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PG RESEARCH DEPARTMENT OF CHEMISTRY

CLASS : II B.Sc CHEMISTRY

SUBJECT CODE : FCH42

SUBJECT NAME : GENERAL CHEMISTRY-IV

SYLLABUS

UNIT- II

Monocarboxylic acids - Acetic acid and Benzoic acid - Preparation by Grignard method - Conversion of Acids to their derivatives - Amide, Ester, Anhydride and Acid Chloride - Strength of Carboxylic Acids - Effect of Substituents on the Strength of Acids - Dicarboxylic acids - Oxalic acid, Malonic acid, Succinic acid, Glutaric acid and Adipic acid - Preparation - Properties - Action of Heat on Dicarboxylic acids - Amines - Ethylamine and Aniline - Preparation - Basicity of Amines - Effect of Substituents on Basicity - Reactivity of Amines - Distinction between Primary,Secondary and Tertiary Amines.

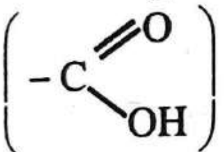
UNIT - II

MONO, Di CARBOXYLIC ACIDS AND AMINES

A

2.1 MONOCARBOXYLIC ACIDS

Carboxylic acid

Organic compounds containing the carboxyl  $\left(-C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}\right)$ group are called carboxylic acids. The name carboxyl is derived from carbonyl (C = O) and hydroxyl (– OH) because in carboxyl group these two groups are directly linked to each other.

2M

Classification of carboxylic acids

Carboxylic acids are classified into three types according to the number of – COOH groups present in the molecule.

1. Monocarboxylic acids
2. Dicarboxylic acids
3. Tricarboxylic acids etc.,

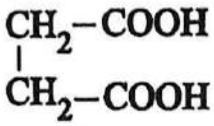
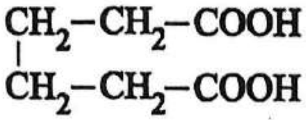
The aliphatic monocarboxylic acids are also called Fatty acids because some higher members occur as glycerides in oils and fats.

Examples

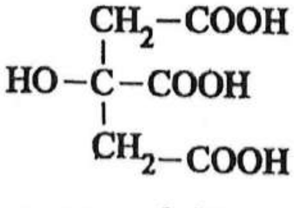
(i) Monocarboxylic acids

Formula	Name
H-COOH	Formic acid
CH_3-COOH	Acetic acid
$CH_3-CH_2-CH_2-COOH$	*n*- Butyric acid

(ii) Dicarboxylic acids

Formula	Name
 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid
 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	Succinic acid
 $\begin{array}{l}CH_2-CH_2-COOH\\ \vert\\ CH_2-CH_2-COOH\end{array}$	Adipic acid

(iii) Tricarboxylic acids



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

Citric acid

2.1.1 General name of Monocarboxylic acids

Compounds containing one-COOH group per molecule are called monocarboxylic acids. They are represented by the general formula, R-COOH (or) $C_n H_{2n+1} COOH$.

2.1.2 Nomenclature

There are three ways of naming monocarboxylic acids. They are

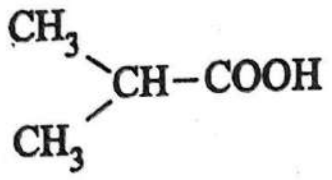
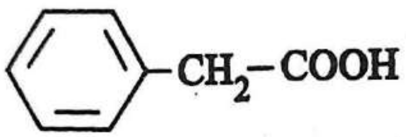
1. Common names
2. IUPAC names
3. Derived names

Formula	Common name	IUPAC name
H-COOH	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-COOH$	*n* – Butyric acid	Butanoic acid
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-COOH$	iso-Butyric acid	2-Methyl propanoic acid.
$CH_3-CH_2-CH_2-CH_2-COOH$	Valeric acid	Pentanoic acid.

Derived names

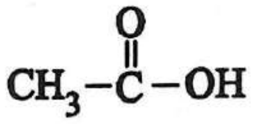
Sometimes fatty acids are named as alkyl derivatives of acetic acid (or) substituted acetic acids.

Examples

Formula	**Name**
CH_3-CH_2-COOH	Methylacetic acid
	Dimethylacetic acid
	Phenylacetic acid

2.1.3 Acetic acid: (Aliphatic carboxylic acid)

Structure:

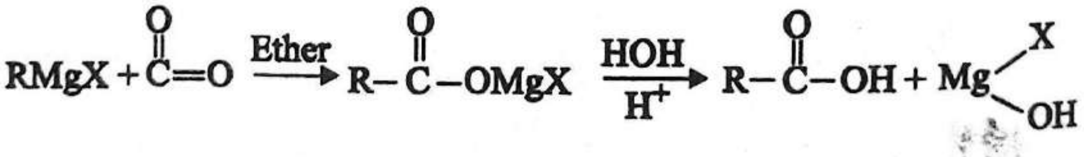


$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$

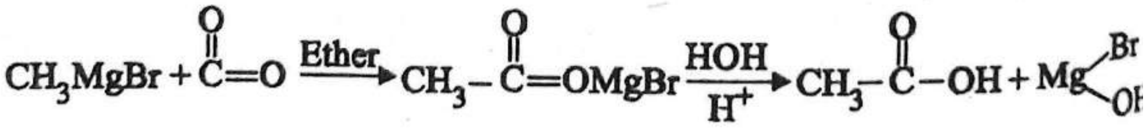
Preparation

1. From Grignard reagent

Grignard reagents react with CO_2 to form additio products which on hydrolysis give carboxylic acids.



$$RMgX + \overset{O}{\overset{\|}{C}}{=}O \xrightarrow{Ether} R-\overset{O}{\overset{\|}{C}}-OMgX \xrightarrow[H^+]{HOH} R-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{smallmatrix}X\\ OH\end{smallmatrix}$$



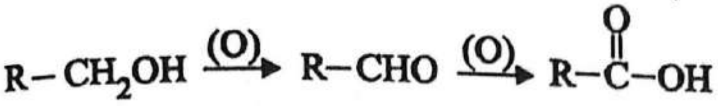
$$CH_3MgBr + \overset{O}{\overset{\|}{C}}{=}O \xrightarrow{Ether} CH_3-\overset{O}{\overset{\|}{C}}{=}OMgBr \xrightarrow[H^+]{HOH} CH_3-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{smallmatrix}Br\\ O\end{smallmatrix}$$

H-COOH cannot be prepared by this method, because i contains only one carbon atom.

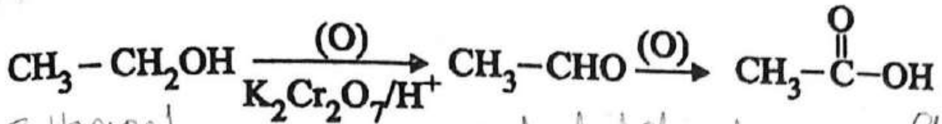
2. Oxidation

Primary alcohols (or) aldehydes undergo oxidation wit a mixture of $K_2Cr_2O_7$ and H_2SO_4 to from carboxylic acids

A secondary alcohol (or) ketone on oxidation gives an acid with lesser number of carbon atoms.

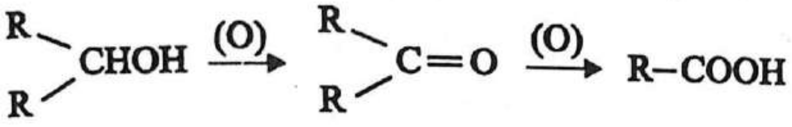


$$R-CH_2OH \xrightarrow{(O)} R-CHO \xrightarrow{(O)} R-\overset{O}{\overset{\|}{C}}-OH$$

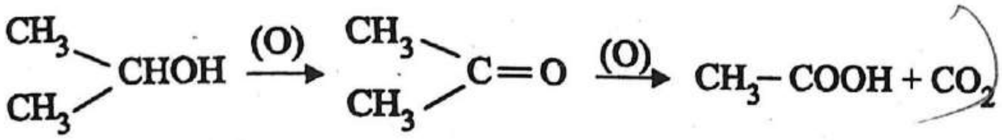


$$CH_3-CH_2OH \xrightarrow[K_2Cr_2O_7/H^+]{(O)} CH_3-CHO \xrightarrow{(O)} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Ethanol Acetaldehyde acetic acid



$$R_2CHOH \xrightarrow{(O)} R_2C=O \xrightarrow{(O)} R-COOH$$

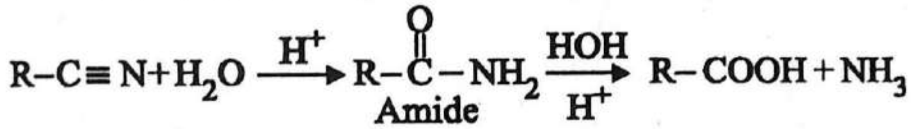


$$(CH_3)_2CHOH \xrightarrow{(O)} (CH_3)_2C=O \xrightarrow{(O)} CH_3-COOH+CO_2$$

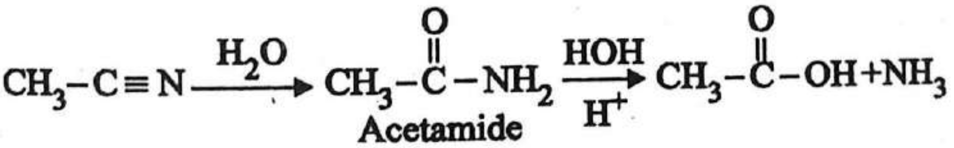
3. Hydrolysis

Hydrolysis of alkyl cyanides, amides and esters with aqueous alkali (or) acid give carboxylic acids.

(i)

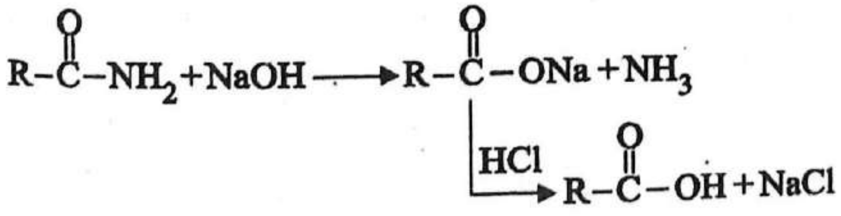


$$R-C\equiv N+H_2O \xrightarrow{H^+} \underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[H^+]{HOH} R-COOH+NH_3$$

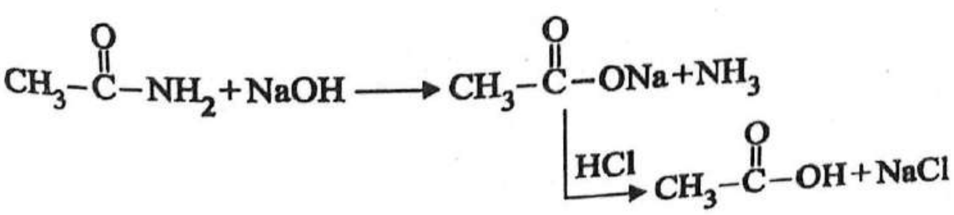


$$CH_3-C\equiv N \xrightarrow{H_2O} \underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[H^+]{HOH} CH_3-\overset{O}{\overset{\|}{C}}-OH+NH_3$$

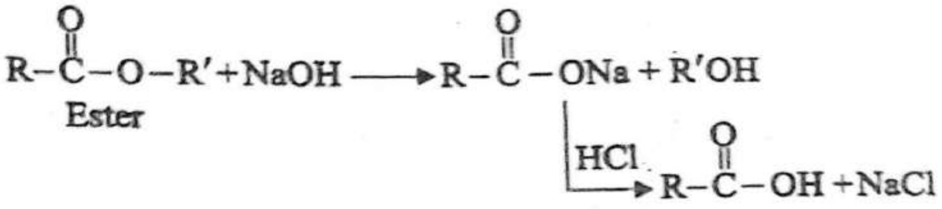
(ii)



$$R-\overset{O}{\overset{\|}{C}}-NH_2+NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa+NH_3 \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH+NaCl$$

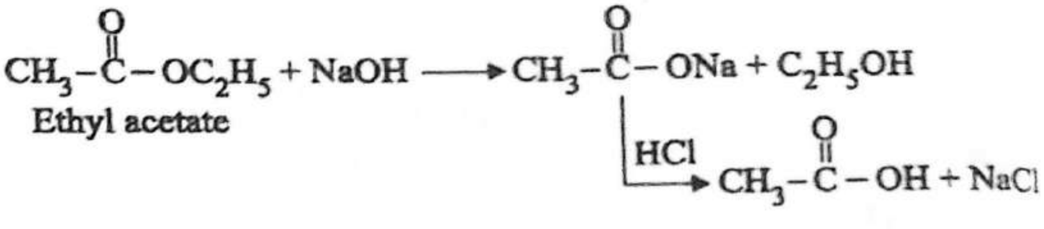


$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2+NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa+NH_3 \xrightarrow{HCl} CH_3-\overset{O}{\overset{\|}{C}}-OH+NaCl$$

(iii) 

$$R-\overset{O}{\overset{\|}{C}}-O-R' + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + R'OH \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH + NaCl$$

Ester



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + C_2H_5OH \xrightarrow{HCl} CH_3-\overset{O}{\overset{\|}{C}}-OH + NaCl$$

Ethyl acetate

Properties

Acetic acid is a colorless, corrosive liquid with vinegar odour and sour taste. Its boiling point is 118° C and m.pt is 16.6° C. The vapours are suffocating and cause damage to the lungs. Pure acetic acid is called Glacial acetic acid because it forms ice-like solid on cooling. It is miscible with H_2O, alcohol and ether.

