ORGANIC CHEMISTRY-II

UNIT 2 NOTES

PHENOLS

- ACIDITY OF PHENOLS
- EFFECT OF SUBSTITUENTS
- STRUCTURE AND USES OF PHENOL, CRESOL, RESOCINOL, NAPHTHOL

AROMATIC AMINES

- BASICITY OF AMINES
- EFFECT OF SUBSTITUENTS
- USES PF ARYL DIAZONIUM SALT

AROMATIC ACIDS

- ACIDITY
- EFFECT OF SUBSTITUENTS
- IMPORTANT REACTIONS OF BENZOIC ACID

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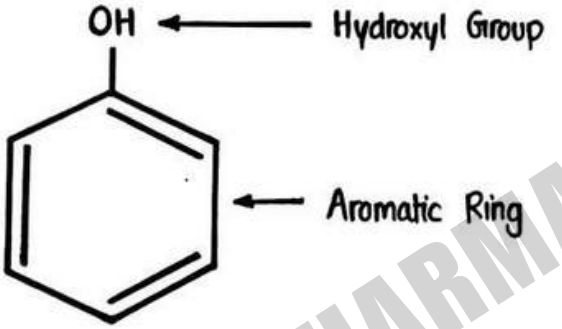
PHENOLS

- Phenols are aromatic organic compound containing hydroxyl group (-OH) directly attached to the carbon atom of aromatic ring.
- It is also known as Carbolic Acid.
- Phenols are nothing but a benzene derivative.
- Phenols are white or colourless crystalline solids.
- General Chemical Formula : C_6H_5OH.



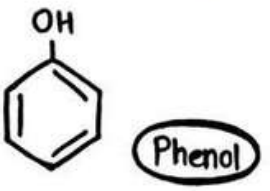
TYPES OF PHENOL

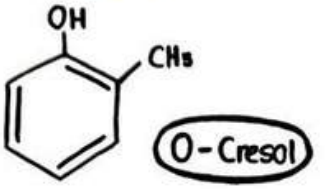
Phenols are of mainly 3 types :

① Monohydric Phenol
② Trihydric Phenol
③ Dihydric Phenol

① MONOHYDRIC PHENOL

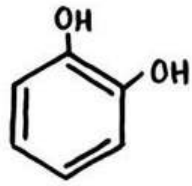
These phenols have only 1 hydroxyl (-OH) group.





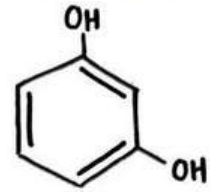
② Dihydric Phenol

These phenols possess two hydroxyl groups.



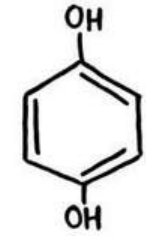
1,2 Dihydroxybenzene

Catechol



1,3 - Dihydroxybenzene

Resorcinol

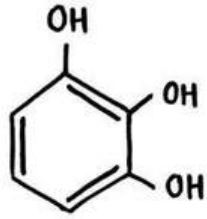


1,4 Dihydroxybenzene

Hydroquinone

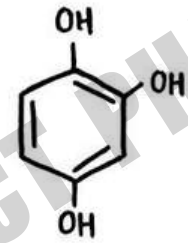
③ Trihydric Phenol

These phenols possess three hydroxyl group.



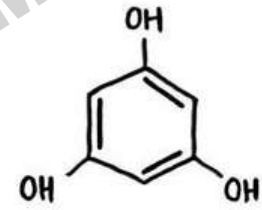
1,2,3 - Trihydroxybenzene

Pyrogallol



1,2,4 - Trihydroxybenzene

Hydroxyquinol



1,3,5 - Trihydroxybenzene

Phloroglucinol

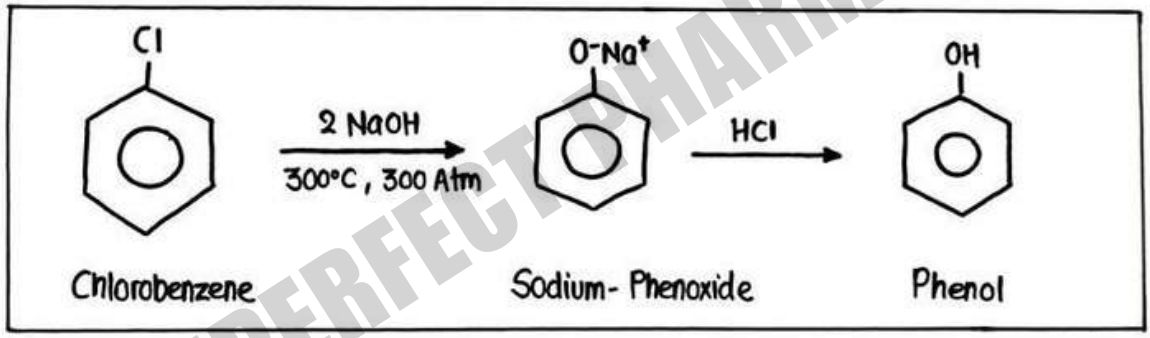
METHOD OF PREPARATION

Phenols can be prepared from various methods in which some of them are as follows :

① From Haloarenes
② From Benzene Sulphonic Acid
③ From Diazonium Salt
④ From Cumene

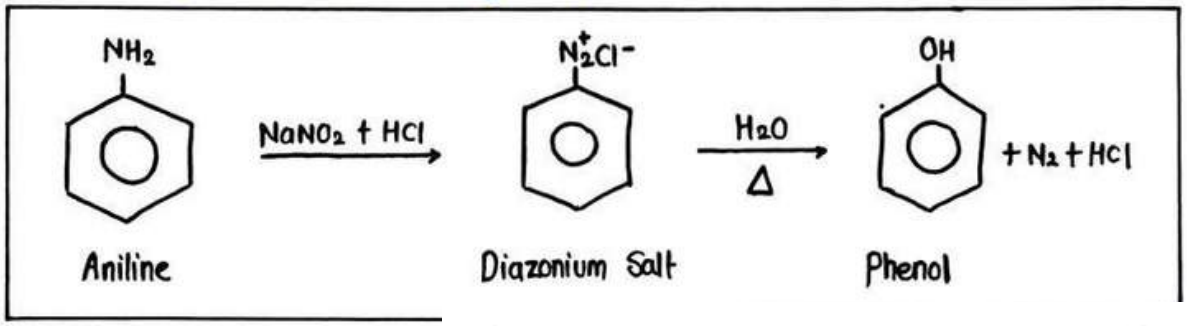
① FROM HALOARENES (Dow's PROCESS)

In this process, Chlorobenzene is heated with concentrated sodium hydroxide at high temperature & high pressure which results in the formation of Sodium Phenoxide which further reacts with HCl to give Phenol.



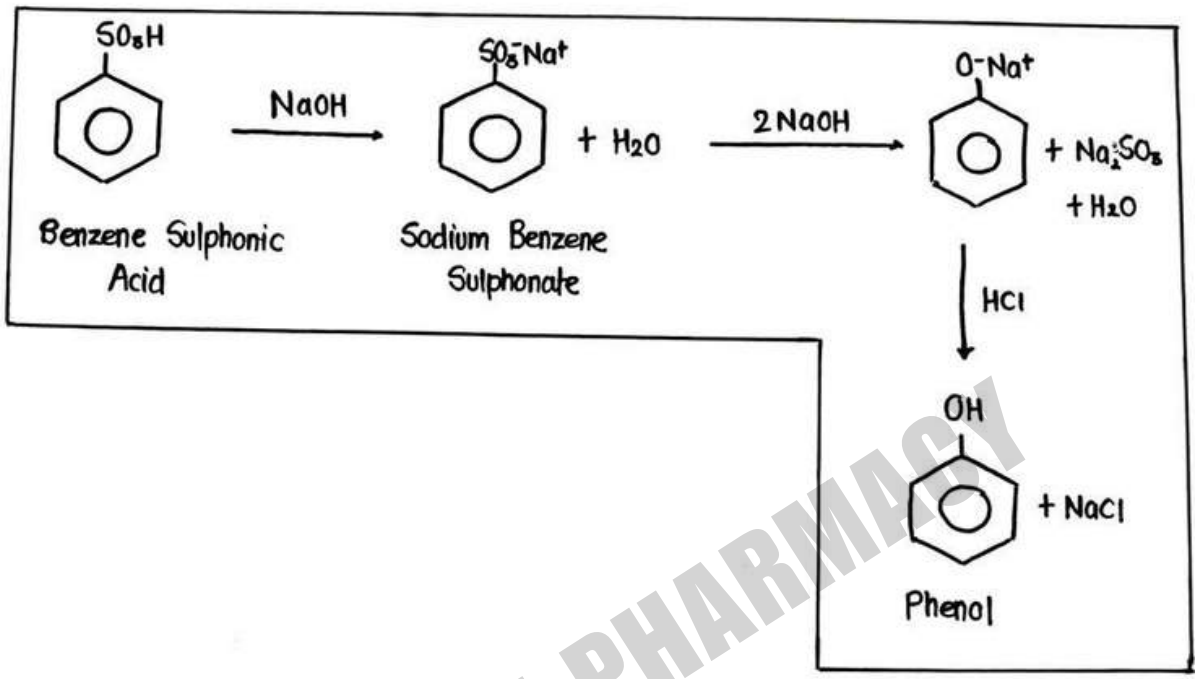
② FROM DIAZONIUM SALT

Aniline reacts with nitrous acid to form diazonium salt which further heated in aqueous medium to give phenol.



