UNIT II

Phenols

Aromatic amines

Aromatic acids

UNIT II

Phenols

Aromatic amines

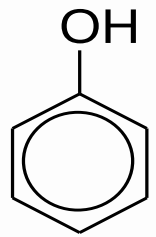
Aromatic acids

- **Phenols: Ar-OH**

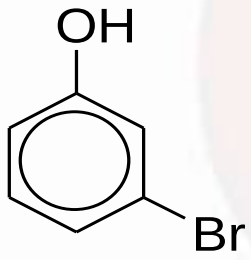
- Phenols are compounds with an –OH group attached to an aromatic carbon. Although they share the same functional group with alcohols, where the –OH group is attached to an aliphatic carbon, the chemistry of phenols is very different from that of alcohols.

Nomenclature.

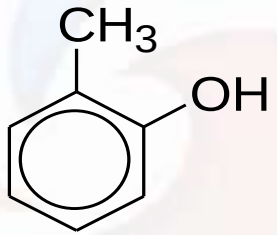
Phenols are usually named as substituted phenols. The methylphenols are given the special name, cresols. Some other phenols are named as hydroxy compounds.



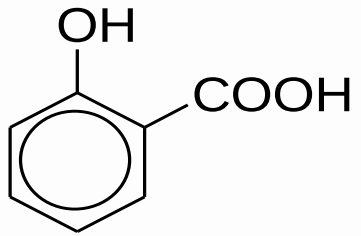
phenol



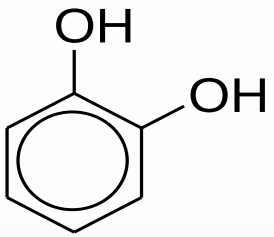
m-bromophenol



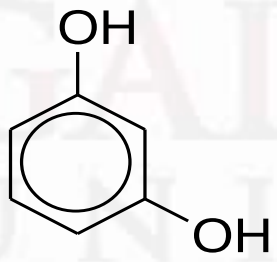
o-cresol



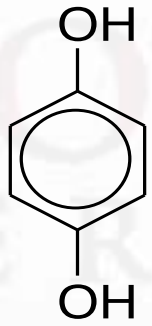
salicylic acid



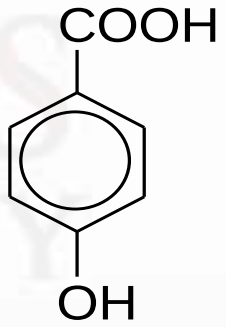
catechol



resorcinol



hydroquinone

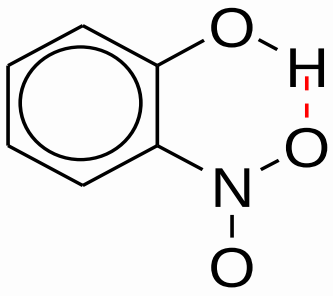


p-hydroxybenzoic acid

physical properties

- Phenols are polar and can hydrogen bond
- Phenols are water insoluble
- Phenols are stronger acids than water and will dissolve in 5% NaOH
- Phenols are weaker acids than carbonic acid and do not dissolve in 5% $NaHCO_3$

Intramolecular hydrogen bonding is possible in some ortho-substituted phenols. This intramolecular hydrogen bonding reduces water solubility and increases volatility. Thus, *o*-nitrophenol is steam distillable while the isomeric *p*-nitrophenol is not.

