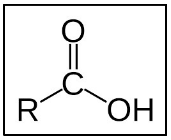
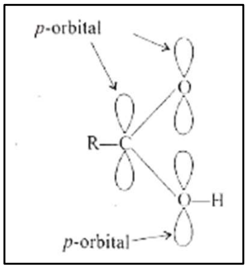
CARBOXYLIC ACIDS

Structure of Carboxylic acid group

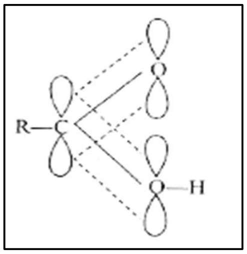
A carboxyl group is made up of a carboxyl group joined to a hydroxyl group. In the carboxyl group, the carbon atom is attached to two oxygen atoms, one by a double bond and the other by a single bond which in turn linked to a hydrogen atom by a single bond. The remaining free valency of the carbon atom of the carboxyl is satisfied by a H atom or an alkyl group.



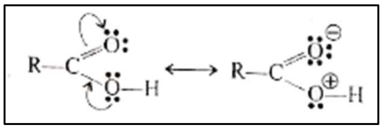
The carbon atom and the two oxygen atoms are sp^2 hybridised. The two sp^2 hybridised orbitals of the carboxyl carbon overlap with one sp^2 hybridised orbital of each oxygen atom while the third sp^2 hybridised orbital of carbon overlaps with either s-orbital of H - atom or a sp^3 hybridised orbital of Carbon atom of the alkyl group to form three σ bonds. Each of the two oxygen atoms are left with one unhybridized p- orbital which is perpendicular to the σ bonding skeleton.



All the three p - orbitals being parallel, overlap to form π bond which is partly delocalised between carbon and oxygen atom on one side and carbon and oxygen of the -OH group on the other side.



In other words, RCOOH may be represented as a resonance hybrid of the following two canonical structures. As a result of resonance (i) the C-O single bond length in carboxylic acids is shorter than the normal C-O single bond in alcohols and ether and (ii) C=O bond length in carboxylic acids is slightly larger than the normal C=O bond length in aldehydes and ketones.



Nomenclature

In IUPAC system of nomenclature, the letter "e" in the name of the parent chain is relaced with "oic acid". Carbon in the Carboxylic acid group has the position 1. For example, CH_3-COOH is named as ethanoic acid since its parent chain is ethane.

S.No	Formula	Common name	IUPAC name
1	HCOOH	Formic acid	Methanoic acid
2	CH_3COOH	Acetic acid	Ethanoic acid
3	CH_3CH_2COOH	Propionic acid	Propanoic acid
4	$CH_3(CH_2)_2COOH$	Butyric acid	Butanoic acid
5	$CH_3(CH_2)_3COOH$	Valeric acid	Pentanoic acid
6	$CH_3(CH_2)_4COOH$	Caproic acid	Hexanoic acid
7	$CH_3(CH_2)_5COOH$	Enanthic acid	Heptanoic acid
8	$CH_3(CH_2)_6COOH$	Caprylic acid	Octanoic acid
9	$CH_3(CH_2)_7COOH$	Pelargonic acid	Nonanoic acid

Classification

Carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids, or tricarboxylic acids, aliphatic carboxylic acids, and aromatic carboxylic acids.

Classification based on the number of carboxyl groups:

Monocarboxylic acids: These carboxylic acids contain one carboxyl group (-COOH). Examples are formic acid (HCOOH) and acetic acid (CH_3COOH).

Dicarboxylic acids: These carboxylic acids contain two carboxyl groups. Examples are oxalic acid (HOOC-COOH) succinic acid (HOOC-CH_2-CH_2-COOH)

Tricarboxylic acids: These carboxylic acids contain three carboxyl groups. An example is citricacid

Methods of preparation

a) From Cyanides or nitriles

Cyanides on ~~hydrolysis~~ hydrolysis in presence of acid or base catalyst to give Carboxylic acids

$$R-C\equiv N \xrightarrow{H_2O/H^{\oplus}/\Delta} RCOOH + \overset{\oplus}{N}H_4$$

$$CH_3-C\equiv N \xrightarrow{H_2O/H^{\oplus}/\Delta} CH_3COOH + \overset{\oplus}{N}H_4$$

b) From Amides

Amides undergo hydrolysis in presence of acids or bases to form Carboxylic acid

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O/H^{\oplus}/\Delta} RCOOH + \overset{\oplus}{N}H_4$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O/\overset{\ominus}{O}H/\Delta} RCO\overset{\ominus}{O} + NH_3$$

$R = -CH_3$

$-C_2H_5$

c) Acidic and alkaline hydrolysis of esters

Hydrolysis of Ester proceeds either by acid catalysed mechanism or by base catalysed mechanism.