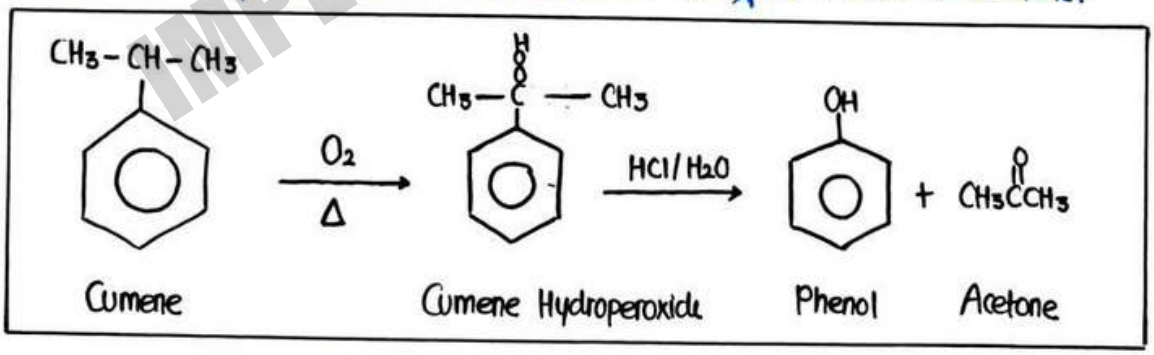
③ From Benzene Sulphonic Acid

Benzene Sulphonic Acid reacts with NaOH to form Sodium Benzene Sulphonate which further reacts with NaOH to form Sodium Phenoxide which on Acidification gives Phenol.



④ From Cumene (Iso-PropylBenzene)

Cumene undergoes oxidation to form Cumene hydroperoxide which further reacts with aqueous acidic medium (HCl) to give Phenol & Acetone.

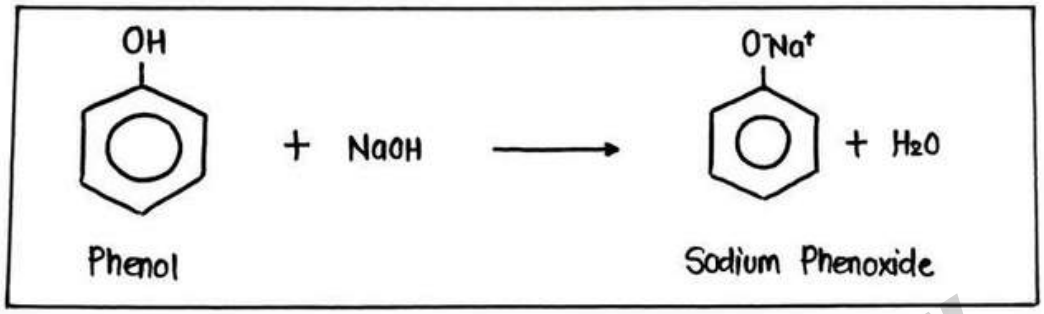


Chemical Reactions Of Phenol

Phenols undergoes following chemical reactions :

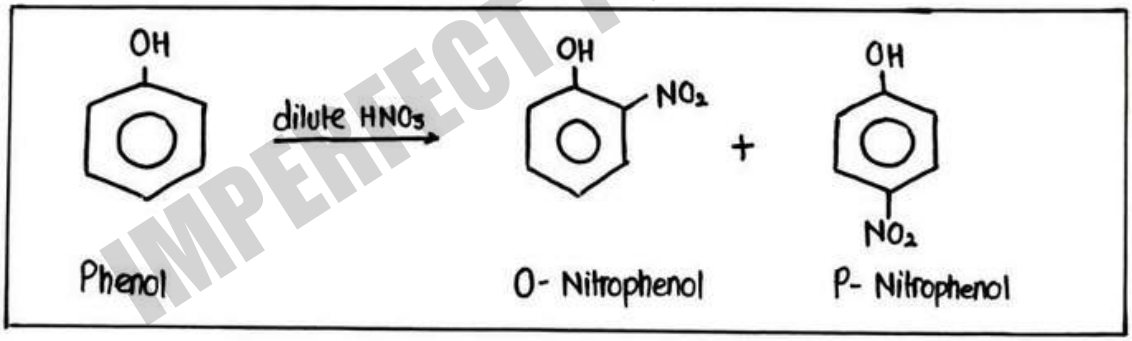
① Salt Formation

Phenols are acidic in nature hence reacts with base like NaOH to form Salt (Sodium Phenoxide)



② Nitration

Phenol reacts with dilute nitric acid to give ortho & para- nitrophenol



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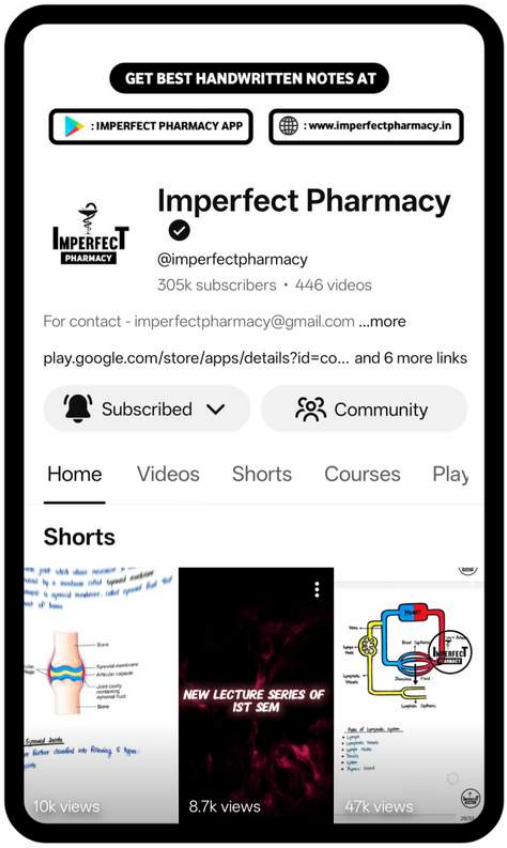

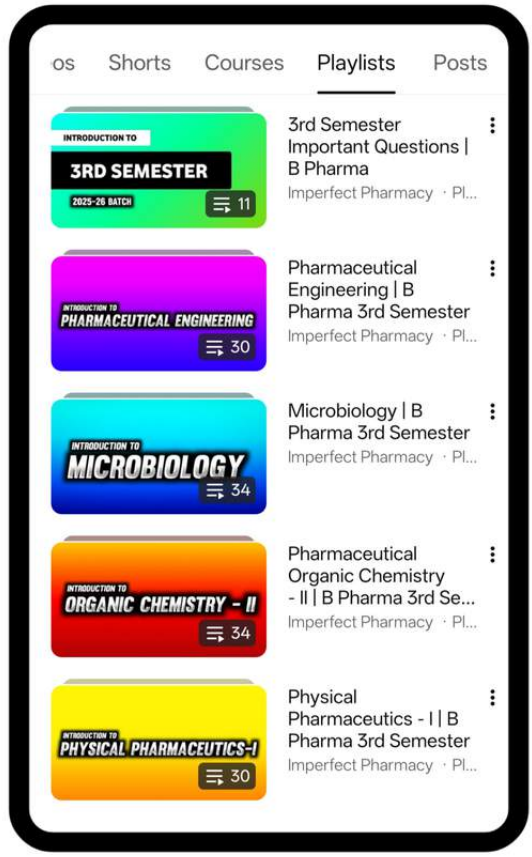

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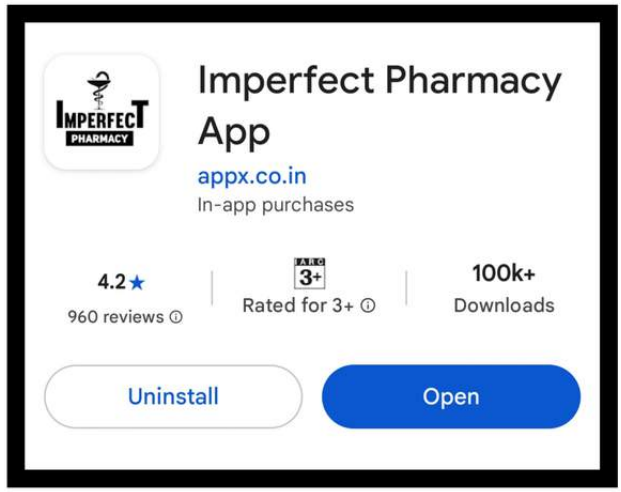
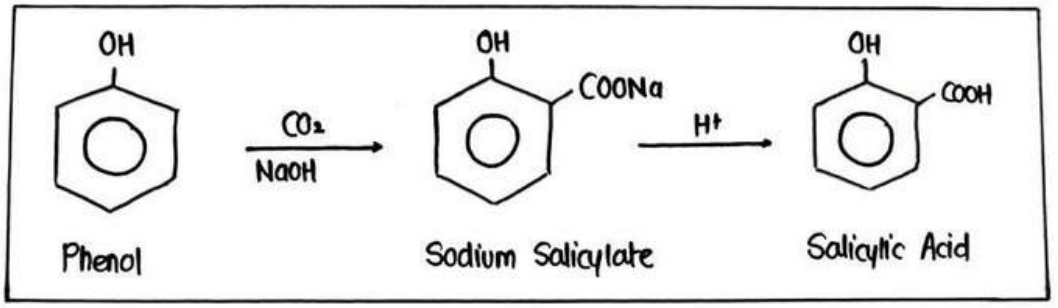


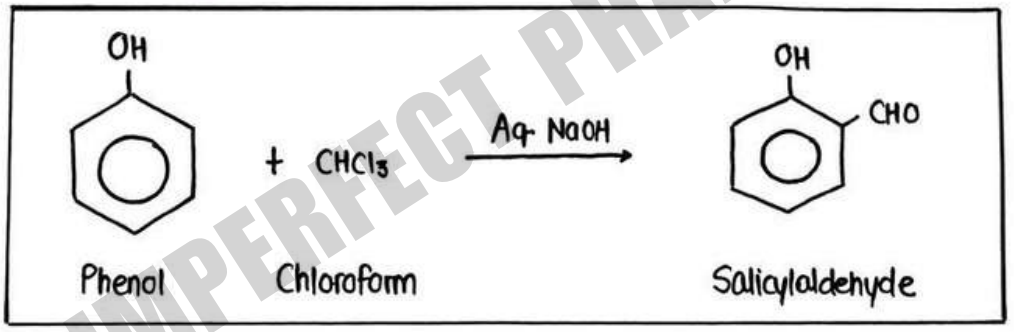
③ KOLBE'S REACTION

Phenol reacts with CO_2 in the presence of NaOH at high atmospheric pressure to give sodium salicylate which on further hydrolysis gives Salicylic Acid (Ortho- Hydroxybenzoic Acid).



