Organic Chemistry

An approach to systematic study of selected topics

Exclusively for Studies at Degree Level

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Shri R.L.T. College of Science, Akola

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Preface ...

It gives me immense pleasure to present the book “Organic Chemistry - An approach to systematic study of selected topics” to the students and teachers learning subject chemistry. Organic chemistry is a rigorous but equally stimulating, exciting and ultimately rewarding subject.

In order to learn organic chemistry, it is necessary to acquire an exhaustive knowledge of the principles and theoretical basis of the subject. In this book, three dimensional illustrations, figures, representations, chemical reactions and numbers of examples are incorporated to make the learning interesting and understandable. The subject matter described in this book covers much of the basic organic chemistry that is needed to study at degree level. I sincerely feel that, the way of presentation of subject matter in the book will help the students and teachers for learning the subject independently. Here in this book, the emphasis is on simplicity and clarity but not at the cost of logical scientific discussion.

Most of the advanced information along with basic aspects and concepts related to the chemistry of organic compounds i.e. aldehydes and ketones, carboxylic acids, aromatic nitro compounds, amino compounds (amines), polynuclear hydrocarbons and reactive methylene compounds is incorporated in this book for undergraduate study. While preparing the book, I have referred numbers of standard books. I wish to put on record my indebtedness to authors of these books.

I take this opportunity to express my sincere and profound gratitude to Hon'ble Adv. Motisingh G. Mohta, President, Hon'ble Shri Pavan N. Maheshwari, Honorary Secretary, The Berar General Education Society, Akola and Respected Dr. Vijay D. Nanoty, Principal, Shri R.L.T. College of Science, Akola for encouraging me to write the book. I would like to acknowledge the support received from Prakash Printers, Akola in preparation of manuscript of this book.

I would like to place on record the love and support of my family members, my wife Harsha and sons Smit and Sparsh to finish this herculean task.

I feel that, a man would do nothing if he waited until he could do it so well that no one would find fault with what he has done. Despite of my sincere efforts, there may have possibility of some errors in the book which might be escaped from my notice. Positive instructions and constructive suggestions for improvement of subject matter and contents of the book are most welcome.

Dr. Pradip P. Deohate

Organic Chemistry

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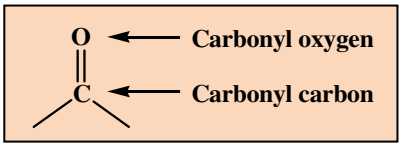
Contents …

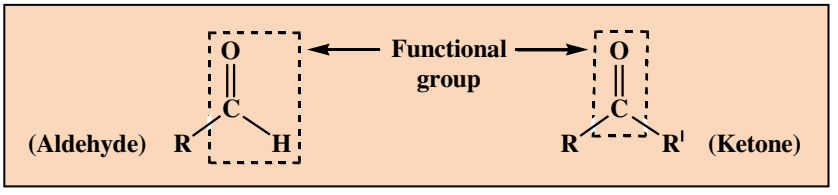
Aldehydes and Ketones

Introduction

Aldehydes and ketones are two important classes of organic compounds. These contains carbonyl group (>C=O) and as it largely determines the chemistry of aldehydes and ketones, these are often collectively referred as carbonyl compounds. These are isomeric with each other and resemble closely in most of their properties.



In aldehydes, carbonyl carbon is bonded to one hydrogen and one alkyl or aryl group. In formaldehyde, HCHO, it is bonded to two hydrogen atoms is an exception. In ketones, carbonyl carbon is bonded to two alkyl or aryl groups. Alkyl or aryl groups may be same or different and accordingly classified as symmetrical or unsymmetrical ketones.



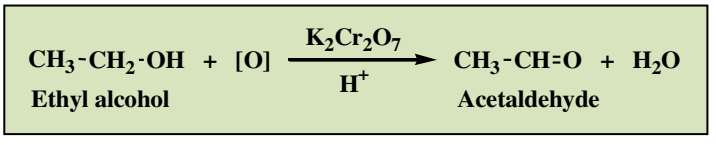
Where, R and R^{I} - alkyl or aryl groups

Aldehydes are quite easily oxidized and are more reactive towards nucleophilic addition than ketones because of the presence of free hydrogen atom.

Preparations

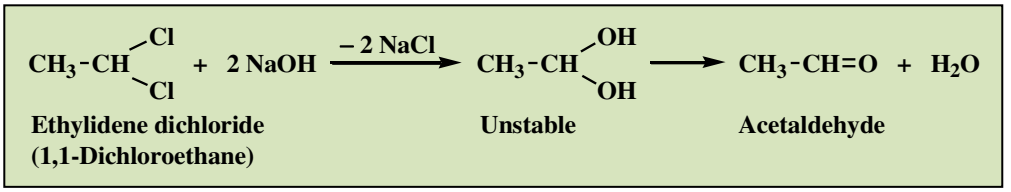
Acetaldehyde or Ethanal (CH_3-CHO)

Oxidation of ethyl alcohol (primary alcohol) - Ethyl alcohol on oxidation using an acidified solution of potassium dichromate under controlled condition (to prevent further oxidation to carboxylic acid) gives acetaldehyde.

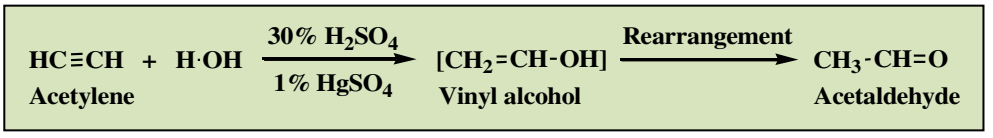


Other oxidizing agents used are alkaline potassium permanganate, chromic anhydride (chromium trioxide) in glacial acetic acid or MnO_2 in acetone.

Hydrolysis of ethylidene dichloride (*gem*-dihalide) - Ethylidene dichloride on hydrolysis in alkaline conditions gives an unstable dihydroxy compound, it readily loses water molecule to produce acetaldehyde.

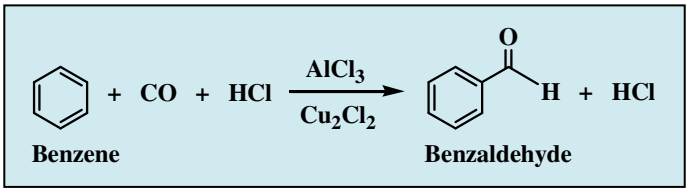


Hydration of acetylene (alkyne) - Acetylene on hydration by bubbling its vapours through 30% sulphuric acid containing 1% mercuric sulphate forms unstable vinyl alcohol (enol intermediate) by addition water molecule to acetylene, it rearranges to give acetaldehyde.

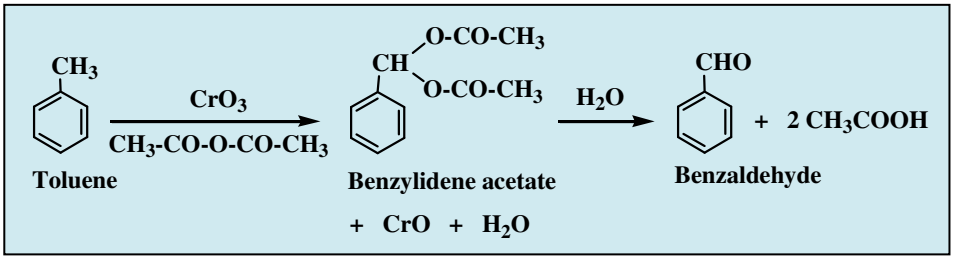


Benzaldehyde (C_6H_5-CHO)

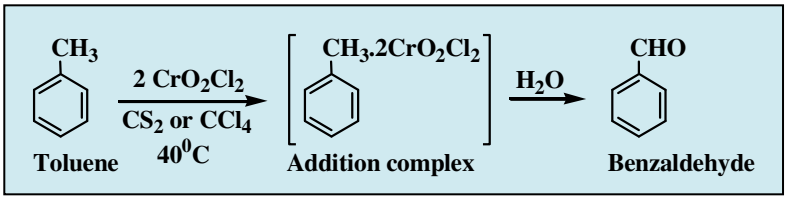
Formylation of benzene (Gattermann-Koch reaction) - Benzene on formylation by passing mixture of carbon monoxide and hydrogen chloride gas through etheral solution of benzene containing aluminium chloride and small amount of cuprous chloride gives benzaldehyde.



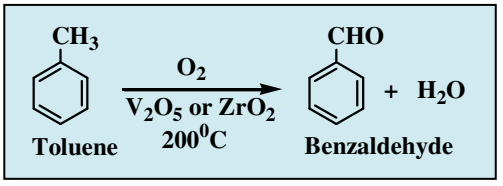
Oxidation of toluene (methyl benzene) - Toluene is oxidized using different methods.
Oxidation - Toluene on oxidation using chromium trioxide (chromic anhydride) in acetic anhydride gives benzylidene acetate, it readily gets hydrolyzed to give benzaldehyde.



Etard reaction - Toluene on oxidation using chromyl chloride in carbondisulphide or carbontetrachloride at 40^0C gives benzaldehyde.

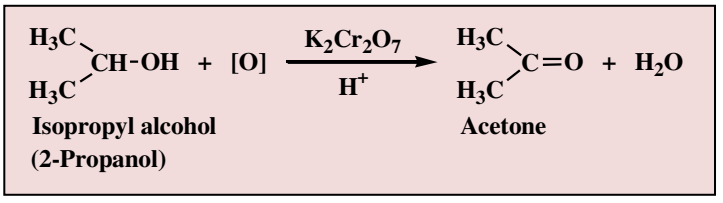


Vapour phase oxidation - Toluene on oxidation by passing its vapours with oxygen or air diluted with nitrogen (to prevent complete oxidation) over vanadium pentaoxide or zirconium dioxide at 200^0C gives benzaldehyde.



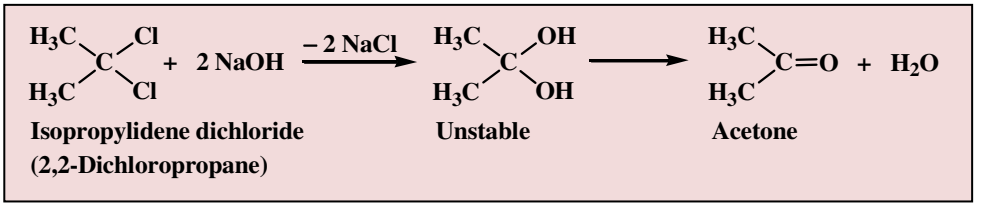
Acetone or Propanone (CH_3-CO-CH_3)

Oxidation of isopropyl alcohol (secondary alcohol) - Isopropyl alcohol on oxidation using an acidified solution of potassium dichromate under controlled condition gives acetone.

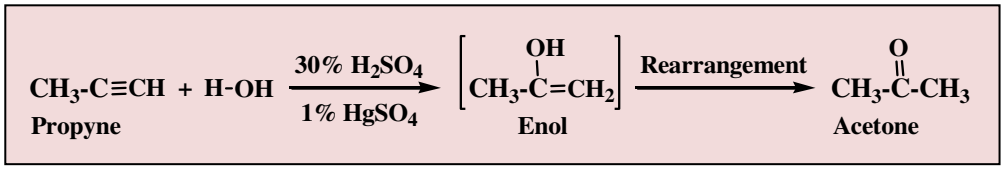


Other oxidizing agents used are alkaline potassium permanganate or chromic anhydride (chromium trioxide) in glacial acetic acid.

Hydrolysis of isopropylidene dichloride (*gem*-dihalide) - Isopropylidene dichloride on hydrolysis in alkaline conditions gives an unstable dihydroxy compound, it readily loses water molecule to produce acetone.

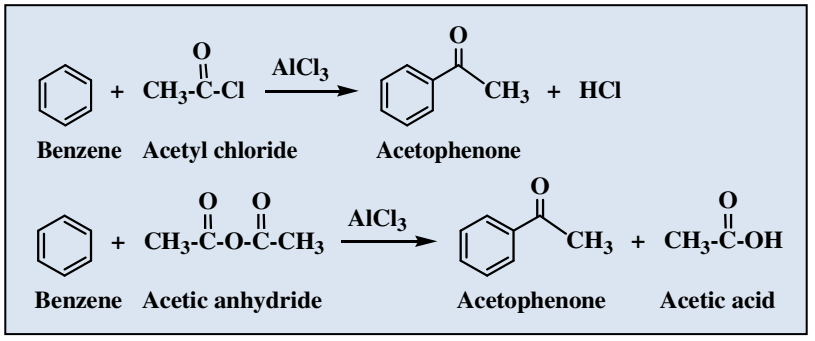


Hydration of propyne (alkyne) - Propyne on hydration by passing its vapours through 30% sulphuric acid containing 1% mercuric sulphate forms unstable enol intermediate (as per Markovnikov rule) by addition of water molecule to propyne, it rearranges to give acetone.

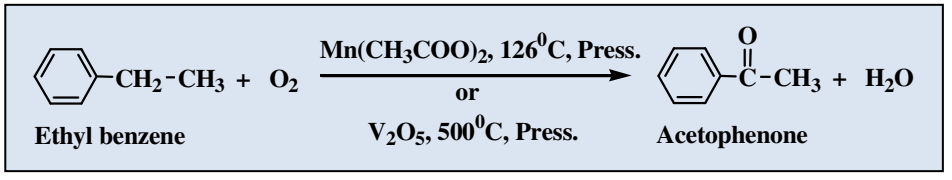


Acetophenone or Methyl Phenyl Ketone (C_6H5-CO-CH_3)

Acetylation of benzene (Friedel-Craft reaction) - Benzene on acetylation by heating with acetyl chloride or acetic anhydride in presence of anhydrous aluminium chloride gives acetophenone.



Oxidation of ethyl benzene - Ethyl benzene on oxidation using oxygen and manganese acetate at 126^0C or oxygen and vanadium pentaoxide at 500^0C under pressure gives acetophenone.

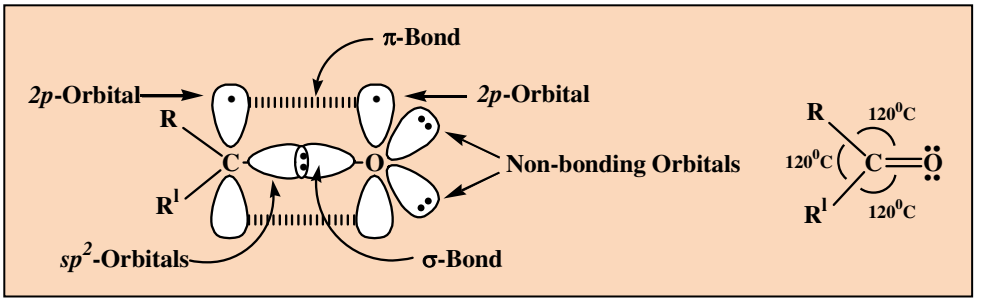


Structure of Carbonyl Group

It can be explained by its geometry and polarity.

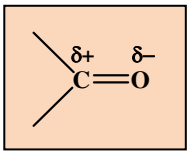
Geometry

In carbonyl group, carbon-oxygen bond is a double bond, it is composed of one σ-bond and one π-bond. Both carbon and oxygen are sp^2 hybridized, three sp^2 hybrid orbitals of carbonyl carbon forms three σ-bonds, one with oxygen by axial overlapping of sp^2 hybrid orbitals of carbon and oxygen and two with other groups attached to it. Fourth unhybridized *2p* orbital of carbon overlap with unhybridized *2p* orbital of oxygen in sidewise fashion (laterally) to form π-bond. Two unused sp^2 orbitals of oxygen are occupied by pairs of electrons. Carbonyl carbon is sp^2 hybridized hence three atoms attached to it lie in same plane and bond angles between attached atoms are approximately 120^0.

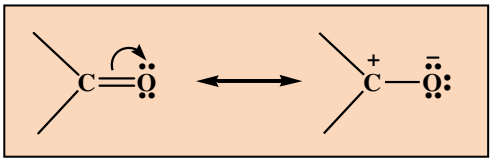


Polarity

Electrons present in π-bond of carbonyl group are not equally shared, these are pulled more toward oxygen because of higher electronegativity of oxygen than carbon. Hence the bond is polarized, with oxygen being slightly negative (δ-) and carbon being slightly positive (δ+).



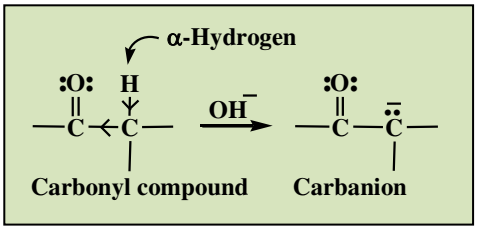
Polar nature of carbonyl group can also be represented by resonance structures which account for high dipole moment (2.3-2.8 D) of carbonyl compounds.

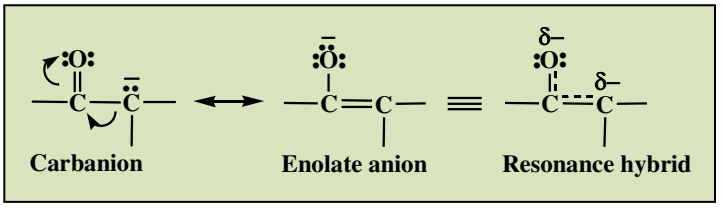


Acidity of α-Hydrogens

α-Carbons - Carbon atoms adjacent to carbonyl carbon.
α-Hydrogens - Hydrogen atoms attached to α-carbons.

Unusual acidity of α-hydrogens in carbonyl compounds is an important characteristic of carbonyl compounds. Carbonyl group is strongly electron withdrawing, oxygen atom attracts electrons towards itself so carbonyl carbon becomes positively charged. This electron withdrawing effect is transmitted next to α-carbon and then to α-hydrogen, because of this bond between α-carbon and α-hydrogen becomes weak. α-Hydrogen is willing to lose electrons to α-carbon because of its lower electronegativity as compared to both α-carbon and oxygen (Electronegativity - H=2.1, C=2.5, O=3.5). So in presence of strong base, α-hydrogen is removed as H^+ to form carbanion, it is stabilized by resonance to give enolate anion, negative charge of anion is delocalized. Thus α-hydrogen in carbonyl compounds is more acidic.





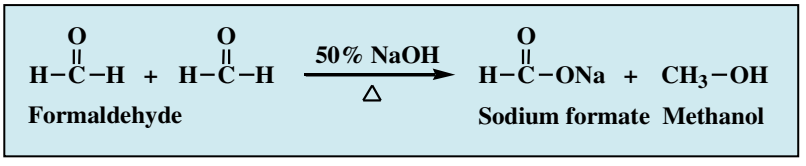
Reactions

Cannizzaro Reaction

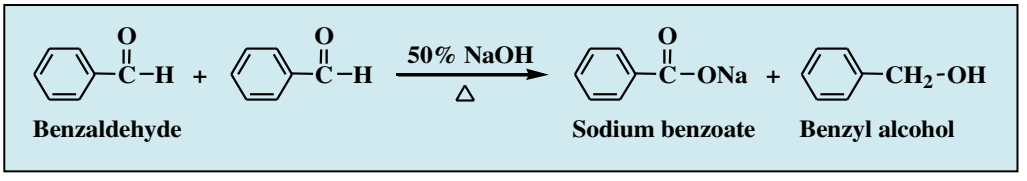
In 1853, Italian chemist Stanislao Cannizzaro gave this disproportion reaction.

In Cannizzaro reaction, aliphatic or aromatic aldehydes do not having α-hydrogen heated with concentrated alkali, one half of aldehydes oxidized to alkali metal salt of carboxylic acid and other half reduced to alcohol.

Example - **Reaction of formaldehyde with 50% NaOH solution**



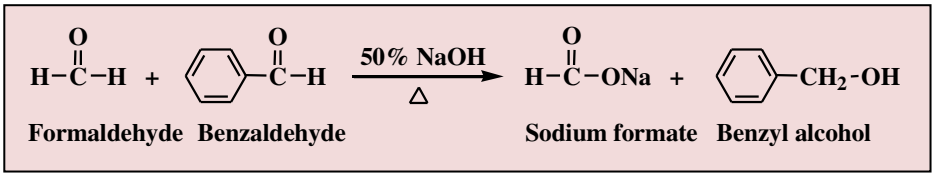
Example - **Reaction of benzaldehyde with 50% NaOH solution**



Cross-Cannizzaro Reaction

In this reaction, two different aldehydes do not having α-hydrogen heated with concentrated alkali, one of aldehydes oxidized to alkali metal salt of carboxylic acid and other reduced to alcohol.

Example - **Reaction of mixture of formaldehyde and benzaldehyde with 50% NaOH**

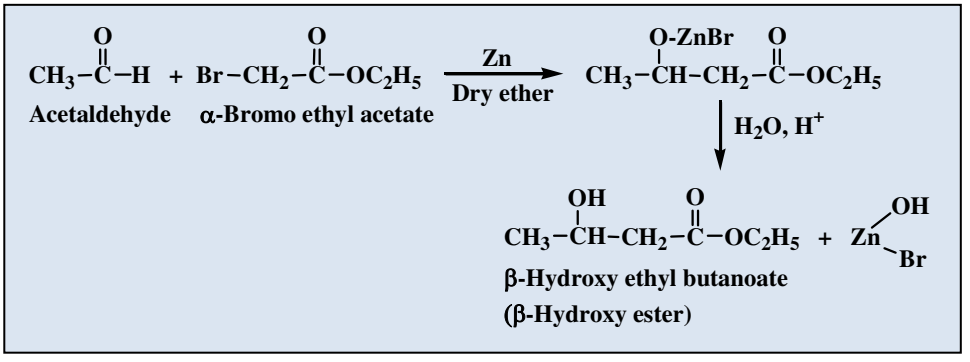


Reformatsky Reaction

In 1887, Russian chemist Sergey Reformatsky gave this reaction.

In Reformatsky reaction, aliphatic or aromatic aldehydes and ketones reacted with α-bromoester and zinc metal in presence of dry ether to give β-hydroxy esters.

Example - **Reaction of acetaldehyde with α-bromo ethyl acetate and zinc metal**



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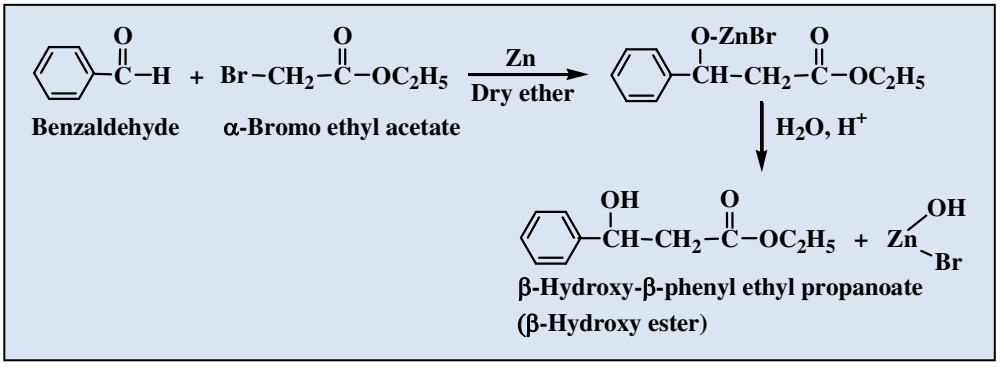
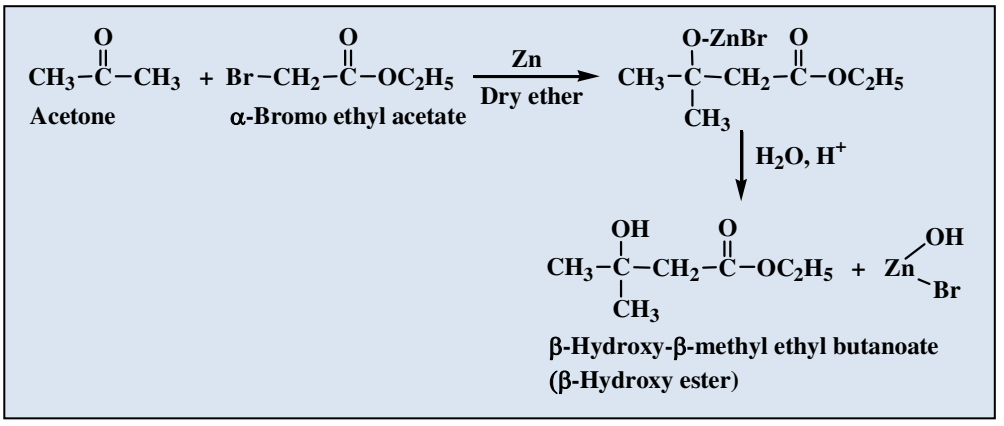
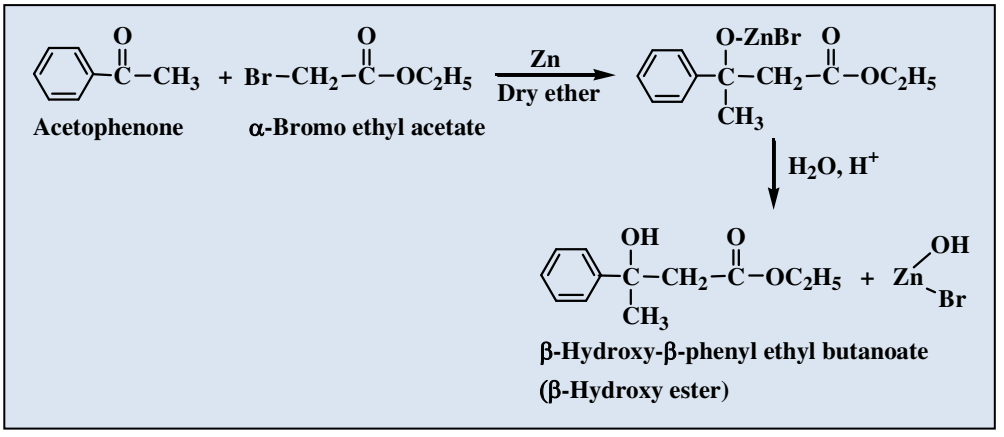


Example - **Reaction of acetone with α-bromo ethyl acetate and zinc metal**



Example - **Reaction of acetophenone with α-bromo ethyl acetate and zinc metal**



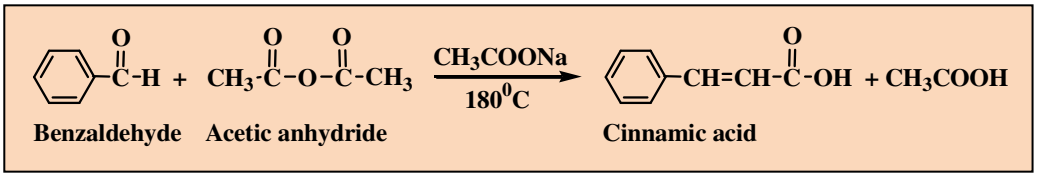
Moreover, these β-hydroxy esters on acid hydrolysis followed by heating yield the α,β-unsaturated acids.