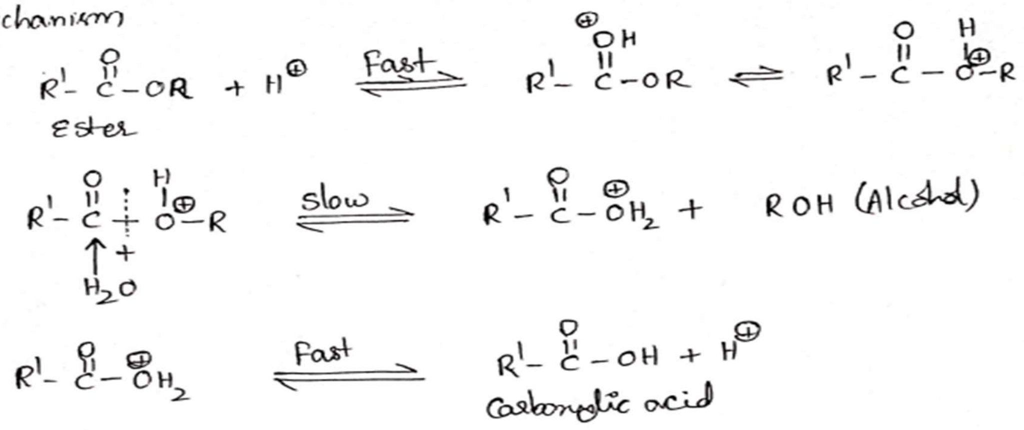
i) Ester hydrolysis ~~by~~ catalysed by acid is reversible

ii) Ester hydrolysis catalysed by Base is irreversible

1) Acid catalysed Ester hydrolysis

The first step of the mechanism is rapid protonation of Ester which is then solvolysed by a water molecule leading to the formation of protonated acid and an alcohol.

Mechanism



$$R'-\overset{O}{\overset{\|}{C}}-OR + H^{\oplus} \underset{}{\overset{Fast}{\rightleftharpoons}} R'-\overset{\overset{\oplus}{O}H}{\overset{\|}{C}}-OR \rightleftharpoons R'-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{\overset{\oplus}{O}}}-R$$

Ester

$$R'-\overset{O}{\overset{\|}{C}} \vdots \overset{H}{\overset{|}{\overset{\oplus}{O}}}-R \;\; \uparrow + H_2O \;\; \overset{slow}{\rightleftharpoons} R'-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{O}H_2 + ROH \text{ (Alcohol)}$$

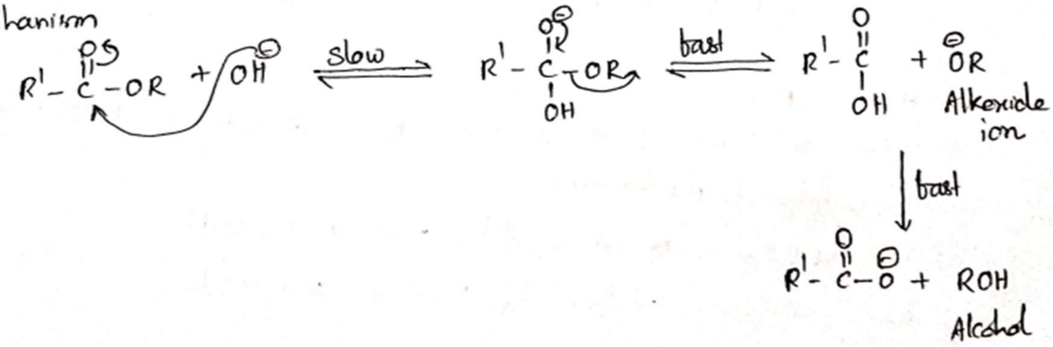
$$R'-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{O}H_2 \overset{Fast}{\rightleftharpoons} R'-\overset{O}{\overset{\|}{C}}-OH + H^{\oplus}$$