④ REIMER- TIEMANN REACTION

Phenol reacts with chloroform in the presence of aqueous sodium Hydroxide to give Salicylaldehyde



QUALITATIVE TEST OF PHENOLS

There are various test performed to identify phenolic group in a compound :

① Litmus Paper Test
② Solubility Test
③ Ferric Chloride Test
④ Libermann's Test
⑤ Bromine Water Test

① LITMUS PAPER TEST

Since, Phenols are acidic in nature, hence they turns blue litmus paper into red.

② SOLUBILITY TEST

Phenols are weak acidic in nature hence they are soluble in sodium hydroxide but insoluble in sodium carbonate or sodium Bicarbonate.

③ FERRIC CHLORIDE TEST

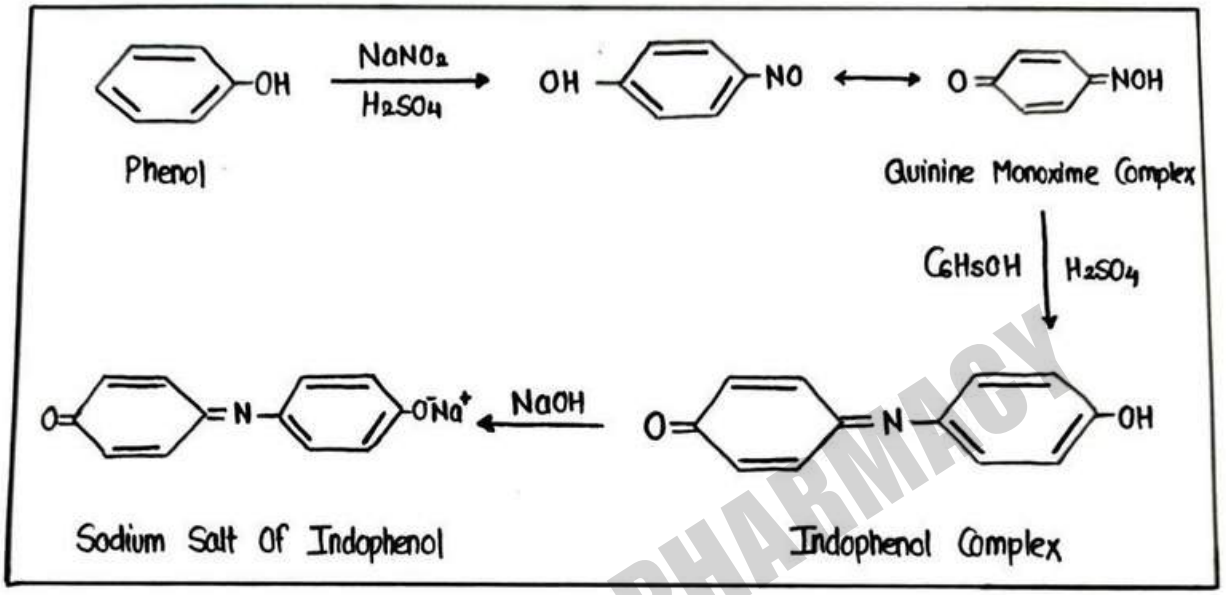
When aqueous solution of Phenol reacts with Ferric Chloride solution then it gives dark coloured complexes. The colour may be violet, Red, Blue or Green

$$6\,C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5)_6]^{3} + 3HCl + 3H^{+}$$

Coloured Complex

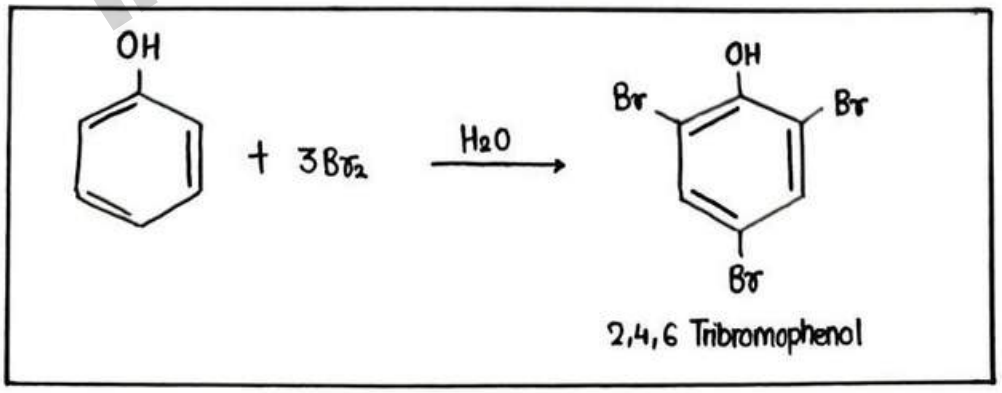
④ LIBERMANN'S TEST

Phenol reacts with concentrated Sulfuric Acid and sodium nitrite forms a yellow colour quinine monoxime complex which further reacts with excess of Phenol & Sulphuric Acid to give deep blue Indophenol complex which after reacting with Sodium Hydroxide forms Sodium Salt of Indophenol



⑤ BROMINE WATER TEST

When Bromine water is added to the aqueous solution of phenol, a white precipitate of Tribromophenol is formed.



Physical Properties Of Phenols

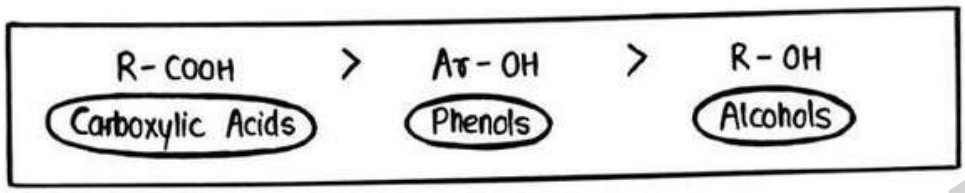
- Phenol is a colourless, crystalline and poisonous substance.
- It is sparingly soluble in water.
- Its melting point is 41°C & boiling point is 182°C.
- It causes blisters on skin.
- It is used as disinfectant & Antiseptics.

Uses Of Phenols

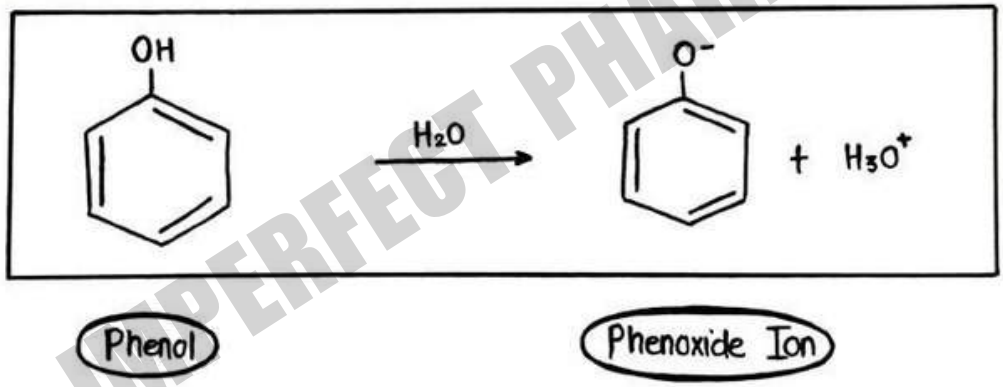
- In industries, phenols are used as Antioxidants & Disinfectants.
- It is also used in Photography, Paint, Rubber, Plastics, Pharmaceutical & Agricultural Industries.
- Phenols are used in manufacturing of cosmetics.
- They are also used in Germicidal Paints, Glue & various Dyes.

Acidity Of Phenols

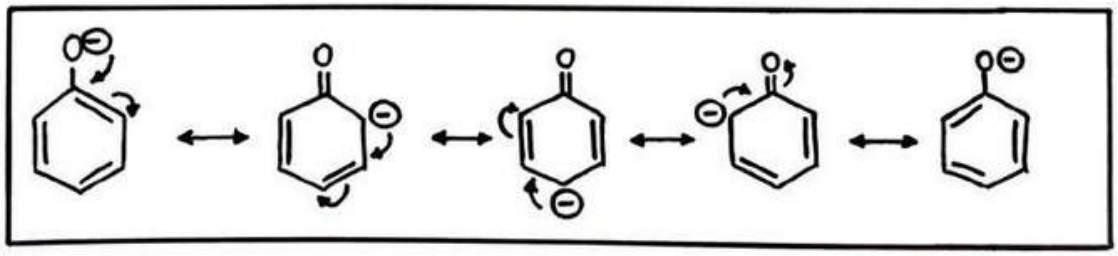
- Phenols are acidic in nature due to the formation of stable Phenoxide Ion after releasing H^+.
- Phenols are not very strong acids, they are weak acids.
- Phenols are more acidic than Alcohol but less acidic than Carboxylic Acids.