2.1.4 Reactions

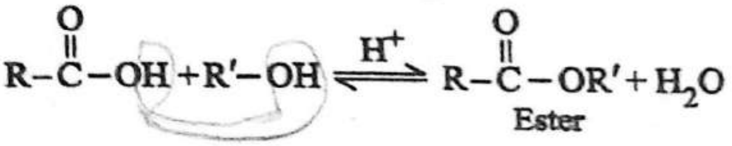
Acetic acid is a typical monocarboxylic acid and gives all the reactions of this class.

Conversion of Acids to their derivatives

1. Formation of Esters

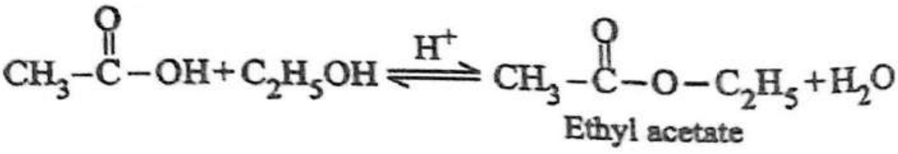
Carboxylic acids react with alcohols in the presence of mineral acid (HCl (or) H_2SO_4) to form esters. This reaction is reversible and is called esterification.

The equilibrium can be shifted to right by using excess of alcohol (or) removal of H_2O by distillation.



$$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Ester



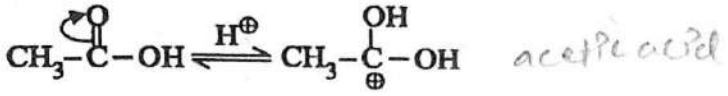
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + H_2O$$

Ethyl acetate

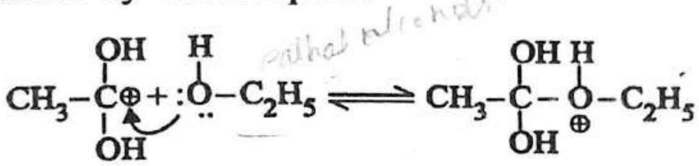
Mechanisms

The mechanism of esterification involves the following steps

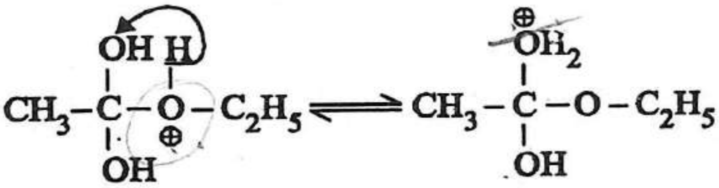
Step 1: Protonation of Carboxylic acid



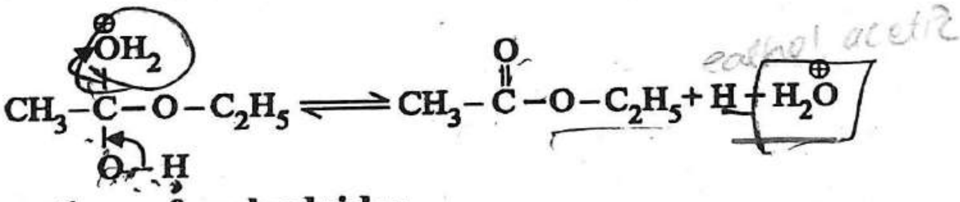
Step 2: Attack by Nucleophile



Step 3: Proton transfer



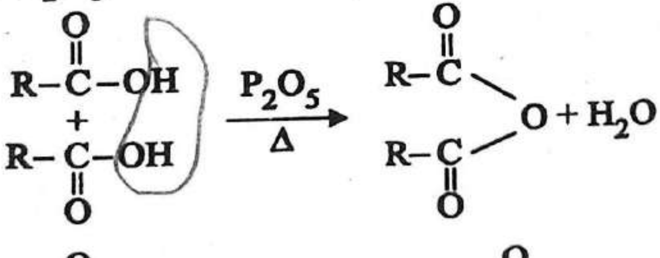
Step 4: Elimination of proton and H_2O

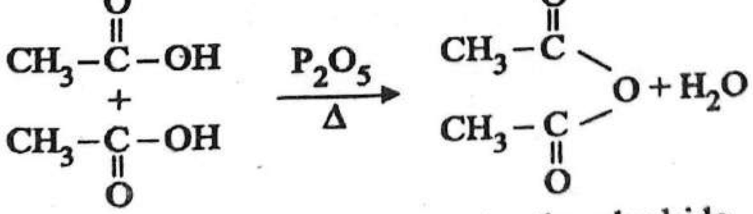


2. Formation of anhydrides

water

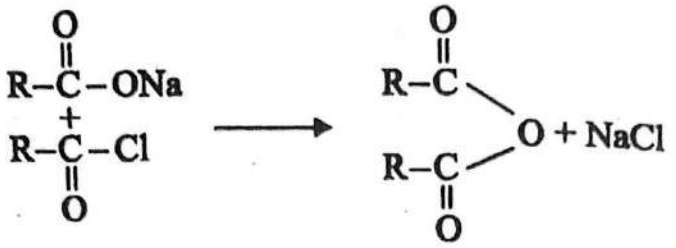
Carboxylic acids undergo intermolecular dehydration on heating with P_2O_5 to form anhydrides.

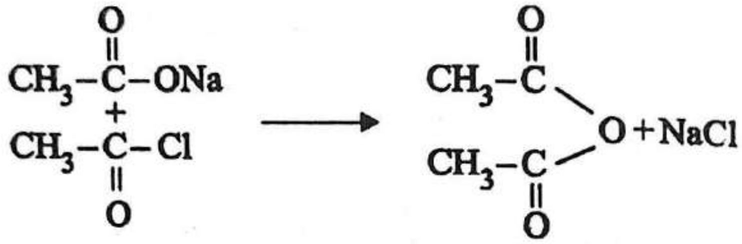




Acetic anhydride

Anhydrides can also be prepared by treating the sodiu salts of the acids with acid chloride.

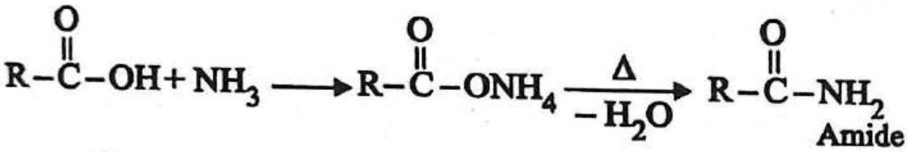




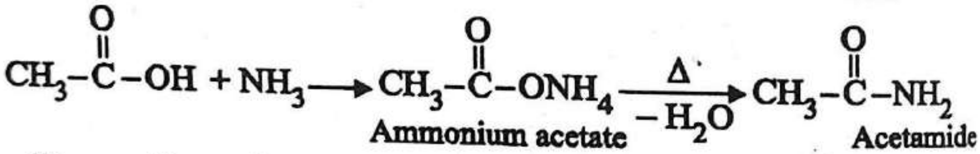
Acetic anhydride

3. Formation of amides

When ammonium salts of carboxylic acids are heate alone, amides are formed.



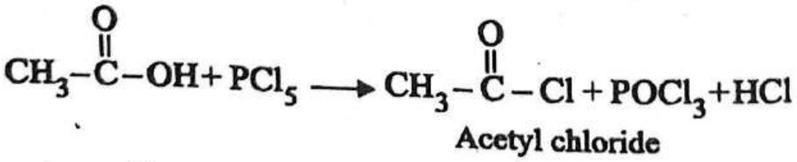
$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2}$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-ONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2}$$

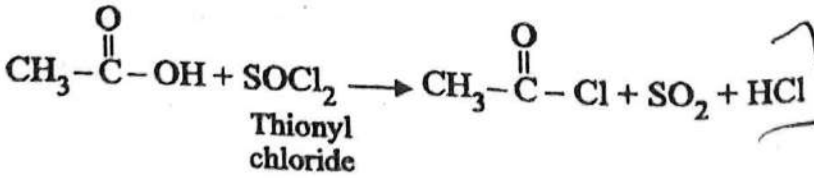
4. Formation of acid chlorides

Carboxylic acids react with PCl_5 (or) PCl_3 (or) SOC to form acid clorides.



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + POCl_3 + HCl$$

$$3\,CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \longrightarrow 3\,CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

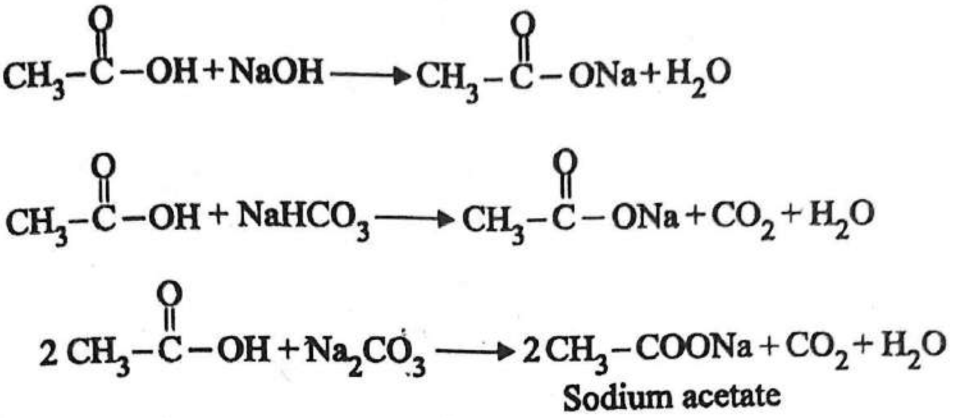


$$CH_3-\overset{O}{\overset{\|}{C}}-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

Other reactions

5. Formation of Salts

Fatty acids react with alkalies, carbonates and bicarbonates to form salts.



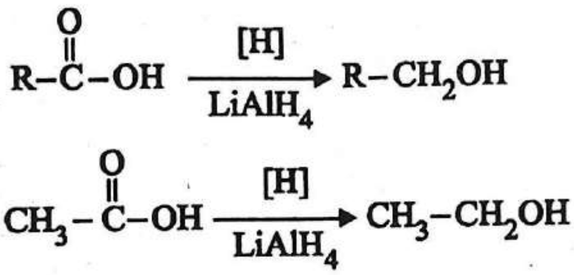
$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NaHCO_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + CO_2 + H_2O$$

$$2\,CH_3-\overset{\overset{O}{\|}}{C}-OH + Na_2CO_3 \longrightarrow 2\,\underset{\text{Sodium acetate}}{CH_3-COONa} + CO_2 + H_2O$$

6. Reduction

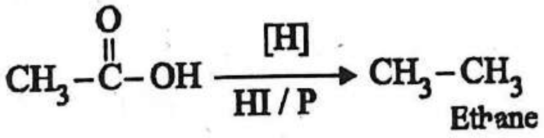
Carboxylic acids undergo reduction with $LiAlH_4$ (or) diborane in THF at 0° C to form primary alcohols.



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[LiAlH_4]{[H]} R-CH_2OH$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[LiAlH_4]{[H]} CH_3-CH_2OH$$

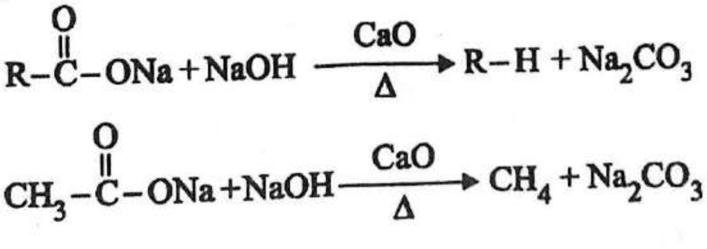
Heating with HI/P converts the carboxylic acids to alkanes.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[HI\,/\,P]{[H]} \underset{\text{Ethane}}{CH_3-CH_3}$$

7. Decarboxylation

When sodium salts of carboxylic acids are heated with soda-lime (NaOH + CaO), alkanes are formed.

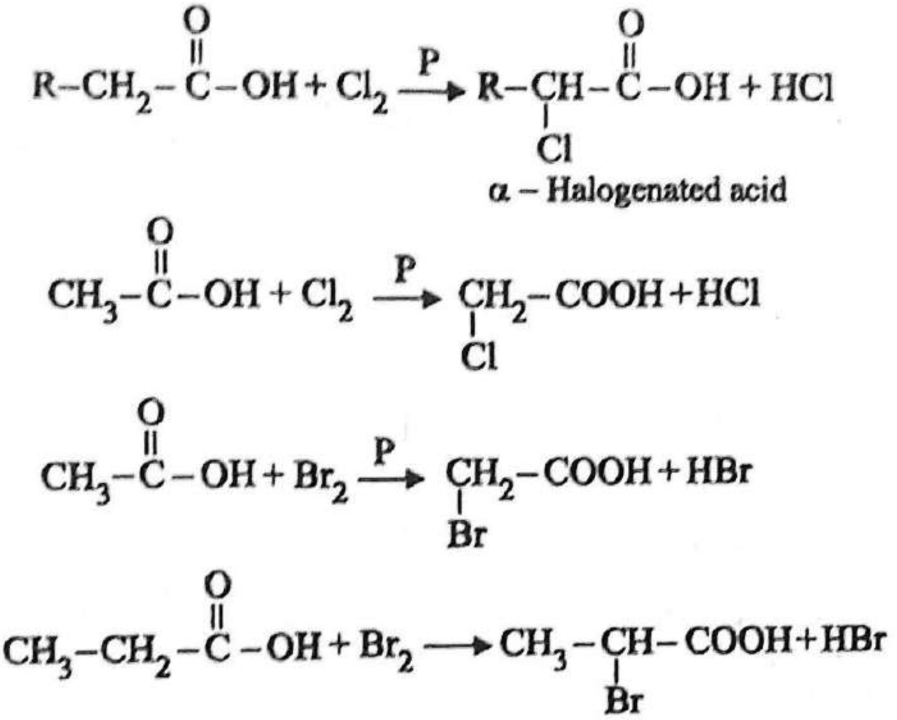


$$R-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

8. Halogenation

When a carboxylic acid (containing $\alpha-$ hydrogen) is treated with Cl_2 (or) Br_2 in the presence of P, the $\alpha-$ hydrogen atoms are substituted by chlorine (or) bromine atoms. This reaction is known as HVZ (Hell-Volhard-Zelinsky) reaction.