Carboxylic acid

Base Catalysed Ester hydrolysis

This reaction involves the nucleophilic attack of Hydroxide ion ($\bullet OH^{\ominus}$) on the Carbonyl group of the ester followed by rapid elemination of alkoxide ion. The next and the irreversible step is the transference of a proton from carboxylic acid to the alkoxide ion

Mechanism



$$R'-\overset{O}{\overset{\|}{C}}-OR + \overset{\ominus}{O}H \overset{slow}{\rightleftharpoons} R'-\underset{OH}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}-OR \overset{fast}{\rightleftharpoons} R'-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + \overset{\ominus}{O}R$$

Alkoxide ion

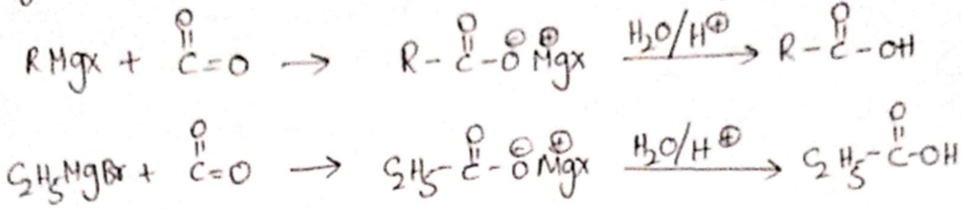
$$\downarrow fast$$

$$R'-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} + ROH$$

Alcohol

d) From Grignard's reagent

Grignard reagents reacts with Carbondioxide to yield Magnesium Carboxylates. These on acidification gives Carboxylic acids



$$RMgX + \overset{O}{\overset{\|}{C}}=O \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{M}gX \xrightarrow{H_2O/H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-OH$$

$$C_2H_5MgBr + \overset{O}{\overset{\|}{C}}=O \rightarrow C_2H_5-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{M}gX \xrightarrow{H_2O/H^{\oplus}} C_2H_5-\overset{O}{\overset{\|}{C}}-OH$$

Special methods of preparation of aromatic acids (Ar-COOH)

a) Oxidation of side chain

Toluene on oxidation with alkaline $KMnO_4$ gives benzoic acid with 40-50% yield. If the same reaction is carried out in presence of Phase Transfer Catalyst like cetyl trimethyl ammonium chloride (CTAC) gives about 80% yield.

$$C_6H_5CH_3 \xrightarrow{\text{Alk } KMnO_4\text{/reflux}} C_6H_5COOH \text{ (40-50 \% yield)}$$

$$C_6H_5CH_3 \xrightarrow{\text{Alk } KMnO_4\text{, CTAC/reflux}} C_6H_5COOH \text{ (>80 \% yield)}$$

b) Hydrolysis by benzotrichlorides

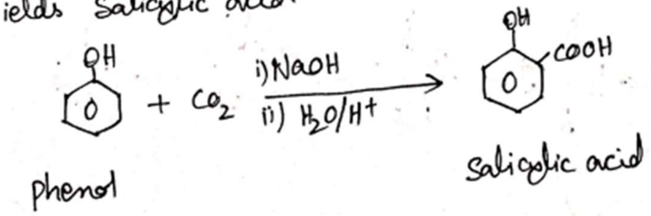
Benzotrichloride readily hydrolyses in the presence of aqueous alkaline solutions, producing benzoic acid.

$$C_6H_5Cl_3 \xrightarrow{Ca(OH)_2\text{/reflux}} C_6H_5COOH$$

c) Kolbe reaction

KOLBE SCHMIDT REACTION

Phenol in presence of Base, (NaOH) reacts with Carbondioxide at high temperature and pressure to yield Sodium salicylate which on acidification yields salicylic acid.