- Aqueous solution of Phenol leads to the formation of Phenoxide ion.

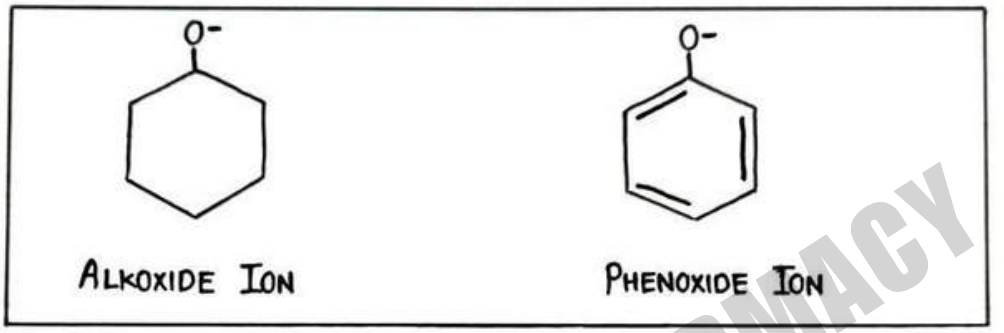


- Now this Phenoxide ion becomes very stable because it undergoes resonance stabilization due to delocalization of π bonds.



Comparison Between Acidity Of Phenols & Alcohol

① Phenols are more acidic in nature compare to Alcohols because when Phenols leaves H^+ ions, Phenoxide Ion becomes very stable due to the resonance stabilization but in the case of Alcohols, when alcohols gives H^+ ions Alkoxide Ion is not stable compare to Phenoxide ion because there is no possibility for the delocalization of negative charge hence no chance of Resonance.



② Atoms with more s character in their hybridization state are more stable when leaves H^+ ions, hence more acidic in nature.

Now Alkoxide Ions have sp^3 hybridization (25% s character)

Phenoxide Ions have sp^2 hybridization (33.33% s character)

Hence Phenoxide Ions becomes more stable & hence Phenols will be more acidic in nature.

Effect Of Substituents On Acidity Of Phenol

There are mainly two types of groups or substituents than can be present on Phenol ring.

- Electron - Withdrawing Group (-I Groups)
- Electron - Releasing Group (+I Groups)

Effect Of Electron Withdrawing Groups

- Electron withdrawing groups takes the electrons from Phenolic ring & thus result in an increase in the positive charge on the oxygen atom present in OH bond. The removal of protons becomes easier with increase in positive charge on oxygen atom & thus the acidity of phenols increases.
- The effect is more on Ortho & Para Positions compare to Meta position.
- Examples : $-NO_2$, $-CHO$, $-COOH$ etc.

Effect of Electron Releasing Group

- Electron releasing groups release the electron towards the ring system & thus the positive charge on oxygen atom is either get neutralised or decreased that leads to the stronger O-H bond & thus removal of proton becomes difficult.
- Thus, lesser the positive charge on oxygen, greater is the strength of O-H bond & lesser the acidity of Phenol.
- The effect is more on Ortho & Para positions
- Examples : $-CH_3$, $-NH_2$, $-OR$ etc.

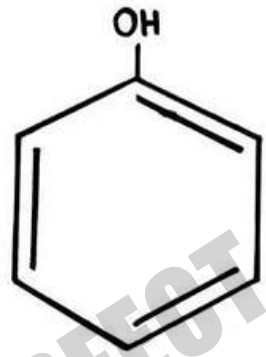
VIDEOS : IMPERFECT PHARMACY

STRUCTURE & USES OF

Given below is discussed the structure & uses of derivatives of Phenols :

① Phenol
② Cresol
③ Resorcinol
④ Napthols

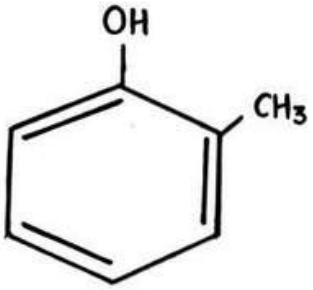
① PHENOL



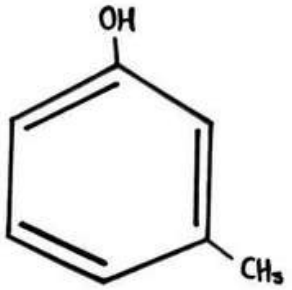
USES

- Phenol is proven to be effective Anti-bacterial, Anti-Fungal & Anti-viral agent.
- It is used as an antiseptic & disinfectant.
- It is also used in the manufacturing of mouthwashes.
- Phenol is also sometimes used as an Oral analgesic & mild anaesthetic.

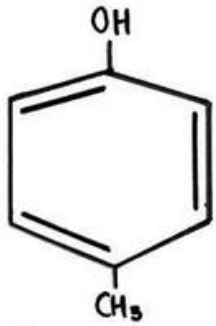
② CRESOL



Ortho - Cresol



Meta - Cresol

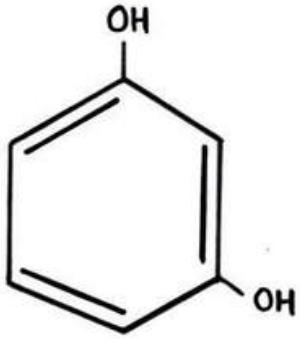


Para - Cresol

USES

- They are used as Germicides.
- They are used as Disinfectant & Antiseptics
- O-cresol & its derivatives are used as herbicides.
- m-cresol used in making photographic developers & explosives.
- P-cresol used in the production of BHT (Butylated Hydroxy Tyloidine) that is used as an Antioxidants.

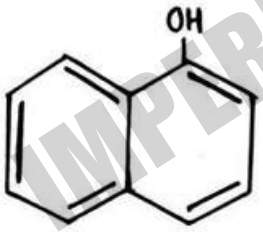
③ RESORCINOL



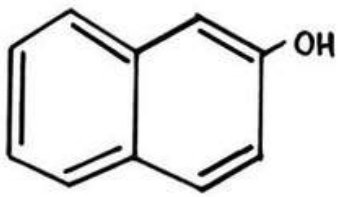
USES

It is used for manufacturing resins, dyes, plastic, medicines & other organic chemical compound.
It is used as an Antiseptics & Disinfectant.
It is also used in the treatment of Gastric Ulcer & Whooping Cough.

④ NAPTHOLS



α- Napthol



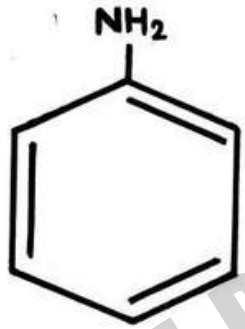
β- Napthol

USES

- They are used in manufacturing of dyes
- α- Napthols used as main ingredient of Molisch reagent.
- β- Napthol used for synthesizing dyes & used as antiseptic & in perfume industries.

AROMATIC AMINES

- These are the derivative of Aromatic hydrocarbons in which a hydrogen of benzene ring is replaced by **Amino Group**.
- Aromatic Amines can also be defined as derivative of Ammonia in which 1 or more hydrogen atom of Ammonia have been replaced by **Aryl Group**.
- In Aromatic Amines, Amino Group is bonded directly to Aromatic Ring.



ANILINE

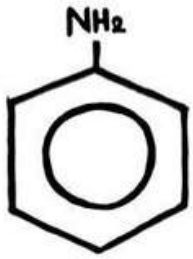
TYPES OF AROMATIC AMINES

Aromatic Amines are generally classified into 3 types

① Primary Aromatic Amines (1°)
② Secondary Aromatic Amines (2°)
③ Tertiary Aromatic Amines (3°)

Primary Aromatic Amines (1°)

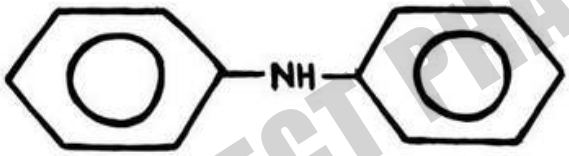
In these amines, one hydrogen atom of ammonia has been replaced by aryl group.



Aniline / Phenyl Amine

Secondary Aromatic Amines (2°)

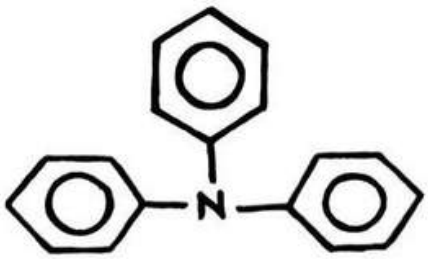
In these amines, two hydrogen atoms of ammonia have been replaced by Aryl Groups



Diphenyl Amine

Tertiary Aromatic Amines (3°)

In these amines, all 3 hydrogen atoms of Ammonia have been replaced by Aryl Groups.