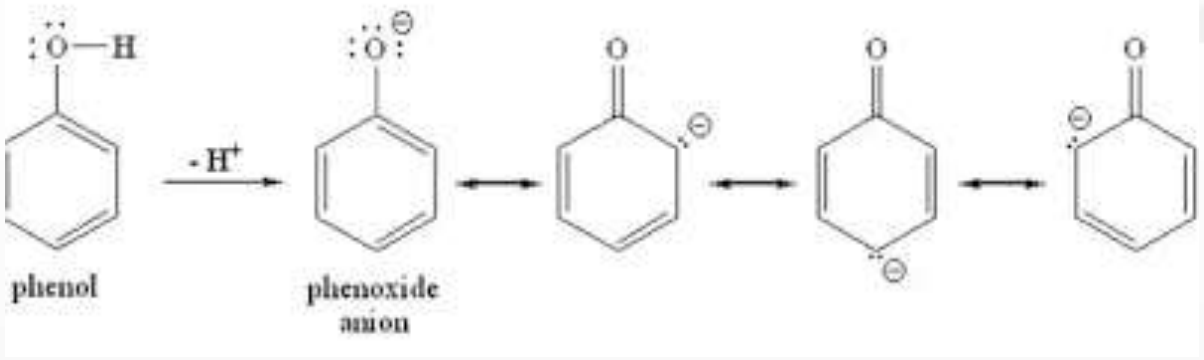


o-nitrophenol
bp 100^{o}C at 100 mm
0.2 g / 100 mL water
volatile with steam

p-nitrophenol
bp *decomposes*
1.69 g / 100 mL water
non-volatile with steam

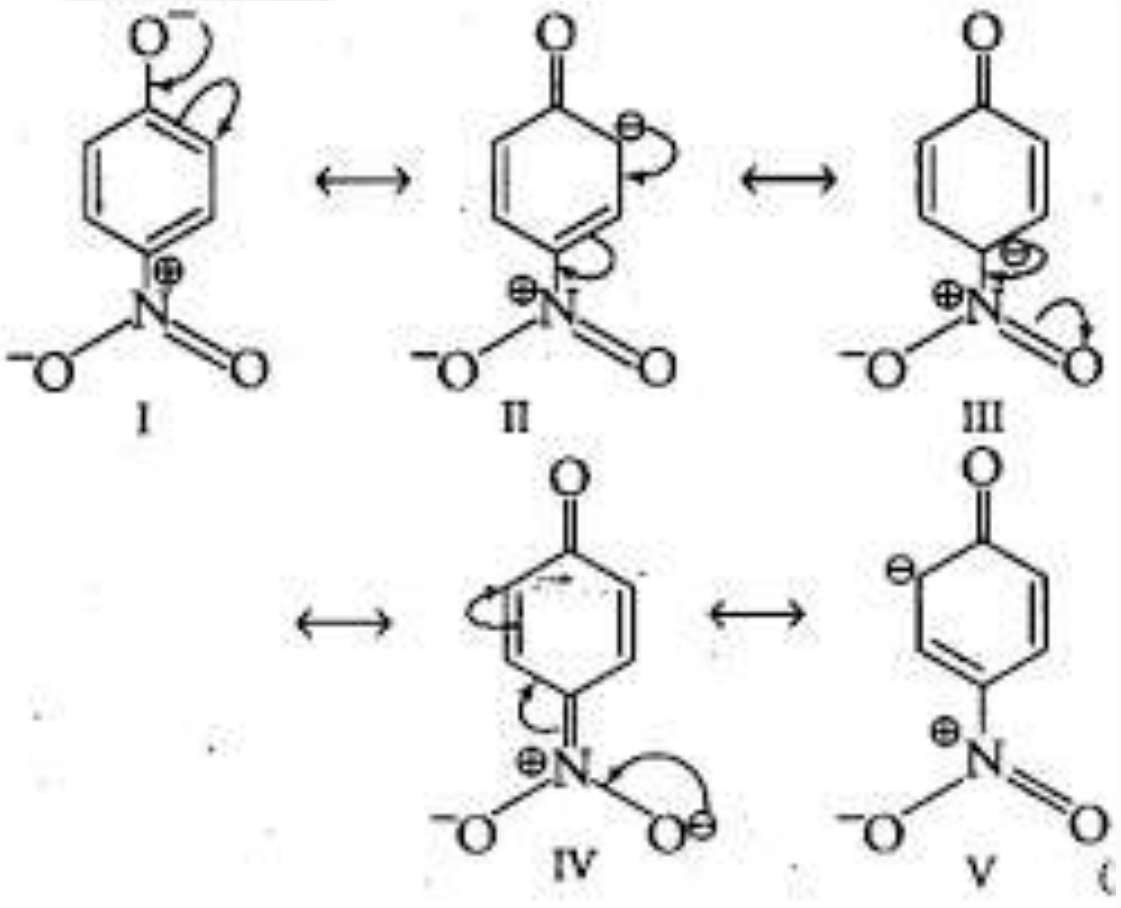
Acidity of phenols

- Phenols are much more acidic than alcohols, but less acidic than carboxylic acids
- They are acidic due to the formation of stable phenoxide ions in aqueous solutions
- The phenoxide ion is stable to resonance
- The negative charge is distributed throughout the benzene ring and thereby effectively dispersed.
- This charge delocalization is a stabilizing factor for the phenoxide ion
- No such resonance is possible in alkoxide ions derived from alcohols, and hence less acidic than phenols.



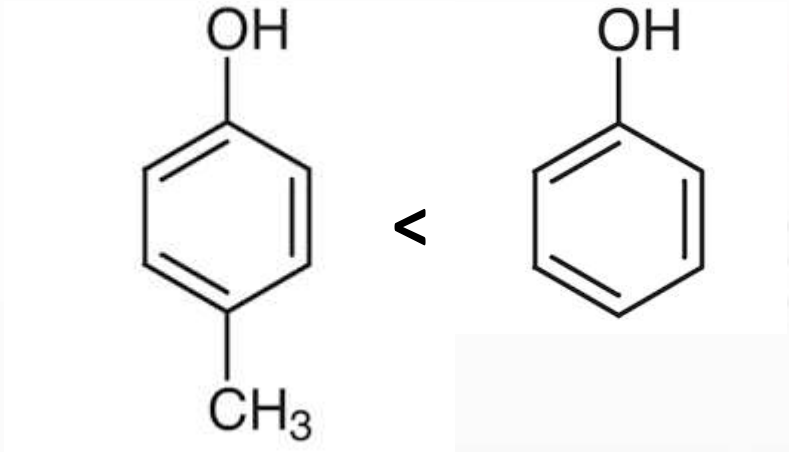
Effect of substituents on acidity of phenols

- Effect of electron withdrawing substituents:
- an electron withdrawing group on the aromatic ring is acid strengthening.
- Ex. NO2, Cl, CN, COOH, etc.
- EWG enables the ring to withdraw more electrons from the phenoxy oxygen and stabilizes the phenoxide ion still further and results in a stronger acid.
- Ex. Para-nitrophenol is more acidic than phenol



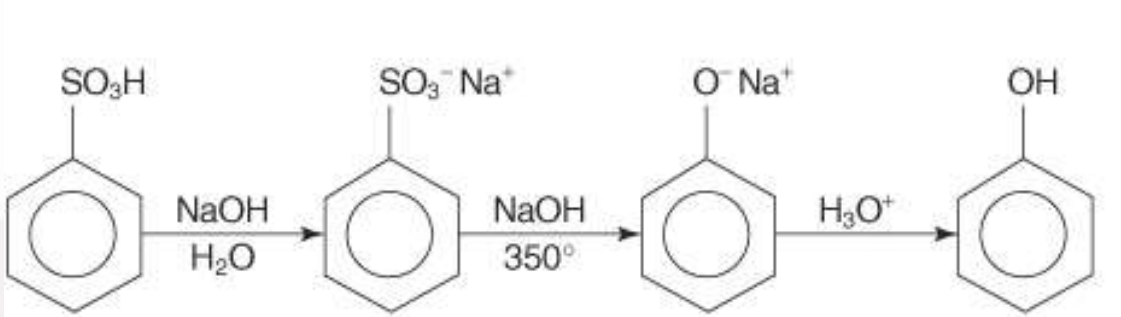
Effect of substituents on acidity of phenols

- Effect of electron releasing substituents:
- an electron releasing group on the aromatic ring is acid weakening.
- Ex. CH3, OCH3, NH2, etc.
- ERG strengthens the negative charge on phenoxy oxygen and inhibits the charge delocalization due to resonance. This destabilizes the phenoxide ion and results in a weaker acid.
- Ex. Para-nitrocresol is less acidic than phenol

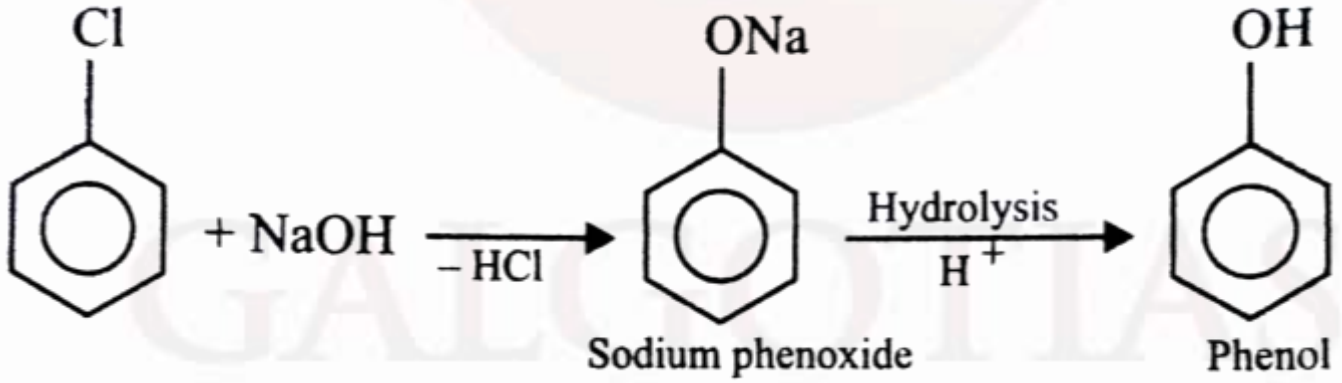


Preparation of phenol

- REACTION OF SODIUM SALT OF BENZENE SULFONIC ACID WITH NaOH:
  - Sodium benzene sulfonate on fusion with strong alkali like NaOH at 300^{o}C give sodium phenoxide which on treatment with HCl gives phenol