Chemical reactions

a) Formation of salts

Acids reacts with bases to form Salts

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}COONa + H_2CO_3$$

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}COONa + H_2O$$

$$R\text{-}COOH + Ca(OH)_2 \longrightarrow (RCOO)_2Ca + 2H_2O$$

$$R\text{-}COOH + NH_3 \longrightarrow RCO\overset{\ominus}{O}\overset{\oplus}{N}H_4$$

$$R\text{-}COOH + AgNO_3 \longrightarrow RCO\overset{\ominus}{O}\overset{\oplus}{Ag} + HNO_3$$

2. Reactions involving -OH of -COOH group

a) Formation of esters

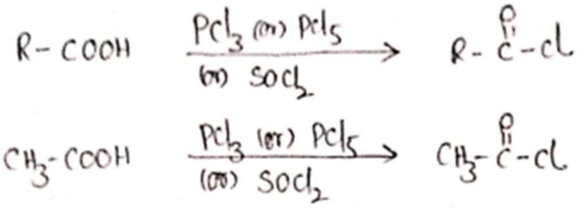
Carboxylic acids reacts with Alcohols to form Esters

$$R\text{-}COOH + HO\text{-}R' \xrightarrow{H^{\oplus}} R\text{-}COOR' \text{ (Ester)}$$

$$CH_3COOH + HO\text{-}C_2H_5 \xrightarrow{H^{\oplus}} CH_3COOC_2H_5$$

b) Formation of acid chlorides

Carboxylic acids reacts with PCl_3, PCl_5 or $SOCl_2$ to form Acid chloride



$$R\text{-}COOH \xrightarrow[\text{(or) } SOCl_2]{PCl_3 \text{ (or) } PCl_5} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$$

$$CH_3\text{-}COOH \xrightarrow[\text{(or) } SOCl_2]{PCl_3 \text{ (or) } PCl_5} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$$

c) Formation of amides

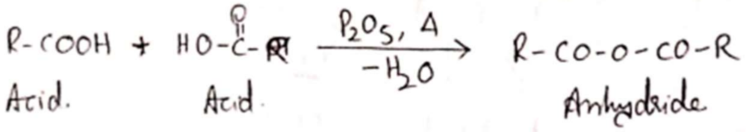
Carboxylic acid reacts with 1° Amines to form Amide

$$R\text{-}COOH + H_2N\text{-}R' \longrightarrow R\text{-}CO\text{-}NH\text{-}R' \text{ (Amide)}$$

$$CH_3COOH + H_2N\text{-}C_2H_5 \longrightarrow CH_3\text{-}CO\text{-}NH\text{-}C_2H_5$$

d) Formation of anhydrides.

Carboxylic acids undergo dehydration to form acid anhydride



$$\underset{\text{Acid.}}{R\text{-}COOH} + \underset{\text{Acid.}}{HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}R} \xrightarrow[-H_2O]{P_2O_5,\ \Delta} \underset{\text{Anhydride}}{R\text{-}CO\text{-}O\text{-}CO\text{-}R}$$

$$CH_3\text{-}COOH + HOOC\text{-}CH_3 \xrightarrow[-H_2O]{P_2O_5,\ \Delta} CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3$$

Acetic anhydride

Reactions involving entire -COOH group

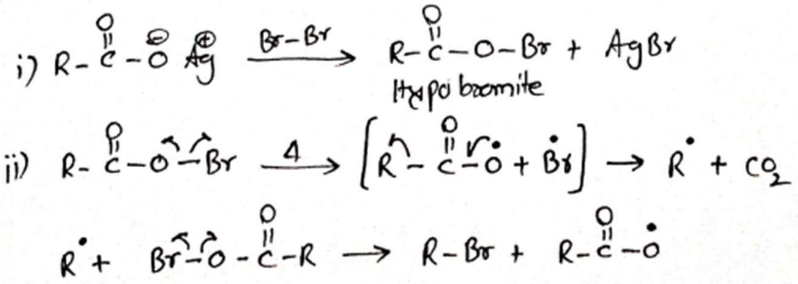
a) Degradation of carboxylic acids by Huns - Diecker’s reaction

Treatment of silversalt of acid with Bromine in presence of CCl_4 to give alkyl (or) Aryl Bromide

$$R-COOH + NaOH \longrightarrow RCOONa \xrightarrow{AgNO_3} R-CO\overset{\ominus}{O}\,\overset{\oplus}{Ag} \xrightarrow[\Delta]{Br_2/CCl_4} R-Br + CO_2 + AgBr$$

$$CH_3-COOH + NaOH \longrightarrow CH_3COONa \xrightarrow{AgNO_3} CH_3CO\overset{\ominus}{O}\,\overset{\oplus}{Ag} \xrightarrow{Br_2/CCl_4} CH_3-Br + CO_2 + AgBr$$