$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH + Cl_2 \xrightarrow{P} R-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH + HCl$$

α – Halogenated acid

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + Cl_2 \xrightarrow{P} \underset{Cl}{\underset{|}{CH_2}}-COOH+HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + Br_2 \xrightarrow{P} \underset{Br}{\underset{|}{CH_2}}-COOH+HBr$$

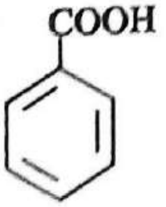
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + Br_2 \longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-COOH+HBr$$

$\alpha-$ Halogenerated acids are the convenient starting materials for preparing other $\alpha-$ substituted acids.

10marks

2.1.5 Benzoic acid (Aromatic carboxylic acid)

Strucutre:



When a carboxyl group is directly linked to the benzene ring, the compounds are called Aromatic carboxylic acids.

ic acid is the simplest of aromatic acids.

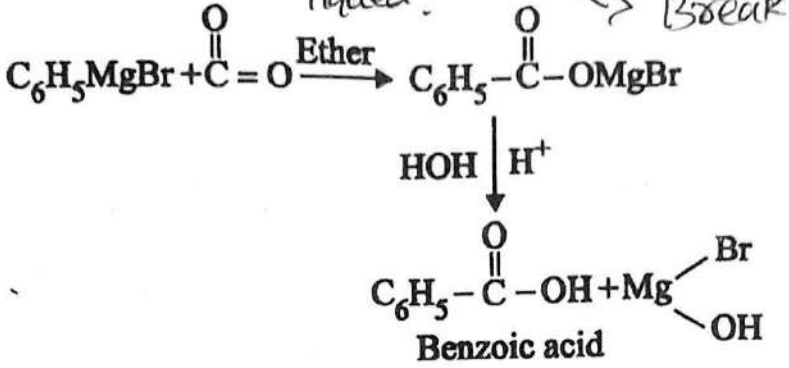
Preparation

1. From Grignard reagent

Phenyl magnesium bromide reacts with CO_2 in ethane to form an addition product which on hydrolysis gives benzoic acid.

~~sous~~ Subsitand.

riqued. → Break down.



$$C_6H_5MgBr + \overset{O}{\overset{\|}{C}} = O \xrightarrow{\text{Ether}} C_6H_5-\overset{O}{\overset{\|}{C}}-OMgBr$$

$$\downarrow \text{HOH} \mid H^+$$

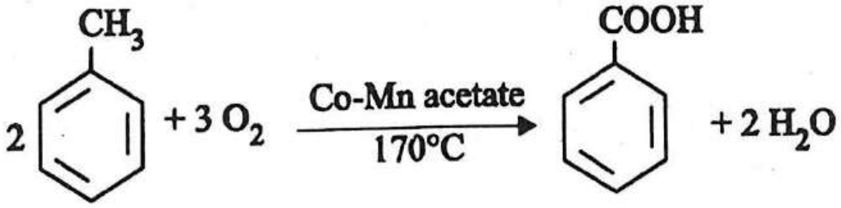
$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{matrix} Br \\ OH \end{matrix}$$

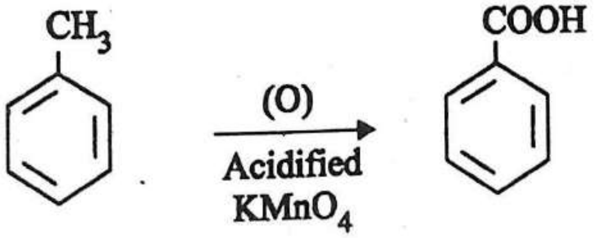
Benzoic acid

2. By Oxidation

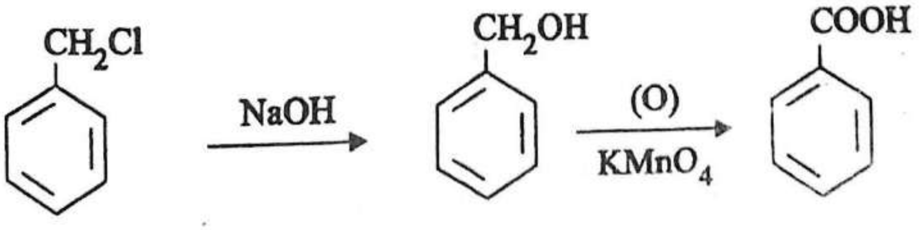
Benzoic acid is prepared by the oxidation of side-chain of benzene derivatives. The side-chain oxidation can be carried out by acid $K_2Cr_2O_7$ (or) $KMnO_4$ (or) alk. $KMnO_4$ (or) air.

(i) By the catalytic oxidation of toluene with air in the presence of Co-Mn acetate (or) by oxidation with acid $KMnO_4$

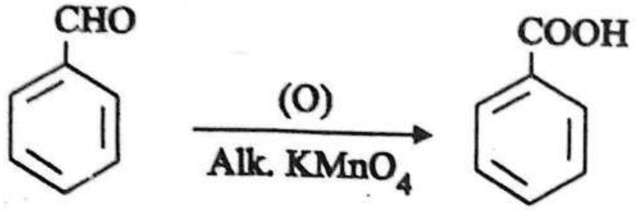




(ii) By the oxidation of benzyl chloride with acidic $KMnO_4$

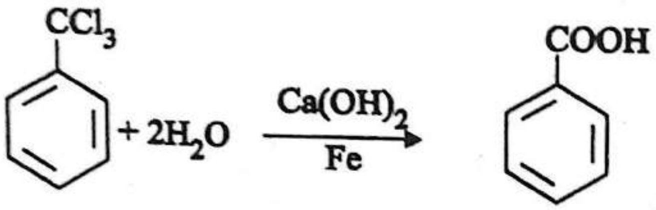


(iii) By the oxidation of benzaldehyde with alk.$KMnO_4$



3. By hydrolysis

Benzoic acid can be prepared by the hydrolysis benzotrichloride with aqueous $Ca(OH)_2$ in the presence of powder.



Properties

Benzoic acid is a white, crystalline solid, m.p 122° It is sparingly soluble in cold H_2O but dissolves readily hot water, ether, ethanol and benzene. It is volatile in stea and may be sublimed to give white plates.

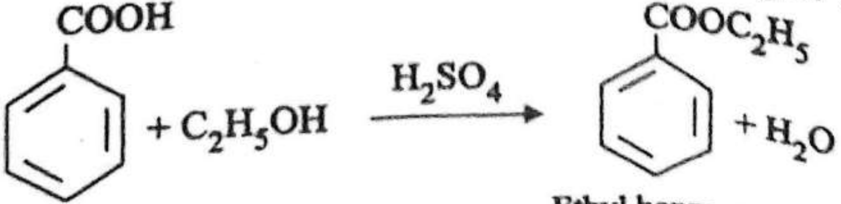
2.1.6 Reactions

Chemically benzoic acid resembles aliphatic acids an gives similar reactions. However, it is a stronger acid tha acetic acid.

Conversion of Acids to their derivatives

1. Ester formation

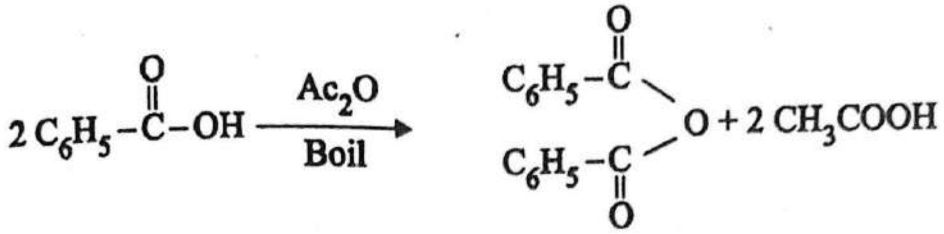
Benzoic acid readily forms esters when it is refluxed wit alcohol in the presence of conc H_2SO_4 (or) hydrogen chloride



Ethyl benzoate

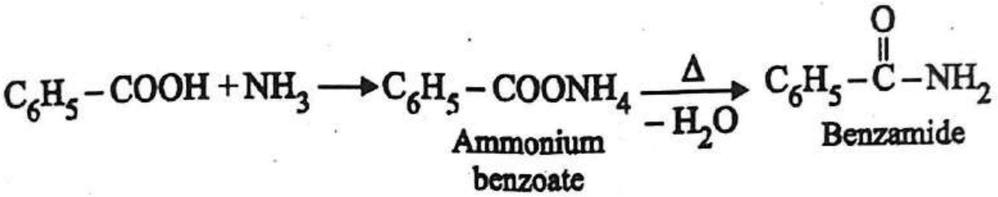
2. Formation of anhydride

Benzoic acid forms the anhydride when it is boiled with acetic anhydride



3. Formation of amide

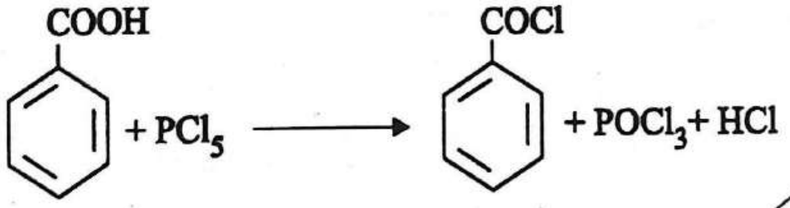
It reacts with NH_3 to form ammonium benzoate which on heating gives benzamide.



$$C_6H_5-COOH+NH_3 \longrightarrow C_6H_5-COONH_4 \xrightarrow[-H_2O]{\Delta} C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$$

4. Formation of acid chloride

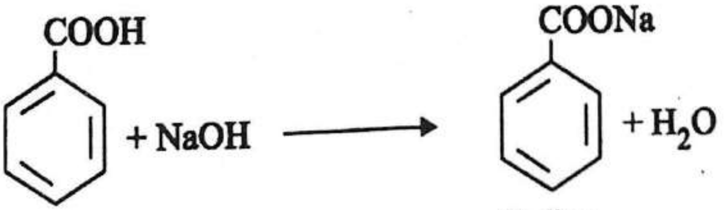
It reacts with PCl_5 (or) $SOCl_2$ to form benzoyl chloride.



Other reactions

5. Salt formation

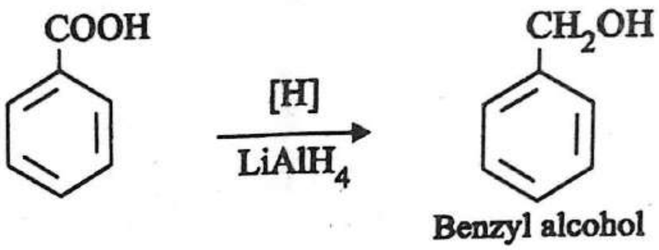
Benzoic acid reacts with strong bases such as NaOH (or) KOH to form salts.



Sodium benzoate

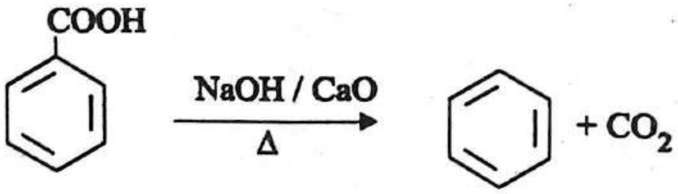
6. Reduction

Benzoic acid can be reduced to benzyl alcohol b $LiAlH_4$ (or) diborane in THF at 0° C



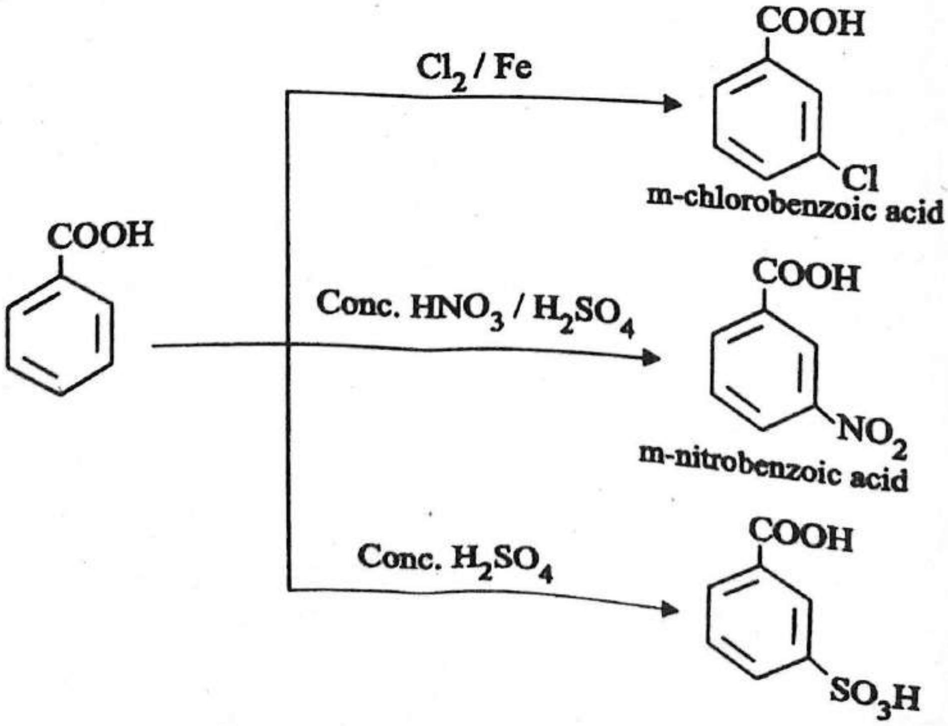
7. Decarboxylation

Benzoic acid undergo decarboxylation when heated wit soda-lime to form benzene.



