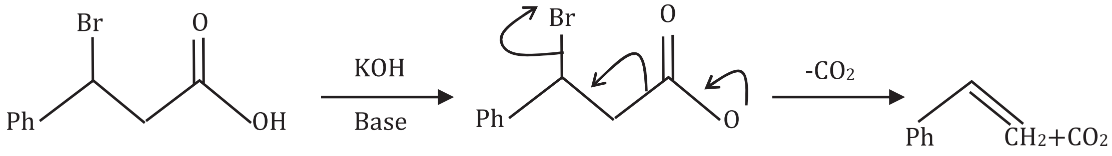
$$H_3C - \underset{\underset{O}{||}}{C} - CH_2\underset{\underset{O}{||}}{C} - OH \longrightarrow H_3C - \underset{\underset{O}{||}}{C} - CH_3 + CO_2$$

Mechanism



Here y can be substituents like

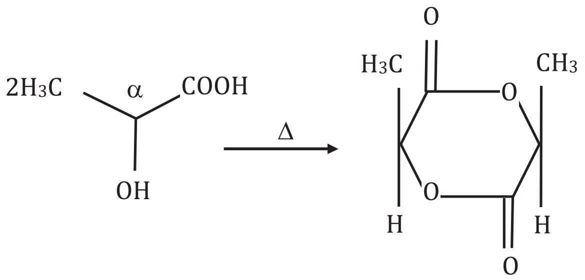
OH – diacid	:	R – β-keto acid
H – β aldehyde acid	:	X – β halo acid



This decarboxylation proceeds through elimination.

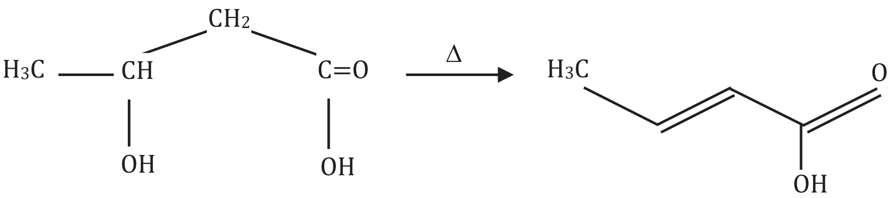
Heating of α, β and γ Hydroxy Acid

(i)



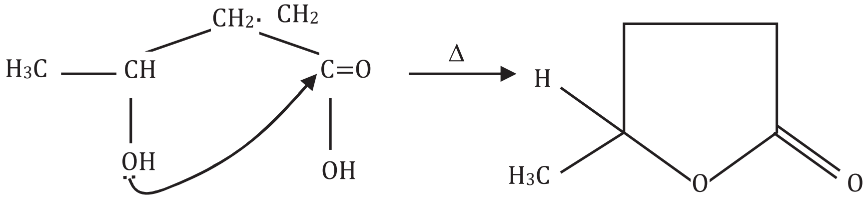
α - hydroxy acid Lactides

(ii)



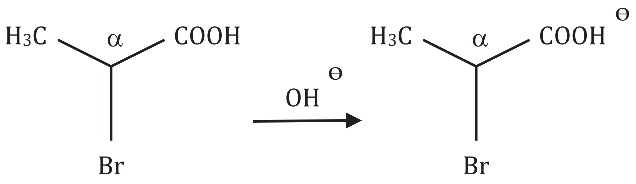
β- hydroxy acid α,β - Unsaturacid carboxylic acid

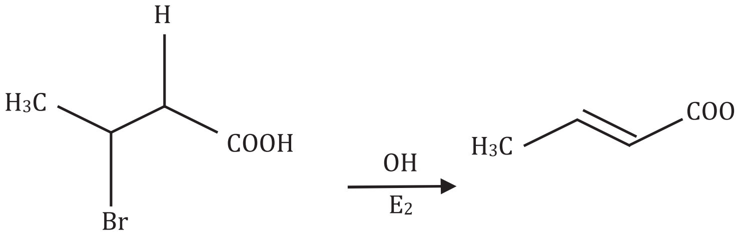
(iii)