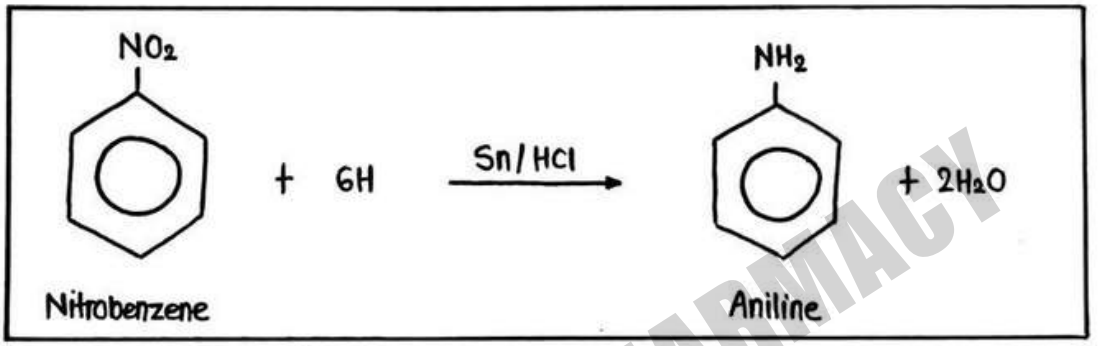
Triphenyl Amine

METHOD OF PREPARATION

Aromatic Amines can be prepared by using any one of the following method.

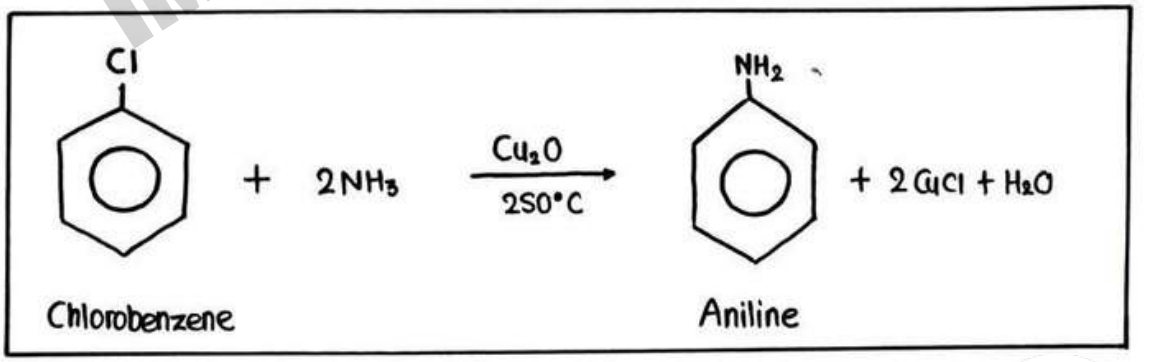
① REDUCTION OF NITRO COMPOUNDS

Aromatic Amines can be prepared by reduction of nitro compounds in the presence of reducing agents like tin & hydrochloric acid.



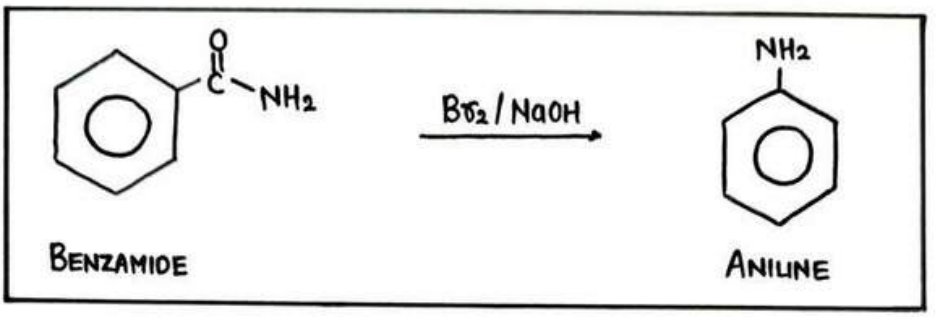
② AMMONOLYSIS OF CHLOROBENZENE

Under high pressure and high temperature Chlorobenzene reacts with Ammonia in the presence of Cuprous Oxide (catalyst) to give Aromatic Amines.



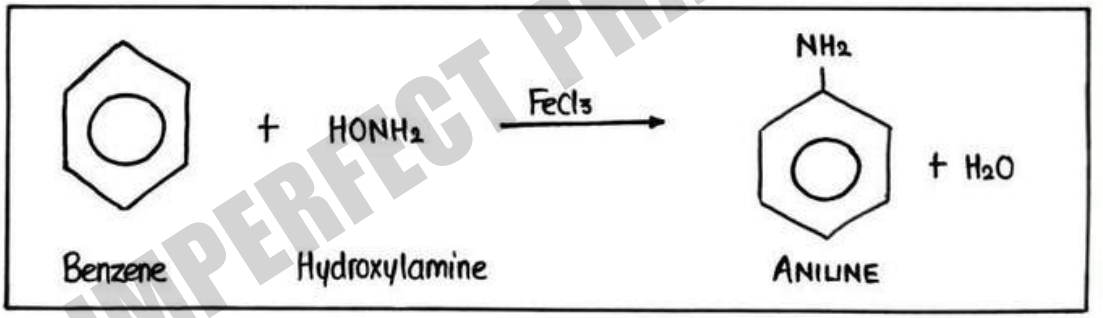
③ Hofmann Rearrangement Reaction

In this reaction, Aromatic Amides treated with bromine & Sodium Hydroxide to give Aromatic Amines.



④ Action Of Hydroxlamine With Hydrocarbons

In this reaction hydroxyamine reacts with Aromatic hydrocarbons in the presence of $FeCl_3$ (catalyst) to give Aromatic Amines.

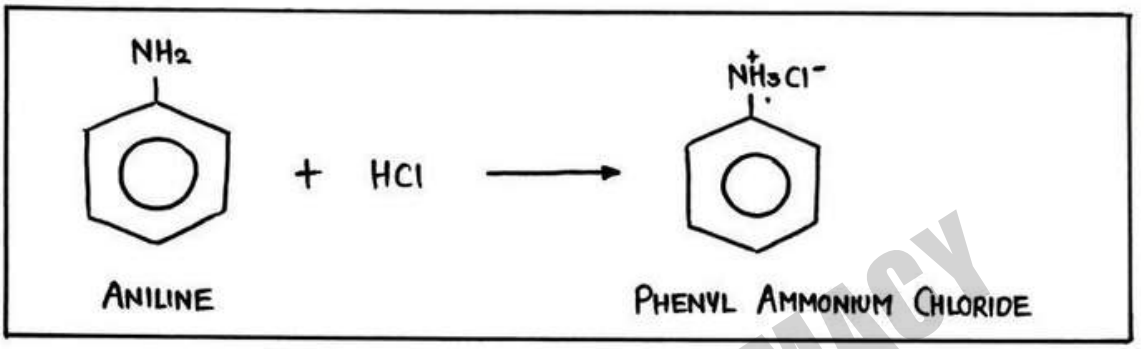


CHEMICAL REACTIONS

Aromatic Amines undergoes following chemical reactions :

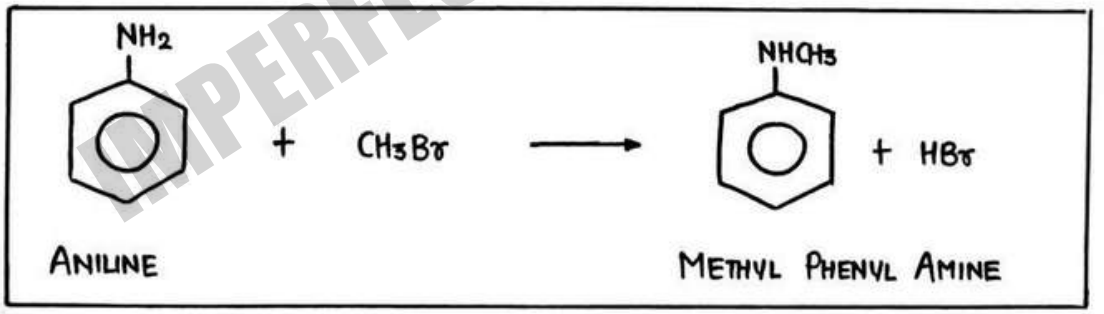
① SALT FORMATION

Aromatic Amines reacts with acids such as Hydrochloric Acids to form Phenyl Ammonium Chloride.



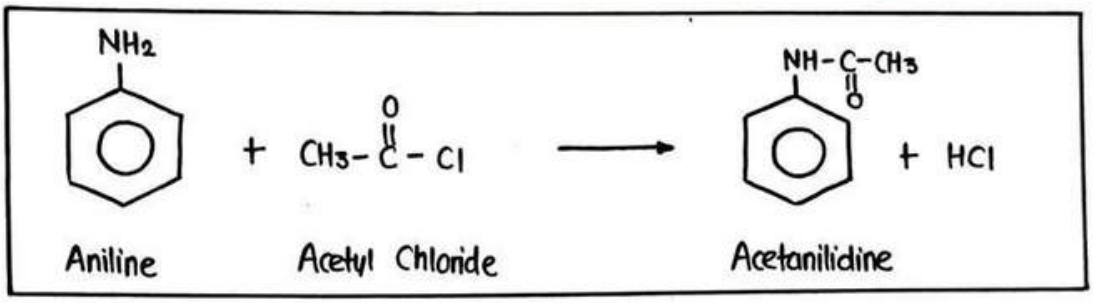
② REACTION WITH ALKYL HALIDES

Aromatic Amines reacts with Alkyl Halides to give Secondary Amines.