Perkin Reaction

In 1868, English chemist William Perkin gave this reaction.

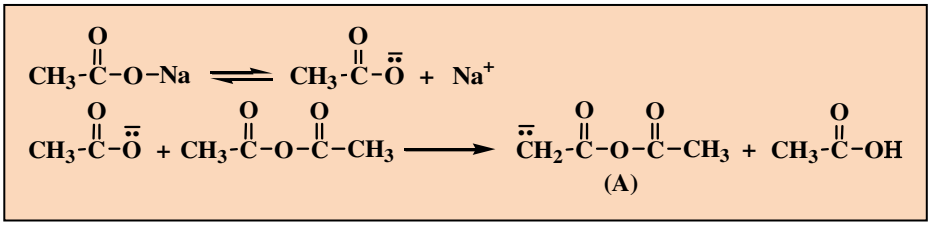
In Perkin reaction, aromatic aldehydes heated with anhydride of aliphatic acid having at least two α-hydrogens and sodium salt of same acid (catalyst) to form α,β-unsaturated acids.

Example - **Reaction of benzaldehyde with acetic anhydride and sodium acetate**

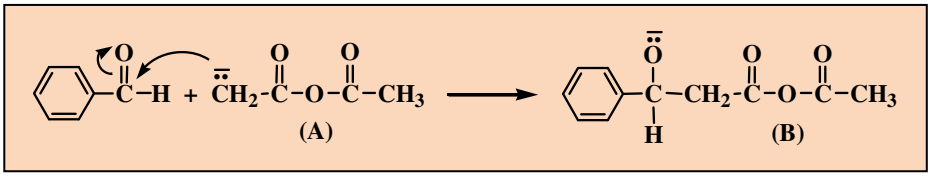


Mechanism

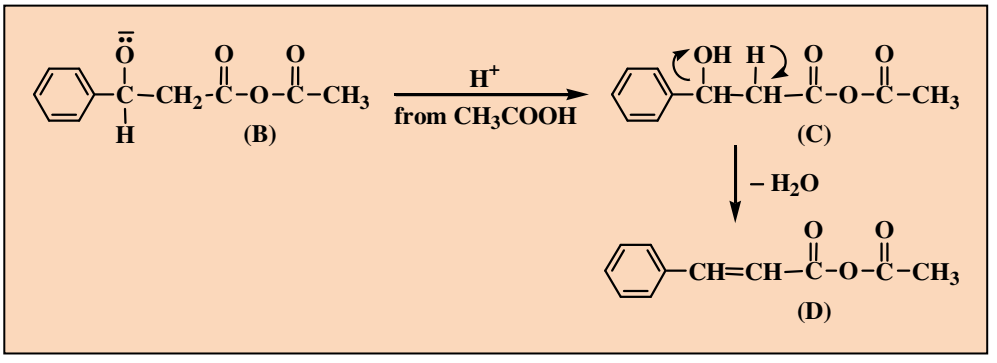
Step-1 : Formation of acetate ion and carbanion (A)



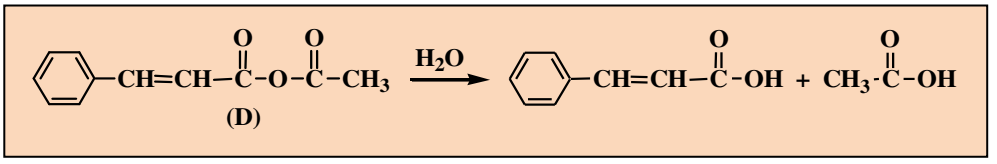
Step-2 : Attack of carbanion (A) on carbonyl carbon of benzaldehyde to give anion (B)



Step-3 : Protonation of anion (B) to give intermediate (C) and formation of α,β-unsaturated mixed anhydride (D)



Step-4 : Hydrolysis of α,β-unsaturated mixed anhydride (D) to give cinnamic acid

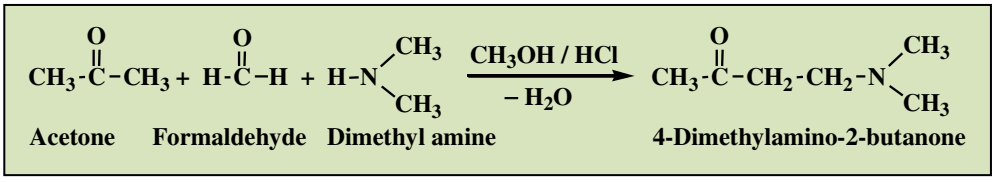


Mannich Reaction

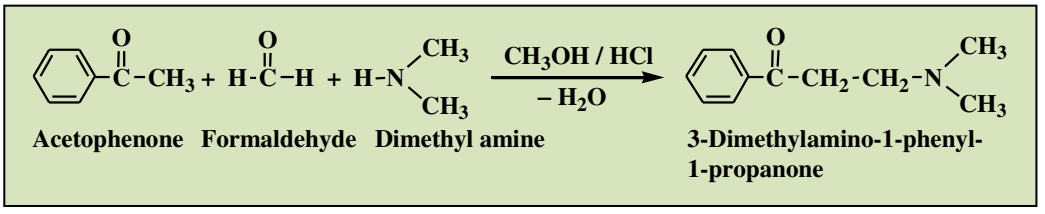
In 1912, German chemist Carl Mannich gave this reaction.

In Mannich reaction, aliphatic or aromatic ketones having α-hydrogen reacted with formaldehyde and ammonia or primary / secondary amine to give β-amino ketones, called Mannich base.

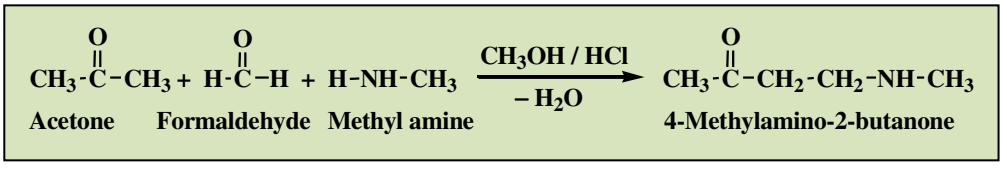
Example - **Reaction of acetone with formaldehyde and dimethyl amine in methanol or hydrochloric acid**



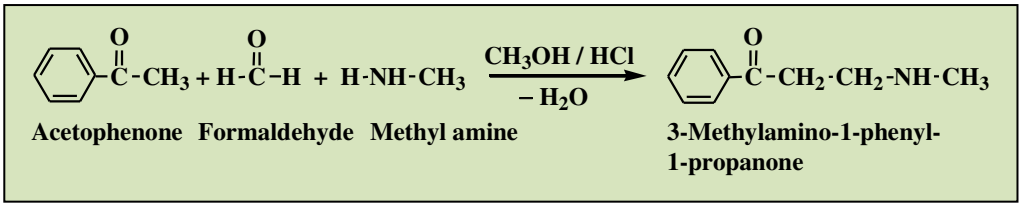
Example - **Reaction of acetophenone with formaldehyde and dimethyl amine in methanol or hydrochloric acid**



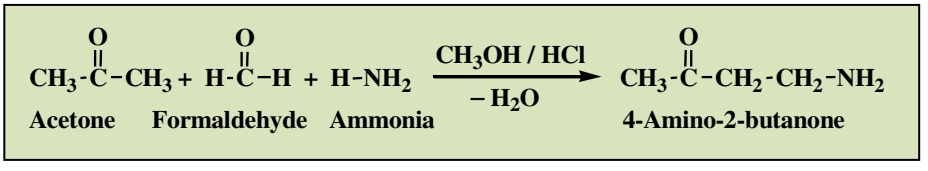
Example - **Reaction of acetone with formaldehyde and methyl amine in methanol or hydrochloric acid**



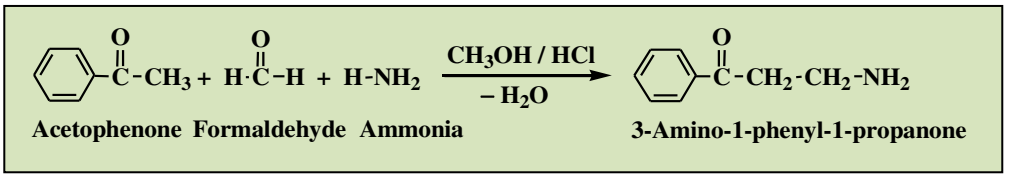
Example - **Reaction of acetophenone with formaldehyde and methyl amine in methanol or hydrochloric acid**



Example - **Reaction of acetone with formaldehyde and ammonia in methanol or hydrochloric acid**



Example - **Reaction of acetophenone with formaldehyde and ammonia in methanol or hydrochloric acid**

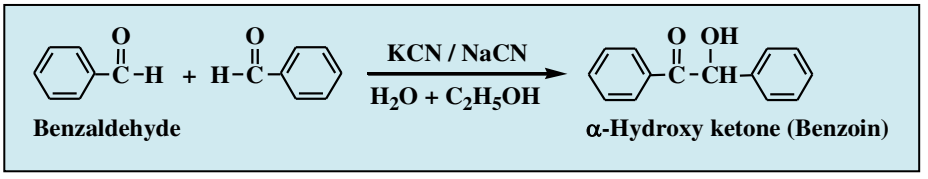


Benzoin Condensation

In 1832, Justus Liebig and Friedrich Wohler observed this reaction for the first time, while use of cyanide as catalyst in the reaction was developed by Nikolay Zinin. In 1903, A. J. Lapworth gave the mechanism of this reaction.

In Benzoin condensation, aromatic aldehydes do not having α-hydrogen treated with aqueous alcoholic potassium cyanide or sodium cyanide to give α-hydroxy ketones called benzoins.

Example - **Reaction of benzaldehyde with aqueous ethanolic solution of potassium cyanide or sodium cyanide**

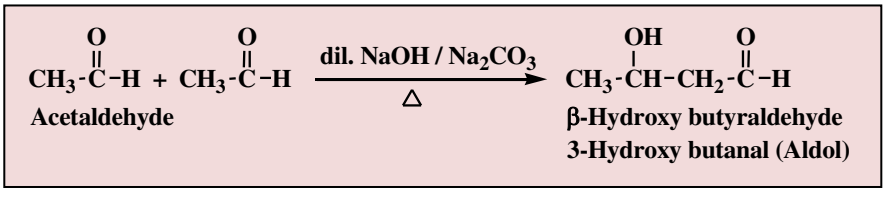


Aldol Condensation

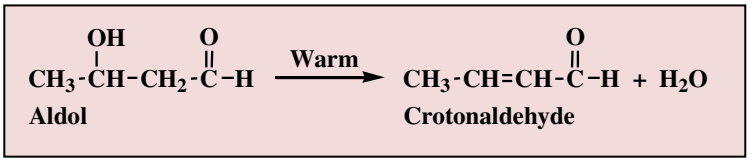
In 1872, Charles Wurtz gave this reaction.

In Aldol condensation, aliphatic or aromatic aldehydes and ketones having α-hydrogen undergo self addition in presence of a base to give β-hydroxy aldehydes (aldols) or β-hydroxy ketones (ketols).

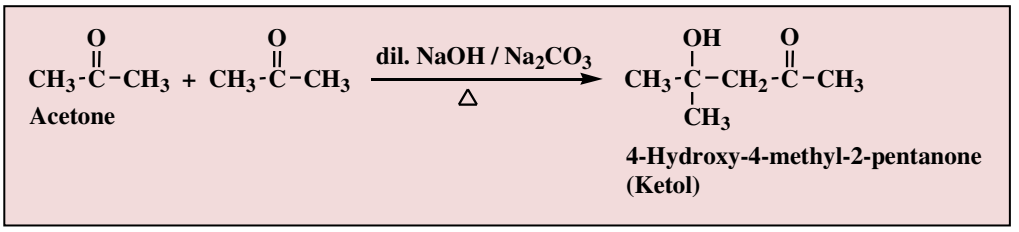
Example - **Reaction of acetaldehyde with dilute sodium hydroxide or sodium carbonate**



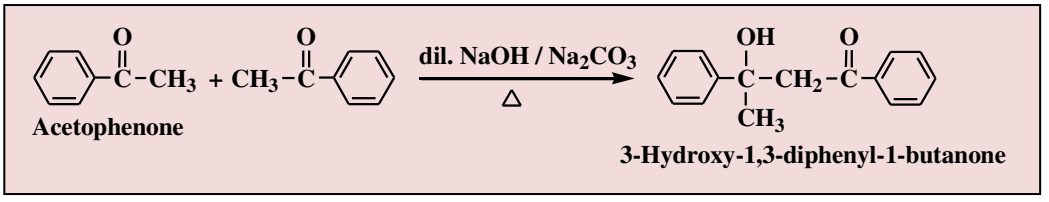
On warming in dilute acid, aldol loses water to form α,β-unsaturated carbonyl compound.



Example - **Reaction of acetone with dilute sodium hydroxide or sodium carbonate**



Example - **Reaction of acetophenone with dilute sodium hydroxide or sodium carbonate**

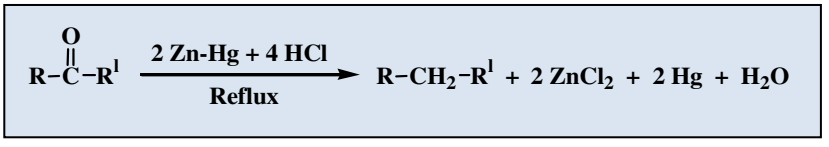


Reductions

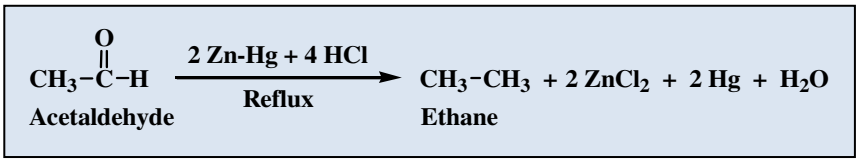
Clemmensen Reduction

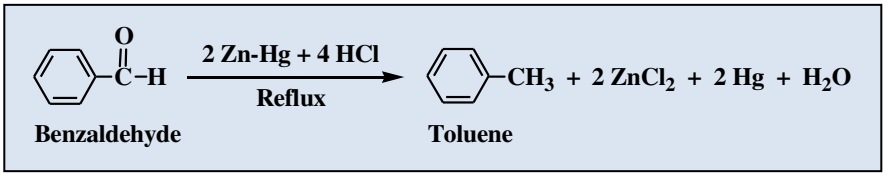
In Clemmensen reduction, aldehydes and ketones refluxed with a large excess of amalgamated zinc i.e. zinc treated with mercury and hydrochloric acid to reduce carbonyl group to methylene group and get corresponding hydrocarbons (actual reduction occurs on surface of zinc).

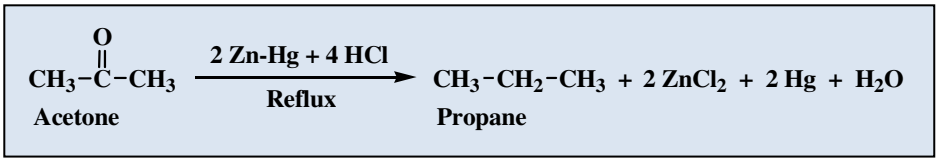
Reagent - **Zn-Hg + HCl** , **Effect** - **>C=O → >CH₂**

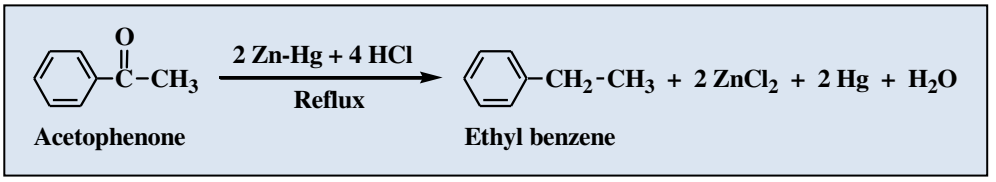


Examples -





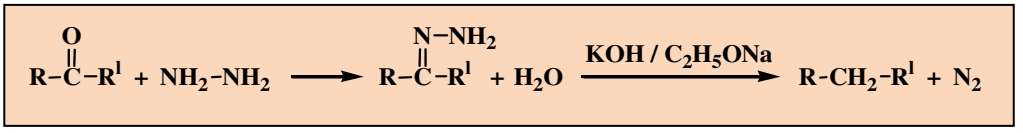




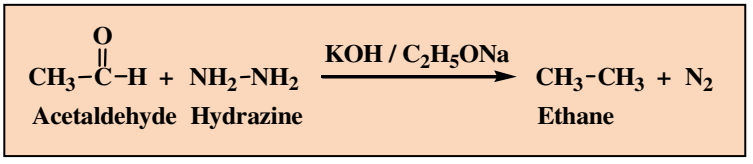
Wolf-Krishner Reduction

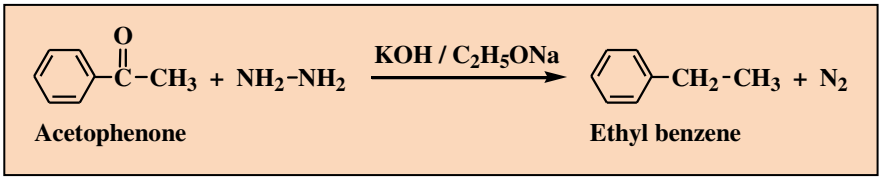
In Wolf-Krishner reduction, aldehydes and ketones heated with hydrazine and a strong base i.e. potassium hydroxide or sodium ethoxide at 450-470^{0}C to reduce carbonyl group to methylene group and get corresponding hydrocarbons (preferably this method is used to reduce ketones).

Reagent - **NH_2-NH_2 + KOH or C_2H_5ONa** , **Effect** - **>C=O → >CH_2**



Examples -

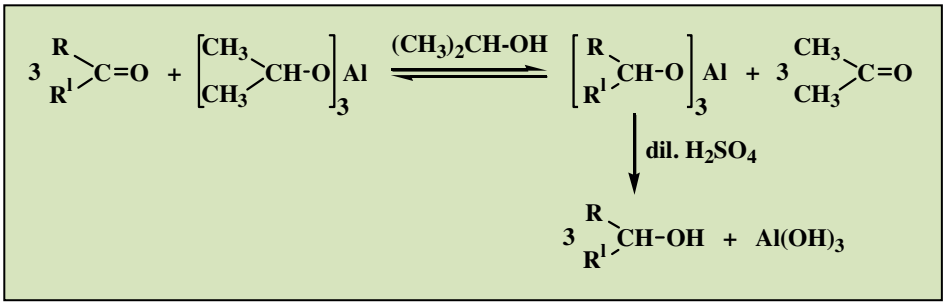




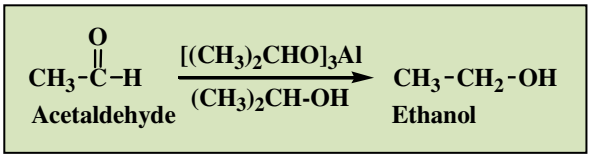
Meerwein-Ponndorf-Verley (MPV) Reduction

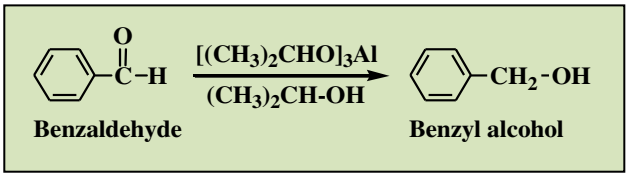
In MPV reduction, aldehydes and ketones treated with aluminium isopropoxide in isopropanol to reduce carbonyl group to alcoholic group and get corresponding alcohols. Aluminium isopropoxide oxidized to acetone during the reaction is continuously removed by slow distillation to shift reaction in forward direction.

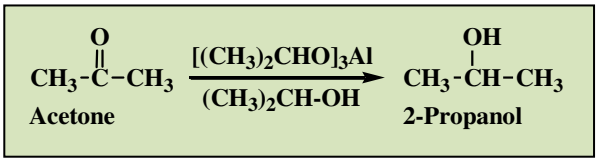
Reagent - **$[(CH_3)_2CHO]_3Al]$ + $(CH_3)_2CH$-OH** , **Effect** - **>C=O → >CH-OH**

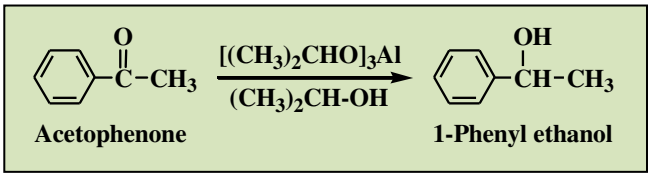


Examples -







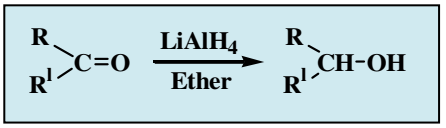


Other reducible groups like double bond, nitro group etc. present in carbonyl compounds remains unaffected in MPV reduction.

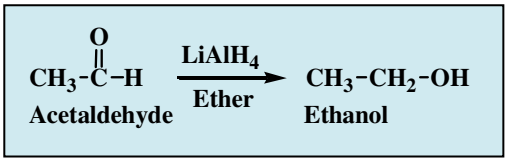
Reduction by Lithium Aluminium Hydride ($LiAlH_4$)

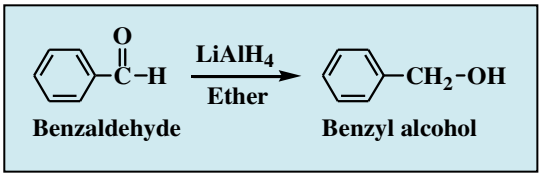
In reduction by lithium aluminium hydride, aldehydes and ketones reacted with lithium aluminium hydride in ether to reduce carbonyl group to alcoholic group and get corresponding alcohols.

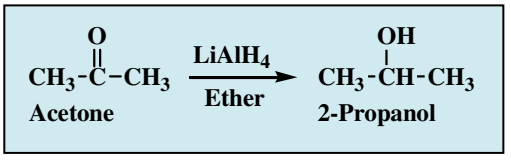
Reagent - **$LiAlH_4$ + ether** , **Effect** - **>C=O → >CH-OH**

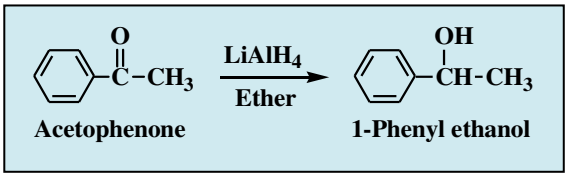

R
R¹
C=O
LiAlH4
Ether
R
R¹
CH-OH

Examples -


O
CH3-C-H
Acetaldehyde
LiAlH4
Ether
CH3-CH2-OH
Ethanol


O
C-H
Benzaldehyde
LiAlH4
Ether
CH2-OH
Benzyl alcohol

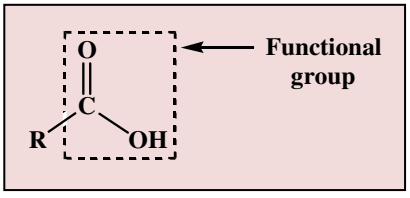

O
CH3-C-CH3
Acetone
LiAlH4
Ether
OH
CH3-CH-CH3
2-Propanol


O
C-CH3
Acetophenone
LiAlH4
Ether
OH
CH-CH3
1-Phenyl ethanol

Carboxylic Acids

Introduction

Carboxylic acids are most common organic compounds. These contains carboxyl group (-COOH) i.e. carbonyl group joined to hydroxyl group and there name is derived from carbonyl (>C=O) and hydroxyl (-OH) groups. Although carboxyl group is virtually a union of one carbonyl and one hydroxyl group, properties of these constituent functional groups are profoundly modified by mutual interaction to give carboxylic acids their own distinctive properties. Carboxyl group is an independent functional group, carbonyl of carboxyl group does not give reactions shown by aldehydes and ketones and its hydroxyl group is not alcoholic.