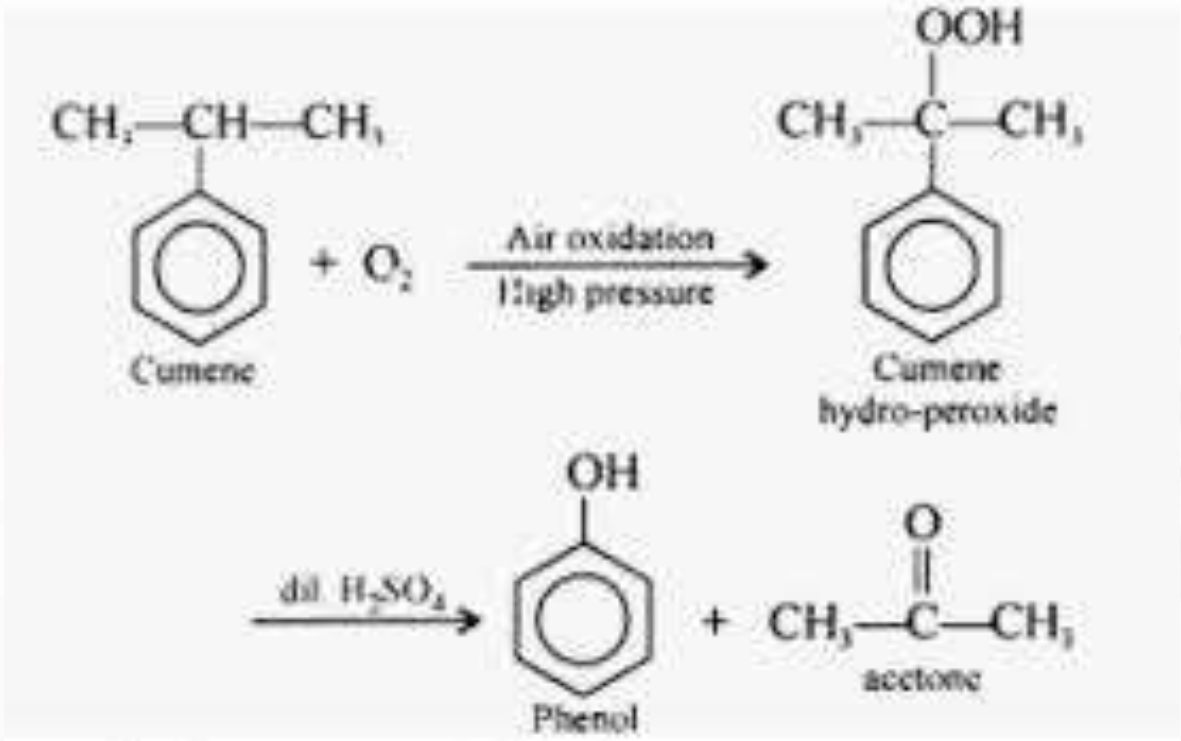


- **BASE HYDROLYSIS OF CHLOROBENZEN (DOW'S METHOD)**
  - Chlorobenzene is hydrolysed by heating with 10% NaOH at 360^{o}C under high pressure to form sodium phenoxide which on treating with HCl gives phenol



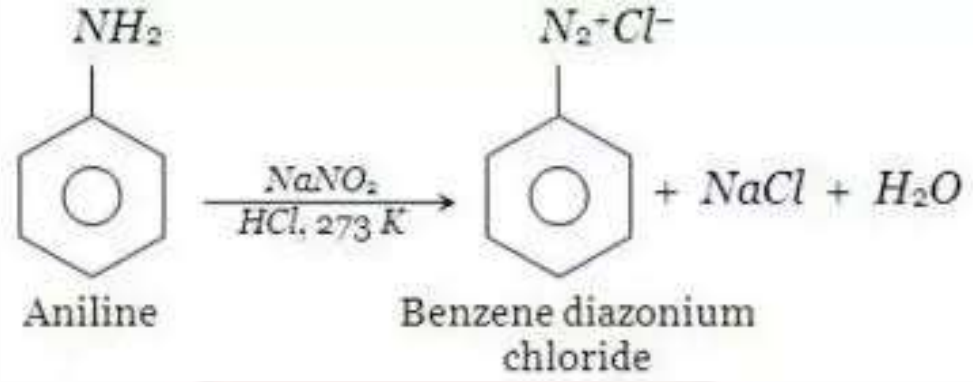
ACIDIC OXIDATION OF CUMENE

- It is recently developed commercial method for preparation of phenol.
- Cumene is oxidized by atmospheric oxygen is presence of metal catalyst into Cumene Hydroperoxide.
- The hydroperoxide is converted into phenol through acid catalyzed arrangement

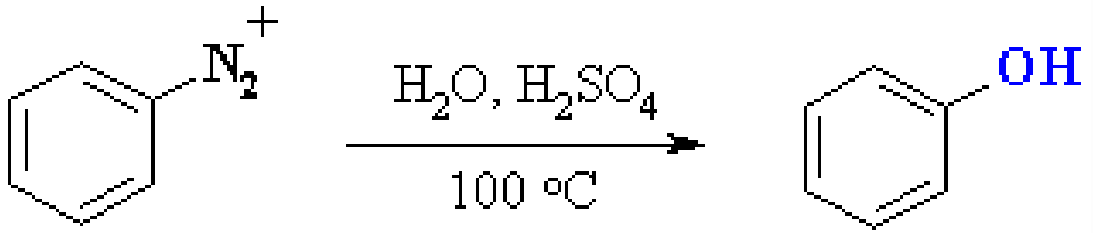


Preparation of phenol from Aryl Diazonium salts

- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid



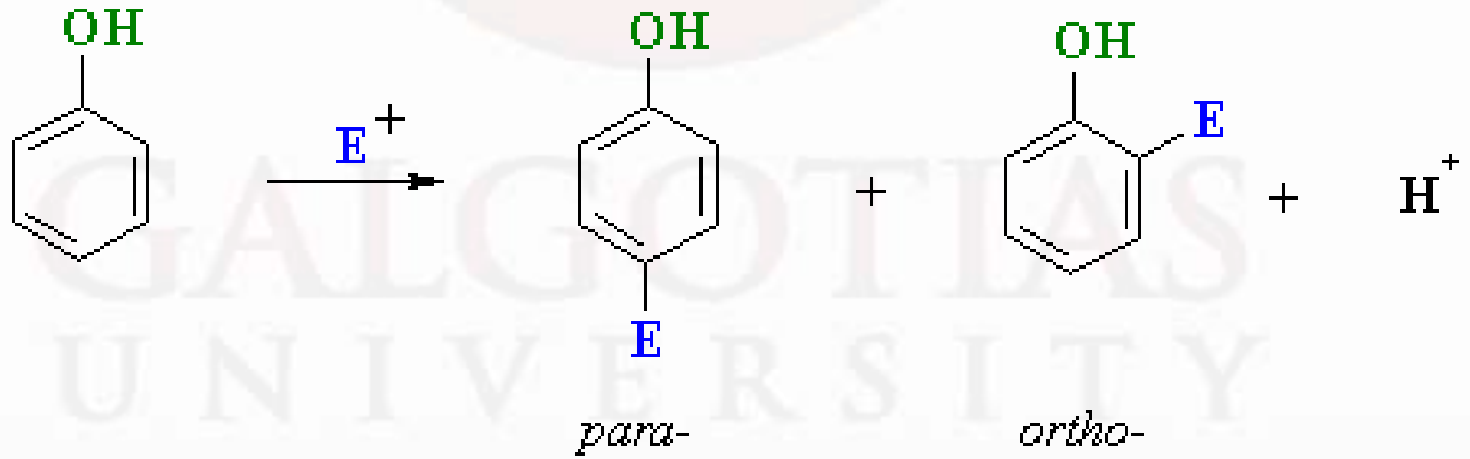
- Aryl diazonium salts can be converted into phenols using H_2O/H_2SO_4/ heat