Mechanism



$$\text{i)}\ R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,\overset{\oplus}{Ag} \xrightarrow{Br-Br} \underset{\text{Hypo bromite}}{R-\overset{O}{\overset{\|}{C}}-O-Br} + AgBr$$

$$\text{ii)}\ R-\overset{O}{\overset{\|}{C}}-O-Br \xrightarrow{\Delta} \left[R-\overset{O}{\overset{\|}{C}}-\dot{O} + \dot{Br}\right] \rightarrow \dot{R} + CO_2$$

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

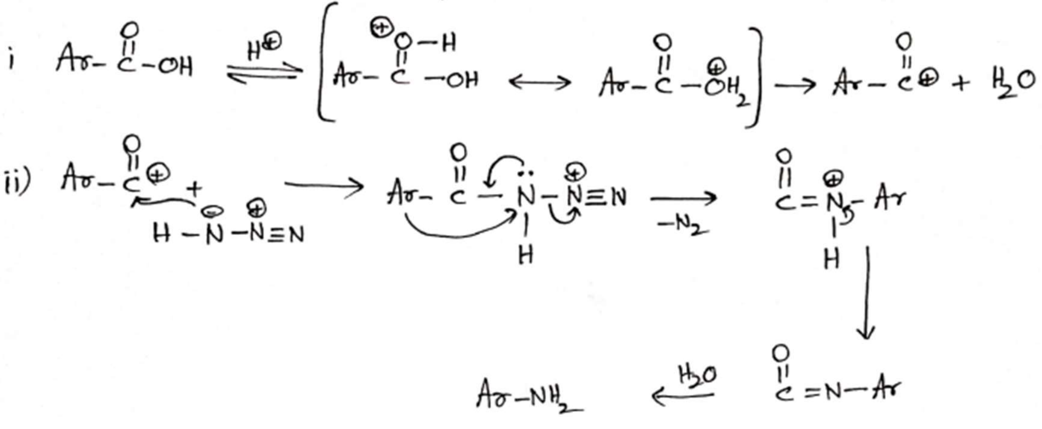
b) Decarboxylation by Schmidt reaction

Carboxylic acids on treatment with Hydrazoic acid gives primary amine

$$R-COOH \xrightarrow[Conc\ H_2SO_4]{N_3H/\Delta} R-NH_2 + N_2 + CO_2$$

$$CH_3COOH \xrightarrow[Conc\ H_2SO_4]{N_3H/\Delta} CH_3NH_2 \ \text{(Methyl amine)}$$

Mechanism



$$\text{i}\ Ar-\overset{O}{\overset{\|}{C}}-OH \overset{H^{\oplus}}{\rightleftharpoons} \left[Ar-\overset{\overset{\oplus}{O}-H}{\overset{\|}{C}}-OH \longleftrightarrow Ar-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{O}H_2\right] \rightarrow Ar-\overset{O}{\overset{\|}{C}}{}^{\oplus} + H_2O$$

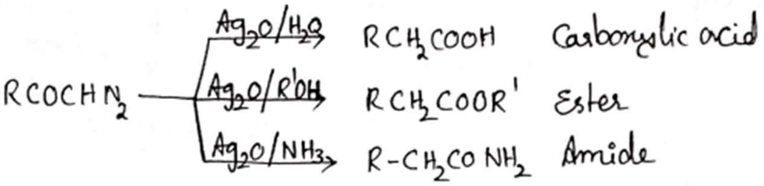
$$\text{ii)}\ Ar-\overset{O}{\overset{\|}{C}}{}^{\oplus} + H-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \longrightarrow Ar-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\ddot{N}}}-\overset{\oplus}{N}\equiv N \xrightarrow{-N_2} \overset{O}{\overset{\|}{C}}=\underset{H}{\underset{|}{\overset{\oplus}{N}}}-Ar$$

$$Ar-NH_2 \xleftarrow{H_2O} \overset{O}{\overset{\|}{C}}=N-Ar$$

c) Arndt-Eistert synthesis

Conversion of an acid into its next higher homologue or to a derivative of the homologous acid, such as amide or ester.

$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow{SOCl_2} \underset{\text{Acid chloride}}{RCOCl} \xrightarrow{CH_2N_2} \underset{\alpha\text{- Diazo ketone}}{RCOCHN_2}$$



Mechanism

i) Carboxylic acid is converted into its acid chloride using Thionyl chloride ($SOCl_2$).