Where, R - alkyl or aryl groups

Carboxylic acid such as acetic acid is known for centuries, numbers of natural products are carboxylic acids or they are derived from them. Carboxylic acids are parent compounds of a large group of derivatives that includes acyl chlorides, acid anhydrides, esters and amides.

According to number of -COOH groups present in molecule, carboxylic acids are classified as mono, di, tri, tetra and poly carboxylic acids. These are aliphatic or aromatic, saturated or unsaturated. Long chain saturated mono carboxylic acids are commonly called as fatty acids because many of them are obtained by hydrolysis of animal fats or vegetable oils.

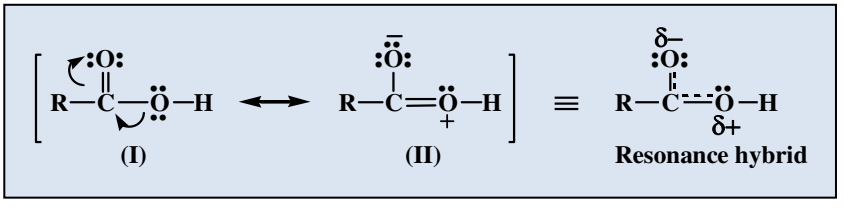
Structure and Reactivity

Structure and Reactivity of Carboxylic Group

It can be explained according to the resonance theory on the basis of non-equivalent resonance stabilization in carboxylic acid and powerful equivalent resonance stabilization in carboxylate anion.

Non-equivalent resonance stabilization in carboxylic acid

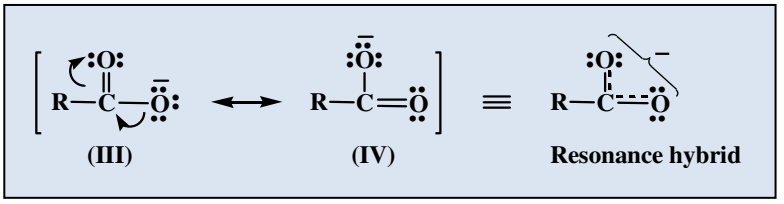
Resonating structures of carboxylic acid -



As resonating structures I, II are non-equivalent, this resonance is not much important.

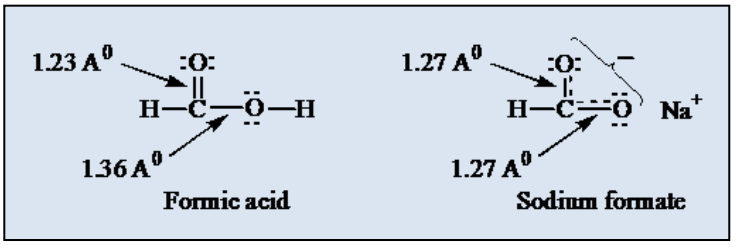
Equivalent resonance stabilization in carboxylate anion

Resonating structures of carboxylate anion -



According to X-ray and electron diffraction studies resonating structures III and IV have equal stability and distribution of negative charge on both oxygens, so equivalent resonance.

Non-equivalent and equivalent resonance was supported by evidence of bond lengths in carboxylic acid (e.g. formic acid) and carboxylate anion (e.g. sodium formate). In formic acid two carbon-oxygen bonds have different bond lengths whereas in sodium formate bond lengths are same. Also, bond lengths in sodium formate are of intermediate length between those of normal double and single carbon-oxygen bonds.

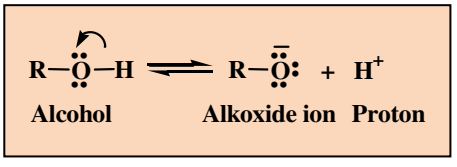


In carboxylic acid, carbonyl group is rather inert. Due to resonance, C=O bond has some single bond character and C-OH bond has some double bond character. So length of C=O bond is more than that of pure C=O bond (1.22 A^0) and length of C-OH bond is less than pure C-OH bond (1.43 A^0).

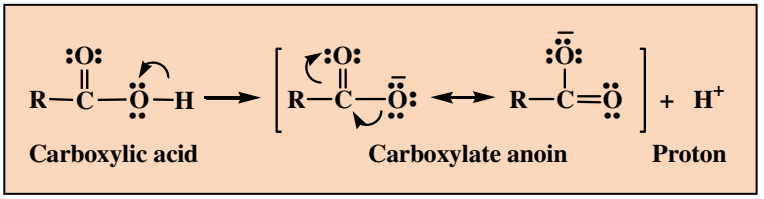
Acidity or Acid Strength

Carboxylic acids are much weaker acids than mineral acids and are more acidic than alcohols and phenols. More acidity of carboxylic acids than alcohols is because of powerful resonance stabilization of carboxylate anion, which is possible only in carboxylic acids.

When alcohol releases proton, alkoxide ion is formed. Oxygen is attached to sp^3 hybridized carbon in alcohols, so resonance stabilization in alkoxide ion is not possible.



When carboxylic acid releases proton, carboxylate anion is formed. Oxygen is attached to sp^2 hybridized carbon in carboxylic acids, so powerful resonance stabilization in carboxylate anion is possible.



More acidity of carboxylic acids than phenols cannot be explained only by resonance stabilization. Here solvation of anion, inductive effect and other factors are equally important.

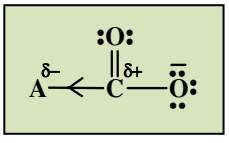
Effect of Substituents on Acidity or Acid Strength

In carboxylic acids, factor that stabilizes carboxylate anion, increases acidity or acid strength and vice versa.

Case-I - 'A' as electron withdrawing group (-I effect)

Electron pair forming A-C bond is pulled towards 'A', so carboxylic carbon develops partial positive charge and helps in dispersing or spreading negative charge on carboxylate anion. It results in stabilization of carboxylate anion and consequently acidity increases.

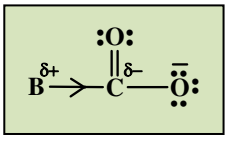
Substituents of type 'A' : -Cl, -Br, -I, -CN, $-NO_2$ etc.



Case-II - 'B' as electron releasing group (+I effect).

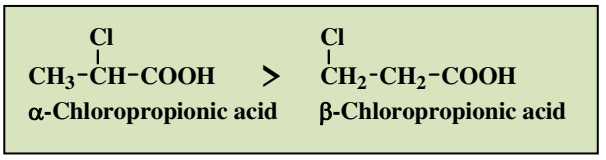
Electron pair forming B-C bond is shifted towards 'C', so carboxylic carbon develops partial negative charge and becomes negatively charged species. It results in destabilization of carboxylate anion and consequently acidity decreases.

Substituents of type 'B' : $-CH_3$, $-C_2H_5$ etc.



Being electron withdrawing, halogens (-Cl, -Br, -I) strengthen acids whereas electron releasing alkyl groups ($-CH_3$, $-C_2H_5$) weaken acids. So acetic acid (CH_3COOH) is ten times weaker than formic acid (HCOOH) while propionic acid (CH_3CH_2COOH) is still weaker than acetic acid. Chloroacetic acid ($Cl-CH_2COOH$) is 100 times stronger than acetic acid whereas trichloroacetic acid ($Cl_3-C-COOH$) is 10,000 times stronger than acetic acid.

α-Chloropropionic acid is stronger than β-chloropropionic acid because of more -I effect of chlorine at α-position than at β-position.



Order of electron withdrawing effect of halogens - F > Cl > Br > I.

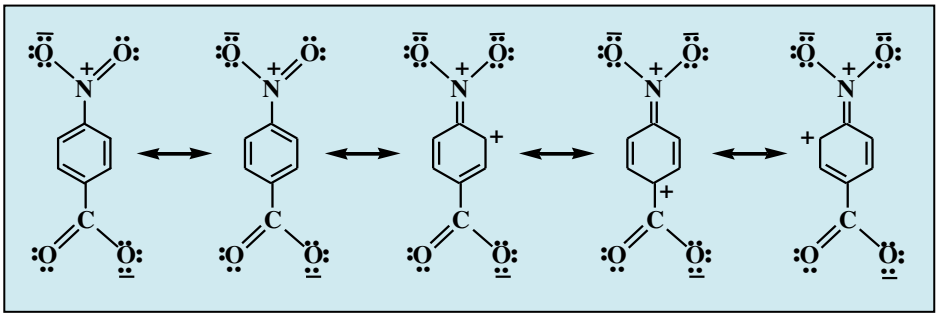
Effect of Substituents on Acidity or Acid strength of Aromatic Acids

Aliphatic carboxylic acids - Acidity or acid strength depends on inductive effect and position of electron withdrawing or releasing group.

Aromatic carboxylic acids - Acidity or acid strength depends on inductive effect, position of electron withdrawing or releasing group and resonance effect.

Here electron withdrawing groups (-CN, $-NO_2$) increases acidity of benzoic acid and makes it stronger whereas electron releasing groups ($-CH_3$, -OH, $-NH_2$) decreases acidity of benzoic acid and makes it weaker.

Electron withdrawing groups i.e. meta directing groups like $-NO_2$ decreases electron density at ortho and para positions of ring by -R effect.

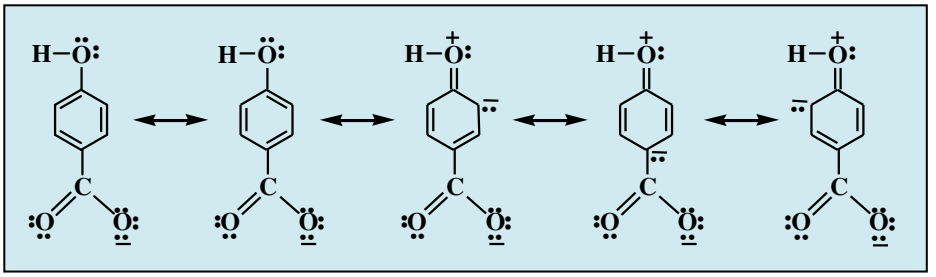


If -COOH group is present at ortho or para positions with respect to electron withdrawing groups, carboxylate anion get stabilized by dispersing of negative charge and results in increase in acidity, so benzoic acid is less acidic than *o,p*-nitrobenzoic acid. *p*-nitrobenzoic acid is weaker than *o*-nitrobenzoic acid due to ortho effect of nitro group. Strong -I effect of nitro group close to carboxylate anion causes strong delocalization of negative charge of carboxylate anion. If -COOH group is present at meta position with respect to electron withdrawing groups, carboxylate anion get stabilized by withdrawing electrons from ring carbon bearing carboxylate anion primarily by -I effect and causes strong delocalization of negative charge.

Sequence of decrease in acidity is -

o-nitrobenzoic acid > *p*-nitrobenzoic acid > *m*-nitrobenzoic acid > benzoic acid

Electron releasing groups i.e. ortho, para directing groups like $-CH_3$, -OH, $-NH_2$ increases electron density at ortho and para positions of ring by +R effect.



If -COOH group is present at ortho or para positions with respect to electron releasing groups, carboxylate anion get destabilized by increasing negative charge and results in decrease in acidity, so benzoic acid is more acidic than *p*-hydroxybenzoic acid. *o*-hydroxybenzoic acid is stronger than benzoic acid due to ortho effect of hydroxy group, strong -I effect of hydroxy group close to carboxylate anion causes strong delocalization of negative charge of carboxylate anion. Nearly all ortho substituents exert an unusually large effect of acid strengthening, whether they are electron withdrawing or releasing. All ortho substituted acids are stronger than para or meta substituted acids, sterric effects and H-bonding are much more important than other factors involved.

Sequence of decrease in acidity is -

o-hydroxybenzoic acid > *m*-hydroxybenzoic acid > benzoic acid > *p*-hydroxybenzoic acid

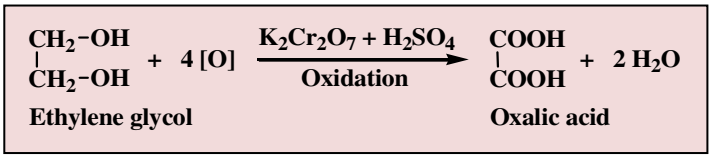
Preparations and Reactions

Oxalic Acid (Ethane-1,2-Dioic Acid or Ethandioic Acid) (HOOC-COOH)

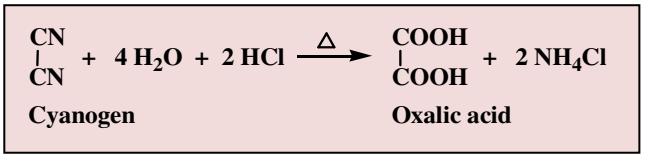
In 1829, French chemist Gay-Lussac discovered isolation of oxalic acid from saw dust with sodium hydroxide. Oxalic acid occurs in wood sorrel (oxalic acetosella) as potassium hydrogen oxalate. It occurs extensively in plant kingdom.

Preparations

Oxidation of ethylene glycol - Ethylene glycol on oxidation using chromic acid gives oxalic acid.

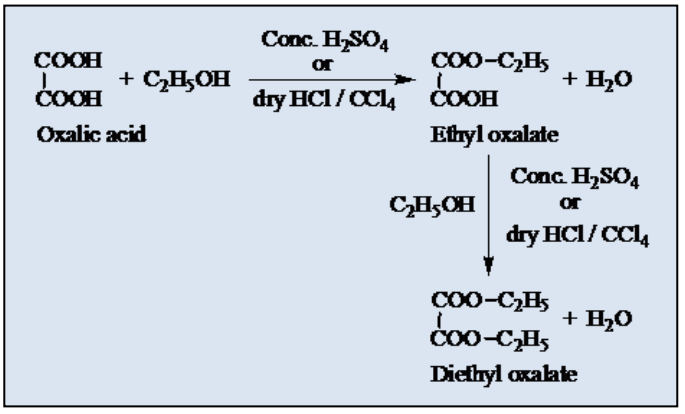


Hydrolysis of cyanogen - Cyanogen on hydrolysis using concentrated hydrochloric acid produces oxalic acid.

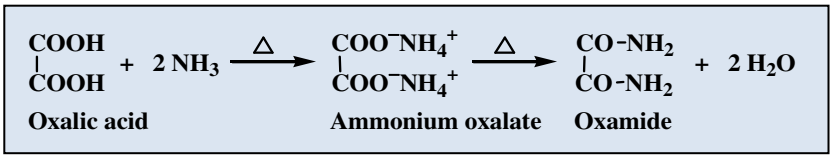


Reactions

Reaction with ethanol (esterification) - Oxalic acid treated with ethanol in presence of concentrated sulphuric acid or dry hydrogen chloride or carbon tetrachloride to give two series of esters i.e. ethyl oxalate and diethyl oxalate.

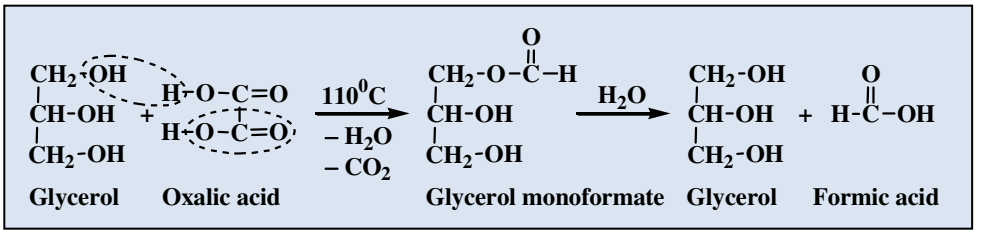


Reaction with ammonia - Oxalic acid reacted with ammonia to form ammonium oxalate, it on heating loses water to give oxamide.

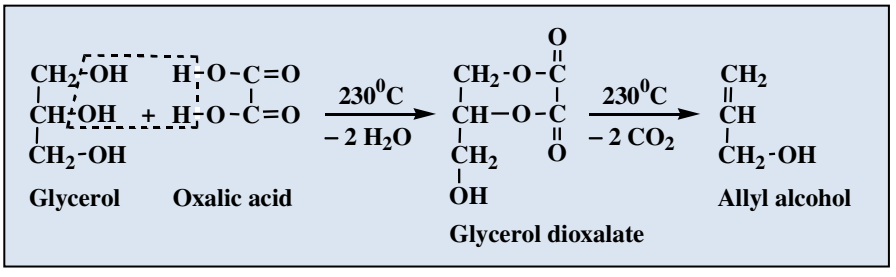


Reaction with glycerol - Oxalic acid reacted with glycerol at different temperatures.

Oxalic acid reacted with glycerol at 110^{0}C to give glycerol monoformate, it on hydrolysis gives formic acid and glycerol is regenerated.

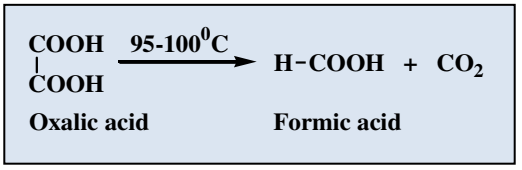


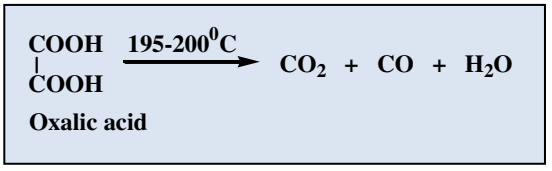
Oxalic acid reacted with glycerol at 230^{0}C to give glycerol dioxalate, it on loss of two molecules of carbondioxide gives allyl alcohol.



Action of heat - Oxalic acid heated at different temperatures to give different products.

Oxalic acid heated at 95-100^{0}C to give formic acid with elimination of carbondioxide and at 195-200^{0}C decomposed into carbon dioxide, carbon monoxide and water.



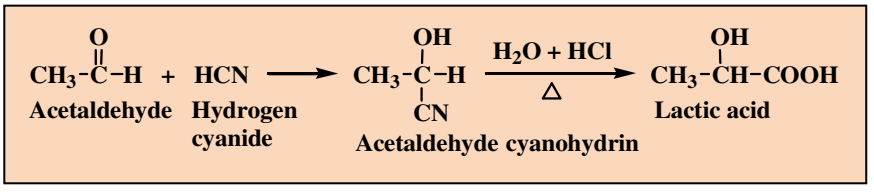


Lactic Acid (α-Hydroxy Propionic Acid or 2-Hydroxy Propanoic Acid) (CH_3-CHOH.COOH)

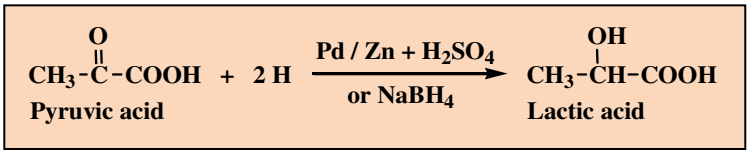
In 1780, Scheele isolated lactic acid from sour milk. It is formed by fermentation of lactose (milk sugar) by lactic ferment or lactic bacilli. It is also found in blood and muscle tissue.

Preparations

Reaction of acetaldehyde with hydrogen cyanide - Acetaldehyde on reaction with hydrogen cyanide forms acetaldehyde cyanohydrin, it is then acid hydrolyzed to give lactic acid.

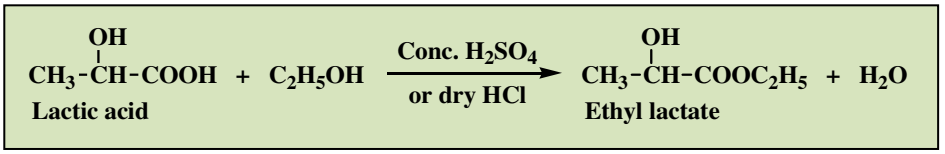


Reduction of pyruvic acid - Pyruvic acid on reduction using palladium or zinc in presence of sulphuric acid or sodium borohydride gives lactic acid.

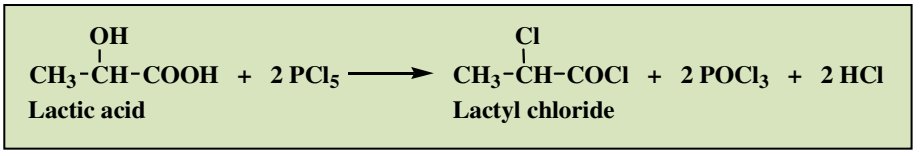


Reactions

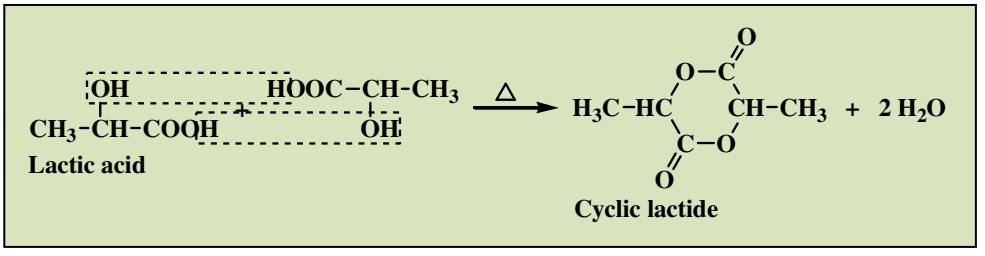
Reaction with ethanol (esterification) - Lactic acid treated with ethanol in presence of concentrated sulphuric acid or dry hydrogen chloride to give ethyl lactate.



Reaction with phosphorous pentachloride - Lactic acid treated with phosphorous pentachloride to give lactyl chloride.

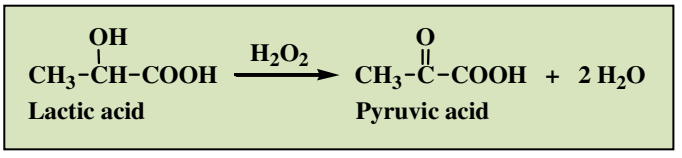


Action of heat - Lactic acid heated to give cyclic ester called lactide.

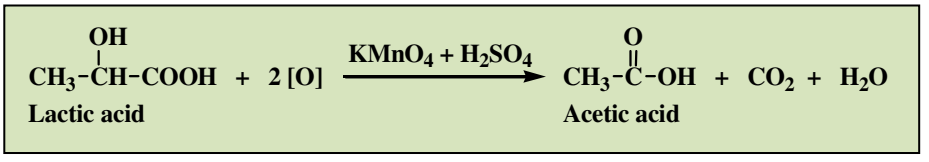


Oxidation - Lactic acid can be oxidized using different oxidizing agents.

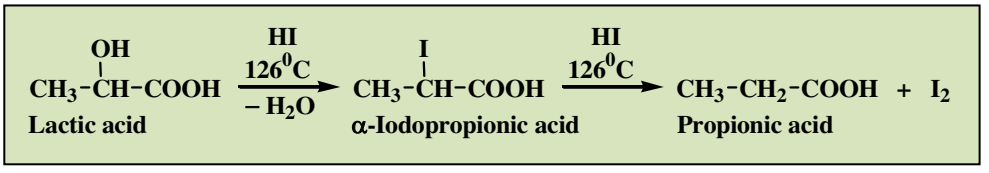
Lactic acid oxidized by weak oxidizing agent like hydrogen peroxide to give pyruvic acid.



Lactic acid oxidized by acidified potassium permanganate to give acetic acid.



Reduction - Lactic acid reduced with hydroiodic acid at 126^{0}C to give propionic acid.

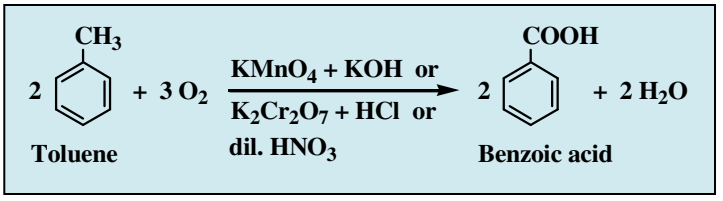


Benzoic Acid (Benzene Carboxylic Acid) (C_6H_5-COOH)

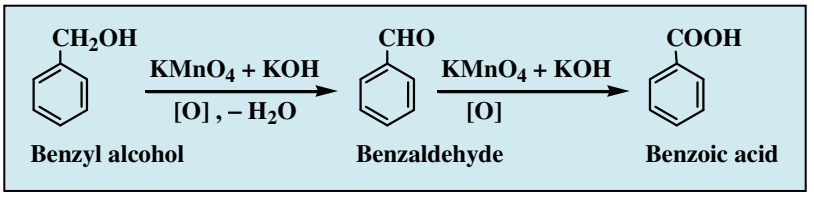
In 1832, Leibig and Wohler established structure of benzoic acid. It is monocarboxylic aromatic acid. It was first obtained by Scheele from gumbenzoin and hence called as benzoic acid. It is found in the form of benzyl ester in resins and peru-balsams. It is also present in urine of horses and oxen in the form of benzoyl glycine (hippuric acid).

Preparations

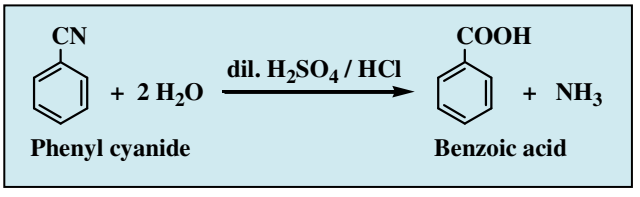
Oxidation of toluene - Toluene on oxidation using alkaline potassium permanganate or dilute nitric acid or acidic potassium dichromate gives benzoic acid.