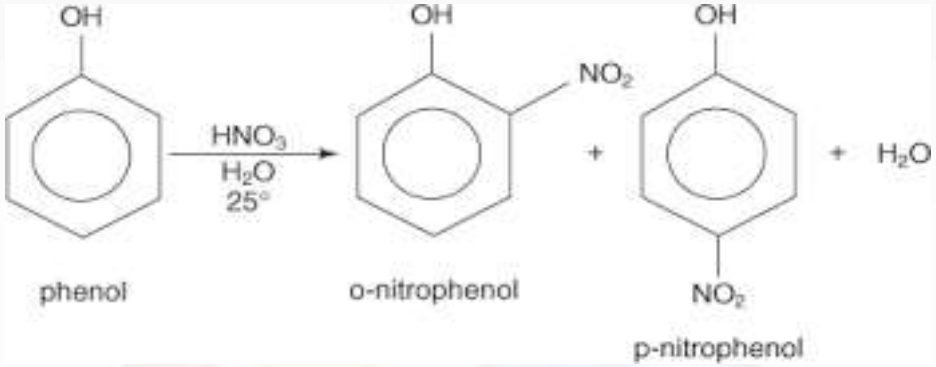


Reactions of phenol

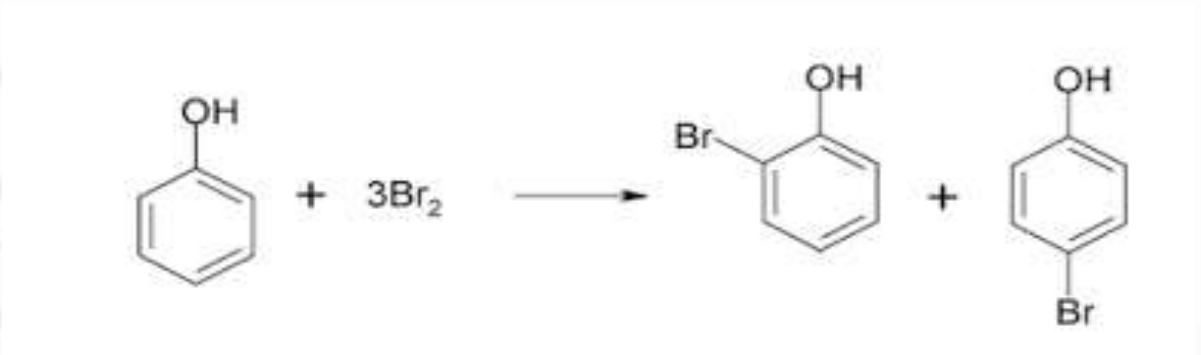
1. Phenol gives a violet colour with ferric chloride. This is a characteristic of all compounds containing OH group linked to benzene ring.

2. Electrophilic substitution reaction: Phenols can be nitrated, halogenated and sulphonated to give ortho and para derivatives.

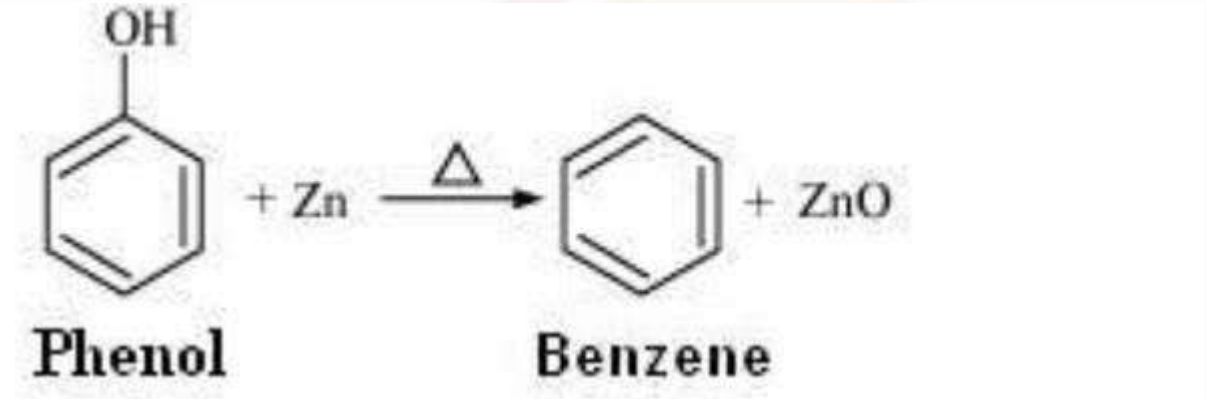



OH
OH
OH
NO2
HNO3
H2O
25°
+
+ H2O
NO2
phenol
o-nitrophenol
p-nitrophenol

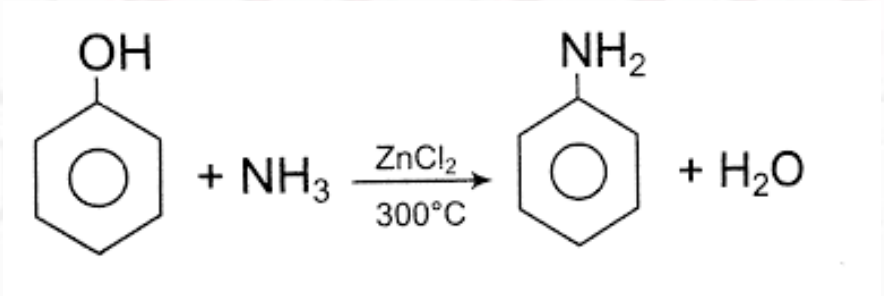

OH
OH
OH
Conc. H2SO4
SO3H
+
SO3H
o-hydroxybenzene sulphonic acid
p-hydroxybenzene sulphonic acid


OH
+ 3Br2
OH
OH
Br
+
Br

3. When phenol is distilled with zinc dust then it gives benzene and zinc oxide.



4. When phenol is heated with ammonia and zinc chloride or calcium chloride, it gives aniline.

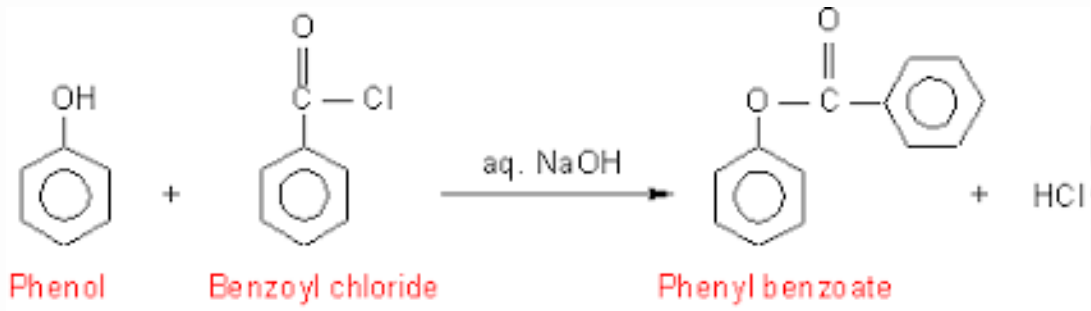


Qualitative tests of phenols

- **Ferric chloride test:** Take a very small amount of phenol and dissolve in 1 ml water or ethanol. Add a few drops of ferric chloride solution. A violet or blue colour indicates phenol, para-cresol or resorsinol. Beta naphthol gives no colour with ferric chloride but it gives a white opalescence
- **Phthalein test:** Take about 0.5 g each of phenol and phthalic anhydride, add 2-3 drops of conc. Sulphuric acid. Heat gently for about 1 min and then cool and add 10% NaOH solution in excess. A red coloration indicates phenol and a green flurescent solution indicates resorcinol. Beta naphthol gives a faint green coloration with slight fluorescence. Para cresol does not give any colour.
- **Bromination test:** Dissolve the sample in water to make a concentrated solution. Add bromine water gradually. First decolorisation of bromine takes place and on adding in excess, a white or yellowish white ppt is formed which indicates phenol.