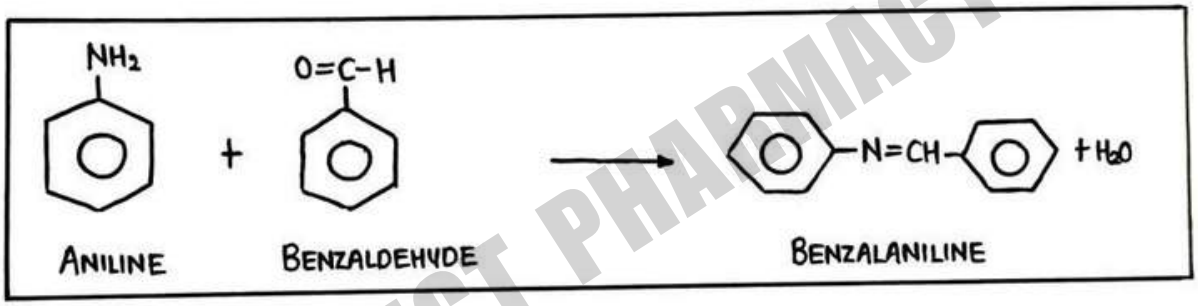
③ ACYLATION

In this, Aromatic Amines reacts with Acetyl Chloride to give Acetanilidine



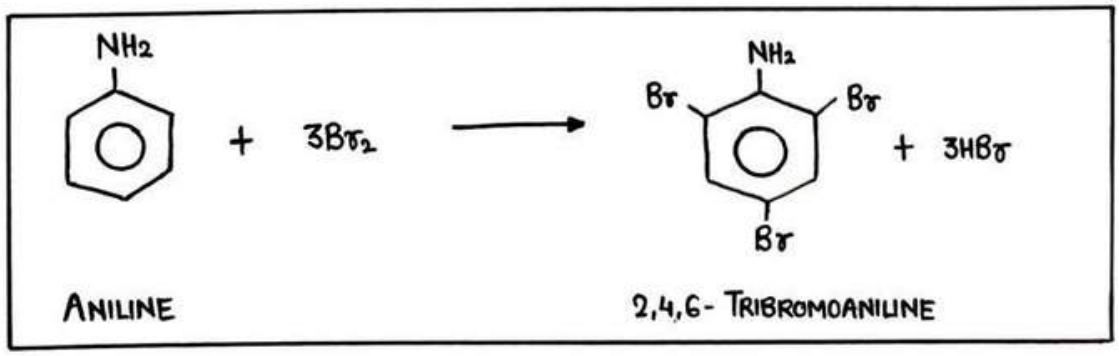
④ REACTION WITH BENZALDEHYDE

Aromatic Amines reacts with benzaldehyde to give benzaliniline.



⑤ HALOGENATION

Benzene reacts with Halogens to give Trisubstituted product.



Physical Properties Of Aromatic Amines

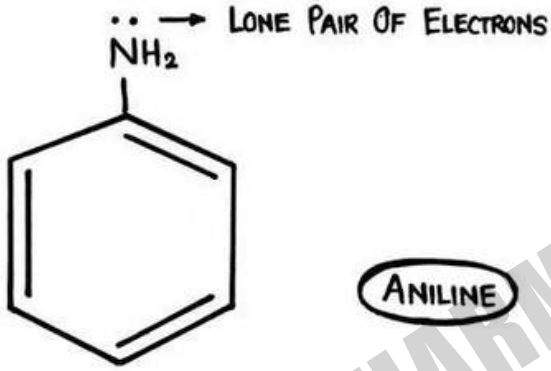
- Aromatic amines are colourless liquids or solids with an unpleasant odour.
- They are sparingly soluble in water & completely soluble in organic solvents.
- They are highly toxic & having carcinogenic effect.
- Its boiling point is approx 184.4°C.

Uses

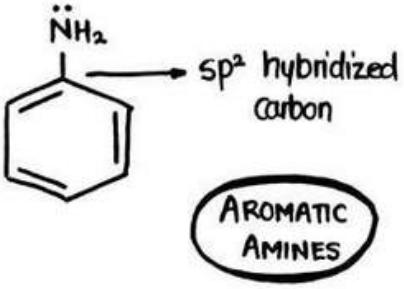
- It can be used in manufacturing of rubber & dyes.
- It can be used as pesticides.
- Often used as indicators like Methyl Orange.
- It can be used in manufacturing of drugs & resins.

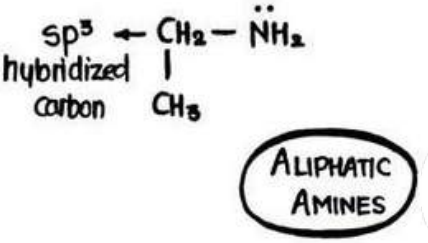
BASICITY OF AMINES

- Aromatic Amines are basic in nature due to the presence of lone pair of electrons on Nitrogen Atom.
- As we know, according to Lewis theory, Substance which can donate lone pair of electrons are basic in nature that's why Aromatic Amines behaves as Lewis Base.
- Also, when Aromatic Amines reacts with Acids they give salts.



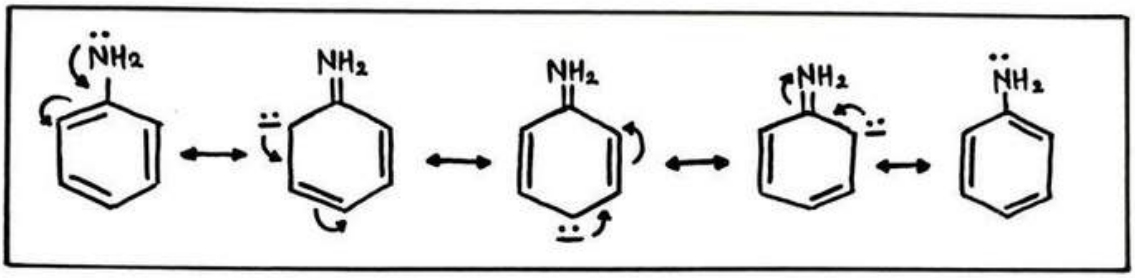
- Now although Aromatic Amines are basic in nature, however basicity of Aromatic Amines is less than Aliphatic Amines & Ammonia.
- The NH_2 group in Aromatic Amines is directly attached to sp^2 hybridised carbon of benzene ring, while in Alophatic Amines it is attached to sp^3 hybridized carbon.
- The electronegativity of sp^2 hybridized carbon is more compare to sp^3, hence aromatic amines attract the lone pair of Nitrogen & thus the availibility of lone pair on nitrogen atom decreased in Aromatic Amines.





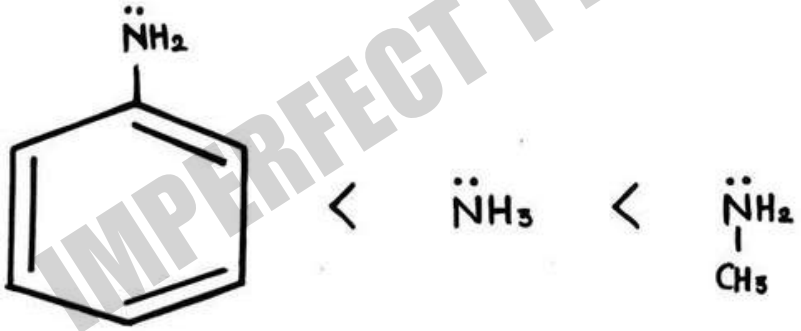
Resonance Effect In Aromatic Amines

Aromatic Amines like Aniline also shows a resonance effect due to which the lone pair on nitrogen atom involves in delocalisation with π electrons that tends to reducing the electron density on aromatic amines that ultimately leads to reducing its Basicity.



Basicity Of Amines In Increasing Order

Basicity of Amines in increasing order is shown below :



Aromatic Amine | Ammonia | Aliphatic Amine

Effect Of Substituents On Basicity Of Aromatic Amines

There are mainly two types of groups that can be present on Aromatic Amines :

① Electron Withdrawing Groups (-I Effect)

② Electron Releasing Groups (+I Effect)

Electron Withdrawing Groups

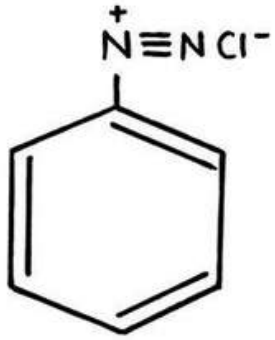
- Electron Withdrawing Groups decreases the electron density on Aromatic Amines, hence they tends to decrease the basicity of Aromatic Amines.
- Example : $-NO_2$, $-NR_3^+$, $-CN$ etc.

Electron Releasing Groups

- Electron releasing groups increases the electron density on Aromatic Amines , hence they tends to increase the basicity of Aromatic Amines.
- Example : $-CH_3$, $-OH$ etc.

ARYL DIAZONIUM SALT

- The word Diazo made from two words 'Di' means 'two' and 'Azo' means 'Nitrogen'
- Aryl Diazonium salt is an organic compound that contains a diazo group ($-N_2^+$) attached to an aromatic ring.
- These salts are important intermediates in organic chemistry & are commonly used in various reactions to synthesize Aromatic Compounds.