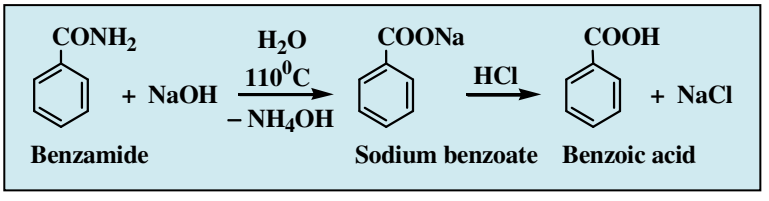
Oxidation of benzyl alcohol - Benzyl alcohol on oxidation using alkaline potassium permanganate gives benzaldehyde, it is then further oxidized to give benzoic acid.



Hydrolysis of phenyl cyanide (phenyl nitrile) - Phenyl cyanide on hydrolysis using mineral acids i.e. dilute sulphuric acid or hydrochloric acid gives benzoic acid.

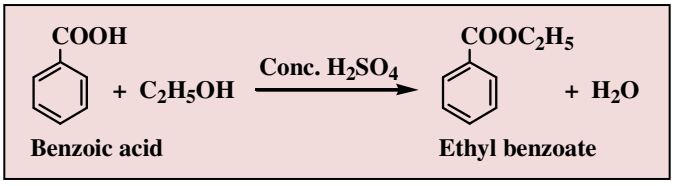


Reaction of benzamide with sodium hydroxide - Benzamide on reaction with sodium hydroxide gives sodium benzoate, it is then acidified to give benzoic acid.

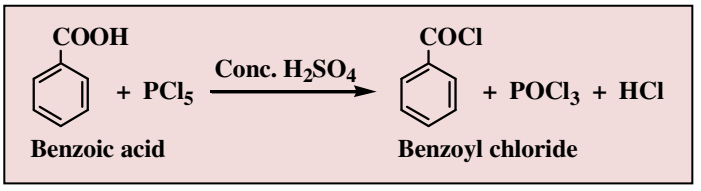


Reactions

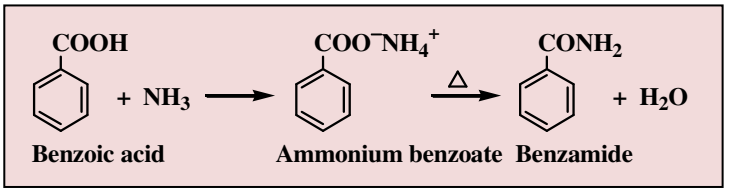
Reaction with ethanol (esterification) - Benzoic acid treated with ethanol in presence of concentrated sulphuric acid to give ethyl benzoate.



Reaction with phosphorous pentachloride - Benzoic acid treated with phosphorous pentachloride to give benzoyl chloride.



Reaction with ammonia - Benzoic acid reacted with ammonia to form ammonium benzoate, it on further heating gives benzamide.

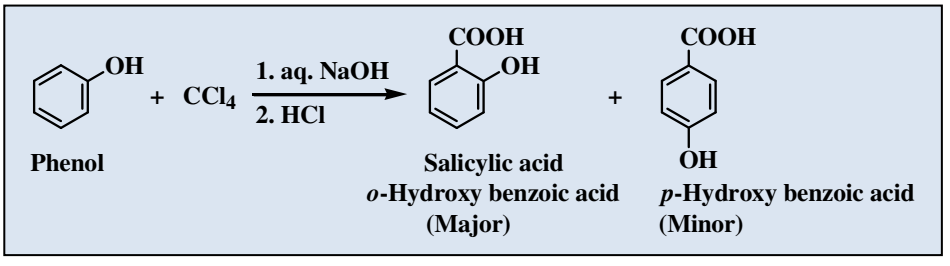


Salicylic Acid (*o*-Hydroxy Benzoic Acid) (C_6H_4-OH.COOH)

Salicylic acid is a naturally occurring carboxylic acid found in certain plants. It is used in making aspirin and in foodstuffs and dyestuffs industries. It is used as fungicide.

Preparations

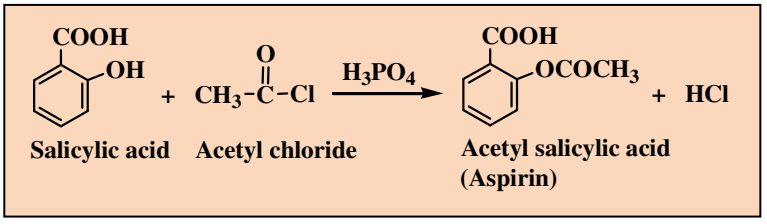
Reimer-Tiemann reaction - Reaction of phenol with carbontetrachloride in aqueous sodium hydroxide solution followed by acid hydrolysis gives salicylic acid.



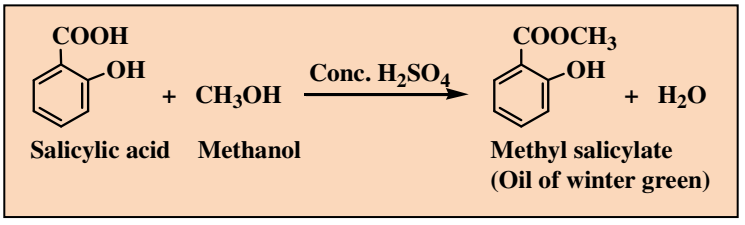
Salicylic acid (*o*-isomer) is more volatile and can be separated by steam distillation.

Reactions

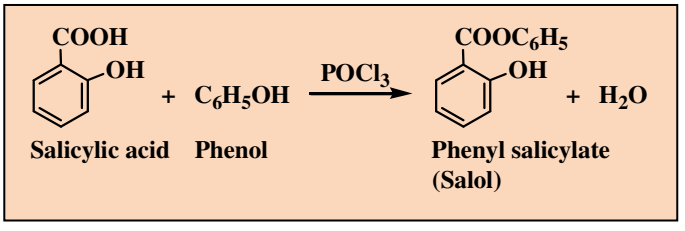
Reaction with acetyl chloride - Salicylic acid heated with acetyl chloride in presence of phosphoric acid, acetylation of -OH group takes place to give acetyl salicylic acid (aspirin).



Reaction with methanol (esterification) - Salicylic acid treated with methanol in presence of concentrated sulphuric acid, esterification of -COOH group takes place to give methyl salicylate (oil of winter green).



Reaction with phenol (esterification) - Salicylic acid treated with phenol in presence of phosphorous oxychloride, esterification of -COOH group takes place to give phenyl salicylate (salol).



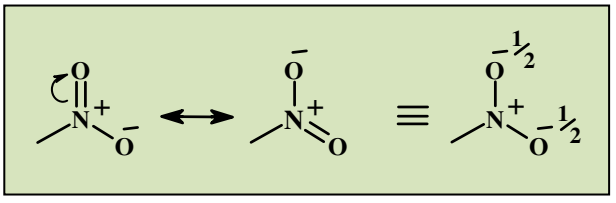
Aromatic Nitro Compounds

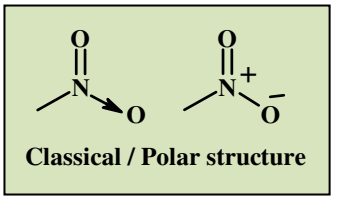
Introduction

Aromatic nitro compounds (nitro arenes) are derivatives of aromatic hydrocarbons in which one or more ring hydrogens are replaced by nitro (-NO_2) group. Process of replacement of one or more hydrogens of benzene nucleus by nitro group is known as nitration. Nitro group is most highly oxygenated form of nitrogen.

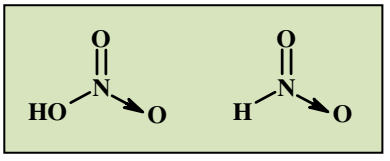
General formula : Ar-NO_2

Representation of Nitro Group





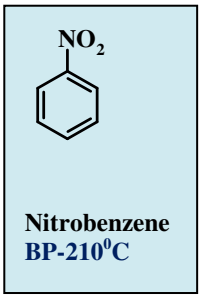
Aromatic nitro compounds are like derivatives of nitric acid (-OH replaced by aromatic substrate) and nitrous acid (-H replaced by aromatic substrate).

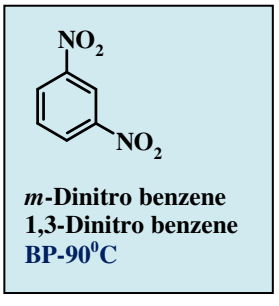


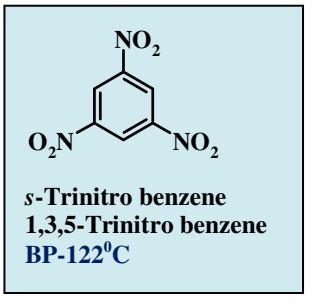
Aromatic nitro compounds are more easily available than aliphatic nitro compounds because introduction of -NO_2 into benzene / aromatic ring is very easy (electrophilic substitution). Replacement of hydrogen by -NO_2 in aliphatic compounds is quite difficult.

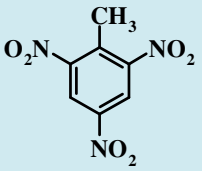
Nomenclature

For naming aromatic nitro compounds, insert word 'Nitro' in front of name of parent hydrocarbon. Here position of -NO_2 is indicated using prefix *o*, *m*, *p* or numerical 1,2,3 ….

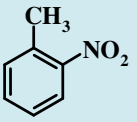




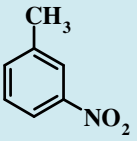




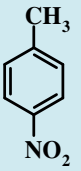
2,4,6-Trinitro toluene
TNT
MP-80^{0}C



***o*-Nitro toluene**
2-Nitro toluene
BP-122^{0}C



***m*-Nitro toluene**
3-Nitro toluene
BP-233^{0}C



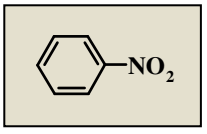
***p*-Nitro toluene**
4-Nitro toluene
MP-52^{0}C

Preparation and Reactions

Nitrobenzene

Nitrobenzene is chemical name of oil of mirbane. It is pale yellow oily liquid, heavier than water, volatile in steams, toxic, quickly absorbed through skin. Its vapours are poisonous. It is insoluble in water but soluble in alcohol, ether, benzene. NO_2 group is highly polar. Its di/tri-nitro derivatives are explosive.

MF : $C_6H_5NO_2$, BP : 210^{0}C , Odour : Pleasant



Nitrating agents - These are compounds / reagents or mixture of compounds / reagents used as the source of electrophilic -NO_2.

1. Conc. HNO_3 (Sp. Gravity - 1.5)
2. Fuming HNO_3 (8-10% N_2O_5 dissolved in Conc. HNO_3)
3. Nitrating mixture (Fuming/Conc. HNO_3 + Conc. H_2SO_4/CH_3COOH/$CH_3COOCOCH_3$/BF_3), H_2SO_4 protonate HNO_3 and produces NO_2^+
4. Dil. HNO_3 (in case of highly activated compounds; Phenol)
5. Pyridinium nitrate + pyridine
6. N_2O_5 + $AlCl_3$

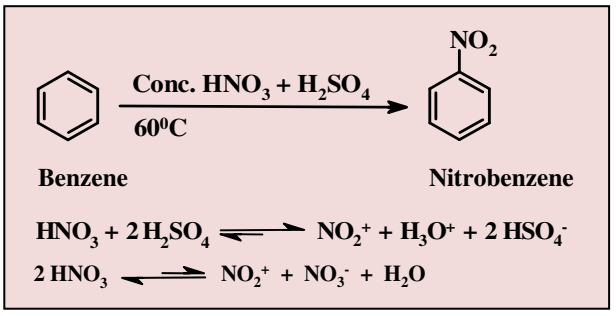
Nitrating agent selection - It depends on the nature of compound and number of -NO_2 to be introduced.

First -NO_2 is easily introduced into aromatic ring but introduction of second -NO_2 is difficult (ring deactivation). So, higher concentration of acid and longer time of reaction is required.

Activating group (-OH, -NH_2, -CH_3) facilitate the nitration whereas deactivating group (-NO_2, -CHO, -COOH) retard nitration.

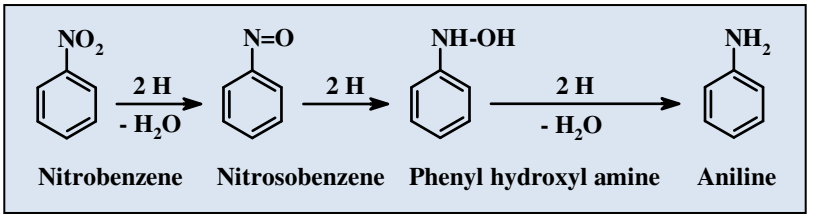
Preparation

Direct nitration of benzene / laboratory method - Benzene on direct nitration using mixture of concentrated nitric acid and sulphuric acid at 60^{0}C gives nitrobenzene.

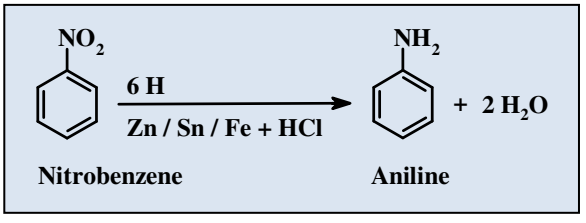


Reactions

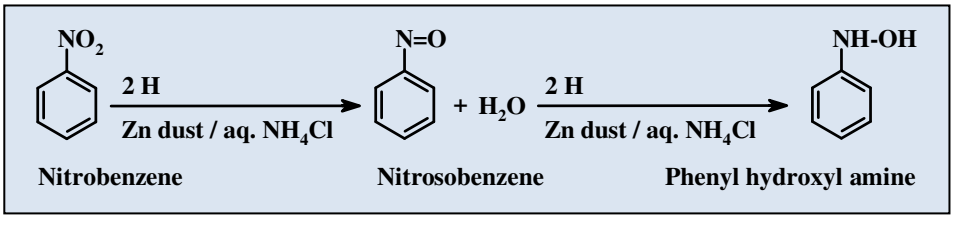
Reduction in acidic and neutral medium - Nitrobenzene reduced with different reducing agents in acidic and neutral medium to give variety of compounds.



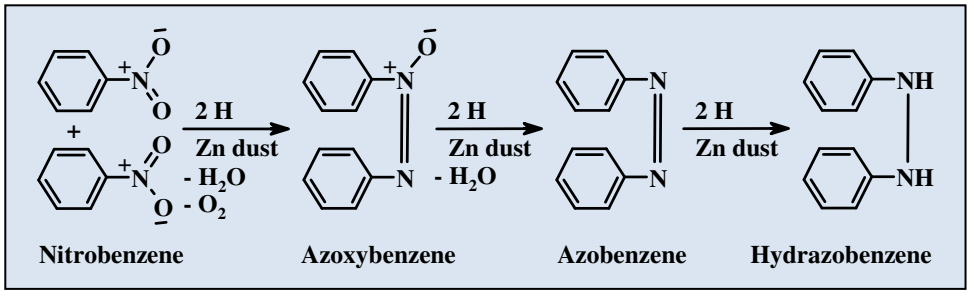
Reduction in acidic medium - Nitrobenzene reduced with metal and acid to give aniline.



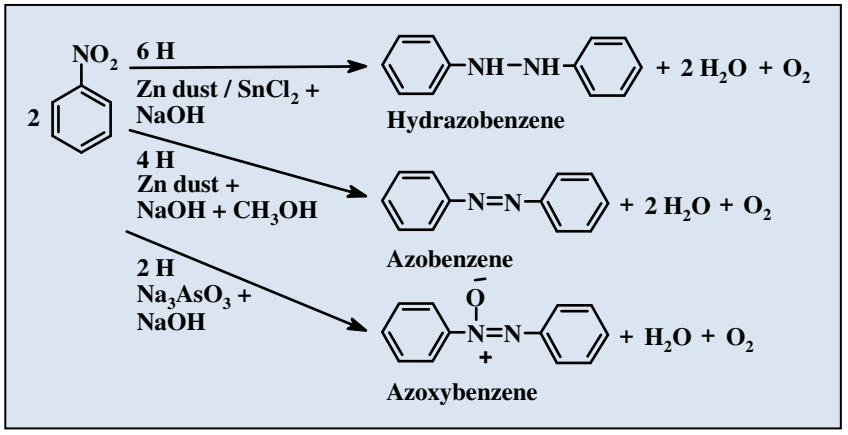
Reduction in neutral medium - Nitrobenzene reduced with zinc dust and boiling aqueous ammonium chloride to give nitrosobenzene, which readily reduced to phenyl hydroxyl amine.



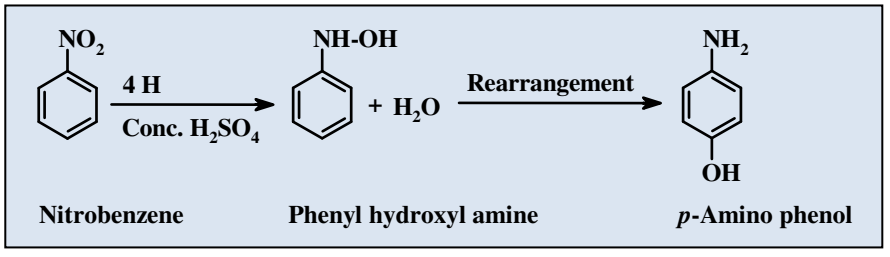
Reduction in alkaline / basic medium - Nitrobenzene reduced with different reducing agents in alkaline / basic medium to give variety of polynuclear compounds.



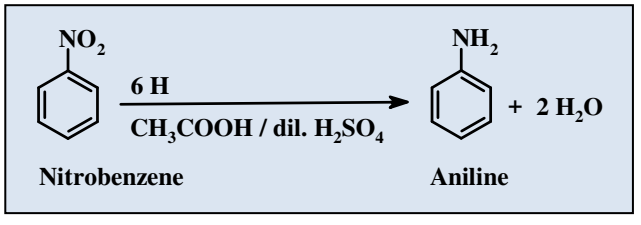
Reduction - Nitrobenzene reduced with zinc dust or stannous chloride in alkaline medium to give hydrazobenzene. It reduced with zinc dust in alkaline ethanolic medium to give azobenzene. It reduced with sodium arsenite in alkaline medium to give azoxybenzene.

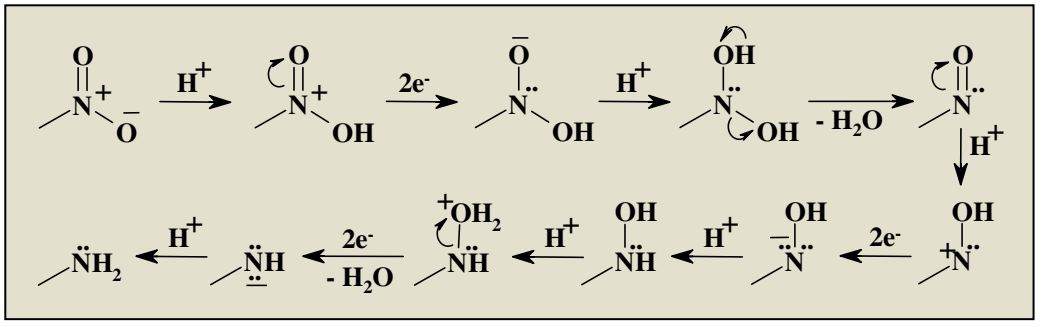


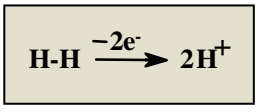
Electrolytic reduction in strongly acidic conditions - Nitrobenzene reduced electrolytically with concentrated sulphuric acid to give phenyl hydroxyl amine, which readily rearranged to give *p*-amino phenol.



Electrolytic reduction in weakly acidic conditions - Nitrobenzene reduced electrolytically with acetic acid or dilute sulphuric acid to give aniline.







In electrolytic reduction, final product depends upon medium and pH of solution.

Amino Compounds (Amines)

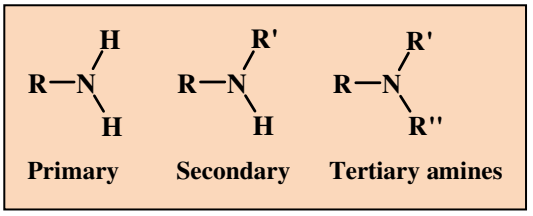
Introduction

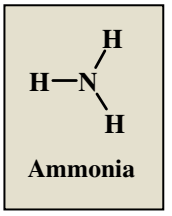
Amino compounds (amines) are derivatives of ammonia in which one or more hydrogens are replaced by alkyl or aryl groups. Amino compounds are of following types.

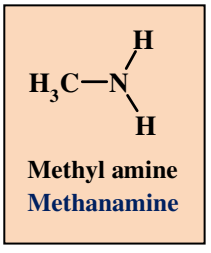
General formula : R-NH_2 / Ar-NH_2

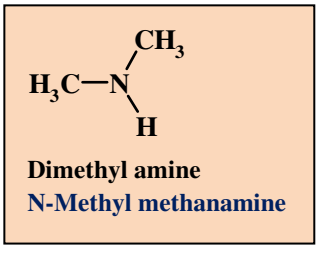
Aliphatic Amino Compounds

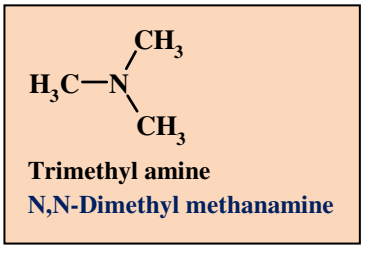
In aliphatic amino compounds, amino group is attached to alkyl groups. These are further classified as primary, secondary and tertiary as per the number of alkyl groups attached to nitrogen.





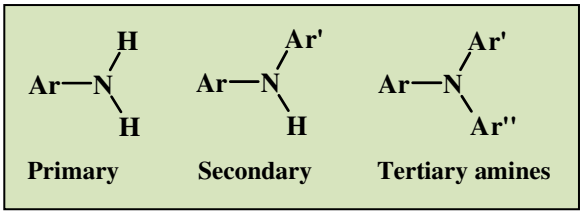


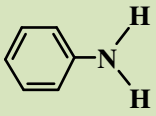




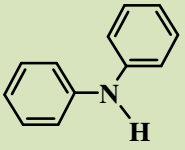
Aromatic Amino Compounds

In aromatic amino compounds, amino group is attached to aryl groups. These are further classified as primary, secondary and tertiary as per the number of aryl groups attached to nitrogen.

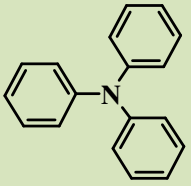




Phenyl amine
Benzenamine
Aniline



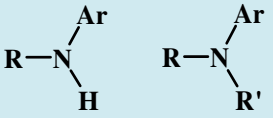
Diphenyl amine
N-Phenyl benzenamine
N-Phenyl aniline



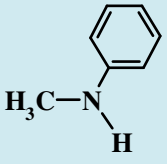
Triphenyl amine
N,N-Diphenyl benzenamine
N,N-Diphenyl aniline

Mixed Amino Compounds

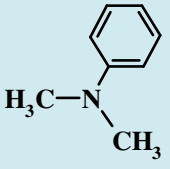
In mixed amino compounds, amino group is attached to both alkyl and aryl groups.



Secondary **Tertiary amines**



N-Methyl aniline
N-Methyl benzenamine
N-Phenyl methanamine
Methyl phenyl amine



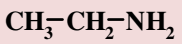
N,N-Dimethyl aniline
N,N-Dimethyl benzenamine
N-Methyl-N-phenyl methanamine
Dimethyl phenyl amine

Nomenclature

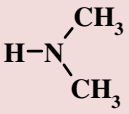
Common - For naming amino compounds, write name of alkyl / aryl group attached to nitrogen of amino group followed by word “amine”. Use prefix di or tri, if two or three different alkyl / aryl groups attached to nitrogen. Follow alphabetical order for naming these alkyl / aryl groups.

IUPAC - For naming amino compounds, replace letter “e” of alkane by word “amine” i.e. alkanamine.

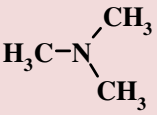
Methyl amine
Methanamine



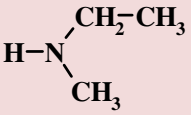
Ethyl amine
Ethanamine



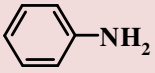
Dimethyl amine
N-Methyl methanamine



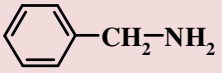
Trimethyl amine
N,N-Dimethyl methanamine



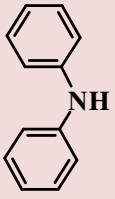
Ethyl methyl amine
N-Methyl ethanamine



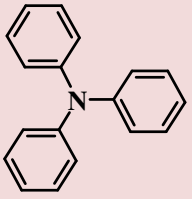
Phenyl amine
Benzenamine
Aniline



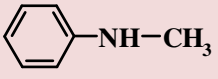
Benzyl amine
Phenyl methanamine



Diphenyl amine
N-Phenyl benzenamine
N-Phenyl aniline

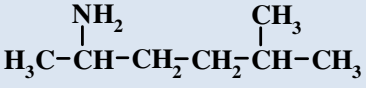


Triphenyl amine
N,N-Diphenyl benzenamine
N,N-Diphenyl aniline

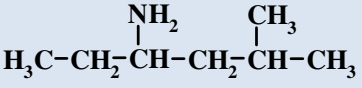


Methyl phenyl amine
N-Phenyl methanamine
N-Methyl benzenamine
N-Methyl aniline

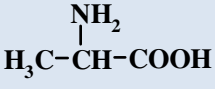
For naming complex amines, use IUPAC system of nomenclature. Consider amino groups as substituents and use lowest possible numbers to indicate their position. Use prefix di, tri etc., if more than one amino groups are present. Retain letter "e" of hydrocarbon.