Qualitative tests of phenols

- **Libermann test:** In 0.5 g sample add few crystals of sodium nitrite (NaNO2). Heat gently for half min, coll and add 1 ml of conc. Sulphuric acid. A deep green or blue violet colour develops. Dilute the mixture with water. The solution turns red. Add and excess of NaOH solution. The solution again becomes green or blue.
- **Benzoylation test**: Take 0.2 g compound and dissolve in 15-20 ml of 10% NaOH solution. Add about 3 ml benzoul chloride and shake vigorously for 10 min. a solid phenyl benzoate separates out.

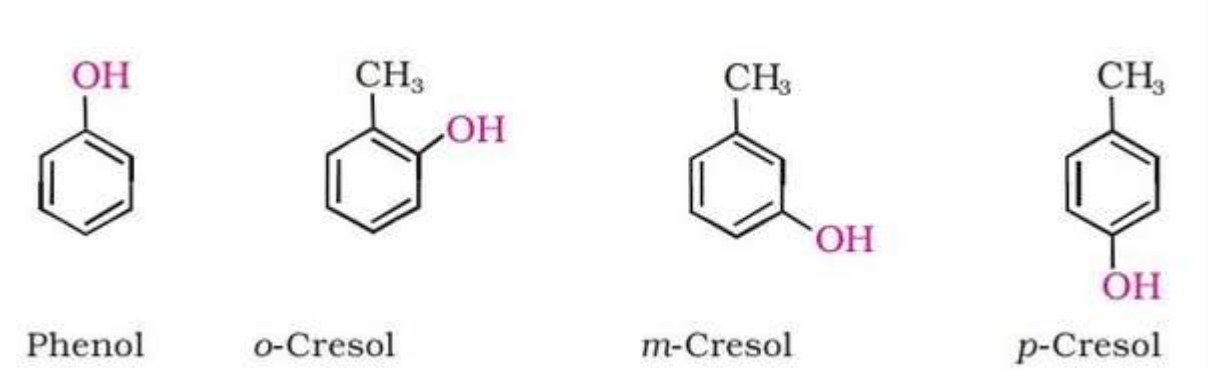


Uses of Phenol

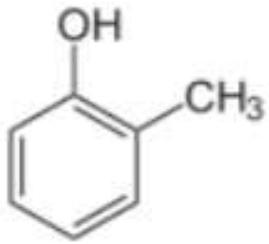
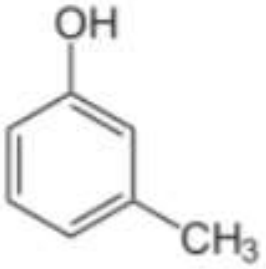
- Approximately two-third of the total phenol produced worldwide is used to prepare reagents used in plastic manufacturing industries
- The polymerization reaction of phenol with formaldehyde is used to commercially prepare phenolic resins
- Phenol is also used in the study and extraction of bio-molecules. Molecular biology finds application of phenol in the extraction of nucleic acids from tissue samples for further investigations.
- Phenol is also used in cosmetic industry in the manufacturing of sunscreens, skin lightening creams and hair coloring solutions
- Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceutical drugs.

CRESOLS

- Cresols (Hydroxytoulene) are organic compounds which are methylphenols.
- They are widely occurring natural and manufactured group of aromatic organic compounds, which are categorized as phenols.
- There are three isomers of cresol: ortho cresol, meta cresol and para cresol.

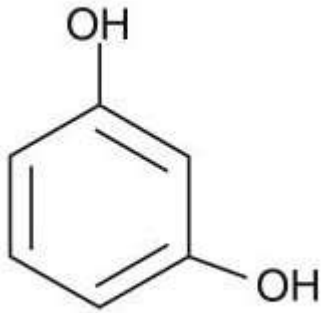


- Uses
- Mixed cresols are used as disinfectants, preservatives and wood preservatives
- o-Cresol is used as a solvent, disinfectane, and chemical intermediate
- m-Cresol is used to produce certain herbicides, as a precursor to the pyrethroid insecticides, to manufacture the explosive 2,4,6-trinitro-m-cresol
- p-Cresol is used in formulation of antioxidant (butylated hydroxy toluene) and in the fragrance and dye industries

Isomers of Cresol			
Structural formula			
General			
Common name	***o*-cresol**	***m*-cresol**	***p*-cresol**
Systematic name	2-methylphenol	3-methylphenol	4-methylphenol
Other names	*ortho*-cresol	*meta*-cresol	*para*-cresol
Molecular formula	C_7H_8O		
Molar mass	108.14 g/mol		
Appearance at room temperature and pressure	colorless crystals	thicker liquid	greasy-looking solid
Properties			
Density and phase	1.05 g/cm^3, solid	1.03 g/cm^3, liquid	1.02 g/cm^3, liquid
Solubility in water at 20–25 °C	2.5 g/100 ml	2.4 g/100 ml	1.9 g/100 ml
Soluble in strongly alkaline water			
Melting point	29.8 °C	11.8 °C	35.5 °C

RESORCINOL

Preferred IUPAC name	Benzene-1,3-diol
Other names	Resorcinol, Resorcin, *m*-Dihydroxybenzene, 1,3-Benzenediol, 1,3-Dihydroxybenzene, 3-Hydroxyphenol, *m*-Hydroquinone, *m*-Benzenediol
Chemical formula	$C_6H_6O_2$
Molar mass	110.1 g/mol
Appearance	White solid, turns pink on exposure to air, light, and
Odor	Faint
Density	1.28 g/cm^3, solid
Melting point	110 °C (230 °F; 383 K)
Boiling point	277 °C (531 °F; 550 K)
Solubility in water	110 g/100 mL at 20 °C



- **Uses**

1. Medicinal uses

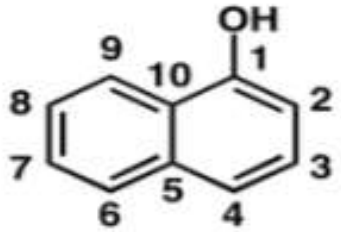
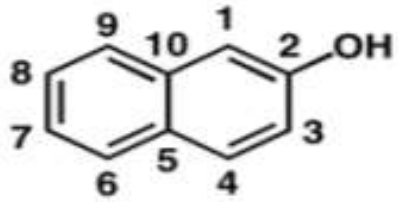
- It is an antiseptic and disinfectant
- 5-10% used in ointments in the treatment of chronic skin diseases such psoriasis, hidradenitis, suppurativa and eczema
- Used in the treatment of gastric ulcers in doses of 125 to 250 mg in pills, and is said to be analgesic and hemostatic (stops bleeding).
- A 2% solution is used to treat external vaginal itching and irritation
- It is a skin protectant and topical analgesic

2. Chemical uses

- Used in the production of diazo dyes and plasticizers and as a UV absorber in resins
- It is used for qualitative determination of ketoses (Seliwanoff's test)
- It is used to form a thermoset resin which is the basis of an aerogen (frozen smoke).