PREPARATION

Aryl Diazonium Salt prepared in following two steps :

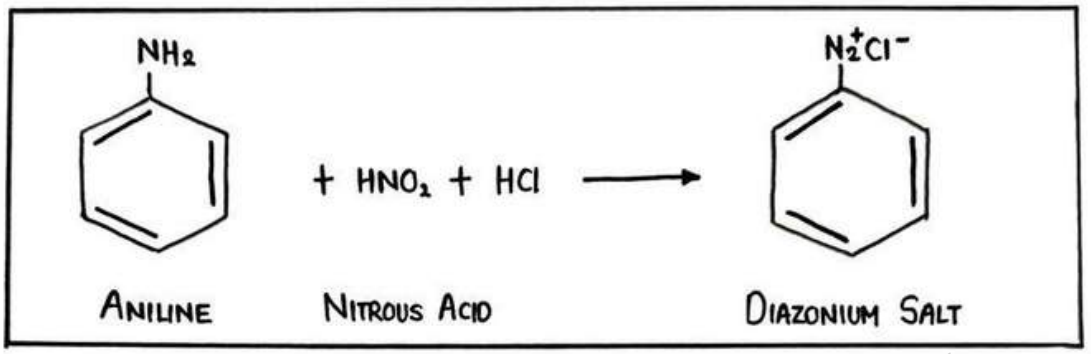
Step-I

In step I Sodium Nitrite ($NaNO_2$) react with HCl to form Nitrous Acid (HNO_2) & Sodium Chloride (NaCl)

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

STEP-II

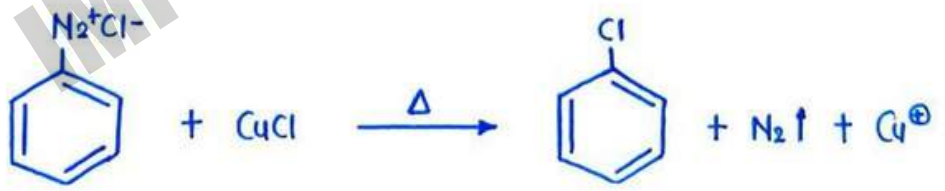
In the second step the formed Nitrous Acid reacts with Aromatic Amines to form Diazonium Salt.



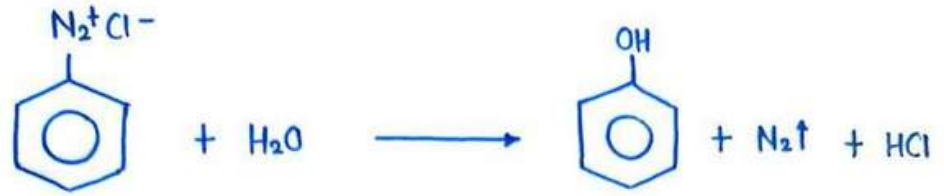
SYNTHETIC USES

- They are used for manufacturing of various dyes.
- They are used in various industries for preparing significant organic compounds.

① Preparation of Halogen Substituted Arenes



② Preparation Of Phenol



Diazonium Salt → Phenol

③ Preparation of Aryl Nitriles

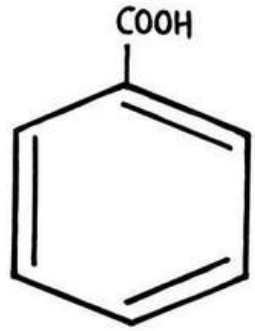
Diazonium Salt → Benzonitrile (Cyanobenzene)

Physical Properties Of Aryl Diazonium Salt

- They are colourless crystalline solids.
- They are highly water-soluble.
- They are ionic in nature.
- They are darken when exposed to air.

AROMATIC ACIDS

- Aromatic Acids are the derivative of Aromatic Hydrocarbons in which 1 Hydrogen of Aromatic ring is replaced by Carboxylic functional group (-COOH).
- These are the organic compounds that contains both Carboxylic Acid Functional Group (-COOH) & an Aromatic Ring.



BENZOIC ACID

PHYSICAL PROPERTIES OF BENZOIC ACID

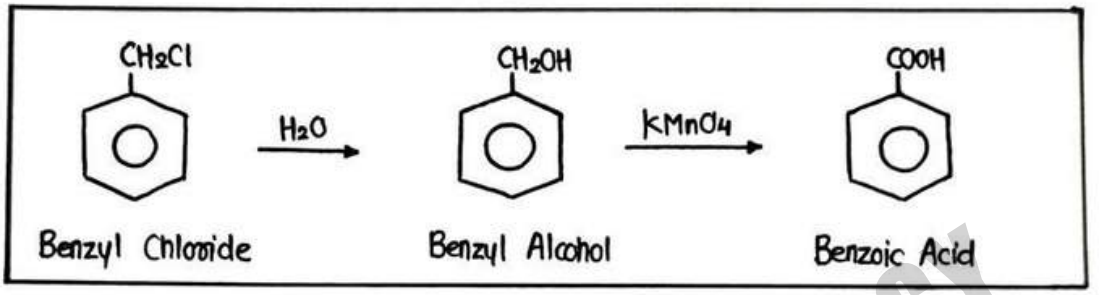
- They are Non-Polar
- They are soluble in hot water & organic solvents.
- They are generally crystalline solids with high melting point.
- They are colourless in nature.
- Its salts are used in medicines

METHOD OF PREPARATION

There are various method of preparation of Aromatic Acids as follows:

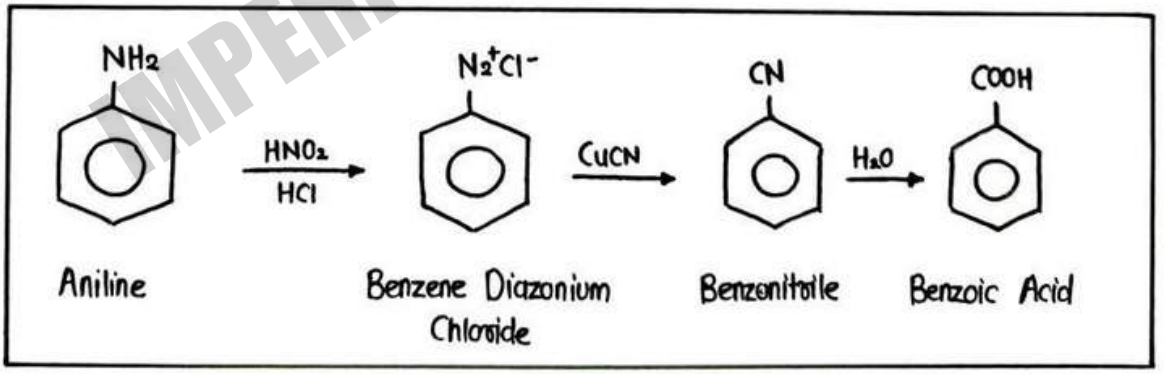
① OXIDATION

Oxidation of Benzyl Chloride with acidic potassium permanganate yeilds the formation of Benzoic Acid.



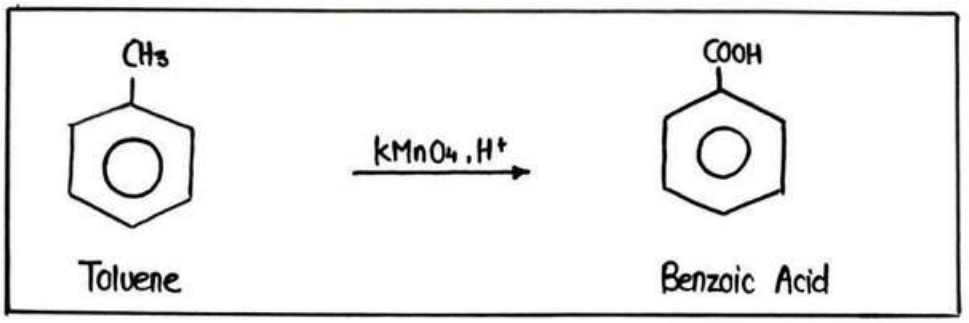
② FROM DIAZONIUM SALT

Aniline on reacting with Nitrous Acid (HNO_2/HCl) gives Benzene diazonium chloride which on reaction with CuCN produce Benzonitrile which on further hydrolysis gives Benzoic Acid



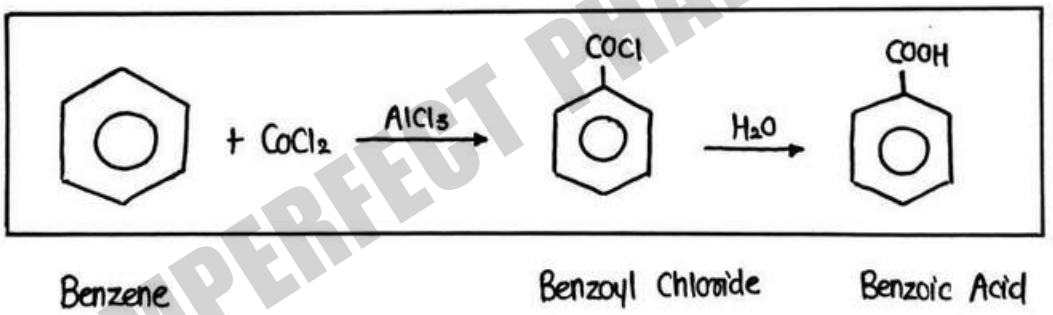
③ By Oxidation Of Alkyl Benzenes

Alkyl Benzenes are oxidized by dilute Nitric Acid or Potassium permanganate to give benzoic Acid.



④ From Benzene

Benzene reacts with Carbonyl Chloride to produce Benzyl Chloride which on further treatment with water to give Benzoic Acid.