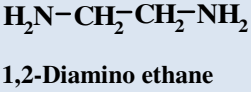
2-Amino-5-methyl hexane



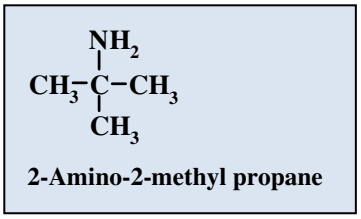
3-Amino-5-methyl hexane



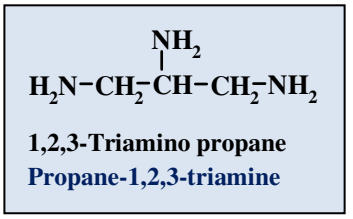
2-Amino propionic acid



1,2-Diamino ethane
Ethane-1,2-diamine



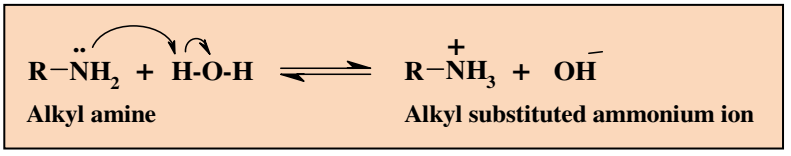
2-Amino-2-methyl propane



1,2,3-Triamino propane
Propane-1,2,3-triamine

Basicity

As per Lewis concept, compounds which donate electrons are called as bases. Basicity of amines is because of presence of unshared pair or lone pair of electrons on nitrogen. On donation of these electrons to a proton, substituted ammonium ions are formed.



Alkyl amine **Alkyl substituted ammonium ion**

Aqueous solutions of amines are basic due to hydroxide ions produced as a result of equilibrium shown above.

Basicity of amines can be measured by base dissociation constant (K_b) for this equilibrium.

$$K_b = \frac{[R\text{-}\overset{+}{N}H_3]\,[\overset{-}{O}H]}{[R\text{-}NH_2]}$$

$pK_b = -\log K_b$
$\log K_b = -pK_b$
$K_b = \text{antilog} -pK_b$
$K_b = 1 / \text{antilog } pK_b$

Concentration of water in aqueous solution remains nearly constant, hence it is omitted. Larger the K_b value or smaller the pK_b value, greater the concentration of OH^- and ammonium ions and hence stronger the base.

pK_b values of some amines

Methyl amine (methanamine)	:	3.38
Dimethyl amine (N-methyl methanamine)	:	3.27
Trimethyl amine (N,N-dimethyl methanamine)	:	4.22
Ethyl amine (ethanamine)	:	3.29
Diethyl amine (N-ethyl ethanamine)	:	3.00
Triethyl amine (N,N-diethyl ethanamine)	:	3.25
Phenyl amine / aniline (benzenamine)	:	9.38
Benzyl amine (phenyl methanamine)	:	4.70
N-Methyl aniline / methyl phenyl amine (N-methyl benzenamine)	:	9.30
N,N-Dimethyl aniline / diphenyl methyl amine (N,N-dimethyl benzenamine)	:	8.92
Ammonia	:	4.75

Aliphatic amines are stronger bases than ammonia due to electron donating nature of alkyl groups (+I effect) and aromatic amines are weaker bases than ammonia due to electron withdrawing nature of aryl groups (-I effect). Effects like solvation, sterric hindrance etc. also affects the basic strength of amines.

Structure - Basicity Relationship

Basicity is related to structure of amine. It depends on how easy the formation of cation takes place by accepting a proton from acid? Amines are more basic, if its cations are more stable relative to amines.

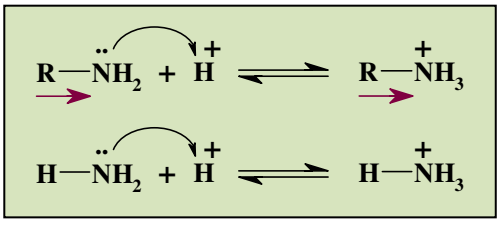
Basicity of Alkyl Amines (Aliphatic Amines)

Alkyl Amines vs. Ammonia

In general aliphatic amines are stronger bases than ammonia. It can be explained on the basis of inductive effect and effect of substituent in alkyl group.

Inductive effect

More the availability of a lone pair of electrons on nitrogen atom more is the strength of base. For comparison, consider the reaction of alkyl amine and ammonia with a proton.



Electron releasing nature of alkyl group increases electron density on nitrogen by +I effect and makes the unshared electron pair more available for sharing with proton of acid. Also, substituted ammonium ion formed from amine gets stabilized due to dispersal of the positive charge by +I effect of alkyl group.

In gaseous phase, basicity of aliphatic amines increases with increase in the number of alkyl groups. Order of basicity of aliphatic amines in gaseous phase is -

R_3N (Tertiary) > R_2NH (Secondary) > RNH_2 (Primary) > NH_3 (Ammonia)

But in aqueous phase, trend of basicity is not regular as in gaseous phase. In aqueous phase, substituted ammonium cations get stabilized not only by electron releasing effect of alkyl group (+I effect) but also by solvation with water molecules. With increase in size of cation, rate of solvation decreases and hence stability of cation decreases. Greater the stability of substituted ammonium cation, stronger the basicity of amine. With increase in size of alkyl group, sterric hindrance to H-bonding increases. Thus change in size of alkyl group results in change in order of basic strength of amines. In aqueous phase, not only inductive effect but also solvation effect and sterric hindrance of alkyl group decides the basicity of alkyl amines. Order of basicity of methyl substituted aliphatic amines in aqueous phase is -

$(CH_3)_2NH$ (Secondary) > CH_3NH_2 (Primary) > $(CH_3)_3N$ (Tertiary) > NH_3 (Ammonia)

Order of basicity of ethyl substituted aliphatic amines in aqueous phase is -

$(C_2H_5)_2NH$ (Secondary) > $(C_2H_5)_3N$ (Tertiary) > $C_2H_5NH_2$ (Primary) > NH_3 (Ammonia)

Effect of substituent in alkyl group

Electron withdrawing group decreases the basicity of amines. It reduces the ability of alkyl group to increase the electron density on nitrogen in amine and hence electrons are less available for donation to proton.

β-Hydroxy ethyl amine is weaker base than ethyl amine.

$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 < CH_3\text{-}CH_2\text{-}NH_2$

Electron withdrawing group reduces the ability of alkyl group to disperse the positive charge on nitrogen in ammonium ion.

$HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ < CH_3\text{-}CH_2\text{-}NH_3^+$

Electron releasing group increases the basicity of amines. It enhances the ability of alkyl group to increase the electron density on nitrogen in amine and hence electrons are more available for donation to proton.

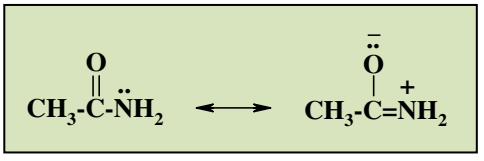
β-Methoxy ethyl amine is stronger base than ethyl amine.

$CH_3O\text{-}CH_2\text{-}CH_2\text{-}NH_2 > CH_3\text{-}CH_2\text{-}NH_2$

Electron releasing group enhances the ability of alkyl group to disperse the positive charge on nitrogen in ammonium ion.

$CH_3O\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ > CH_3\text{-}CH_2\text{-}NH_3^+$

Carbonyl group adjacent to the amino group makes it less basic due to resonance and inductive effect. Thus acetamide is neutral in nature.



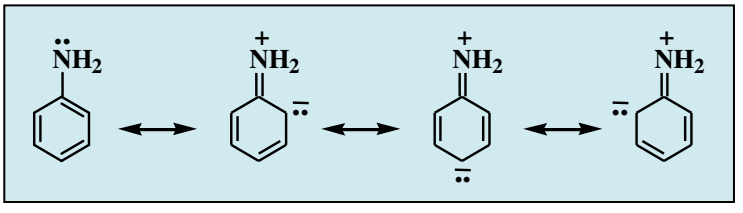
Basicity of Aryl Amines (Aromatic Amines)

Aryl Amines vs. Ammonia

In general aromatic amines are weaker bases than ammonia and aliphatic amines. It can be explained on the basis of resonance effect, stability of aryl ammonium ions, inductive effect and effect of substituent in aryl group.

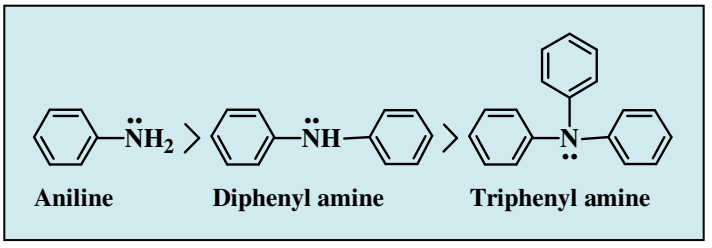
Resonance effect

More the availability of a lone pair of electrons on nitrogen atom more is the strength of base. Resonance mechanism in aromatic amines (aniline) is as shown below.



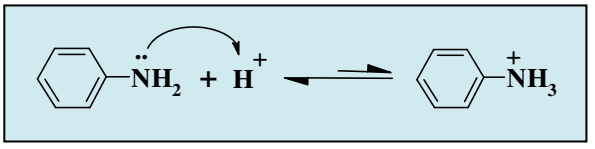
Due to resonance, a lone pair of electrons on nitrogen interacts with pi electron density of benzene ring, it involves in delocalization over the benzene ring and hence less available for donation to the proton. Nitrogen acquires little positive charge, which tends to repel proton instead of accepting it.

In aniline one benzene ring is attached to nitrogen whereas in diphenyl amine two benzene rings are attached to nitrogen. Hence in diphenyl amine there is more resonance stabilization and it is weak base than aniline. In triphenyl amine three benzene rings are attached to nitrogen, there is much more resonance stabilization, above effect is still further and hence triphenyl amine is not basic in aqueous solution.



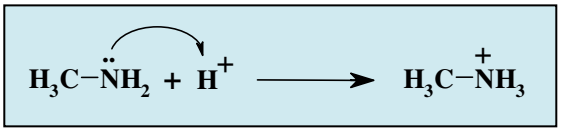
Stability of aryl ammonium ions

Aryl amine i.e. aniline accepts proton to form anilinium ion.



In aniline, a lone pair of electrons interacts with pi electrons of benzene ring, hence there is resonance stabilization but in anilinium ion, a lone pair of electrons is utilized in bonding the proton and so it is not available for interacting with pi electrons of benzene ring, hence no resonance stabilization. Thus stability of aniline is more than anilinium ion, so in equilibrium mixture, concentration of anilinium ion is less.

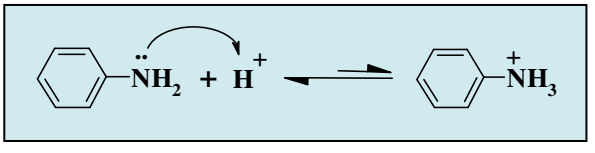
In aliphatic amines, no issue of resonance either in amine or ammonium ion.



So aniline is weaker base than aliphatic amines as well as ammonia.

Inductive effect

Less the availability of a lone pair of electrons on nitrogen atom less is the strength of base.



Electron withdrawing groups (-NO_2, -SO_3H, -COOH, -X etc.) in the ring decreases the basicity of amines by pulling electrons towards itself. Electron withdrawing effect of phenyl ring decreases electron density on nitrogen by -I effect and make the unshared electron pair less available for sharing with proton of acid. Also, substituted ammonium ion (anilinium ion) formed from amine (aniline) gets destabilized due to increase in positive charge by -I effect of phenyl ring.

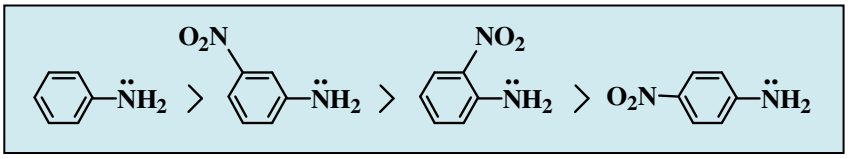
Carbons of phenyl group are sp^2 hybridized and are more electronegative. So they are more electron withdrawing than sp^3 hybridized carbons of alkyl groups.

Effect of substituent in aryl group

Ring substituted aromatic amines

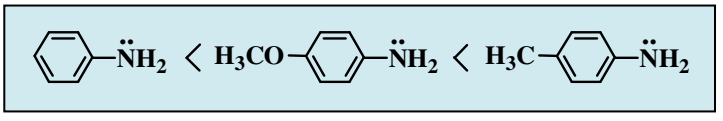
Electron withdrawing groups (-NO_2, -SO_3H, -COOH, -X etc.) in the ring decreases the basicity of amines by pulling electrons towards itself

Basicity - Aniline > *m*-Nitro aniline > *o*-Nitro aniline > *p*-Nitro aniline



Electron releasing groups (-CH_3, -OCH_3 etc.) in the ring increases the basicity of amines by donating electrons to nitrogen.

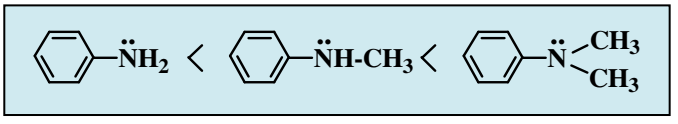
Basicity - Aniline < p-Methoxy aniline < *p*-Toluidine



N-Substituted aromatic amines

Electron releasing groups (-CH_3, -C_2H_5 etc.) attached to nitrogen increases the basicity of amines by pushing electrons towards nitrogen.

Basicity - Aniline < N-Methyl aniline < N,N-Dimethyl aniline

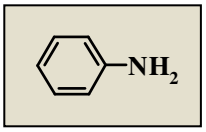


Preparations and Reactions

Aniline (Phenyl Amine / Benzenamine / Amino benzene)

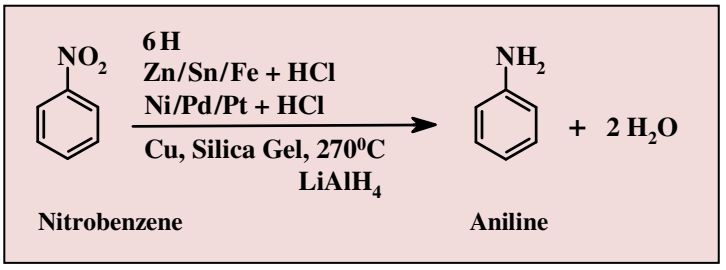
Aniline is a colourless oily liquid when it is freshly prepared. It becomes pale yellow and rapidly darkens on exposure to light. It has characteristic unpleasant odour. It is steam volatile, toxic. Its prolong inhalation may cause death. It is sparingly soluble in water (3%) but soluble in alcohol, ether, benzene.

MF : C_6H_7N , BP : 184^0C , Odour : unpleasant

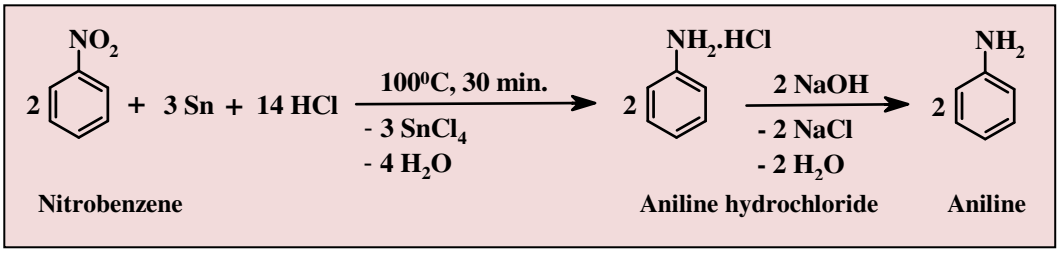


Preparations

Reduction of nitrobenzene - Nitrobenzene on reduction using metals like zinc, tin, iron along with concentrated hydrochloric acid or using hydrogen gas in presence of metal catalyst like nickel, palladium, platinum or finely divided copper metal on silica as catalyst or using lithium aluminium hydride gives aniline.

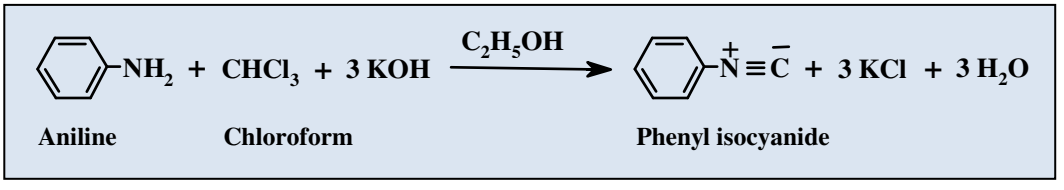


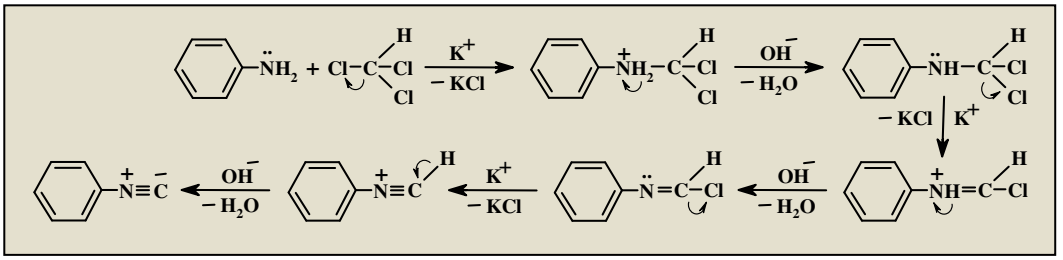
Laboratory method - Nitrobenzene on reduction with tin metal and concentrated hydrochloric acid at 100^0C gives acid salt i.e. aniline hydrochloride, it is then treated with sodium hydroxide to give aniline.



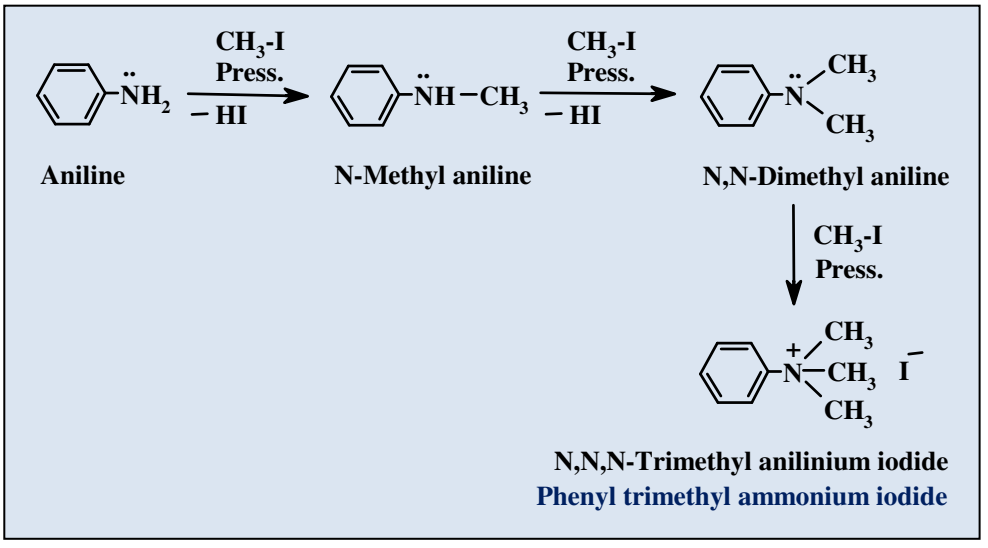
Reactions

Carbylamine reaction (isocyanide test) - Aniline reacted with chloroform and alcoholic potassium hydroxide to give phenyl isocyanide (phenyl carbyl amine) having intolerable characteristic smell.

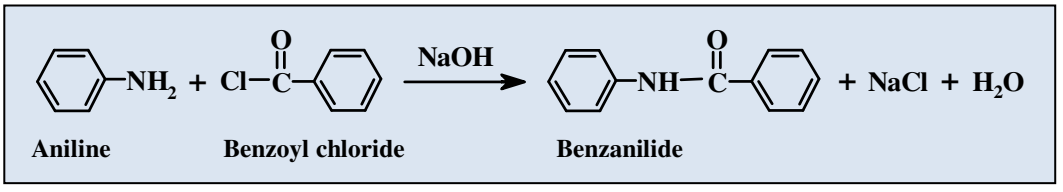




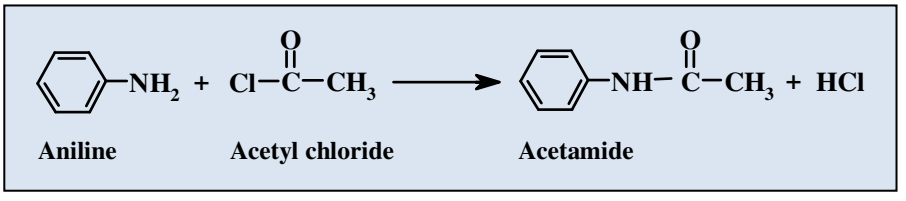
Alkylation (formation of quaternary ammonium salt) - Aniline heated with methyl iodide under pressure to give methyl aniline (secondary amine), it is then converted to dimethyl aniline (tertiary amine) and finally to N,N,N-trimethyl anilinium iodide (quaternary ammonium salt).

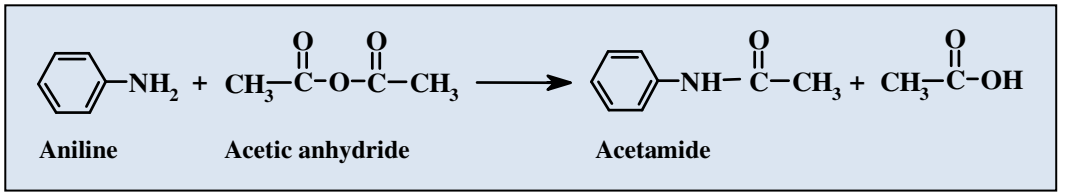


Benzoylation - Aniline reacted with benzoyl chloride in presence of sodium hydroxide to give benzanilide.

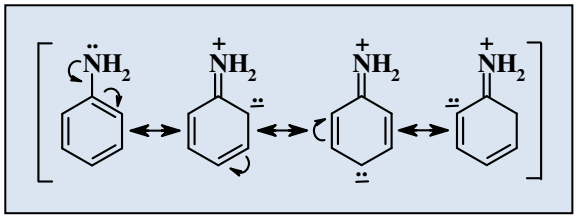


Acetylation - Aniline reacted with acetyl chloride or acetic anhydride to give acetanilide.

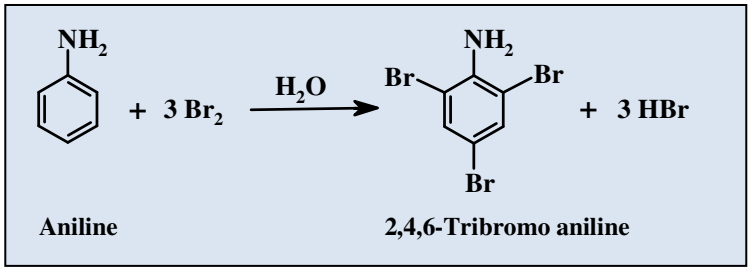




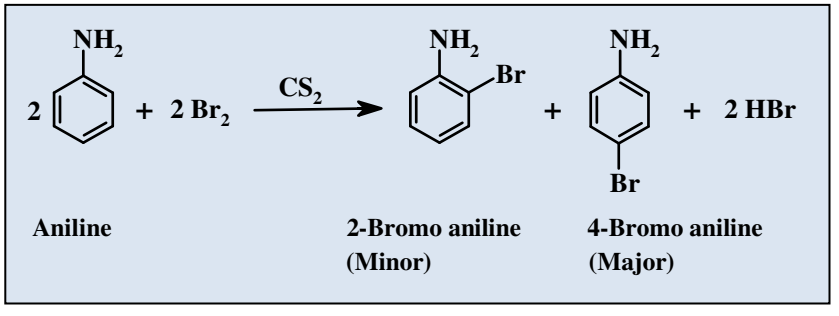
Bromination (electrophilic substitution) - As amino group in aniline is ring activating, it activates ring at *o*,*p*-positions by resonance mechanism, thus increases electron density at *o*,*p*-positions and undergoes electrophilic substitution (halogenation, nitration, sulphonation). During electrophilic substitution, generally poly-substitution occurs instead of mono-substitution. Mono-halogenated products can be obtained by protecting amino group by acetylation followed by substitution and then hydrolysis.



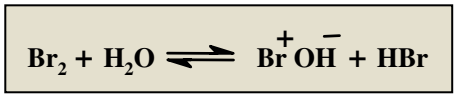
In aqueous medium - Aniline reacted with bromine in polar solvent like water to give 2,4,6-tribromo aniline.



In CS_2 medium - Aniline reacted with bromine in non-polar solvent like carbondisulphide to give mixture of 2-bromo aniline and 4-bromo aniline.