NAPHTHOL

- Naphthol is a dihydroxy phenol derivative
- It has two isomers, 1-naphthol and 2-naphthol

Isomers of Napthol		
Structural formula	 1-naphthol	 2-naphthol
IUPAC name	Naphthalen-1-ol	Naphthalen-2-ol
Other names	1-Hydroxynaphthalene; 1-Naphthalenol; alpha-Naphthol	2-Hydroxynaphthalene; 2-Naphthalenol; beta-Naphthol; Naphth-2-ol
Molecular formula	$C_{10}H_8O$	$C_{10}H_8O$
Molar mass	144.17 g/mol	144.17 g/mol
Appearance at room temperature and pressure	Colorless or white solid; commercial material is often strongly colored	Colorless crystalline solid
Density	1.10 g/cm^3	1.280 g/cm^3
Solubility	Both isomers are soluble in simple alcohols, ethers, and chloroform.	
Melting point	95 to 96 °C	121 to 123 °C

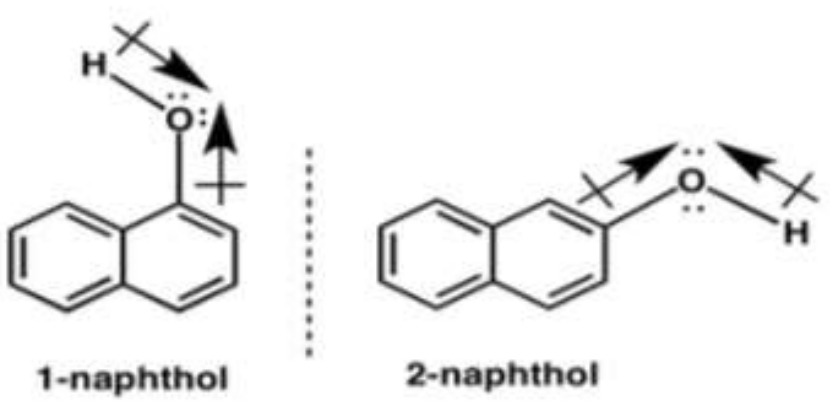
Polarity of naphthols

-Since naphthols contain a hydroxyl group, it's a highly polar molecule, with the oxygen atom attracting electron density through the bonds toward itself. For a molecule to be polar, there has to be a difference in electronegativity (the ability of an atom to attract electrons to itself) between one or more atoms, and in the case of naphthol, oxygen is more electronegative than both carbon and hydrogen.

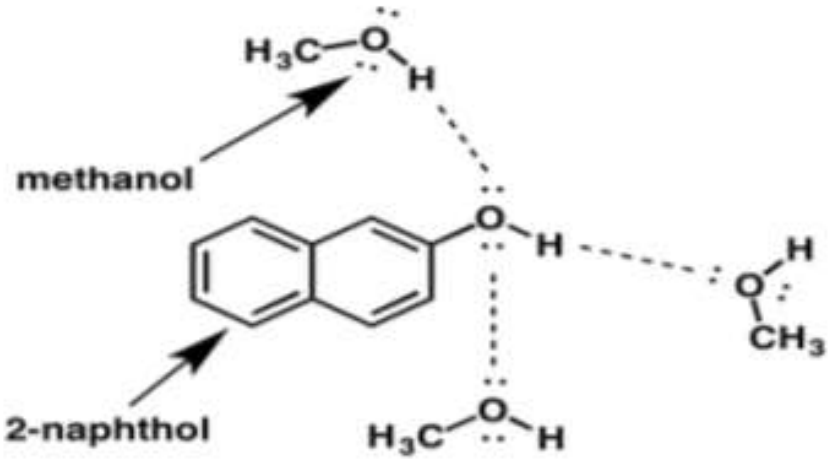
- **For this reason, it can 'hog' more of the electron density in the form of the bonds, making it polar**.

Solubility

- In terms of the solvents that naphthol is soluble in (things it will form solutions with), it's very versatile. Because of the presence of the hydroxyl group, it can hydrogen bond with other alcohol-based (polar) solvents like ethanol, methanol, and isopropanol. The ability to form these hydrogen bonds makes it readily soluble in these kinds of solvents. For example, consider the case of 2-naphthol forming hydrogen bonds with methanol molecules



Polarity of naphthol



Naphthol forming hydrogen bonds with methanol molecules

Uses of naphthols

- Naphthols (both 1 and 2 isomers) are used as biomarkers for livestock and humans exposed to polycyclic aromatic hydrocarbons
- 1-Naphthol is a precursor to a variety of insecticides including carbaryl and pharmaceuticals including nadolol. It undergoes azo coupling to give various azo dyes, but these are generally less useful than those derived from 2-naphthol.
- In Molisch's test, 1-naphthol dissolved in ethanol, known as Molisch's reagent, is used as reagent for detecting the presence of carbohydrates.
- The Sakaguchi test uses 1-naphthol with sodium hypobromite to detect the presence of arginine in proteins.
- The Voges–Proskauer Test uses 1-naphthol in potassium hydroxide (KOH) solution to detect the breakdown of glucose into acetoin which is used by bacteria for external energy storage. A positive test will be indicated by the appearance of a red color of the original yellow solution.

UNIT II

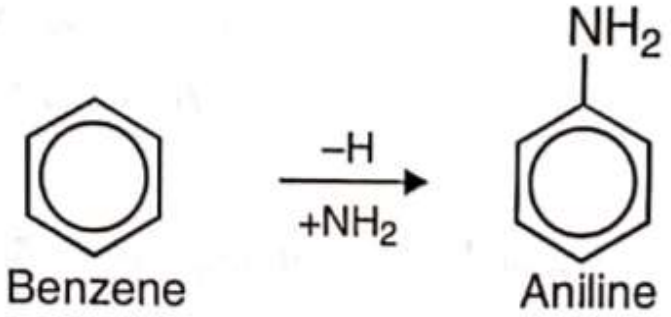
Phenols

Aromatic amines

Aromatic acids

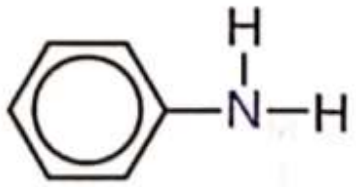
AROMATIC AMINES

These are the derivatives of aromatic hydrocarbons in which a hydrogen of the benzene ring has been replaced by an amino group, $-NH_2$.

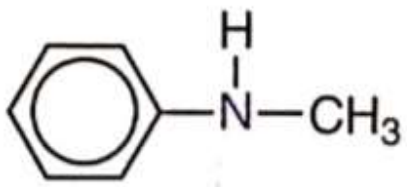


All such compounds in which an amino or substituted amino group is bonded directly to an aromatic ring are termed Aromatic amines.