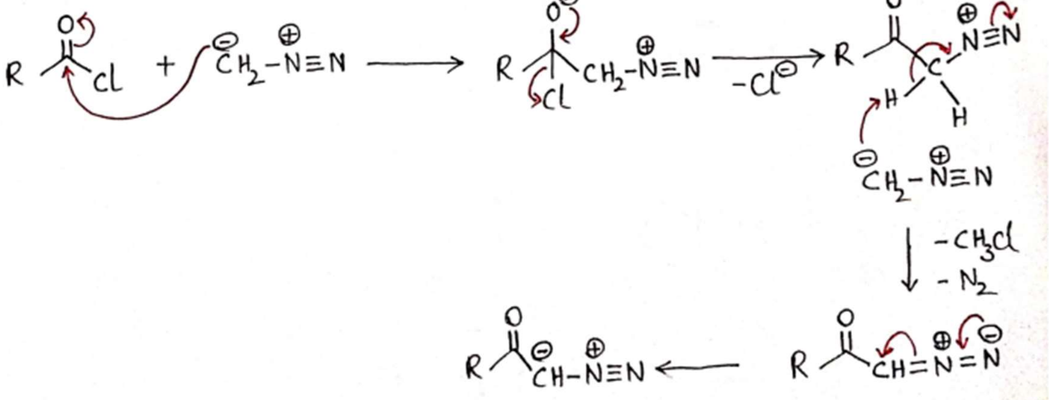
ii) Acid chloride reacts with Diazomethane gives α-diazo ketone (1)

iii) α- Diazoketone (1) eleminates N_2 molecule and rearranges to Ketene (2) in poesence of Ag_2O (or) hν

iv) Ketene is converted into an acid (or) amide (or) ester

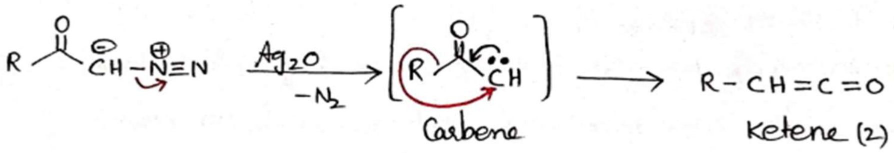
i) $RCOOH \xrightarrow{SOCl_2} RCOCl$ (Acid chloride)

ii)

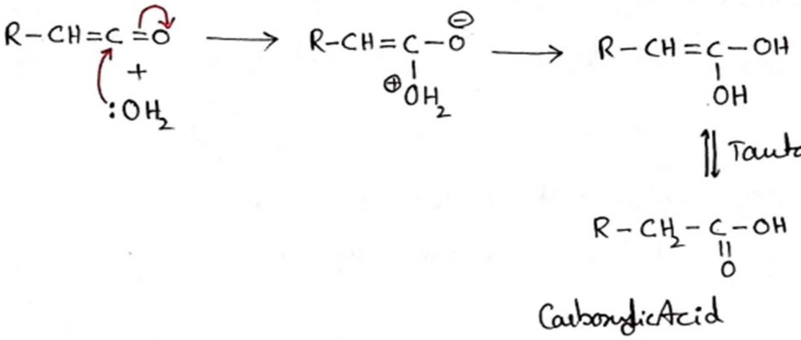


α- Diazoketone.

iii)



iv)