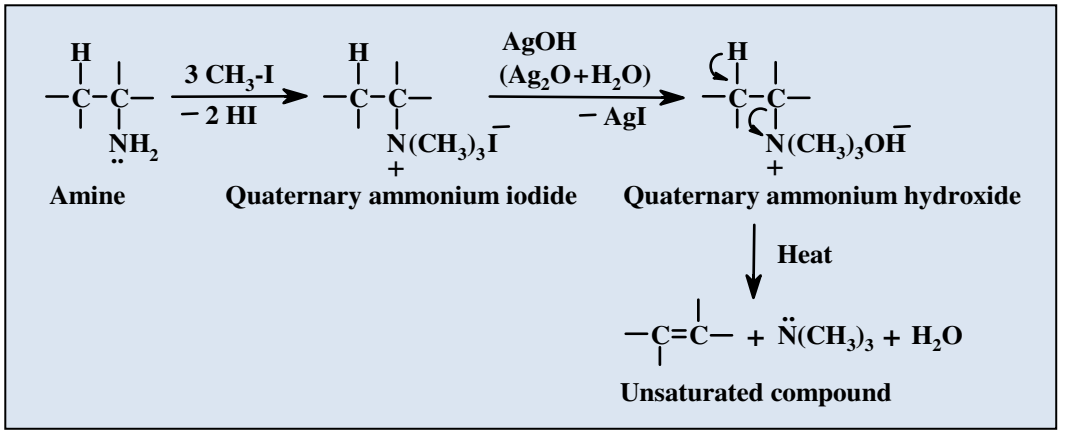


In aqueous medium, water molecule polarizes bromine molecule to some large extent than in CS_2 medium.

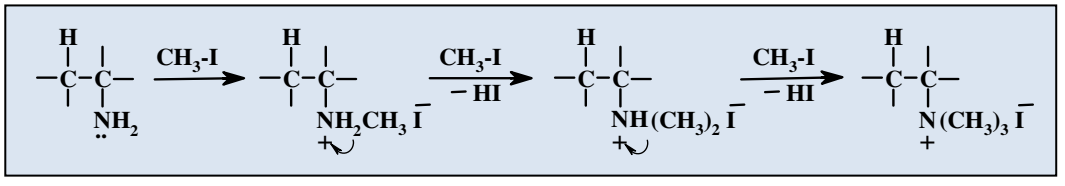


Hence reactivity of bromine increases and Br^+ ions become readily available for electrophilic substitution. As a result tri-substitution occurs in aqueous medium. Also because of sterric hindrance at *o*-position, usually *p*-substituted product is major product.

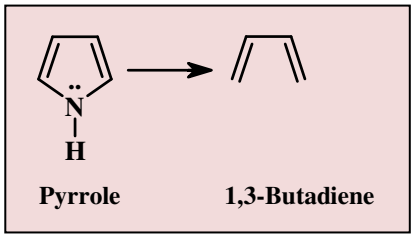
Hoffmann's exhaustive methylation (Hoffmann's degradation) - Primary, secondary or tertiary amines converted to unsaturated compounds by pyrolytic decomposition (heating) of quaternary ammonium hydroxide. Herein amines treated with excess of methyl iodide to give quaternary ammonium iodide which is then hydrolyzed with moist silver oxide to give quaternary ammonium hydroxide. Finally quaternary ammonium hydroxide heated to obtain unsaturated compounds.

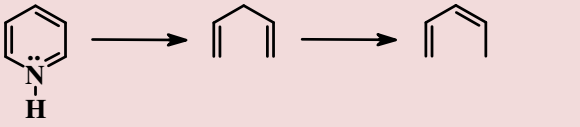


Conversion of amine to quaternary ammonium iodide is SN^2 reaction. Amine is incoming nucleophile whereas iodine is leaving. During elimination of water molecule in pyrolytic decomposition, loss of hydrogen is from β-position with respect to nitrogen to give alkene.

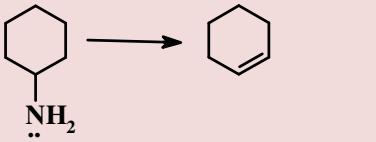


Examples -





Pyridine 1,4-Pentadiene 1,3-Pentadiene



Cyclohexyl amine Cyclohexene

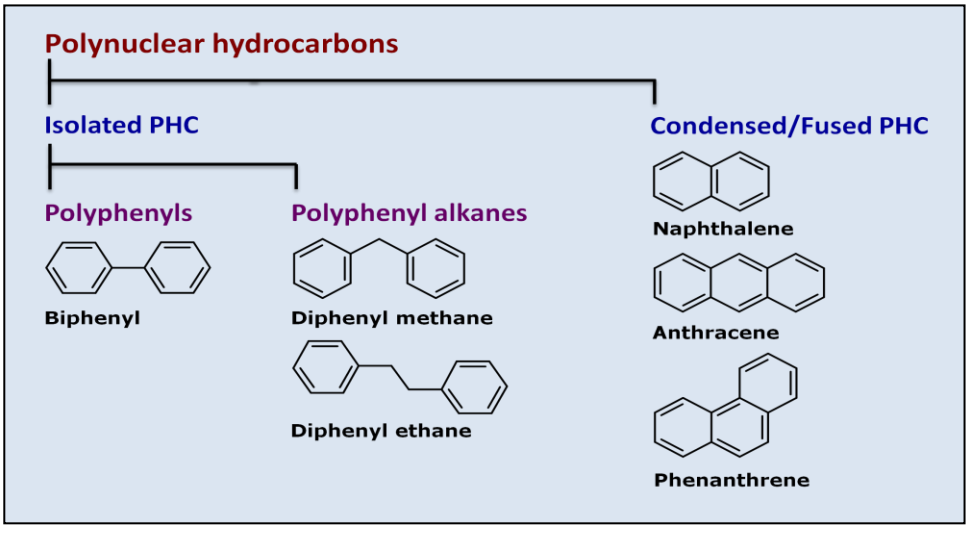
Polynuclear Hydrocarbons and Derivatives

Introduction

Polynuclear hydrocarbons are organic compounds containing two or more benzene nuclei or aromatic rings. These are polycyclic benzenoid aromatic hydrocarbons belong to class arenes. Polynuclear hydrocarbons are of following two types.

Isolated polynuclear hydrocarbons - In isolated systems, two or more benzene nuclei are linked either directly to each other or through one or more carbon atoms. Here carbons are not shared by two or more benzene nuclei.

Condensed or fused polynuclear hydrocarbons - In condensed or fused systems, two or more benzene nuclei are fused together. Here two carbons are shared by two or more benzene nuclei.

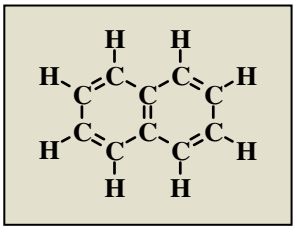


Condensed Polynuclear Hydrocarbons and Derivatives

Naphthalene

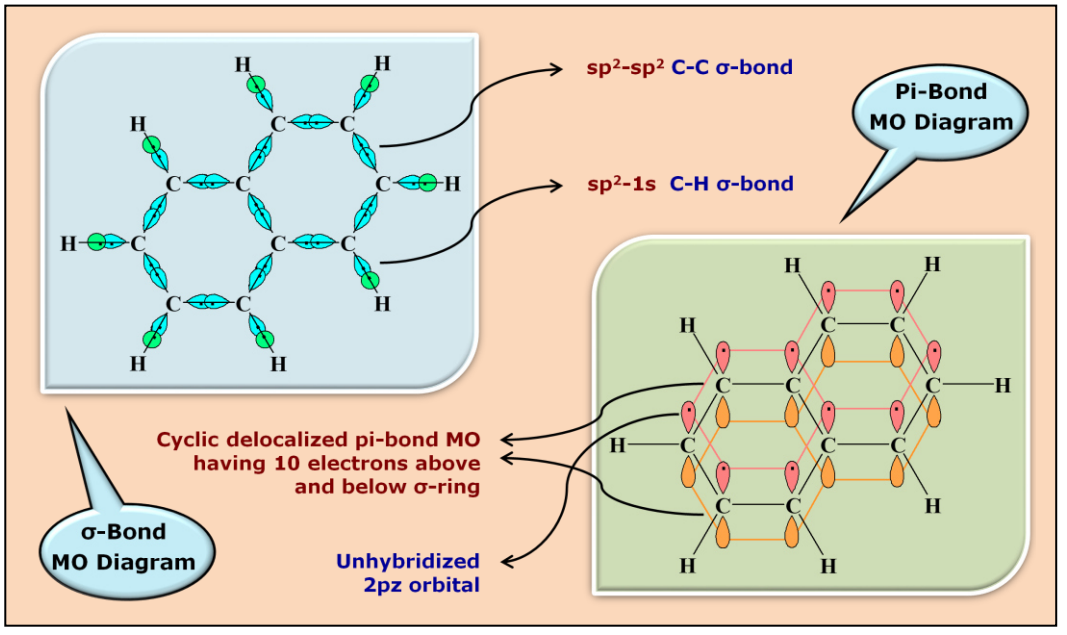
Naphthalene is a condensed polynuclear hydrocarbon having two benzene nuclei or aromatic rings fused at ortho position. It is white crystalline volatile solid, sublimes at room temperature. It is obtained from coal tar to the extent of 5 to 10 % and isolated from oil fraction. It is insoluble in water but soluble in alcohol, ether, benzene.

MF : $C_{10}H_8$, MP : 80^0C , Odour : Like moth balls



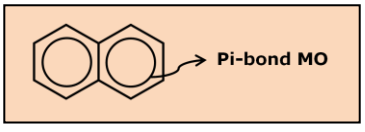
Molecular Orbital Diagram

As suggested by X-ray diffraction study, naphthalene is a co-planer molecule i.e. all carbon and hydrogen atoms lie in same (one) plane. All C-C-C and C-C-H bonds angles are of 120^0. All carbons are in sp^2 hybridized state i.e. all carbon contain three half filled sp^2 hybridized orbitals and one half filled 2pz unhybridized orbital. All C-C bonds are strong σ-bonds formed by sp^2-sp^2 axial overlapping and all C-H bonds are strong σ-bonds formed by sp^2-1s axial overlapping. Unhybridized 2pz orbitals of all carbon atoms lie perpendicular to plane of σ-ring. They overlap laterally (sidewise) and equally in both directions to form cyclic delocalized pi-bond molecular orbital having 10 pi-electrons. One half of pi-bond molecular orbital lie above and other half lie below the plane of σ-ring and thus σ-ring is sandwiched between pi-bond molecular orbitals.

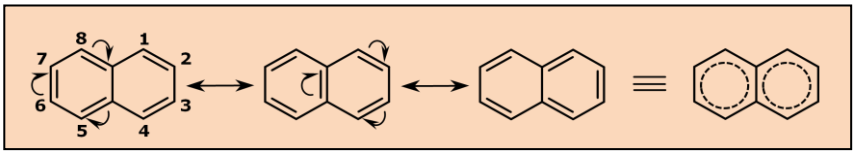


Naphthalene is stabilized due to delocalization of pi-bond molecular orbital having 10 electrons. Delocalization energy is 61 Kcal/mole.

Common short hand representation -



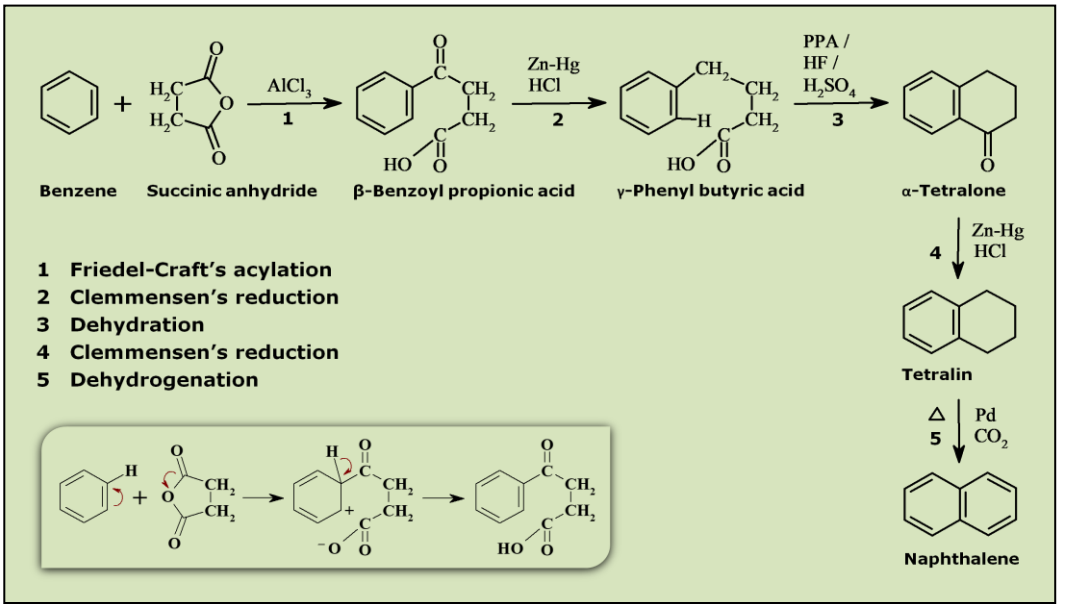
According to resonance theory, naphthalene is considered to be a hybrid of following three resonating structures.



As per X-ray diffraction study, unlike benzene, all C-C bonds in naphthalene are not of same length. In particular, C1-C2 bond is considerably shorter (1.36 A^0) than C2-C3 bond (1.40 A^0). This is because C1-C2 bond is double in two resonating structures and single in only one whereas C2-C3 bond is single in two resonating structures and double in only one. Hence C1-C2 bond has more double bond character (shorter bond length) and C2-C3 bond has more single bond character (longer bond length). In general, C1-C2, C3-C4, C5-C6 and C7-C8 bonds have shorter bond length as compared to other bonds.

Preparation

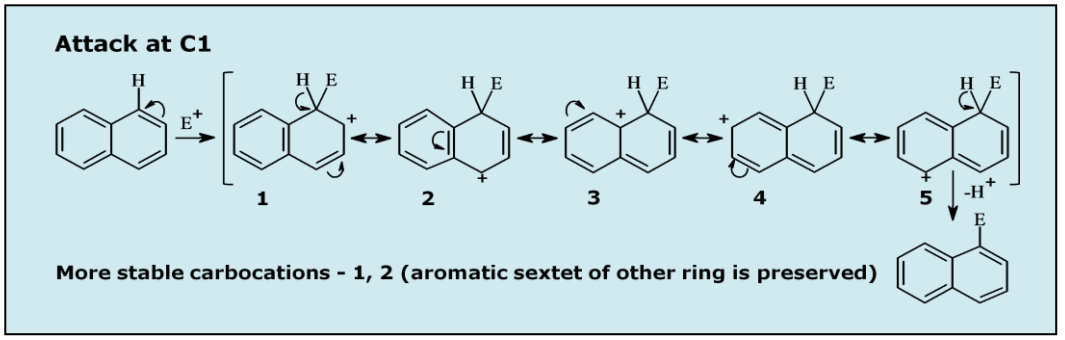
Haworth synthesis - Benzene is subjected to Friedel-Craft acylation with succinic anhydride to yield β-benzoyl propionic acid (Haworth synthesis), which on Clemmensen reduction gives γ-phenyl butyric acid. This γ-phenyl butyric acid is treated with acid catalyst like poly-phosphoric acid (PPA) or hydrogen fluoride (HF) or sulphuric acid (H_2SO4) to give α-tetralone. It is then converted to tetralin by Clemmensen reduction again and finally tetralin is dehydrogenated to naphthalene by heating with paladized charcoal.



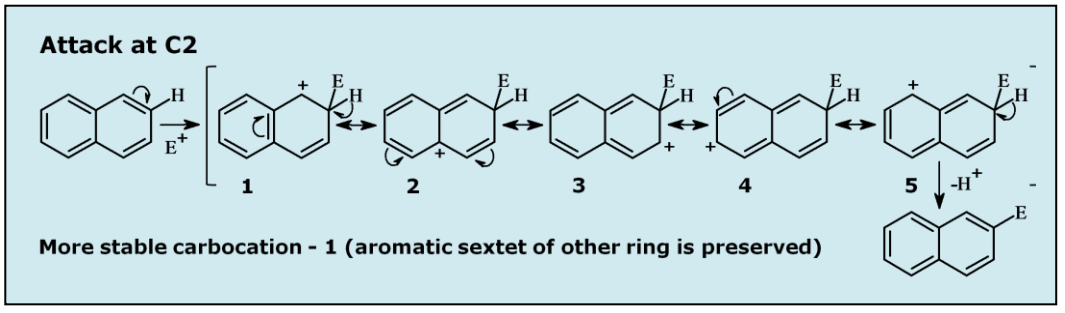
Orientation of Electrophilic Substitution

When naphthalene is subjected to electrophilic substitution, it occurs primarily at C1(α)-position. Controlling step in this reaction is attachment of an electrophile to aromatic ring to form an intermediate carbocation. This attachment takes place in such a way to give more stable carbocation.

When naphthalene is attacked by electrophile at C1(α)-position, an intermediate carbocation is formed which is a resonance hybrid of structures 1 to 5. Here two structures 1 and 2 are more stable (aromatic sextet of other ring is preserved) and hence stability of intermediate carbocation is more.



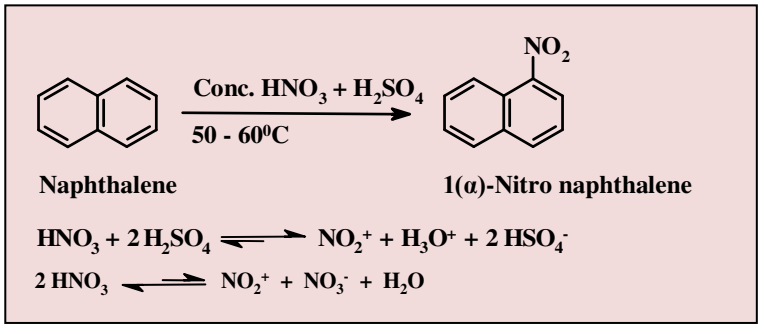
If attack of electrophile is at C2(β)-position, then so formed intermediate carbocation is a resonance hybrid of structures 1 to 5. Here only one structure 1 is more stable (aromatic sextet of other ring is preserved) and hence stability of intermediate carbocation is somewhat less as compared to attack at C1(α)-position.



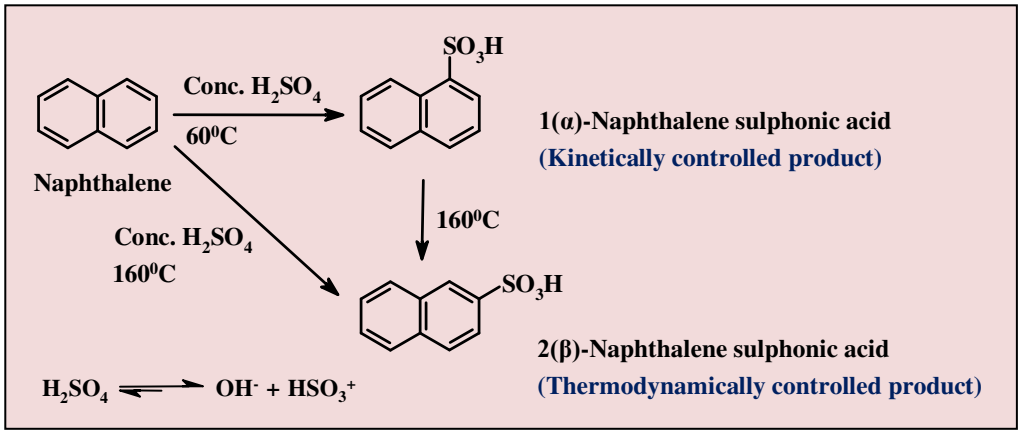
Substitution at C2(β)-position occurs only when the reactions are carried out at higher temperatures or when bulkier solvents are used. In general, under equilibrium conditions, substitution is preferred at C2(β)-position (sulphonation reaction).

Reactions

Nitration - Naphthalene treated with mixture of concentrated nitric acid and sulphuric acid at 50-60^{0}C to give 1(α)-nitro naphthalene.

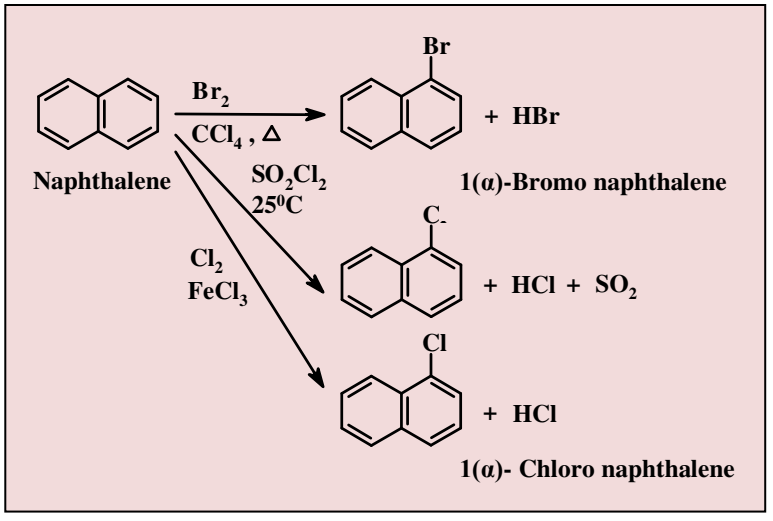


Sulphonation - Naphthalene treated with concentrated sulphuric acid at 60 and 160^{0}C to give 1(α)-naphthalene sulphonic acid and 2(β)-naphthalene sulphonic acid respectively.

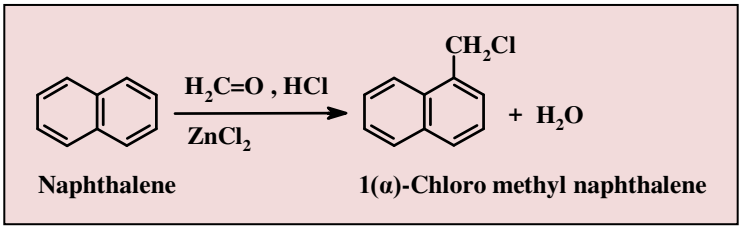


When 1(α)-naphthalene sulphonic acid is heated at 160^{0}C, most of it is converted to 2(β)-naphthalene sulphonic acid. Even at high temperature, initial attack takes place more readily at 1(α)-position since it gives a more stable intermediate. However reaction being reversible, desulphonation at 1(α)-position is equally easy. Whereas 2(β)-position is attacked more slowly, but once formed, 2(β)-isomer is more stable and resists desulphonation. Relative instability of 1(α)-isomer is due to large sterric interaction between bulky SO_3H group at 1(α)-position and hydrogen at 8-position. There is no such interaction in 2(β)-isomer, so it is more stable. Thus formation of 1(α)-isomer is kinetically controlled and that of 2(β)-isomer is thermodynamically controlled.

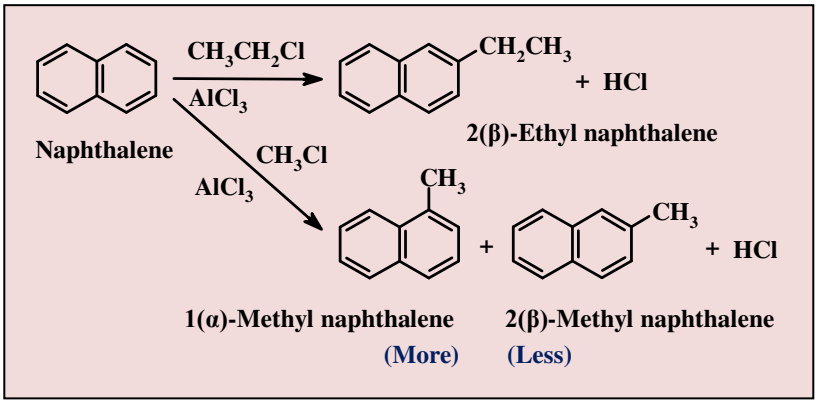
Halogenation - Naphthalene treated with liquid bromine in carbontetrachloride to give 1(α)-bromo naphthalene. Naphthalene can also be halogenated by reacting it with sulphuryl chloride at 25^{0}C or by chlorination in presence of ferric chloride to give 1(α)-chloro naphthalene .



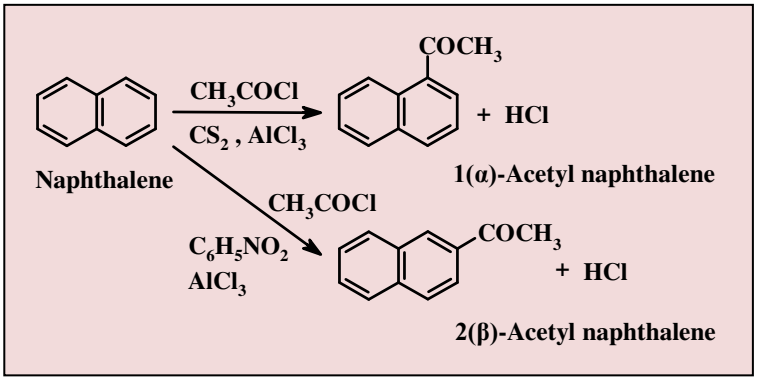
Chloromethylation - Naphthalene reacted with mixture of formaldehyde and hydrochloric acid in presence of zinc chloride to give 1(α)-chloro methyl naphthalene.