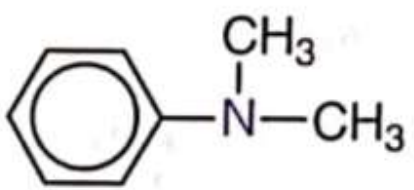
They are also designated as primary, secondary or tertiary amines.



Aniline
(1° amine)



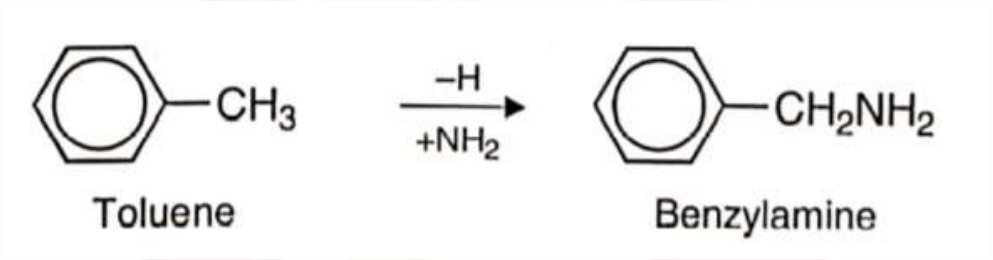
N-Methylaniline
(2° amine)



N,*N*-Dimethylaniline
(3° amine)

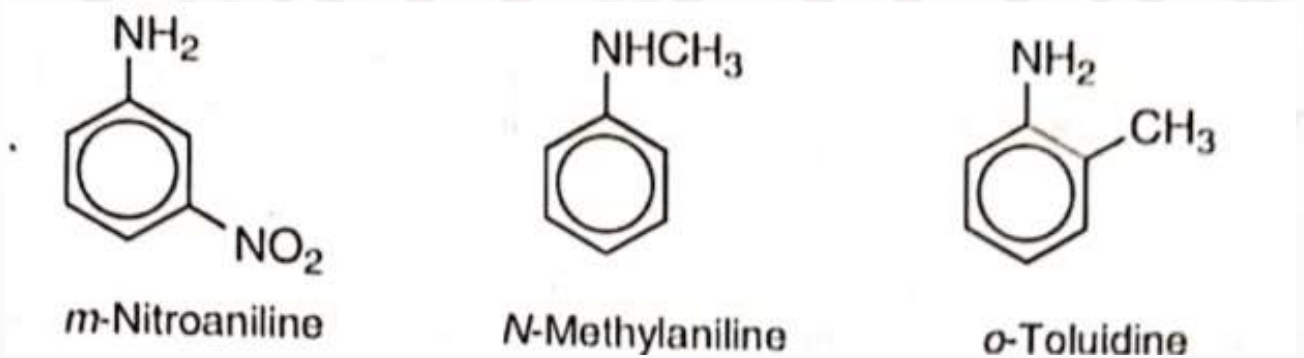
AROMATIC AMINES

- The derivatives of arenes in which NH2 is bonded to a side-chain are to be regarded as arylsubstituted aliphatic amines.



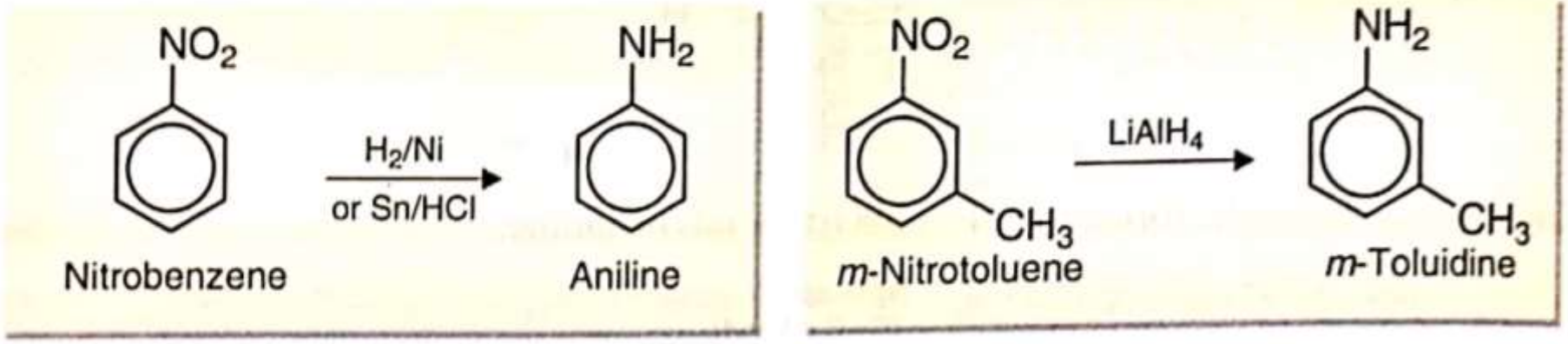
Nomenclature

- Simple aromatic amines are named as derivatives of aniline. An aminotoluene is given the special name of toluidine.
- Substituents on the nitrogen atom are named as prefixes preceded by N-, or N-

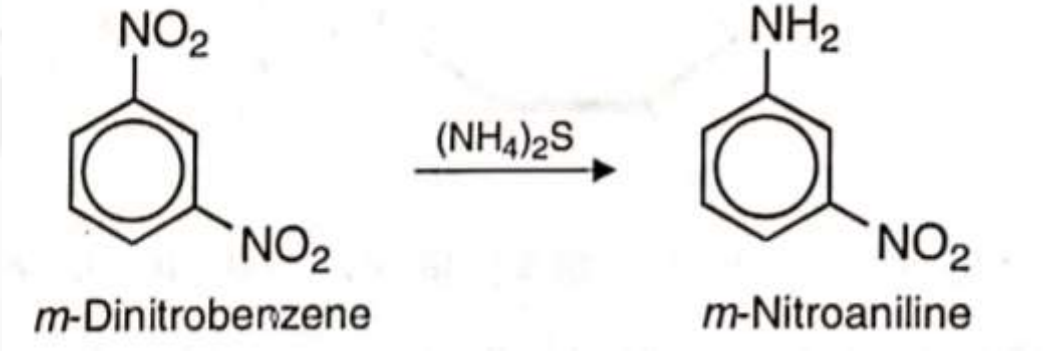


Preparation of aromatic amines

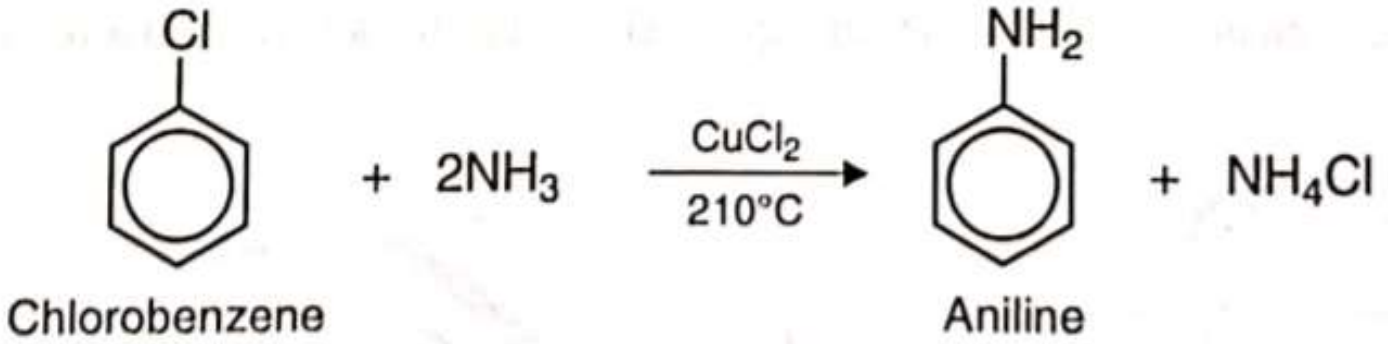
1) **Reduction of Nitro compounds:** This is a very convenient and most widely used method. The reduction is carried wity (a) H2 in the presence of Ni, Pd or Pt as catalyst, (b) Sn or Fe and HCl and (c) Lithium aluminium hydride.