8. Electrophilic substitutations

Benzoic acid undergoes the usual electrophilic substitutions at meta position.



Uses

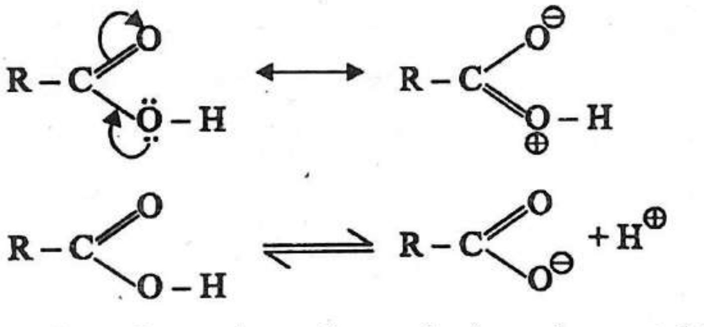
1. Benzoic acid is used in medicine as urinary antiseptic and its vapours for disinfecting bronchial tubes.
2. Na benzoate is used as food preservative.
3. It is used in dye industry for making aniline-blue.

ella

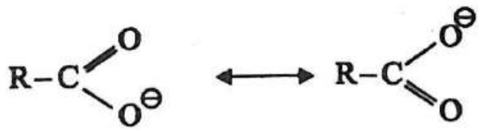
2.1.7 Strength of Carboxylic acids

An acid is a proton donor. The strength of an acid depends upon the ease with which it can release the proton.

Carboxylic acids are acidic in nature. Due to resonance, the electron density on the hydroxyl oxygen decreases. Hence the bonding pair of electrons between oxygen and hydrogen in O-H group is shifted towards oxygen and the proton is released readily.



The carboxylate ion formed is also stabilized by resonance which is much more effective than in carboxyl group. The resonating structures in carboxylate ion are of equal energy.



X-ray studies support the fact that carboxylate ion exists as a resonance hybrid. Greater the stability of the anion of the acid, higher is its strength.

2.1.8 Effects of substituents on the strength of acids (acidity)

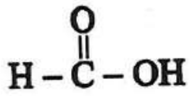
Any factor that stabilizes the carboxylate anion more than it stabilizes the acid, should increase the acidity. Similarly any factor that makes the anion less stable should decrease the acidity of the carboxylic acid.

Factors explaining acidity of acids

The most important factor affecting the acidity is the inductive effect of the substituents (or) groups on the α-carbon atom.

1. Electron-releasing substituents

Electron-releasing + I effect of alkyl groups decrease the acidity. Electron-releasing alkyl groups increase the electron density around the carboxyl group which makes the proton release difficult. Further they increase the negative charge on the carboxylate ion and destabilize it. Also, as the size of the alkyl group increases, acidity decreases.

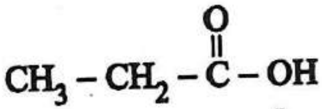


$$H-\overset{\overset{O}{\parallel}}{C}-OH$$

$K_a = 17.7 \times 10^{-5}$

CH_3-COOH

$K_a = 1.8 \times 10^{-5}$



$$CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-OH$$

$K_a = 1.34 \times 10^{-5}$

2. Electron-withdrawing substitutents

Electron-withdrawing substituents (F, Cl, Br, – CN and – NO_2) increase the acidity. Electron-withdrawing groups (with - I effect) decrease the electron density around the – COOH group and thereby make the release of proton easy. These groups decrease the negative charge on the carboxylate ion and stabilize it.

Example

Chloroacetic acid is about 100 times stronger than acetic acid.

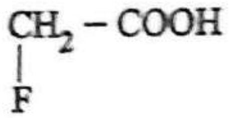
CH_3-COOH $\qquad$ $Cl\,CH_2-COOH$

$K_a = 1.8 \times 10^{-5}$ $\qquad$ $K_a = 136 \times 10^{-5}$

The strength of the electron-withdrawing substituents determines the magnitude of its effect on acidity.

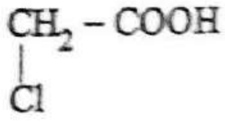
Example

Fluoroacetic acid is stronger than chloroacetic acid.



$CH_2(F)-COOH$

$K_a = 260 \times 10^{-5}$



$CH_2(Cl)-COOH$

$K_a = 136 \times 10^{-5}$

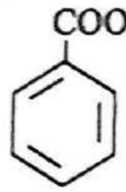
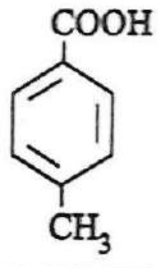
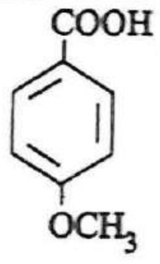
Acidity also increases as the number of electron-withdrawing groups ((or) substituents) increases.

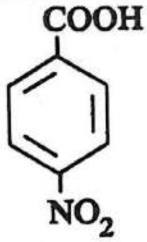
CCl_3-COOH	$CHCl_2-COOH$	$Cl\,CH_2-COOH$
$K_a = 23{,}200 \times 10^{-5}$	$K_a = 5{,}530 \times 10^{-5}$	$K_a = 136 \times 10^{-5}$

The distance between the carboxyl group and the substituent also determines its strength.

2.1.9 Acidity of substituted benzoic acids

The acidity of substituted benzoic acids depends on the nature and position of the substituent group. The K_a values for some substituted benzoic acids are given below:

Name	Formula	K_a
Benzoic acid		6.52×10^{-5}
p-Methylbenzoic acid		4.3×10^{-5}
p-Methoxybenzoic acid		3.38×10^{-5}

Name	Formula	K_a
p-Chlorobenzoic acid		10.4×10^{-5}
p-Nitrobenzoic acid		40×10^{-5}

The prensece of electron-releasing substituents like $-CH_3$, $-OCH_3$ etc., decrease the acidity of benzoic acid. On the other hand, electron-withdrawing substituents like $-NO_2$, $-Cl$, $-CN$ etc., increase the acidity of benzoic acid.

Factors explaining acidity

The effect of substituents on the acidity of benzoic acid can be explained by the following two factors

(i) Inductive effect of the substitutent

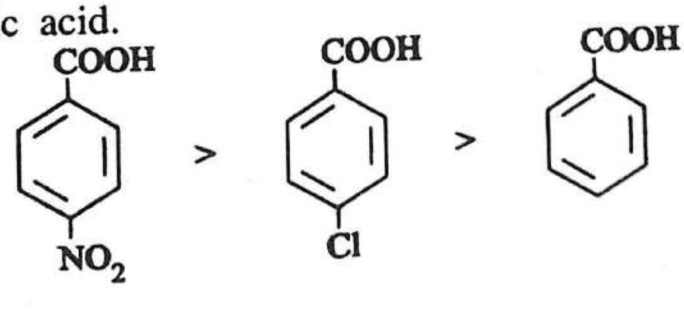
(ii) Resonance effect (or) Mesomeric effect.

(i) Effects of electron-withdrawing substituents

Electron-withdrawing substitutents increase the acidity of aromatic acids also.

Example

p-nitrobenzoic acid and p-chlorobenzoic acid are stronger than benzoic acid.



p-Nitrobenzoic acid is stronger than p-chlorobenzoic acid because both -I effect and -R effect of nitro group are important in stabilizing the carboxylate anion. But in p-chlorobenzoic acid, -I effect and +R effect are opposing each other.

$$-I > +R$$

(ii) Effect of electron-releasing substituents

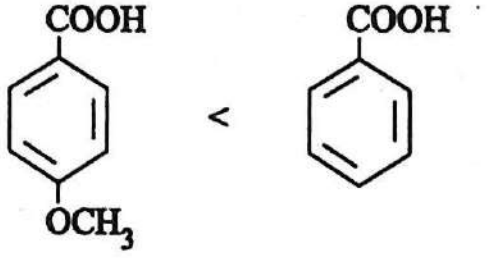
Electron-releasing substituents generally decrease the acidity.

Example

In p-methlybenzoic acid, the electron-releasing +I effect of the methyl group destabilizes the carboxylate ion. Hence p-methylbenzoic acid is weaker than benzoic acid. The -OH (or) $-OCH_3$ groups attached to the benzene ring exert resonance effect and inductive effect in opposite directions.

$$+R > -I.$$

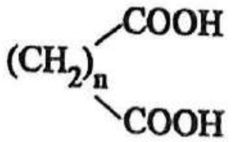
The electron-releasing resonance effect predominates in $-OCH_3$ group. Hence p-methoxybenzoic acid is weaker than benzoic acid.



From the above discussion it is clear that the net effect of two factors (Inductive effect and resonance effect) determines the actual acidity of a particular substituted benzoic acid.

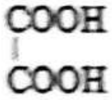
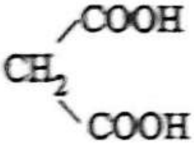
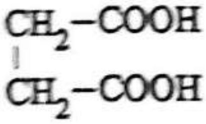
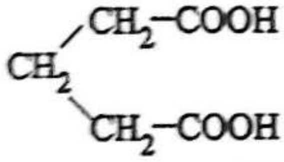
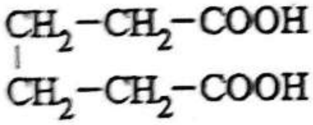
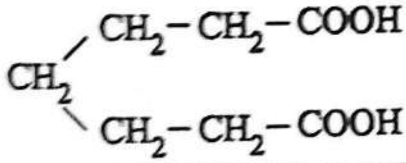
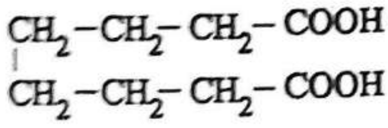
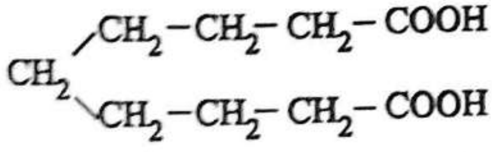
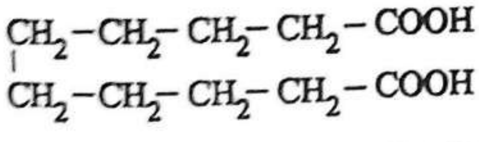
2.2 DICARBOXYLIC ACIDS

Compounds containing two $-COOH$ groups in their molecules are called dicarboxylic acids. Saturated dicarboxylic acids have the general formula:



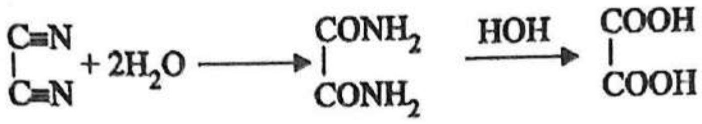
$$(CH_2)_n(COOH)_2 \qquad n = 0, 1, 2, 3 \ldots$$

2.2.1 Nomenclature of Dicarboxylic acids

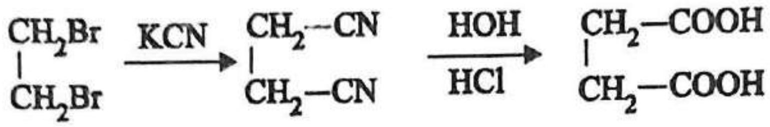
Formula	Common name	IUPAC name
 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Ethanedioic acid
	Malonic acid	Propanedioic acid
 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	Succinic acid	1,4-Butanedioic acid
	Glutaric acid	1,5-Pentanedioic acid
 $\begin{array}{l}CH_2-CH_2-COOH\\ \vert\\ CH_2-CH_2-COOH\end{array}$	Adipic acid	1,6-Hexanedioic acid
	Pimelic acid	1,7-Heptanedioic acid
 $\begin{array}{l}CH_2-CH_2-CH_2-COOH\\ \vert\\ CH_2-CH_2-CH_2-COOH\end{array}$	Suberic acid	1,8-Octanedioic acid
	Azelaic acid	1,9-Nonanedioic acid
 $\begin{array}{l}CH_2-CH_2-CH_2-CH_2-COOH\\ \vert\\ CH_2-CH_2-CH_2-CH_2-COOH\end{array}$	Sebacic acid	1,10-Decanedioic acid