Friedel-Craft's alkylation - Naphthalene treated with alkyl halides in presence of aluminium chloride to give 2(β)-alkyl naphthalene or mixture of 1(α)-alkyl naphthalene and 2(β)-alkyl naphthalene, depending on the bulkiness of alkyl halide. On alkylation, ethyl chloride gives 2(β)-ethyl naphthalene whereas methyl chloride gives mixture of 1(α)-methyl naphthalene (more) and 2(β)-methyl naphthalene (less).



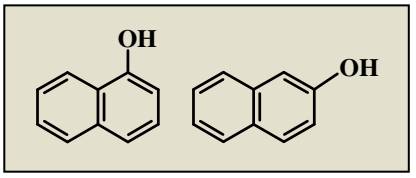
Friedel-Craft's acylation - Naphthalene treated with acetyl chloride in presence of aluminium chloride using carbondisulphide and nitrobenzene as solvents to give 1(α)-acetyl naphthalene and 2(β)-acetyl naphthalene respectively.



Naphthols

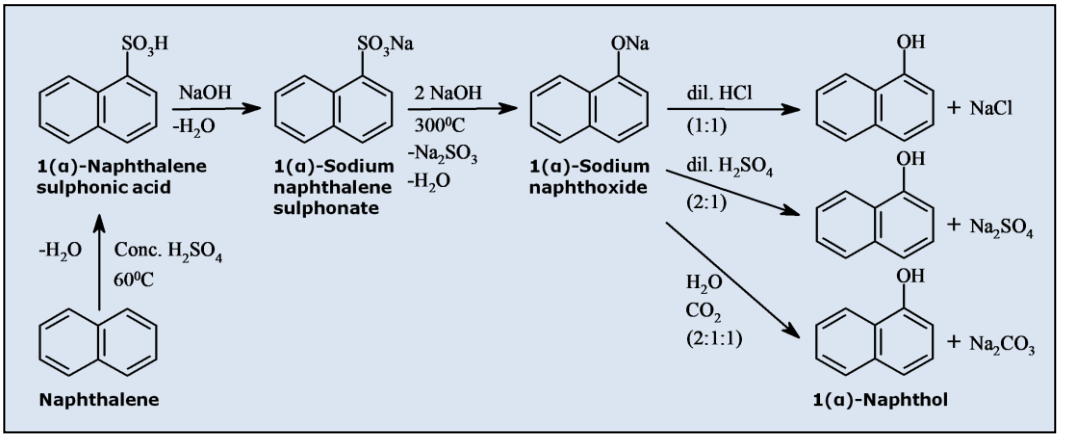
Naphthols are two important isomeric mono-hydroxy derivatives of naphthalene belong to phenol family. 1(α)-Hydroxy derivative of naphthalene is called as 1(α)-naphthol whereas 2(β)-hydroxy derivative of naphthalene is called as 2(β)-naphthol. Naphthols are colourless crystalline solids in pure state but become pinkish on exposure to air. These are obtained from coal tar. These are insoluble in water but soluble in alcohol, ether, benzene.

MF : $C_{10}H_8O$, MP : 95^0C and 123^0C , Odour : Phenolic



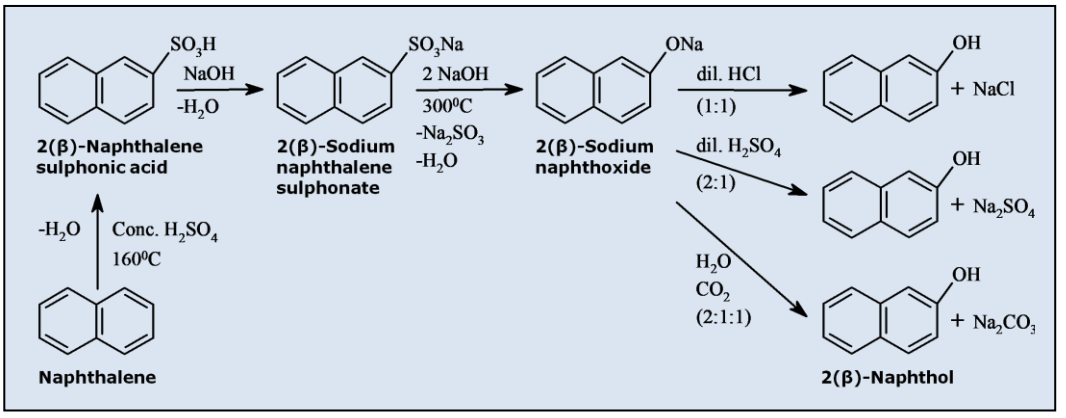
Preparations

Synthesis 1(α)-naphthol from 1(α)-naphthalene sulphonic acid - 1(α)-Naphthalene sulphonic acid treated with sodium hydroxide to give 1(α)-sodium naphthalene sulphonate. It is then fused again with sodium hydroxide at 300^0C in presence of little water to obtain solid mass of sodium salt i.e. 1(α)-sodium naphthoxide. Finally 1(α)-naphthol is obtained by extracting sodium salt with water and by passing carbondioxide or by adding dilute sulphuric acid or hydrochloric acid through it. Initially 1(α)-naphthalene sulphonic acid obtained by treating naphthalene with concentrated sulphuric acid at 60^0C.



Synthesis of 2(β)-naphthol from 2(β)-naphthalene sulphonic acid - 2(β)-Naphthalene sulphonic acid treated with sodium hydroxide to give 2(β)-sodium naphthalene sulphonate. It is then fused again with sodium hydroxide at 300^0C in presence of little water to obtain solid mass of sodium salt i.e. 2(β)-sodium naphthoxide. Finally 2(β)-naphthol is obtained by extracting sodium salt with water and by passing carbondioxide or by adding dilute sulphuric acid or hydrochloric acid through it. Initially

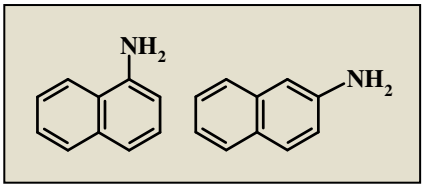
2(β)-naphthalene sulphonic acid obtained by treating naphthalene with concentrated sulphuric acid at 160^0C.



Naphthylamines

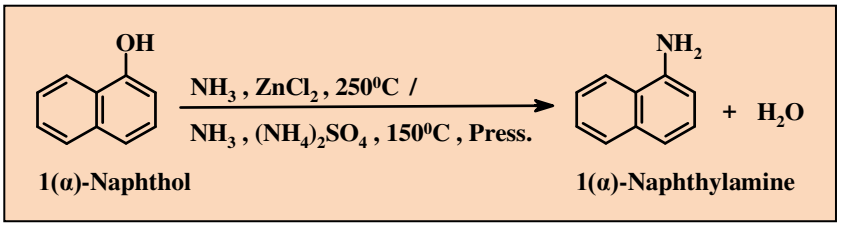
Naphthylamines are two important isomeric mono-amino derivatives of naphthalene. 1(α)-Amino derivative of naphthalene is called as 1(α)-naphthylamine whereas 2(β)-amino derivative of naphthalene is called as 2(β)-naphthylamine. These are also called as amino naphthalenes i.e. 1(α)-amino naphthalene and 2(β)-amino naphthalene. Naphthylamines are colourless crystalline solids. These are obtained from coal tar. These are insoluble in water but soluble in alcohol, ether, benzene. 2(β)-Naphthylamine is toxic, on prolong exposure it may cause cancer of bladder.

MF : $C_{10}H_9N$, MP : 50^0C and 112^0C , Odour : Foul

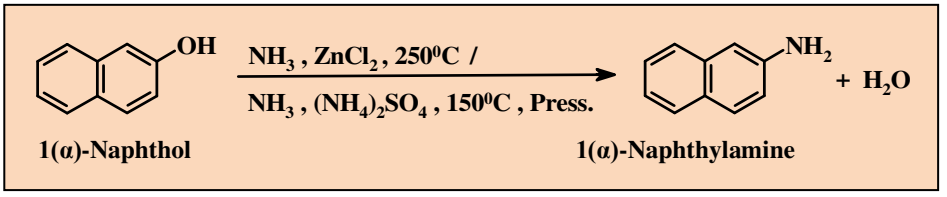


Preparations

Synthesis of 1(α)-naphthylamine from 1(α)-naphthol - 1(α)-Naphthol heated with ammonia in presence of zinc chloride at 250^0C or ammonium sulphite at 150^0C under pressure to give 1(α)-naphthylamine.



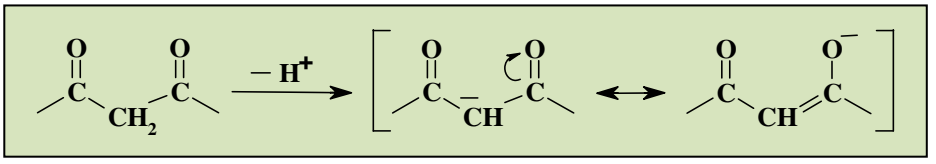
Synthesis of 2(β)-naphthylamine from 2(β)-naphthol - 2(β)-Naphthol heated with ammonia in presence of zinc chloride at 250^0C or ammonium sulphite at 150^0C under pressure to give 2(β)-naphthylamine.



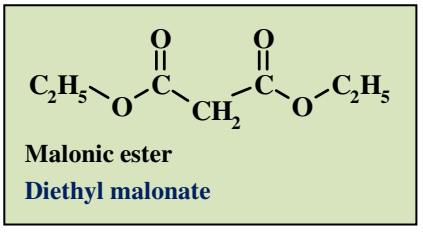
Reactive Methylene Compounds

Introduction

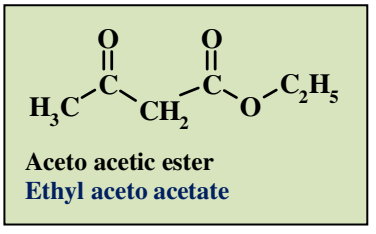
In reactive methylene compounds, methylene group lies between strong electronegative (electron withdrawing/attracting) groups like >C=O (-$COCH_3$, -$COOC_2H_5$), -C≡N, -NO_2 etc. which makes it reactive. Electronegative groups attract electrons towards themselves, weaken the C-H bond, increases acidity and release H. Resulting carbanions undergo resonance stabilization and facilitate the release of H.



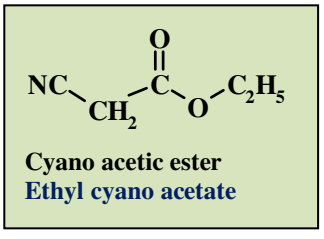
Examples



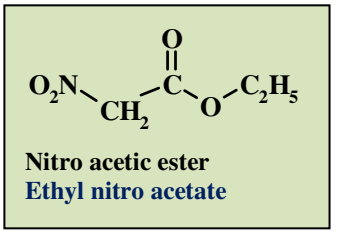
Malonic ester
Diethyl malonate



Aceto acetic ester
Ethyl aceto acetate

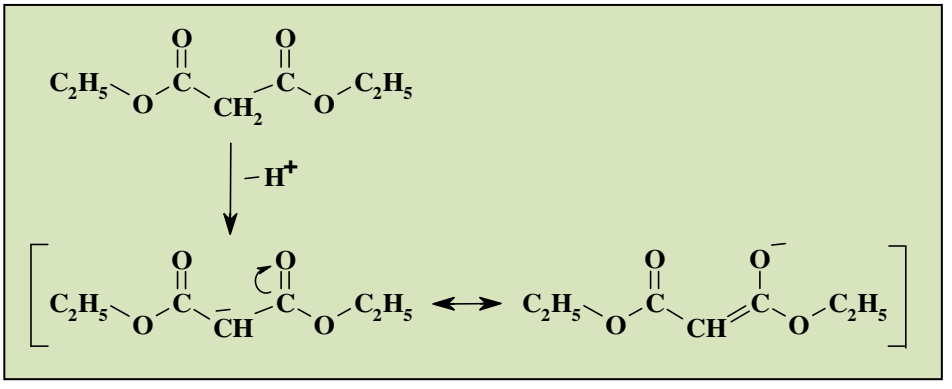


Cyano acetic ester
Ethyl cyano acetate



Nitro acetic ester
Ethyl nitro acetate

In all the above compounds, methylene group (CH_2) is flanked by strong electron withdrawing groups, which attract electrons towards themselves and increases acidity. Such compounds releases H easily and form carbanions more fastly.

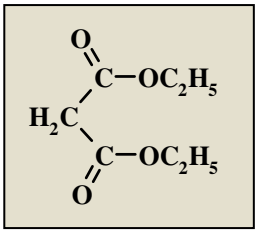


Preparation and Reactions

Malonic Ester (Diethyl Malonate)

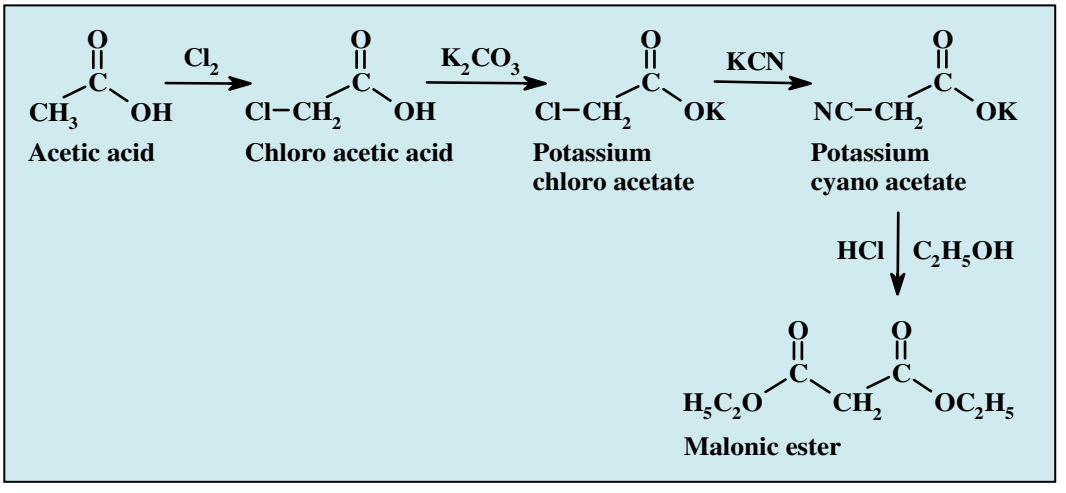
Malonic ester is diethyl ester of malonic acid. It is colourless liquid, important synthetic reagent. It is sparingly soluble in water but soluble in alcohol, ether, benzene.

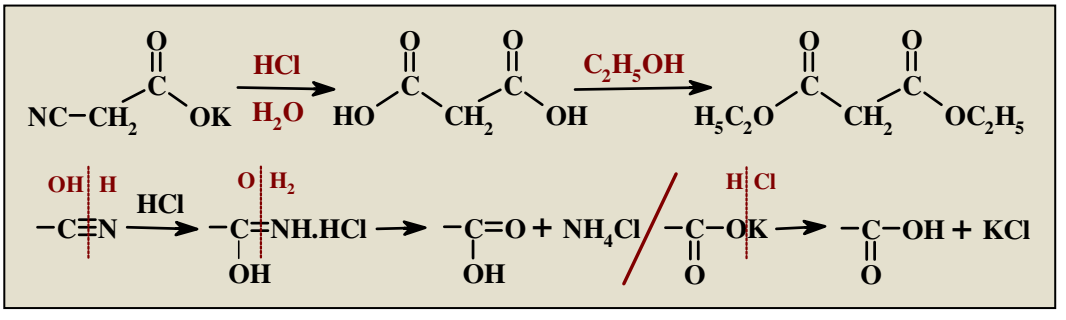
MF : $C_7H_{12}O_4$, BP : 199^0C , Odour : Pleasant



Preparation

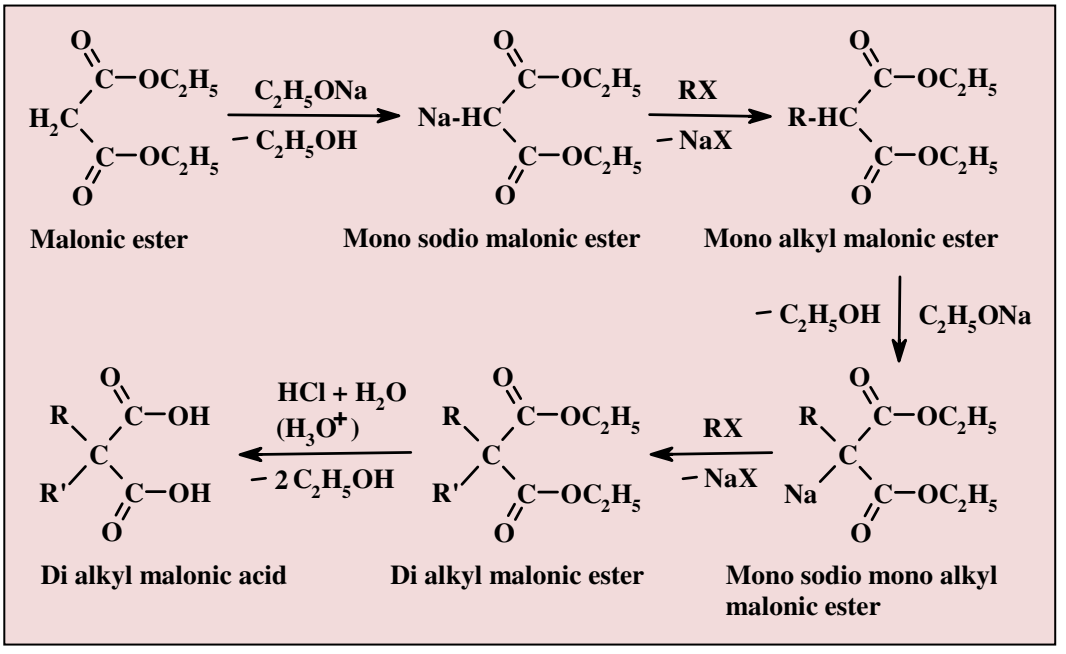
Laboratory method - Acetic acid is first chlorinated to give α-chloro acetic acid. It is neutralized with potassium carbonate to form potassium α-chloro acetate, which is heated strongly with potassium cyanide and evaporated to dryness. Dry potassium α-cyano acetate is heated with absolute ethanol and concentrated hydrochloric acid. Hydrolysis and esterification takes place simultaneously to form malonic ester.



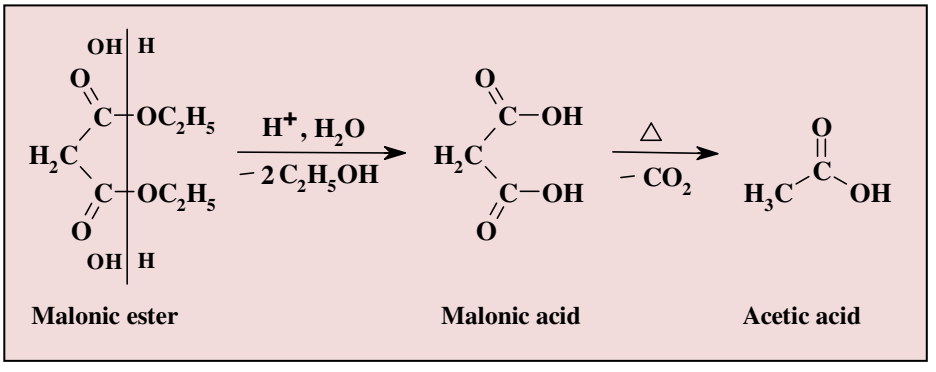


Reactions

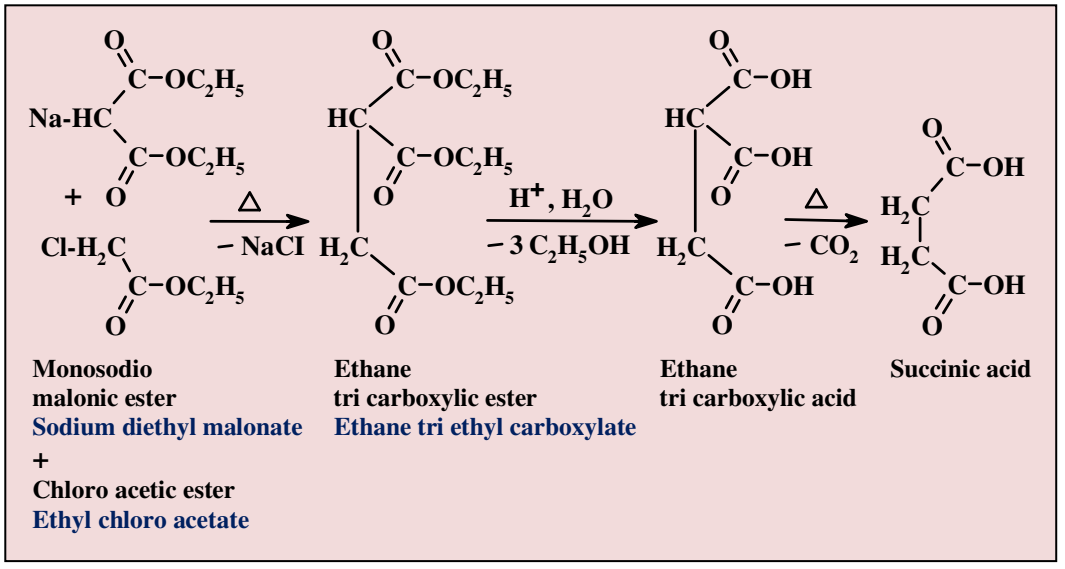
Synthetic application / alkylation - Malonic ester reacted with base to form mono sodio malonic ester (sodium diethyl malonate), which reacted with alkyl halide to give mono alkyl malonic ester. It further reacted with base to form mono sodio mono alkyl malonic ester, which reacted with alkyl halide to give di alkyl malonic ester. Its hydrolysis gives di alkyl malonic acid.



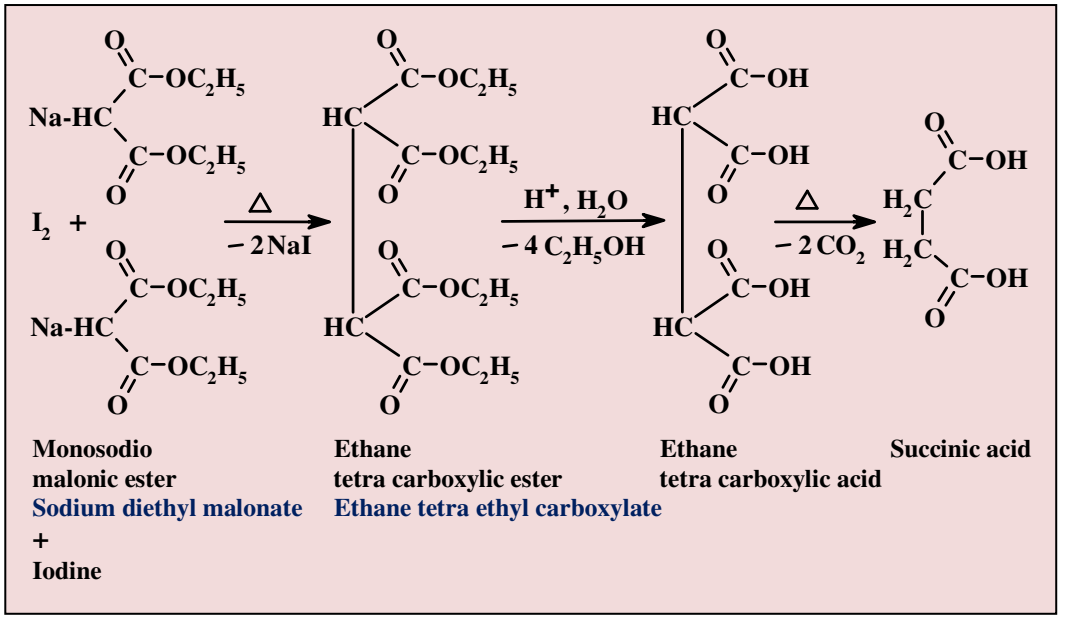
Formation of monobasic acid (acetic acid) - Malonic ester hydrolyzed with dilute hydrochloric acid to give malonic acid and then decarboxylated to form acetic acid.



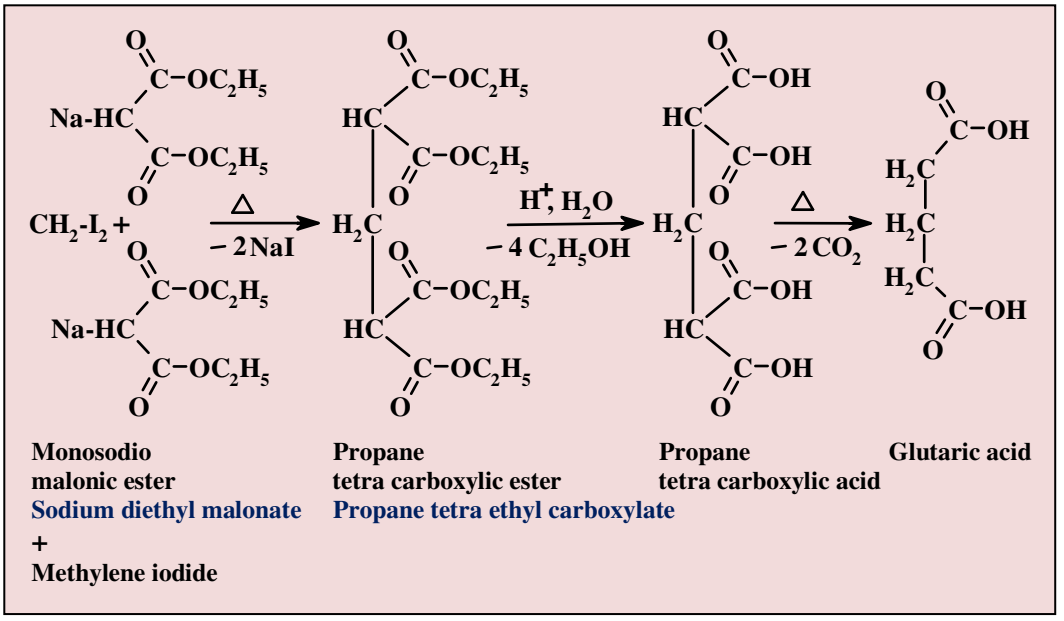
Formation of dibasic acid (succinic acid) - Mono sodio malonic ester reacted with chloro acetic ester to give ethane tri carboxylic ester. It is hydrolyzed with dilute hydrochloric acid to give ethane tri carboxylic acid and then decarboxylated to form succinic acid.