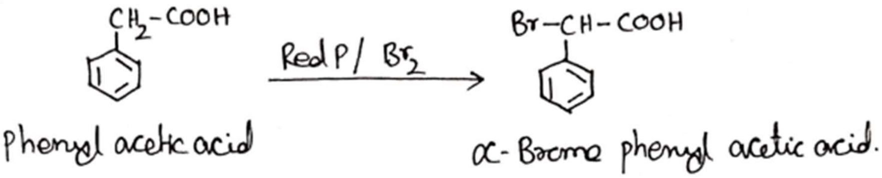


d) Halogenation by Hell- Volhard- Zelinsky reaction

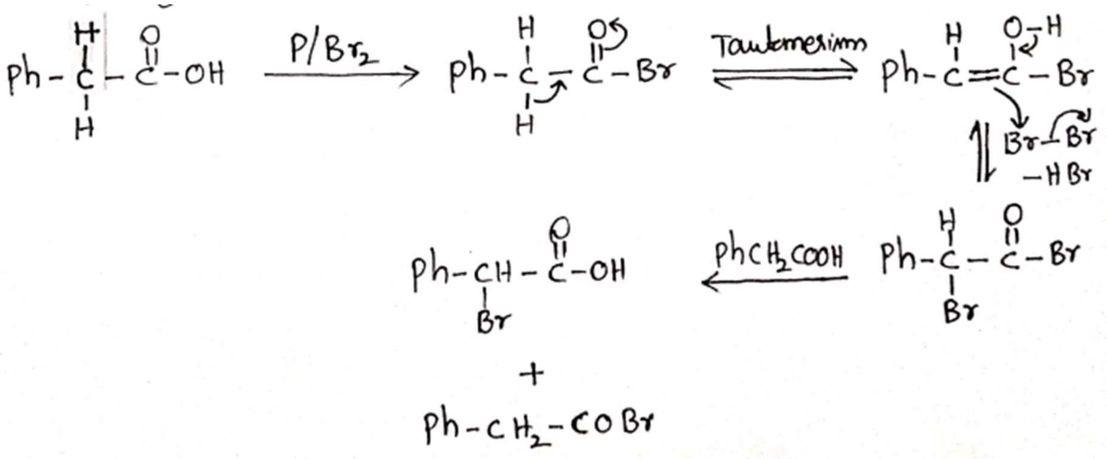
Preparation of α-chloro (or) bromo carboxylic acids by the action of chlorine (or) Bromine on mono carboxylic acids having α-hydrogens in presence of Red phosphorus.

Example:

Preparation of α-Bromo phenyl acetic acid from phenyl acetic acid in presence of Red phosphorus and Bromine.

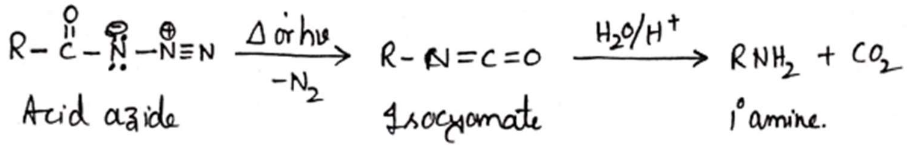


Mechanism



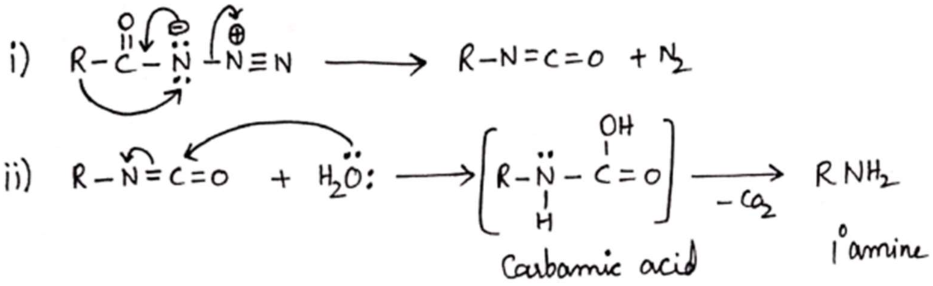
Curtis Rearrangement

Thermal rearrangement of Acid azides to isocyanates in presence of aqueous solvents such as Chloroform is known as Curtius rearrangement



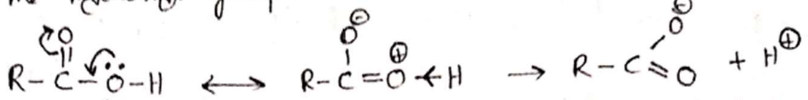
Isocyanate on hydrolysis gives 1° amines.

Mechanism:



Strength of acids with examples of trimethyl acetic acid and trichloroacetic acid.