2.2.2 General methods of preparation

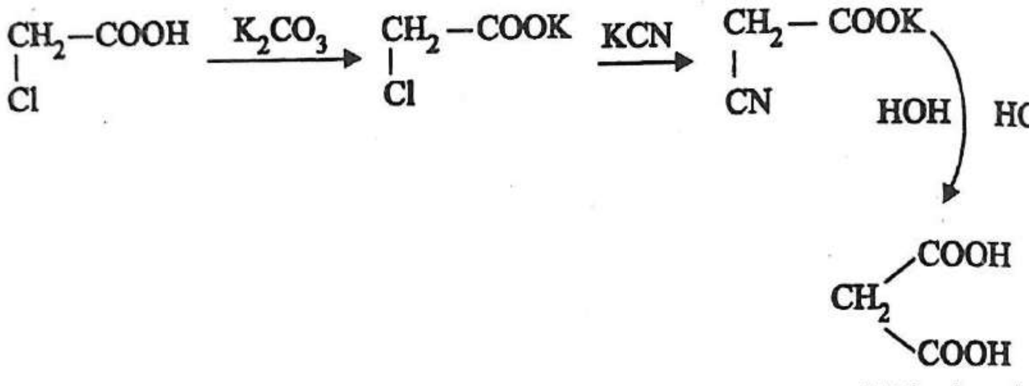
1. By the hydrolysis of dicyanides (or) cyanomonocarboxylic aci



$$\begin{array}{l}C\equiv N\\ |\\ C\equiv N\end{array} + 2H_2O \longrightarrow \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} \xrightarrow{HOH} \begin{array}{l}COOH\\ |\\ COOH\end{array}$$



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} \xrightarrow{KCN} \begin{array}{l}CH_2-CN\\ |\\ CH_2-CN\end{array} \xrightarrow[HCl]{HOH} \begin{array}{l}CH_2-COOH\\ |\\ CH_2-COOH\end{array}$$

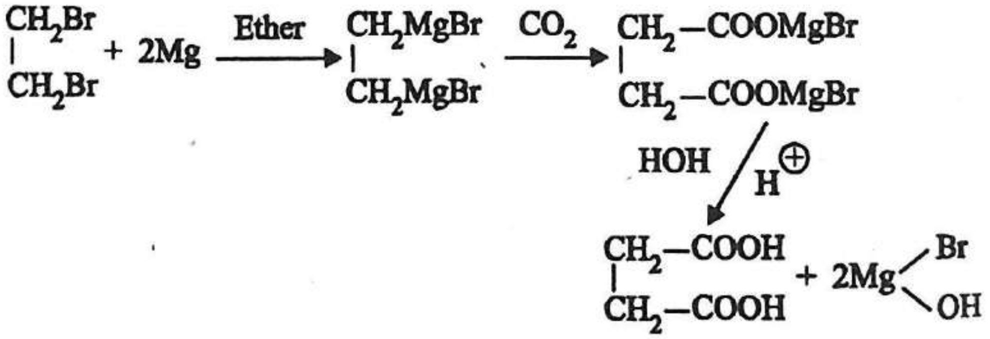


$$\begin{array}{l}CH_2-COOH\\ |\\ Cl\end{array} \xrightarrow{K_2CO_3} \begin{array}{l}CH_2-COOK\\ |\\ Cl\end{array} \xrightarrow{KCN} \begin{array}{l}CH_2-COOK\\ |\\ CN\end{array} \xrightarrow{HOH\quad H} CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$$

Malonic aci

2. From Grignard reagents

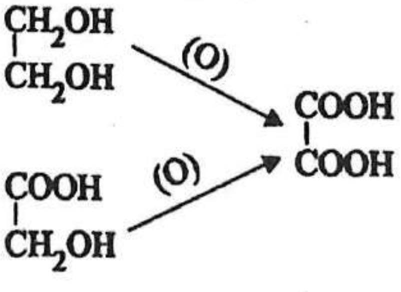
By treating Grignard reagents, obtained from t corresponding dihalides, with CO_2 and subsequent hydrolysi



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + 2Mg \xrightarrow{Ether} \begin{array}{l}CH_2MgBr\\ |\\ CH_2MgBr\end{array} \xrightarrow{CO_2} \begin{array}{l}CH_2-COOMgBr\\ |\\ CH_2-COOMgBr\end{array} \xrightarrow{HOH\ /\ H^{\oplus}} \begin{array}{l}CH_2-COOH\\ |\\ CH_2-COOH\end{array} + 2Mg\begin{array}{l}\diagup Br\\ \diagdown OH\end{array}$$

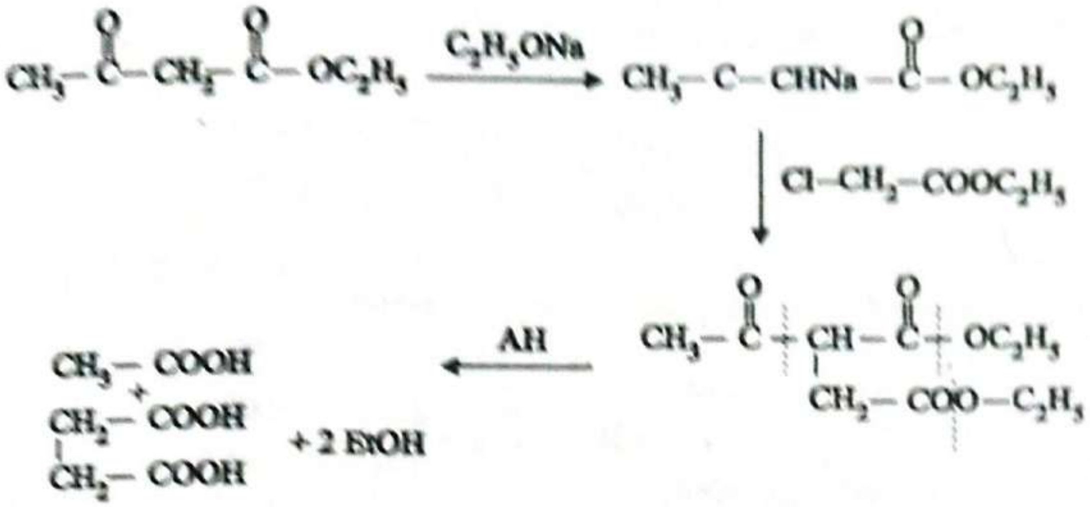
3. By oxidation

By the oxidation of diprimary alcohols (or) hydro acids with $KMnO_4$ (or) $K_2Cr_2O_7$

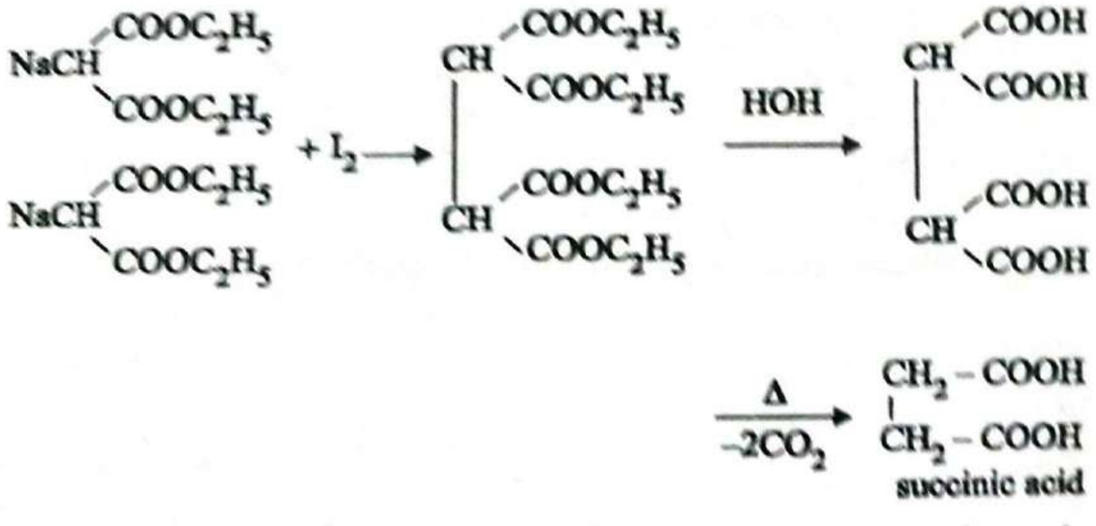


$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \xrightarrow{(O)} \begin{array}{l}COOH\\ |\\ COOH\end{array} \xleftarrow{(O)} \begin{array}{l}COOH\\ |\\ CH_2OH\end{array}$$

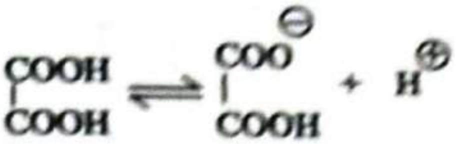
4. From acetoacetic ester



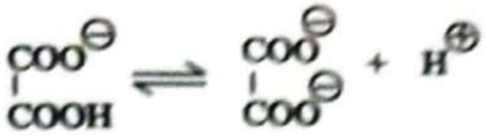
5. From malonic ester



If CH_2I_2 is used instead of I_2, glutaric acid is formed. Similarly when ethylene dibromide is used, adipic acid is obtained.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \rightleftharpoons \begin{matrix} COO^{\ominus} \\ | \\ COOH \end{matrix} + H^{\oplus}$$



$$\begin{matrix} COO^{\ominus} \\ | \\ COOH \end{matrix} \rightleftharpoons \begin{matrix} COO^{\ominus} \\ | \\ COO^{\ominus} \end{matrix} + H^{\oplus}$$

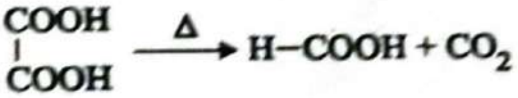
The dicarboxylic acids are much stronger than monocarboxylic acids. The acid strength decreases with increase in molecular weight. The dicarboxylic acids dissociate in two stages $K_{a1} > K_{a2}$.

Chemical properties

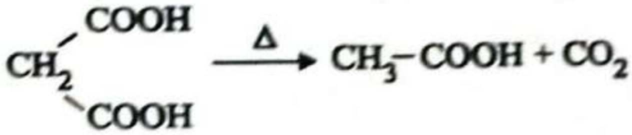
1. Action of heat

Different products are obtained on heating depending upon the relative positions of the two $-COOH$ groups.

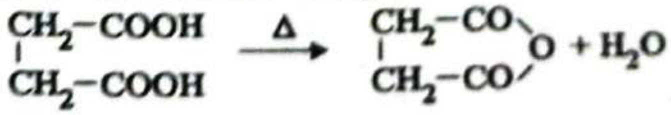
(a) Dicarboxylic acids in which the two $-COOH$ groups are directly linked (or) to the same carbon atom (1,2 (or) 1,3) lose CO_2 to form fatty acids.

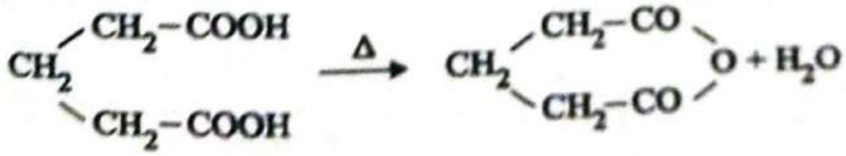


$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\Delta} H-COOH + CO_2$$

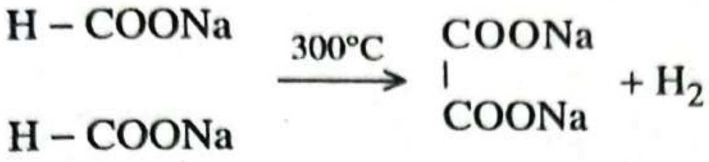


(b) The dicarboxylic acids, separated by two (or) three carbon atoms, lose a molecule of H_2O on heating (or) better by distillation with acetic anhydride.

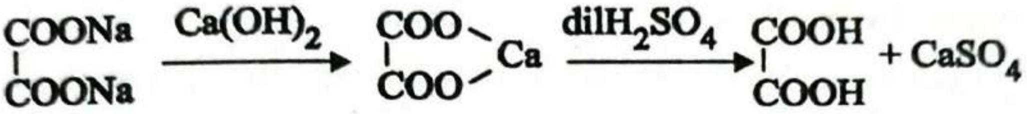




2. Oxalic acid is prepared industrially by heating HCOONa rapidly at 360°C when sodium oxalate is formed. This is then converted into Ca oxalate by treatment with lime which then reacts with dil H_2SO_4 forming oxalic acid.

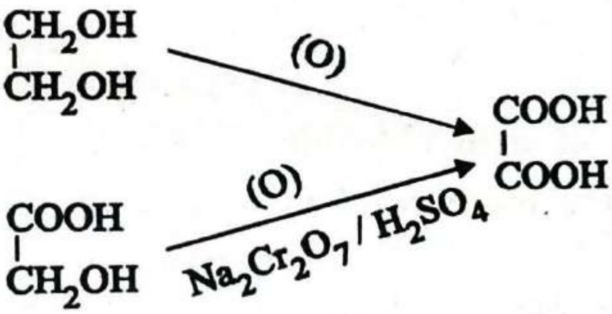


$$\begin{matrix} H-COONa \\ H-COONa \end{matrix} \xrightarrow{300^\circ C} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$



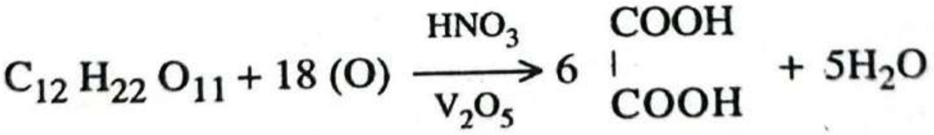
$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow{Ca(OH)_2} \begin{matrix} COO \\ | \\ COO \end{matrix}\!\!>Ca \xrightarrow{dil H_2SO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix} + CaSO_4$$

3. Oxalic acid is prepared by the oxidation of ethylene glycol (or) glycollic acid with $Na_2Cr_2O_7$ / H_2SO_4



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow{(O)} \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xleftarrow[Na_2Cr_2O_7 / H_2SO_4]{(O)} \begin{matrix} COOH \\ | \\ CH_2OH \end{matrix}$$

4. In the laboratory oxalic acid is prepared by the oxidation of cane-sugar with conc HNO_3 in the presence of V_2O_5:

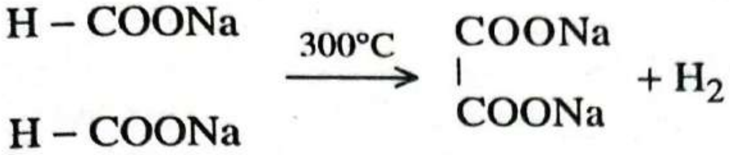


$$C_{12}H_{22}O_{11} + 18\,(O) \xrightarrow[V_2O_5]{HNO_3} 6 \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 5H_2O$$

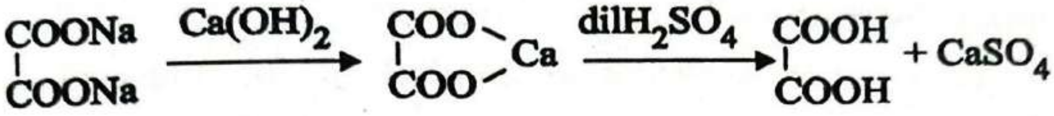
Properties

Oxalic acid is a colourless, crystalline solid. It is soluble in H_2O and alcohol but almost insoluble in ether. It is poisonous.