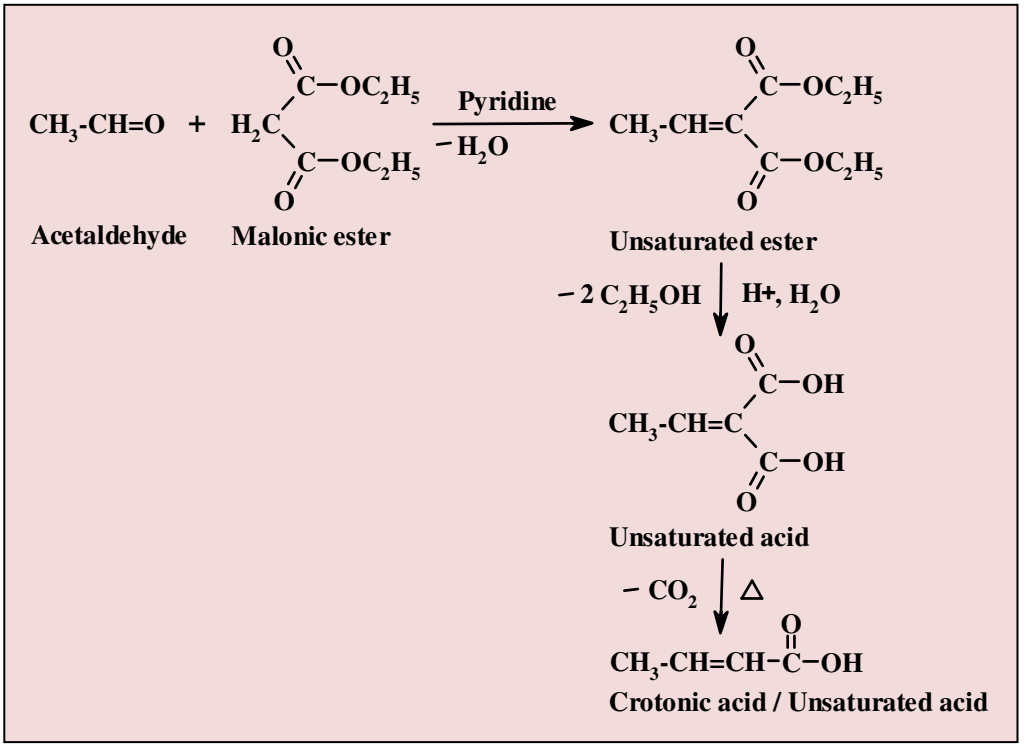
Formation of dibasic acid (succinic acid) - Mono sodio malonic ester reacted with iodine to give ethane tetra carboxylic ester. It is hydrolyzed with dilute hydrochloric acid to give ethane tetra carboxylic acid and then decarboxylated to form succinic acid.



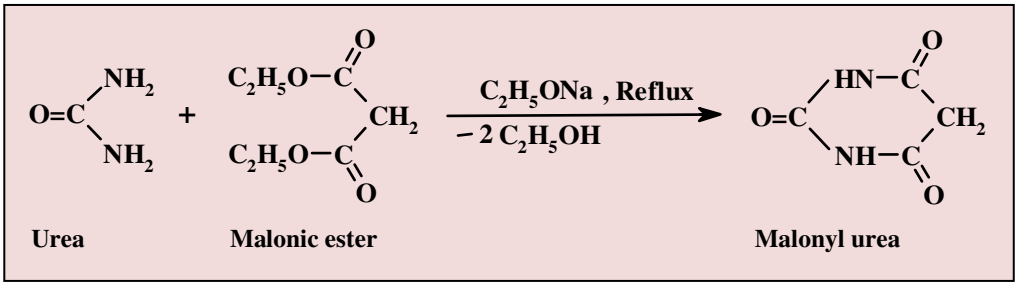
Formation of higher dibasic acid (glutaric acid) - Mono sodio malonic ester reacted with methylene iodide to give propane tetra carboxylic ester. It is hydrolyzed with dilute hydrochloric acid to give propane tetra carboxylic acid and then decarboxylated to form glutaric acid.



Formation of α,β-unsaturated acid (crotonic acid) - Malonic ester condensed with acetaldehyde in presence of base pyridine to give α,β-unsaturated ester. It is hydrolyzed with dilute hydrochloric acid and subsequently decarboxylated to give α,β-unsaturated crotonic acid.



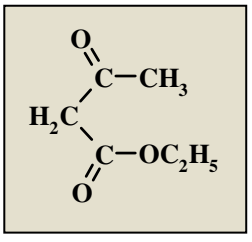
Formation of heterocyclic compound (malonyl urea) - Malonic ester condensed with urea to give malonyl urea (barbituric acid).



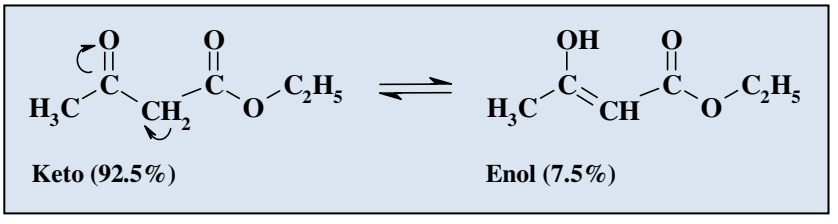
Aceto Acetic Ester (Ethyl Aceto Acetate)

Aceto acetic ester is ethyl ester of aceto acetic acid. It may called as acetyl derivative of ethyl acetate. It is colourless liquid, important synthetic reagent. It is sparingly soluble in water but soluble in alcohol, ether, benzene.

MF : $C_6H_{10}O_3$, BP : 181^0C , Odour : Pleasant

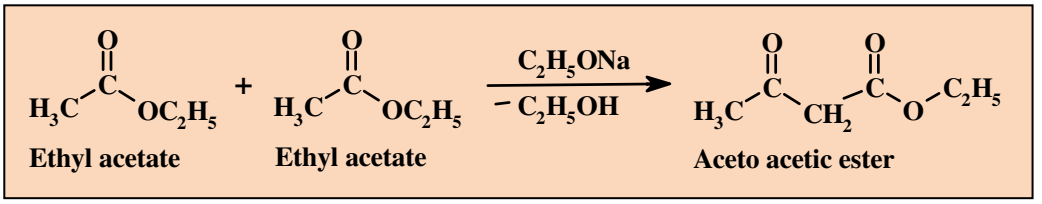


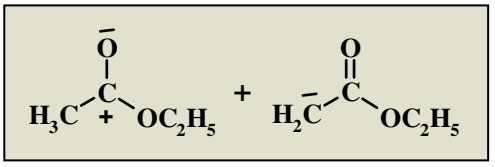
Keto-enol tautomerism - Aceto acetic ester is an equilibrium mixture of keto and enol forms. It behaves as ketone as well as alcohol.



Preparation

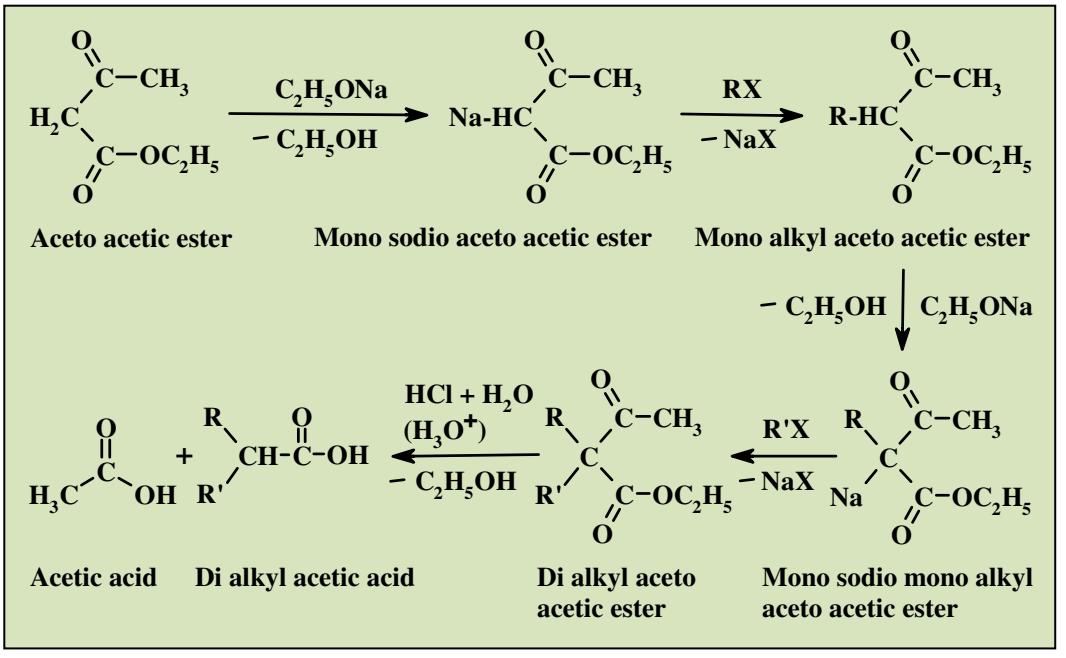
Laboratory method - Two molecules of ethyl acetate condensed in presence of a base sodium ethoxide to give aceto acetic ester (Claisen's condensation). During preparation, ethyl acetate is mixed with little absolute ethanol and sodium metal is added. Mixture is refluxed, cooled, acidified with dilute acetic acid and then treated with saturated sodium chloride solution to form separate layers of ethyl acetate and aceto acetic ester, which then separated by fractional distillation.



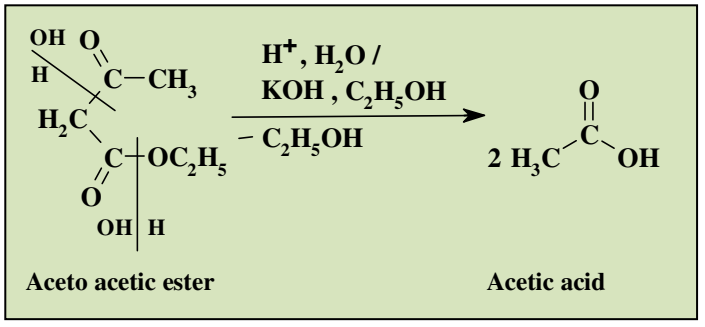


Reactions

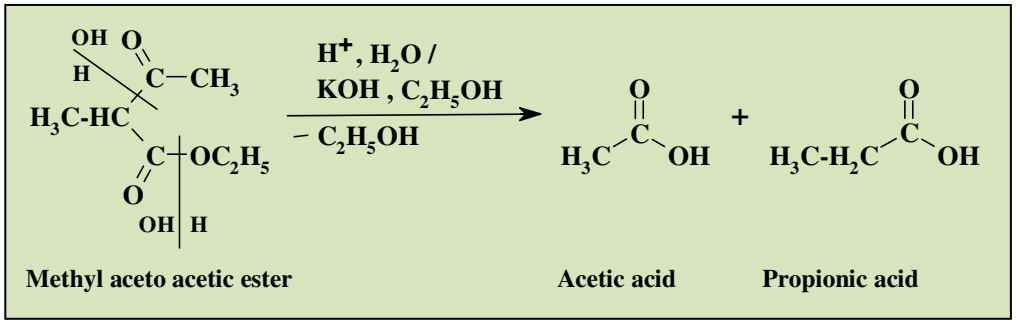
Synthetic application / alkylation - Aceto acetic ester reacted with base to form mono sodio aceto acetic ester (sodium ethyl aceto acetate), which reacted with alkyl halide to give mono alkyl aceto acetic ester. It further reacted with base to form mono sodio mono alkyl aceto acetic ester, which reacted with alkyl halide to give di alkyl aceto acetic ester. Its hydrolysis gives di alkyl acetic acid and acetic acid.



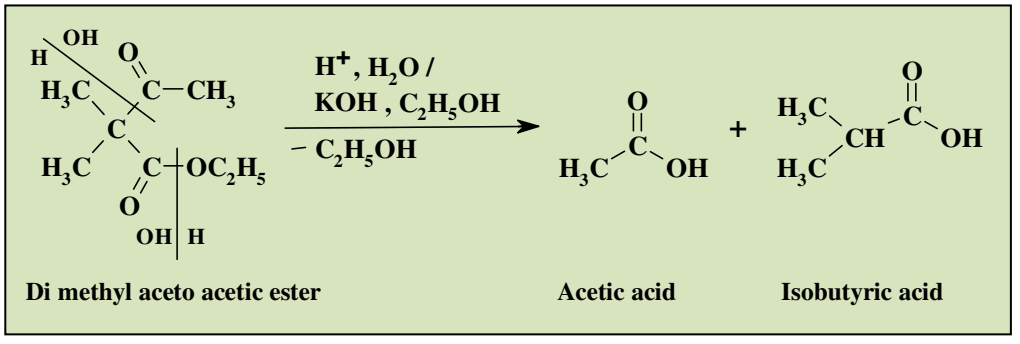
Formation of monobasic acid (acetic acid) - Aceto acetic ester hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give acetic acid.



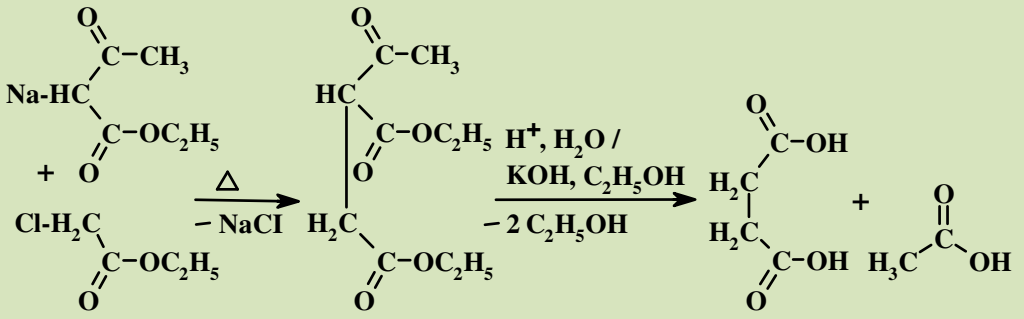
Formation of monobasic acid (propionic acid) - Methyl aceto acetic ester hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give acetic acid and propionic acid.



Formation of monobasic acid (isobutyric acid) - Dimethyl aceto acetic ester hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give acetic acid and isobutyric acid.



Formation of dibasic acid (succinic acid) - Mono sodio aceto acetic ester reacted with chloro acetic ester to give ethane aceto di carboxylic ester. It is hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give succinic acid and acetic acid.



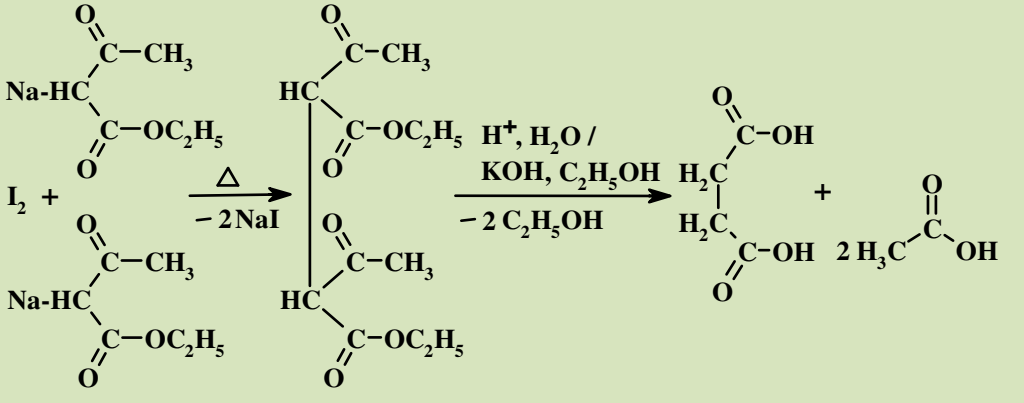
Monosodio aceto acetic ester
Sodium ethyl aceto acetate
+
Chloro acetic ester
Ethyl chloro acetate

Ethane aceto di carboxylic ester
Ethane aceto di ethyl carboxylate

Succinic acid

Acetic acid

Formation of dibasic acid (succinic acid) - Mono sodio aceto acetic ester reacted with iodine to give ethane di aceto di carboxylic ester. It is hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give succinic acid and acetic acid.



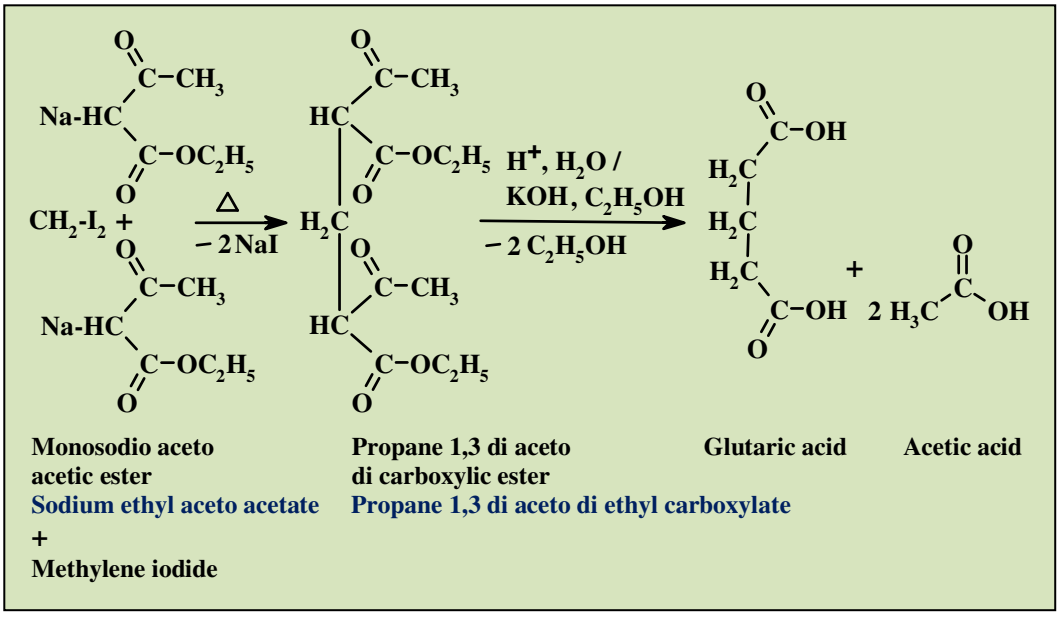
Monosodio aceto acetic ester
Sodium ethyl aceto acetate
+
Iodine

Ethane di aceto di carboxylic ester
Ethane di aceto di ethyl carboxylate

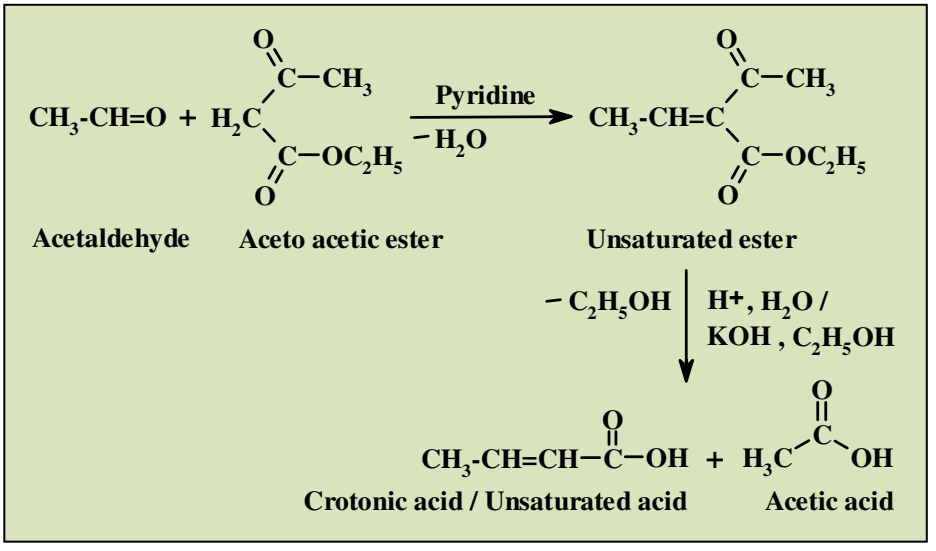
Succinic acid

Acetic acid

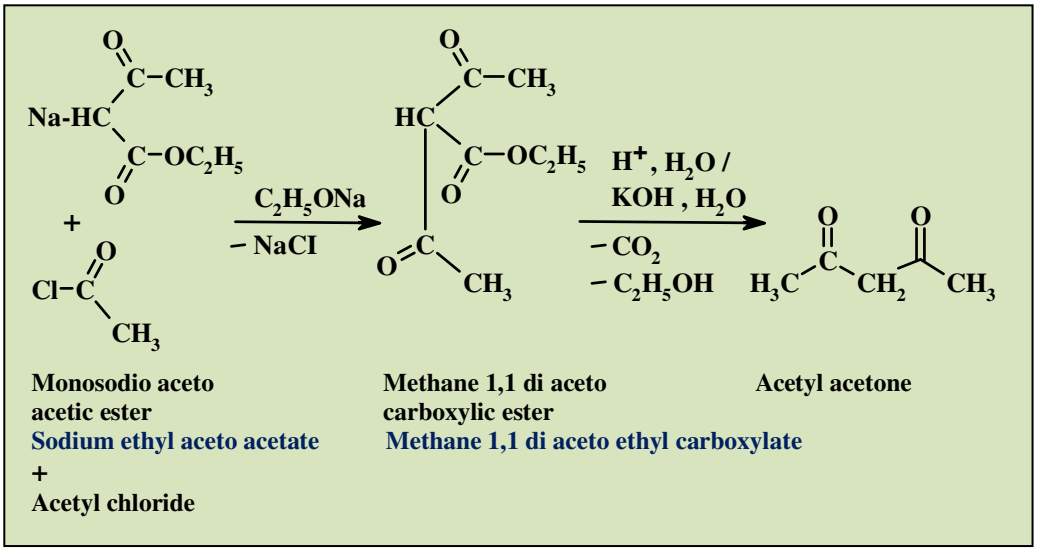
Formation of higher dibasic acid (glutaric acid) - Mono sodio aceto acetic ester reacted with methylene iodide to give propane 1,3 di aceto di carboxylic ester. It is hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give glutaric acid and acetic acid.



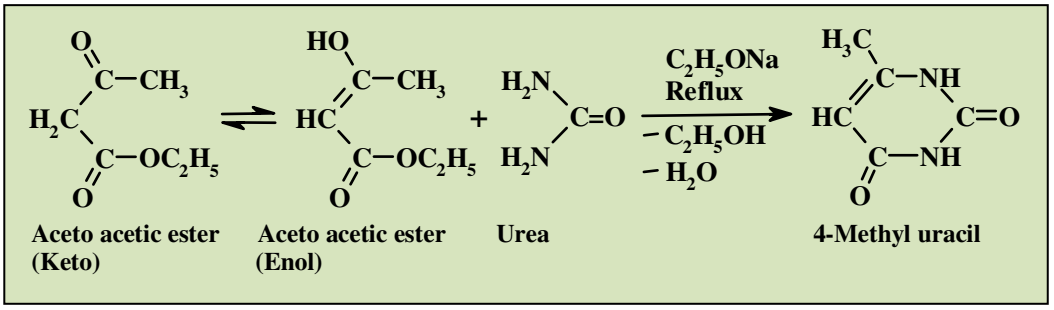
Formation of α,β-unsaturated acid (crotonic acid) - Aceto acetic ester condensed with acetaldehyde in presence of base pyridine to give α,β-unsaturated ester. It is hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give α,β-unsaturated crotonic acid and acetic acid.



Formation of ketone (acetyl acetone) - Mono sodio aceto acetic ester reacted with acetyl chloride in presence of base sodium ethoxide to give methane 1,1 di aceto carboxylic ester. It is hydrolyzed with dilute hydrochloric acid or concentrated alcoholic potassium hydroxide to give acetyl acetone (ketonic hydrolysis).



Formation of heterocyclic compound (4-methyl uracil) - Aceto acetic ester condensed with urea to give 4-methyl uracil.



Aceto acetic ester also condensed with ammonia, hydrazine, phenyl hydrazine, hydroxyl amine, thiourea etc. to give heterocyclic compounds.

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- 22 Years of teaching experience.
- 19 Years of research experience.
- 03 Students are awarded with Ph.D.
- 03 Students are awarded with M.Phil.
- 77 Research papers are published.
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