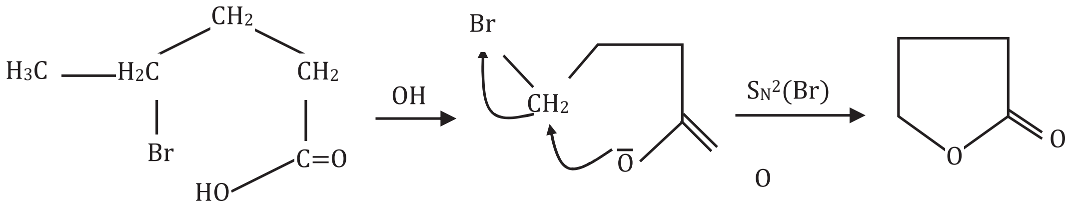


γ - hydroxy acid 5 – Methyldihydrofuran – 2 - one

8. Reaction of α, β and γ halo carboxylic acid with aq. NaOH

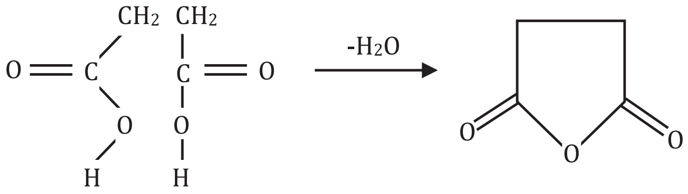




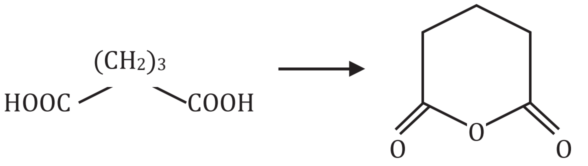


Cyclization of γ haloacid

Heating of Dicarboxylic Acids



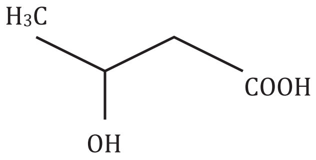
Succinic acid Succinic anhydride



Glutamic anhydirde

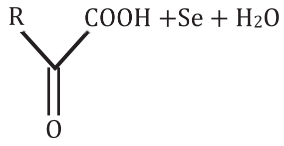
Oxidation of Carboxylic acid at Alkyl Group

Acid on treatment with mild oxidising agent such as H_2O_2, is oxidized at the β position.



$CH_3\ CH_2 - CH_2COOH = [O] \xrightarrow{H_2O_2}$ 3 – Hydroxy butanoic acid

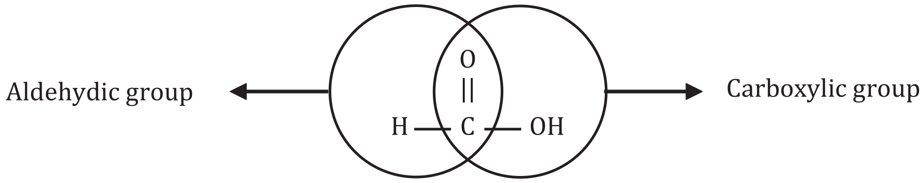
Oxidation can also occur at α carbon atom on treatment with oxidizing agent like selenium dioxide SeO_2.



$$RCH_2COOH + [O] \xrightarrow[\triangle]{SeO_2} \alpha\text{Keto acid}$$

Abnormal Behaviour of Formic Acid

Formic acid exhibits distinct behavior compared to other carboxylic acids due to the presence of an aldehydic group.



Reaction with

(a) Tolle's reagents: Formic acid behaves as a reducing agent and reduces Tolle's reagent or Fehling solution. But others acid fails to do so.

$$H\text{–}COOH + Ag_2O \longrightarrow CO_2 + H_2O + 2Ag\downarrow \text{ Silver mirror}$$

$$H\text{–}COOH + 2CuO \longrightarrow CO_2 + H_2O + Cu_2O\downarrow \text{ Red ppt.}$$

(b) Reaction with $HgCl_2$: Formic acid reacts with $HgCl_2$ to produce a white precipitate of Hg_2Cl_2, which can be transformed into a gray precipitate of mercury.

$$2HCOOH + HgCl_2 \longrightarrow CO_2 + \underset{\text{white ppt.}}{Hg_2Cl_2\downarrow} + 2HCl$$

Applications of Formic Acid

(i) Employed as an antiseptic.
(ii) Utilized for fruit preservation.
(iii) Involved in leather tanning.
(iv) Used in dyeing wool and cotton textiles.
(v) Serves as a coagulating agent for rubber.
(vi) Applied in the hydrogenation of oil, often in the form of Ni-format.

Applications of Acetic Acid

(i) Found in vinegar, commonly as a 6-10% solution, used for culinary purposes and in pickle production.
(ii) In its salt forms, it is employed in medicine and the paint industry.
(iii) Used as a coagulant for the manufacture of rubber from latex and casein from milk.
(iv) Aluminum and chromium acetates are used as mordants.
(v) Essential in the production of dyes and perfumes.
(vi) Functions as a solvent and laboratory reagent.