2. Oxalic acid is prepared industrially by heating HCOONa rapidly at 360°C when sodium oxalate is formed. This is then converted into Ca oxalate by treatment with lime which then reacts with dil H_2SO_4 forming oxalic acid.

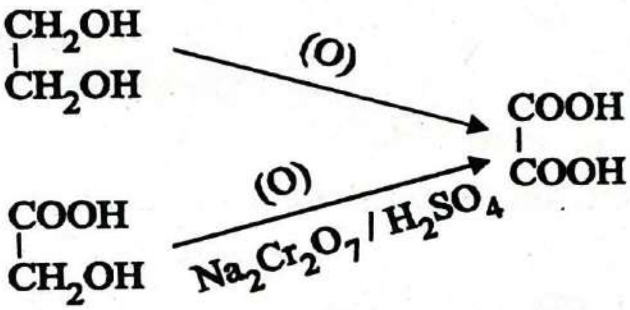


$$\begin{matrix} H-COONa \\ H-COONa \end{matrix} \xrightarrow{300^\circ C} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$



$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow{Ca(OH)_2} \begin{matrix} COO \\ | \\ COO \end{matrix}\!\!>Ca \xrightarrow{dil H_2SO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix} + CaSO_4$$

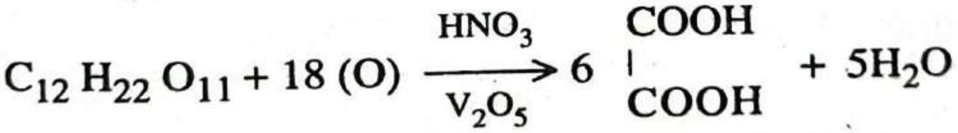
3. Oxalic acid is prepared by the oxidation of ethylene glycol (or) glycollic acid with $Na_2Cr_2O_7$ / H_2SO_4



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow{(O)} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

$$\begin{matrix} COOH \\ | \\ CH_2OH \end{matrix} \xrightarrow[Na_2Cr_2O_7 / H_2SO_4]{(O)} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

4. In the laboratory oxalic acid is prepared by the oxidation of cane-sugar with conc HNO_3 in the presence of V_2O_5:



$$C_{12}H_{22}O_{11} + 18\,(O) \xrightarrow[V_2O_5]{HNO_3} 6 \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 5H_2O$$

Properties

Oxalic acid is a colourless, crystalline solid. It is soluble in H_2O and alcohol but almost insoluble in ether. It is poisonous.

6. Oxidation

Oxalic acid is oxidised to CO_2 by acidified $KMnO_4$:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\,(O)$$

$$5H_2C_2O_4 \longrightarrow 5H_2O + 5CO + 5CO_2$$

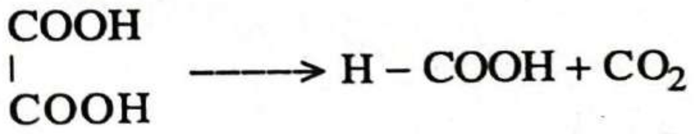
$$5CO + 5\,(O) \longrightarrow 5CO_2$$

$$2KMnO_4 + 3H_2SO_4\ 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10\,CO_2$$

---

7. Action of heat

When oxalic acid is heated above its melting point, it decomposes to give H–COOH, CO_2 and H_2:

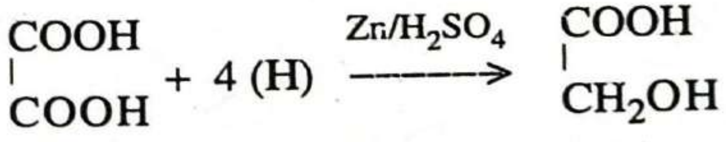


$$\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix} \longrightarrow H-COOH + CO_2$$

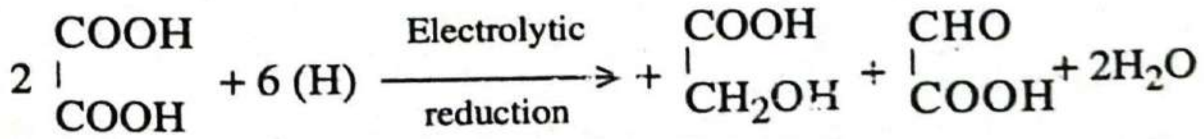
$$H-COOH \longrightarrow H_2 + CO_2$$

8. Reduction

Oxalic acid is reduced to glycollic acid by Zn/H_2SO_4 while electrolytic reduction using lead cathode leads to the formation of glycollic and glyoxylic acids.



$$\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix} + 4\,(H) \xrightarrow{Zn/H_2SO_4} \begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{CH_2OH}\end{matrix}$$

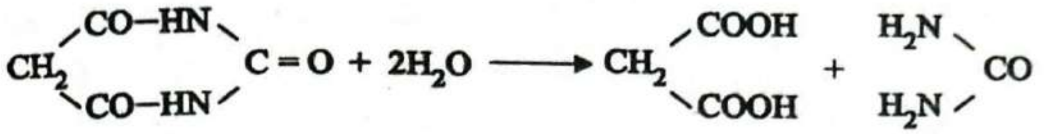


$$2\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix} + 6\,(H) \xrightarrow[\text{reduction}]{\text{Electrolytic}} + \begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{CH_2OH}\end{matrix} + \begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{matrix} + 2H_2O$$

9. With glycerol

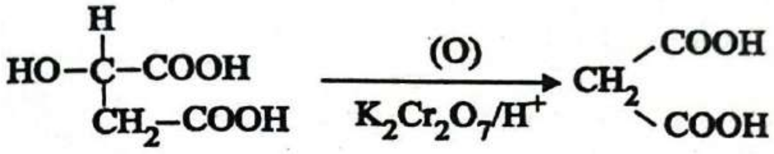
When crystalline oxalic acid is heated with glycerol at 110°C, formic acid is formed. But when heating is done at 260°C, allyl alcohol is formed.

2. It is prepared by the hydrolysis of malonylurea (barbituric acid):



$$CH_2\begin{matrix}CO-HN\\ CO-HN\end{matrix}C=O + 2H_2O \longrightarrow CH_2\begin{matrix}COOH\\ COOH\end{matrix} + \begin{matrix}H_2N\\ H_2N\end{matrix}CO$$

3. Malonic acid is also prepared by the oxidation of malic acid with acidified $K_2Cr_2O_7$:



$$HO-\overset{H}{\underset{CH_2-COOH}{C}}-COOH \xrightarrow[K_2Cr_2O_7/H^+]{(O)} CH_2\begin{matrix}COOH\\ COOH\end{matrix}$$

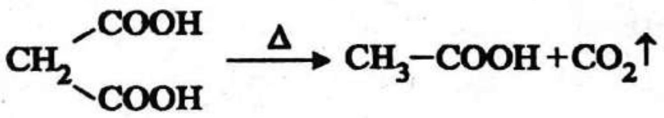
Properties

Malonic acid is a colorless, crystalline solid. It is readily soluble in H_2O and alcohol, but sparingly soluble in ether.

Reactions

1. Action of heat

When heated at 140°C, malonic acid decomposes into CH_3 COOH and CO_2:



$$CH_2\begin{matrix}COOH\\ COOH\end{matrix} \xrightarrow{\Delta} CH_3-COOH + CO_2\uparrow$$

2. With P_2O_5

When malonic acid is heated with P_2O_5, it loses two molecules of H_2O to form carbon suboxide (C_3O_2). This when dissolved in H_2O again forms malonic acid.

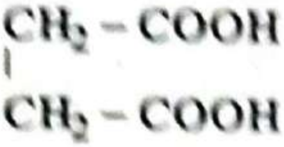
$$CH_2\begin{matrix}COOH\\ COOH\end{matrix} \longrightarrow C_3O_2 + 2H_2O$$

3. With HNO_2

Malonic acid on treatment with HNO_2 followed by hydrolysis forms mesoxalic acid:

2.2.6 Succinic acid

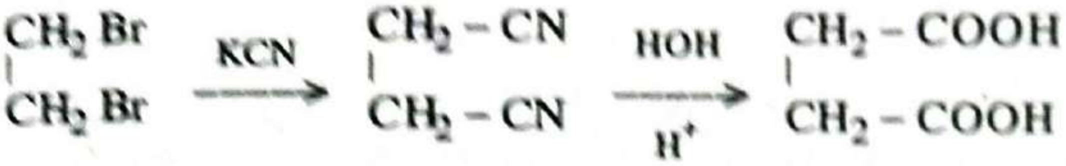
Structure:



$$\begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

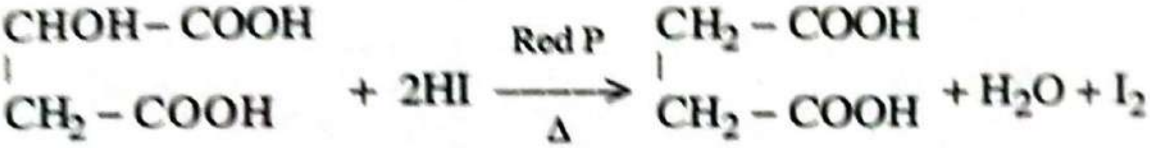
Preparation

1. Succinic acid is prepared by treating ethylene dibromide with KCN followed by hydrolysis:



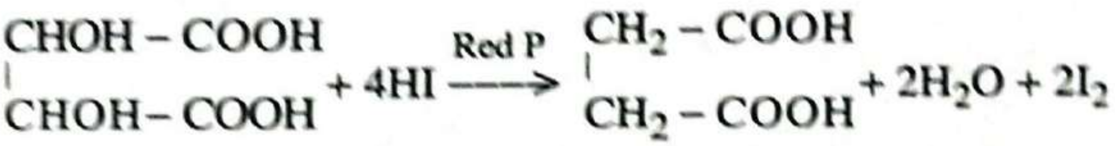
$$\begin{array}{l} CH_2\,Br \\ | \\ CH_2\,Br \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2-CN \\ | \\ CH_2-CN \end{array} \xrightarrow[H^+]{HOH} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

2. It is also prepared by the action of HI and red P on malic acid (or) tartaric acid:



$$\begin{array}{l} CHOH-COOH \\ | \\ CH_2-COOH \end{array} + 2HI \xrightarrow[\Delta]{Red\ P} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array} + H_2O + I_2$$

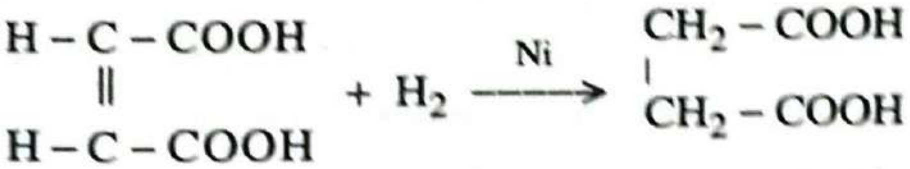
Malic acid



$$\begin{array}{l} CHOH-COOH \\ | \\ CHOH-COOH \end{array} + 4HI \xrightarrow{Red\ P} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array} + 2H_2O + 2I_2$$

Tartaric acid

3. It is prepared on a large scale by the catalytic reduction of maleic acid:



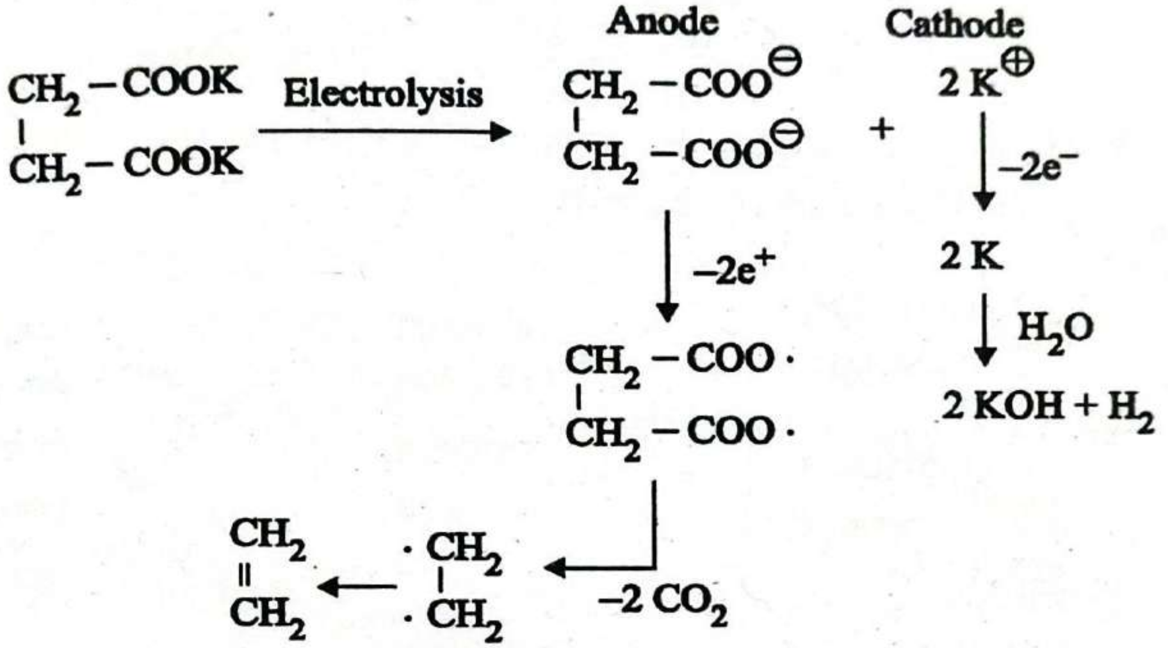
$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} + H_2 \xrightarrow{Ni} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

Properties

Succinic acid is a white, crystalline solid. It is moderately soluble in H_2O, but sparingly soluble in ether.