The acidic character of Carboxylic acids is due to resonance in the acid group which imparts electron deficiency (+ve charge) on oxygen atom of the Hydroxyl group



The +ve charge on oxygen atom causes a displacement of electron pair of O−H bond towards oxygen atom, with this the Hydrogen atom of O−H group is eliminated as proton, and a carboxylate ion is formed which is stabilised by resonance

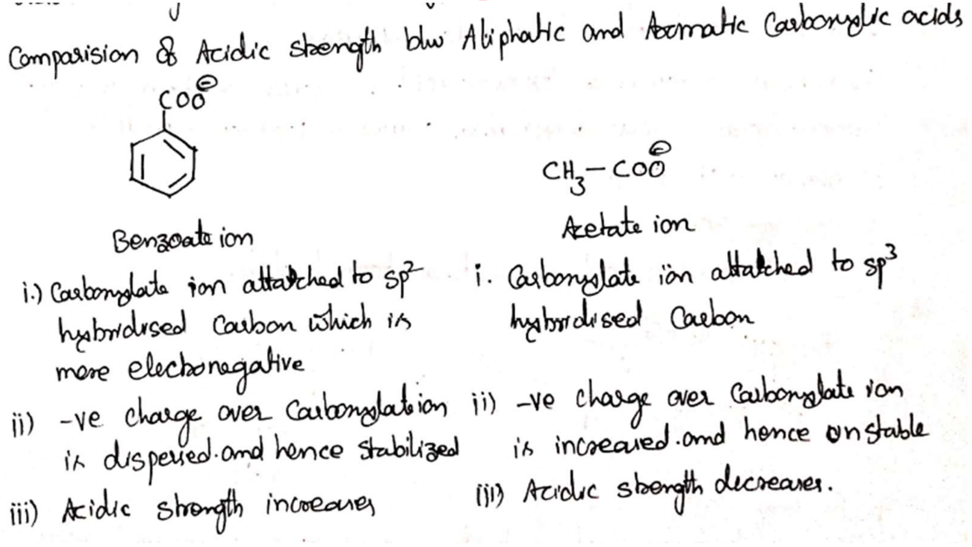
In Trimethyl acetic acid [$(CH_3)_3$-C-COOH], three methyl groups which are electron releasing in nature releases electrons on to the carboxylate ion and destabilises the carboxylate anion and hence decreases the acid strength.

Whereas in case of Trichloro acetic acid [CCl_3-COOH], three Chlorine groups which are electron withdrawing in nature withdraws electrons from the carboxylate ion, stabilises the carboxylate anion and hence increases the acid strength.

Relative differences in the acidities of aromatic and aliphatic acids

or

Comparision of acidities of aromatic and aliphatic acids



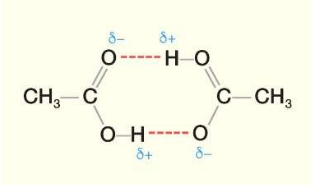
Comparision of Acidic strength b/w Aliphatic and Aromatic Carboxylic acids

$CH_3-COO^{\ominus}$

Benzoate ion	Acetate ion
i.) Carboxylate ion attached to sp² hybridised carbon which is more electronegative	i. Carboxylate ion attached to sp³ hybridised carbon
ii) -ve charge over carboxylate ion is dispersed and hence stabilized	ii) -ve charge over carboxylate ion is increased and hence unstable
iii) Acidic strength increases	iii) Acidic strength decreases.

Hydrogen bonding in Carboxylic acids - Dimeric Association

In hydrogen bonding, Hydrogen Bond Donar is the hydroxyl (-OH) group can donate a hydrogen atom to form a hydrogen bond. Hydrogen Bond Acceptor is the oxygen atom of the carbonyl (C=O) group in another molecule can act as an acceptor for the hydrogen bond. Two carboxylic acid molecules can form two hydrogen bonds with each other to create a stable, cyclic dimer. This forms a strong, associated structure that requires significant energy to break.



Effect of Hydrogen bonding in Carboxylic acids

High Boiling Points:

Due to the strong, two-fold hydrogen bonding that forms stable dimers, a large amount of energy (heat) is needed to separate these molecules, resulting in higher boiling points compared to alcohols, aldehydes, or ketones of comparable molecular weight.

High Water Solubility:

Simple carboxylic acids (with up to four carbon atoms) are highly soluble in water because the carboxyl group can form hydrogen bonds with water molecules, both as a donor and an acceptor. This interaction increases the affinity of the acid for water.

Stronger Than Alcohols:

The hydrogen bonds in carboxylic acids are generally stronger than those in alcohols because the adjacent electron-withdrawing carbonyl group makes the O-H bond in carboxylic acids even more polarized.