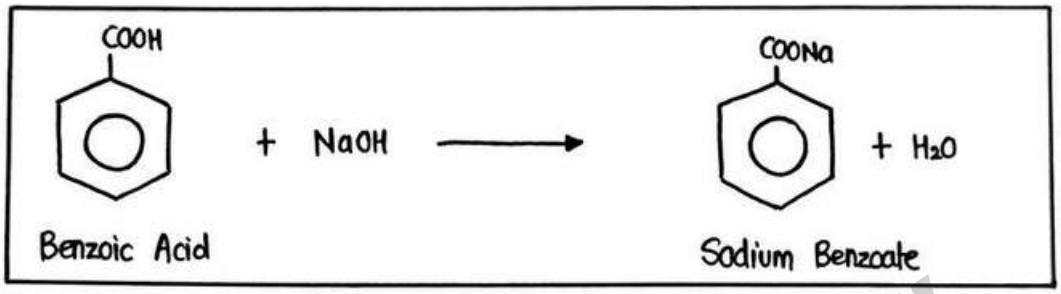


CHEMICAL REACTIONS

Aromatic Acids (Benzoic Acid) undergoes following chemical reactions :

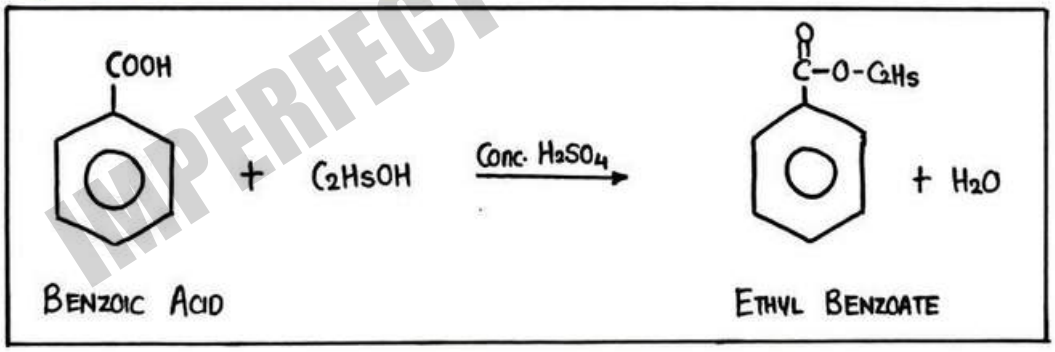
① SALT FORMATION

When Benzoic Acid reacts with base it forms salt.



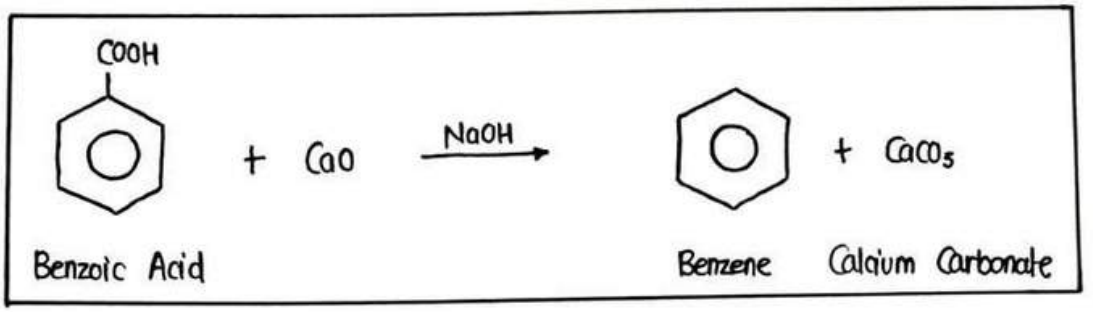
② ESTERIFICATION

Benzoic Acid reacts with Alcohols in the presence of concentrated Sulphuric Acid to form Ester.



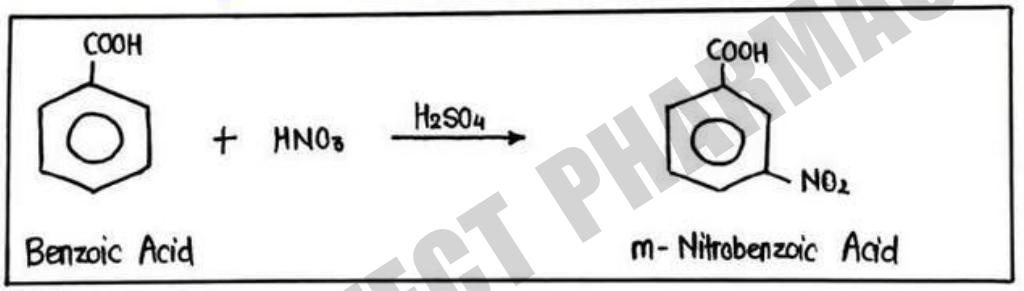
③ Decarboxylation

When Benzoic Acid reacts with Calcium Oxide in the presence of NaOH it gives Benzene & Calcium Carbonate.



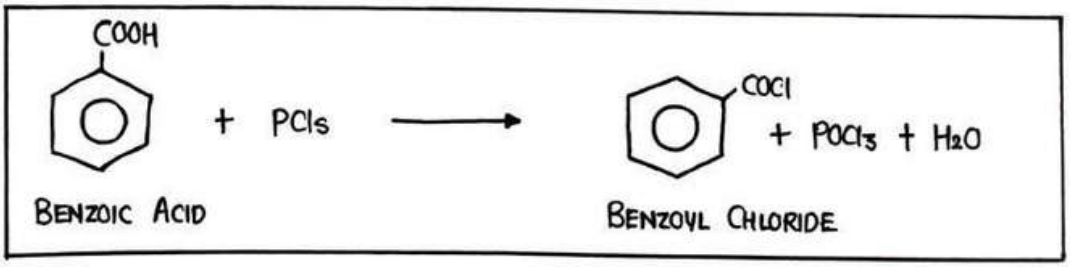
④ Nitration

When Benzoic Acid reacts with concentrated HNO_3 in the presence of H_2SO_4 it gives Nitrobenzoic Acid.



⑤ Formation of Benzoyl Chloride

Benzoic Acid reacts with Phosphorus Pentachloride to form Benzoyl Chloride.

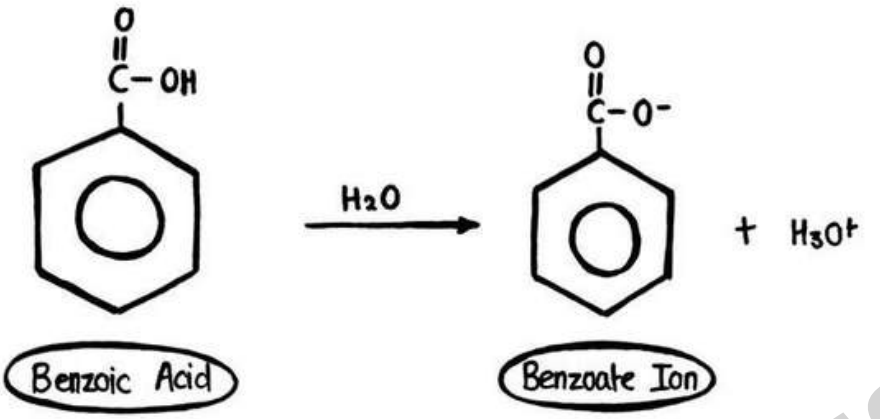


Uses Of Benzoic Acid

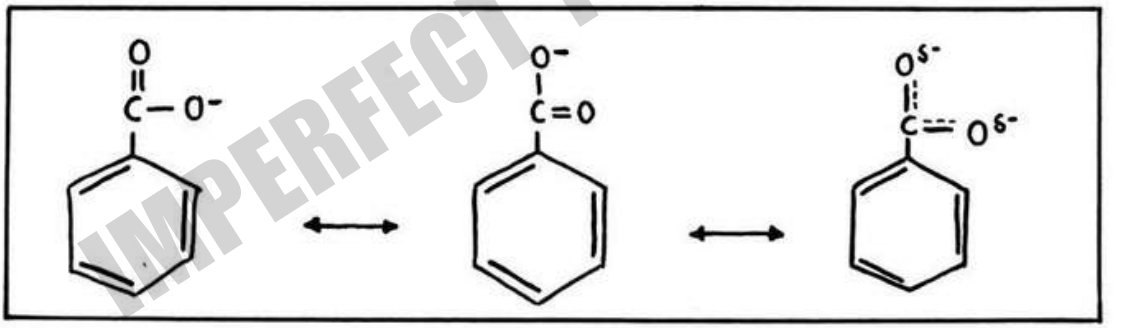
- Its salts are used in medicines.
- Its sodium salt is used as food preservatives.
- Its used for synthesizing various organic compounds.
- It is used for treating infection in bronchial tubes.
- It is also used in cosmetic products & various dyes.

Acidity Of Aromatic Acids

- Aromatic Acids as the name says are acidic in nature because they release H^+ ions when dissociate in aqueous solution.



- The negative charge on benzoate ion is effectively shared by both the oxygen atoms that maintains the stability of Benzoate Ion.



- The acidity of Aromatic Carboxylic Acids is even more than Aliphatic Acids, this is because sp^2 hybridized carbon of benzene ring is more electronegative compare to sp^3 hybridized carbon of Aliphatic Acids.

Effect Of Substituents On Acidity

There are mainly two types of groups present on Aromatic Acids:

① Electron Withdrawing Groups

② Electron Releasing Groups

Electron Withdrawing Groups

- Electron withdrawing groups tends to decrease the electron density on aromatic ring that ultimately increases the stability of Ring ⊖ hence Acidity increases.
- Example: $-NO_2$, $-CHO$ etc.

Electron Releasing Groups

- Electron releasing groups tends to increase the electron density on Aromatic Ring that ultimately decreases the stability of Ring ⊖ hence Acidity decreases.
- Example: $-CH_3$, $-OH$ etc.

THANK YOU

FOR CHOOSING IMPERFECT PHARMACY AS YOUR STUDY PARTNER

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