4. Electrolysis of $Na^{\oplus}$ (or) $K^{\oplus}$ salts

The electrolysis of a solution of Na (or) K salt of succinic acid yields ethylene:



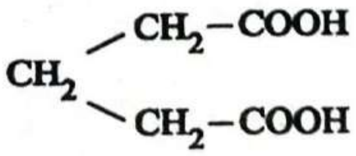
Uses

Succinic acid is used

1. In the manufacture of high polymer esters (or) polyester resins.
2. In medicine.
3. As a reagent in volumetric analysis.
4. In the manufacture of dyes and perfumes.

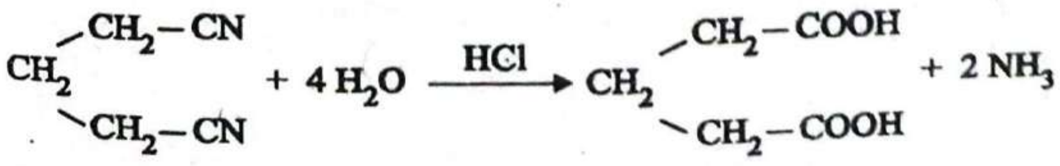
2.2.7 Glutaric acid

Structure:



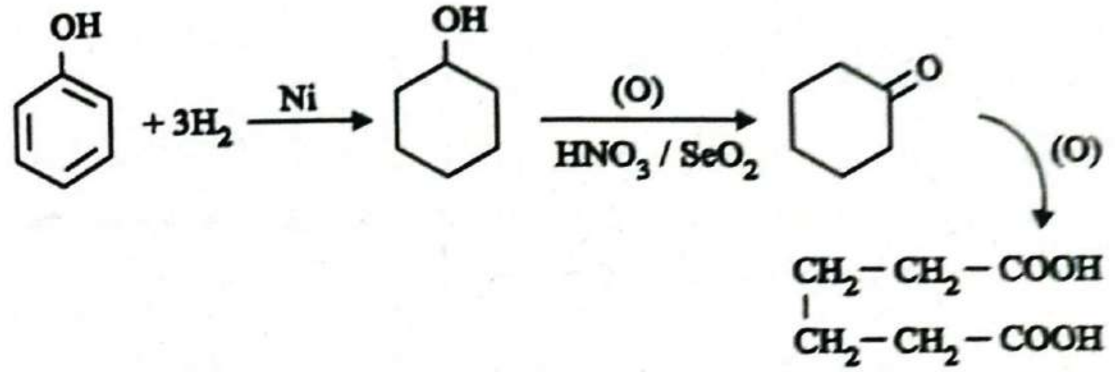
Preparation

1. Glutaric acid is prepared by the hydrolysis of trimethylene-dicyanide with HCl:

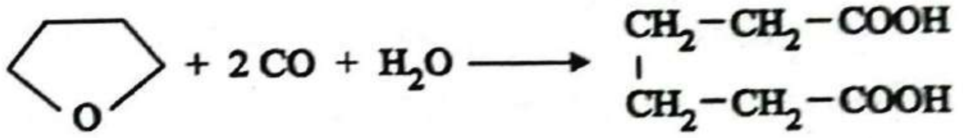


Preparation

1. Adipic acid is prepared industrially by the oxidation of phenol (or) cyclohexanone with HNO_3 in the presence of SeO_2:



2. It is also prepared on a large scale by the reaction of THF with CO and H_2O:



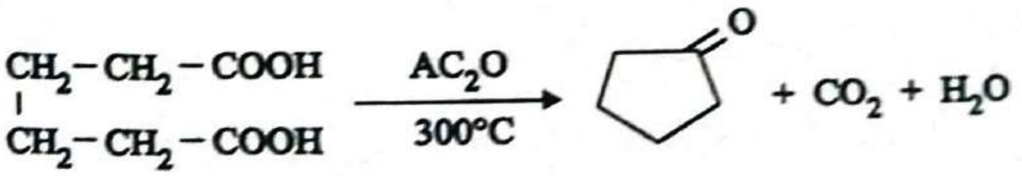
3. Adipic acid is prepared by the reaction of sodio malonic ester with ethylene dibromide.

Properties

Adipic acid is a crystalline solid melting point 150°C.

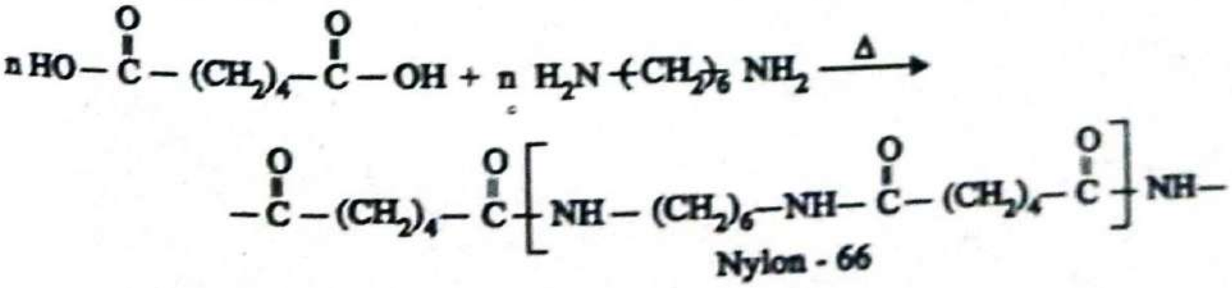
1. Action of heat

When adipic acid is distilled with acetic anhydride, it loses H_2O and CO_2 to form cyclopentanone:



2. Condensation reaction

It undergoes condensation with 1,6-hexamethylenediamine to give a polyamide called Nylon-66.

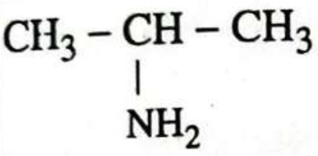
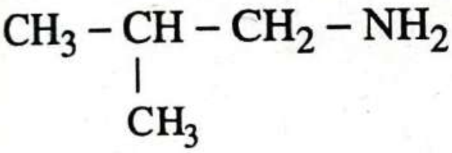
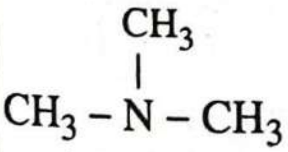


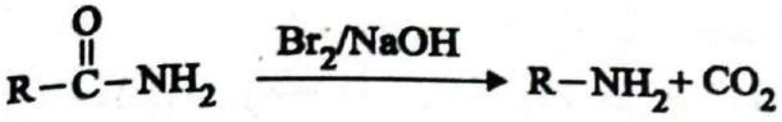
$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,H_2N{(CH_2)}_6NH_2 \xrightarrow{\Delta}$$

$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\left[NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]NH-$$

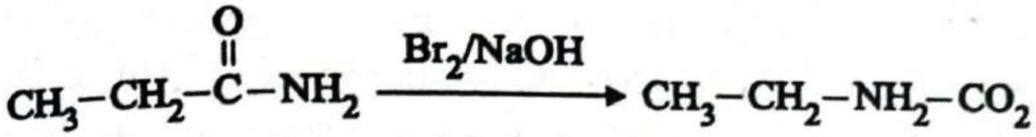
Nylon - 66

2.3.2 Nomenclature of Amines

Formula	Common name	IUPAC name
CH_3-NH_2	Methylamine	Amino methane
$CH_3-CH_2-NH_2$	Ethylamine	Amino ethane
$CH_3-CH_2-CH_2-NH_2$	n-Propylamine	1-Amino propane
 $CH_3-\underset{\underset{NH_2}{\vert}}{CH}-CH_3$	iso-Propylamine	2-Amino propane
$CH_3-CH_2-CH_2-CH_2-NH_2$	n-Butylamine	1-Amino butane
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-NH_2$	iso- Butylamine	2-Methyl-amino propane
$CH_3-NH-CH_3$	Dimethylamine	(N-Methylamino)-methane
$CH_3-NH-CH_2-CH_3$	Ethylmethylamine	(N-methylamino)-ethane
 $CH_3-\overset{\overset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	(N,N-Dimethylamino)-methane

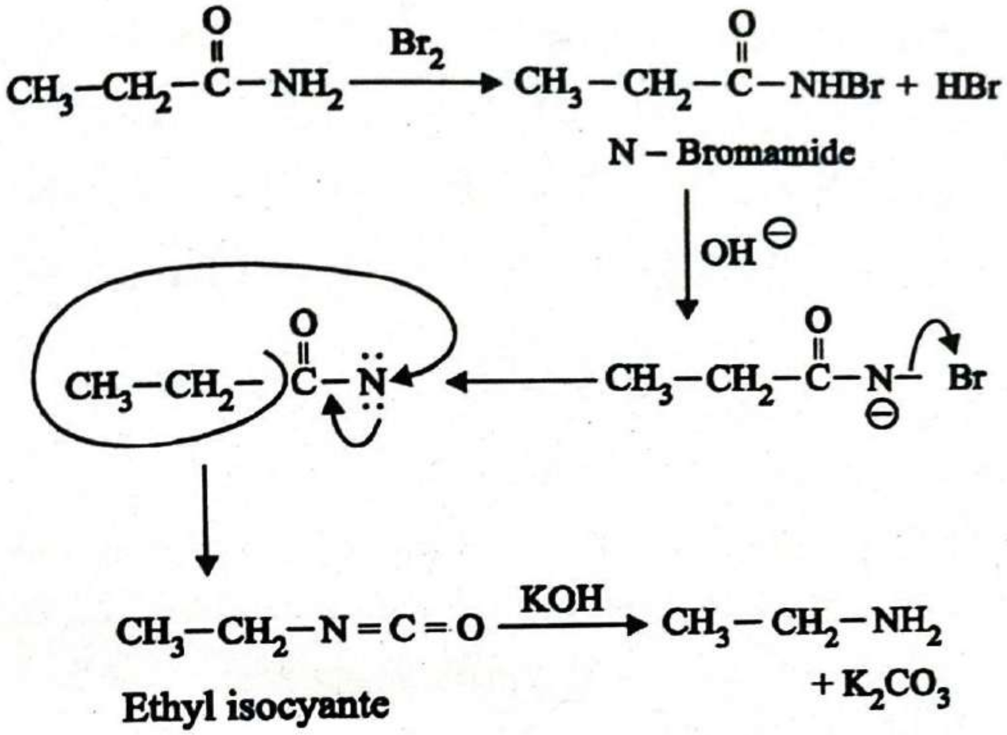


$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/NaOH} R-NH_2 + CO_2$$



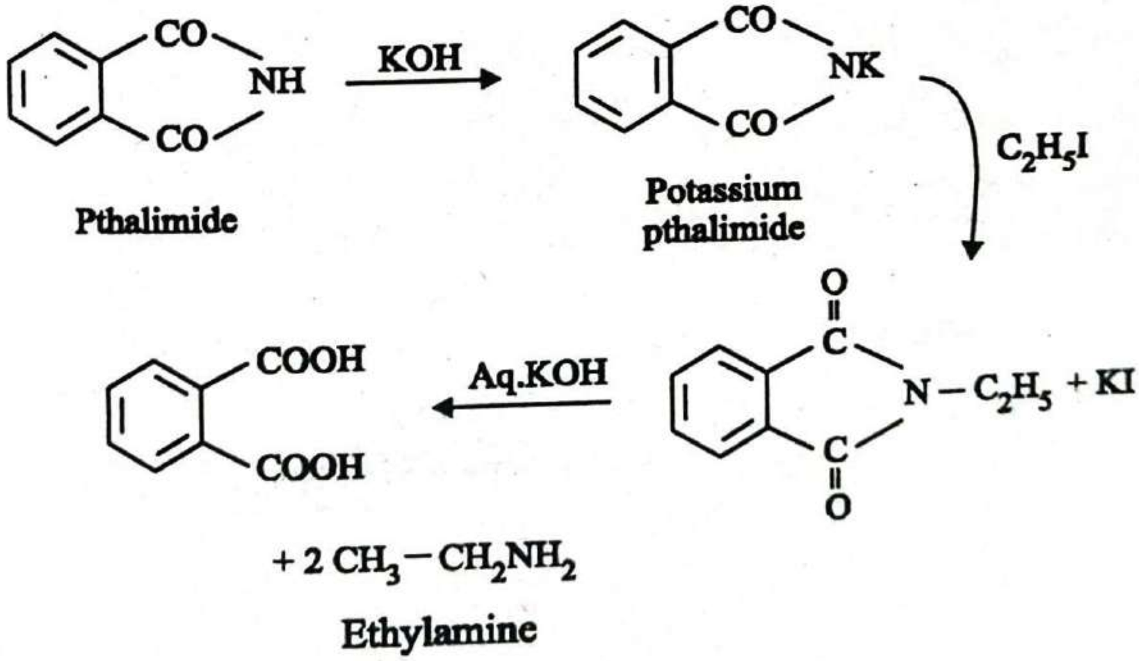
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/NaOH} CH_3-CH_2-NH_2-CO_2$$

Mechanism



5. By Gabriel phthalimide synthesis

Ethylamine (or primary amine) can be prepared in the following steps:

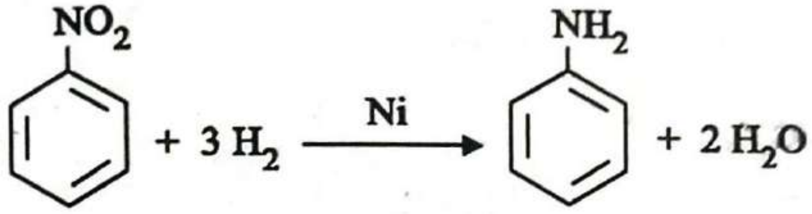


Preparation

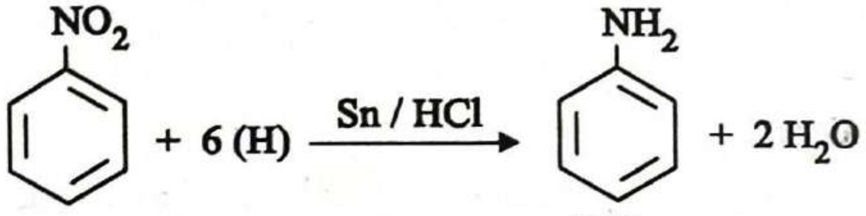
1. By catalytic (or) chemical reduction of nitrobenzene

This is a very convenient and most widely used method of preparing aniline. The reduction is carried out with (a) H_2 in the presence of Ni, Cu, Pd (or) Pt catalyst, (b) Sn (or) Fe and HCl and (c) $LiAlH_4$.

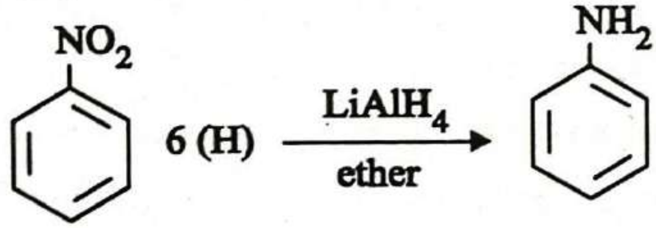
(a)



(b)

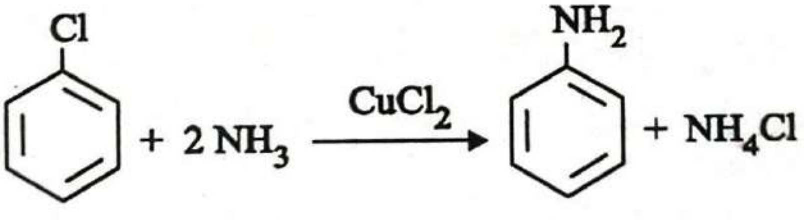


(c)



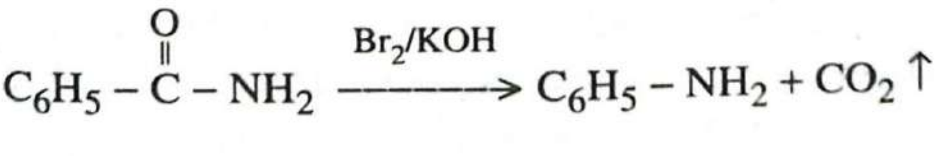
2. By ammonolysis of aryl halides

Aniline is prepared by heating chlorobenzene with ammonia in the presence of Cu salts at 210°C and high pressure.



3. By Hofmann's hypobromite reactions

When benzamide is treated with Br_2 and alkali, the amide is converted into aniline containing one carbon atom less.



$$C_6H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 \xrightarrow{Br_2/KOH} C_6H_5 - NH_2 + CO_2 \uparrow$$

$$R{-}NH_2 + H_2O \rightleftharpoons R{-}\overset{\oplus}{N}H_3 + \overset{\ominus}{OH}$$

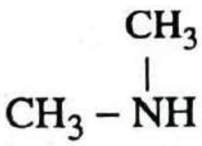
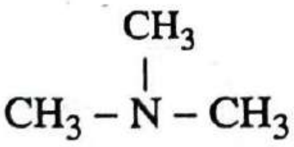
Applying law of mass action,

$$K_b = \frac{\left[R - \overset{\oplus}{N}H_3\right][\overset{\ominus}{OH}]}{[R - NH_2]}$$

K_b – Basicity constant.

The extent of ionisation is described by Basicity constant. It is an equilibrium constant for the ionisation reaction of the base. The basicity constant values describe the relative strength of the bases. Stronger bases will have higher numerical values of K_b.

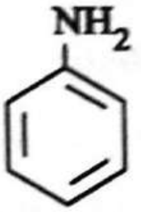
Table 2.1: K_b values of some amines

Base	**K_b**
NH_3	1.8×10^{-5}
$CH_3 - NH_2$	37×10^{-5}
 $CH_3 - \overset{\overset{CH_3}{\vert}}{N}H$	54×10^{-5}
 $CH_3 - \overset{\overset{CH_3}{\vert}}{N} - CH_3$	6.5×10^{-5}

Relative basicities of amines

Aliphatic amines are stronger bases than ammonia. This is because the alkyl groups are electron-releasing. They increase the electron density around the nitrogen atom, thereby increasing the availability of the lone pair for protonation.

K_b values of some aromatic amines

Name	Formula	K_b
Aniline		4.2×10^{-10}
p-Taludine		2×10^{-9}

2.3.6 Effect of substituents on basicity

Effect of various substituents on the basicity of aniline depends on the nature of the group and its position in the benzene ring. Further its ability to enter into resonance with the amino group should also be considered.

Example

1. p-Toludine is more basic than aniline

p-Toludine is more basic than aniline. The CH_3- (Methyl) group has a +I effect. Therefore it increases the electron density on the nitrogen atom. The effect is more when CH_3- group in p-position than in meta position. This is due to reason that the electron-withdrawing (or) electron-releasing effect is more at o- and p-positions than at the meta position.

2. m-Nitro aniline is more basic than o & p nitro toludine

In o-nitroaniline (or) p-nitroaniline the NO_2- group exerts −R as well as −I effects and, therefore, decreases the basicity tremendously. In meta position, it cannot exert −R effect. Decrease in basicity is only due to −I effect. The order of basicity in nitroanilines is as follows:

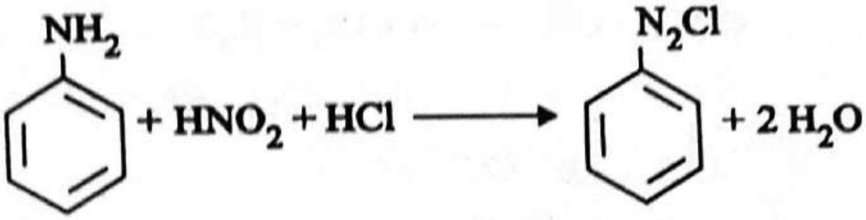
$$R_2NH + HO - N = O \dashrightarrow \underset{\text{N – Nitrosoamine}}{R_2N - NO} + H_2O$$

(iii) Tertiary amines react with HNO_2 to form the nitrite salts in the cold. These salts are soluble in water.

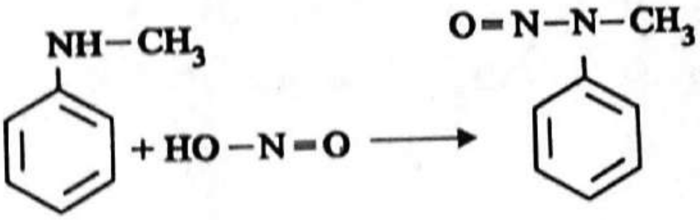
$$R_3N + HNO_2 \dashrightarrow \underset{\text{salt}}{\left[R_3\overset{\oplus}{N}H \right]} \overset{\ominus}{NO_2}$$

Aromatic amines

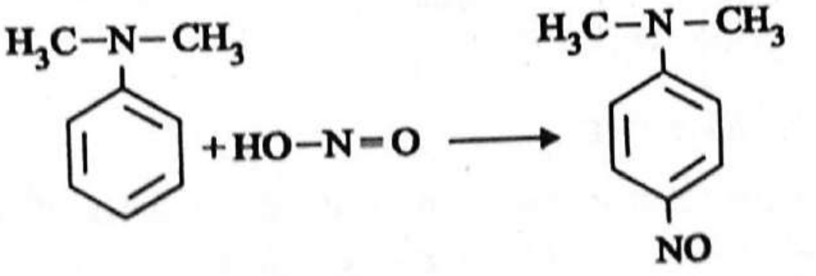
(i) Aromatic primary amines form diazonium salts (diazotisation) with HNO_2



(ii) Secondary amines form N-Nitrosoamine



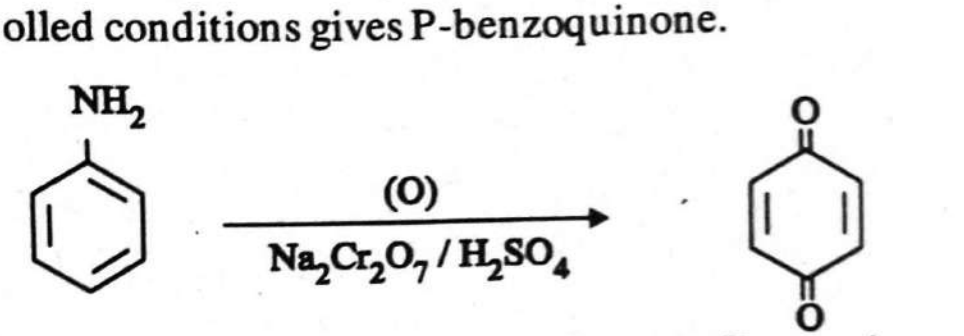
(iii) Tertiary amines undergo nitrosoation in the para-position.



p – nitroso - N, N
dimethylaniline

(i) Primary amine

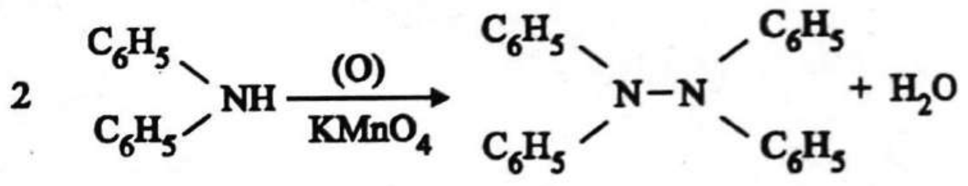
Oxidation of aniline with $Na_2Cr_2O_7/H_2SO_4$ under controlled conditions gives P-benzoquinone.



p – Benzoquinone

(ii) Secondary amine

Diphenylamine on oxidation by $KMnO_4$ gives tetraphenyl hydrazine.



Tetraphenyl-hydrazine

2.3.8 Distinction between Primary, Secondary and Tertiary amines

	Reagent (or) Test	Primary amine	Secondary amine	Tertiary amine
1.	With HNO_2	Forms alcohol with the evolution of N_2	Forms yellow oily nitroso-amine which answers Liebermann's nitroso reaction.	Forms nitrite salt in the cold.
2.	With $CHCl_3/KOH$	Forms Carbylamine with obnoxious smell	No reaction	No reaction

	Reagent (or) Test	Primary amine	Secondary amine	Tertiary amine
3.	With $CS_2/HgCl_2$	Forms alkyl isothiocyanate (Mustard oil reaction)	No reaction	No reaction
4.	With $C_6H_5SO_2Cl$ (Hinsberg's reagent)	Forms N-alkyl sulphonamide soluble in alkali	Forms N, N - dialkyl sulphonamide insoluble in alkali.	No reaction.
5.	With diethyl oxalate $\left(\begin{array}{l} COOC_2H_5 \\ \vert \\ COOC_2H_5 \end{array}\right)$	Forms a solid dialkyl oxamide at room temperature. $\left(\begin{array}{l} CO-NH-R \\ \vert \\ CO-NH-R \end{array}\right.$	Forms oxamic ester which is a liquid $\left(\begin{array}{l} CONR_2 \\ \vert \\ COOC_2H_5 \end{array}\right)$	No reaction.
6.	With acetyl chloride.	Forms N-alkyl acetamide	Forms N,N-dialkyl acetamide	No reaction.
7.	With Grignard reagent (RMgX)	Forms alkane	Forms alkane	No reaction.
8.	With alkyl iodide under ordinary conditions.	Forms Quaternary salt with three moles of RI.	Forms Quaternary salt with two moles of RI.	Forms Quaternary salt with one mole of RI.