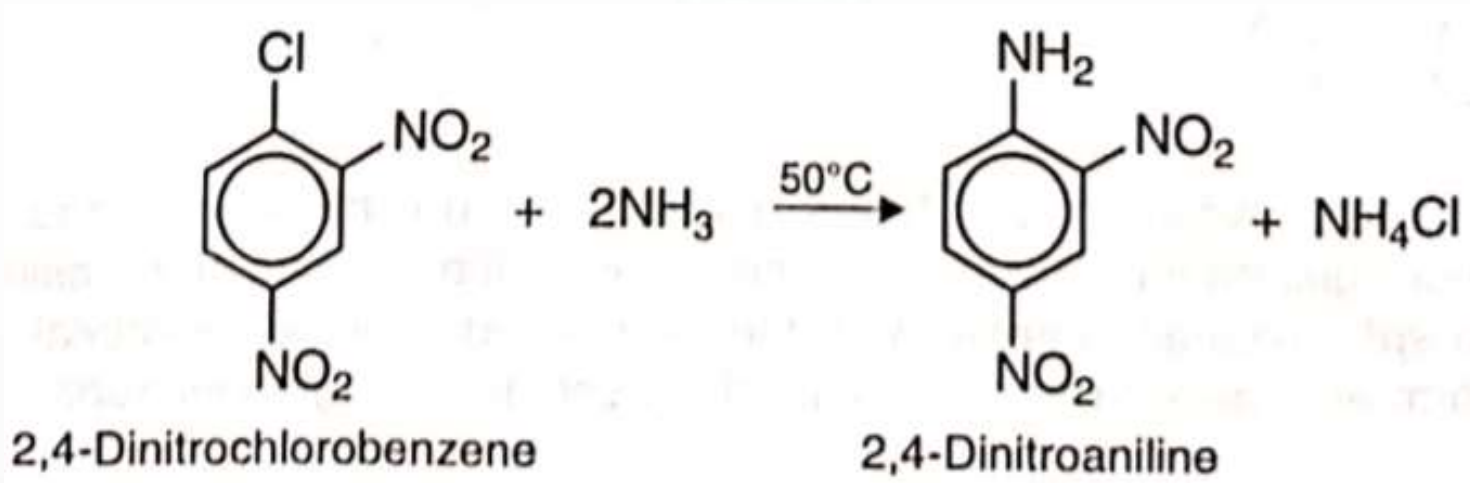
Selective reduction with ammonium sulfide is used to prepare an amino compound such as m-dinitrobenzene when only one –NO2 group need be reduced.



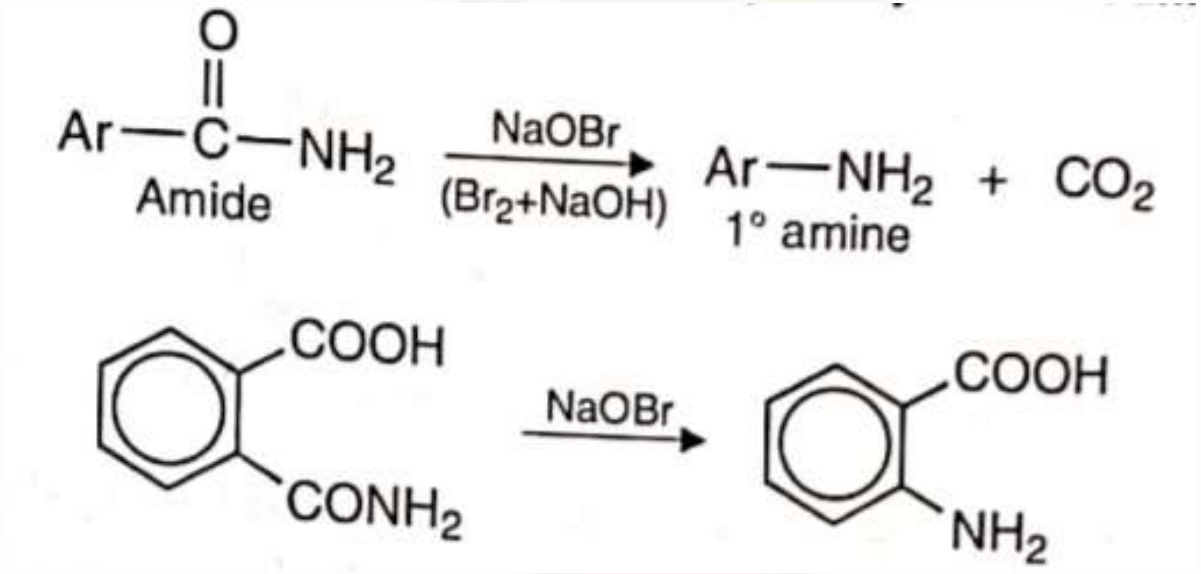
2) **Ammonolysis of aryl chlorides:** Aniline is prepared by treating chlorobenzene with ammonia in the presence of copper salts at high temperature and pressure.



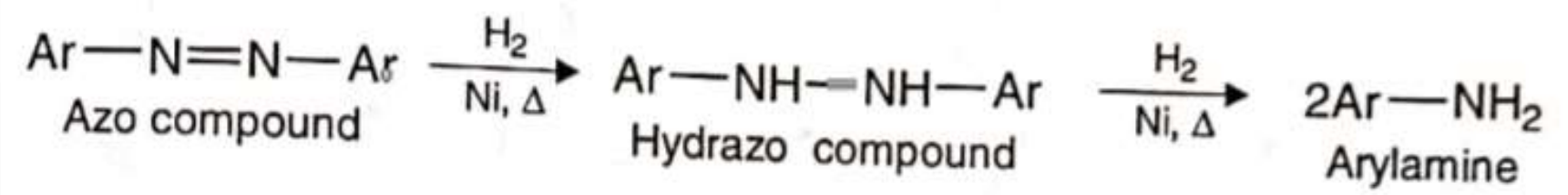
This method is useful and can be carried under ordinary conditions if a strongly EWG such as –NO2 is present ortho or para to –Cl.



3) **Hoffmann Rearrangement:** When treated with bromine or chloine in an alkaline solution, an arylamide undergoes Hofmann rearrangement to yield a primary aromatic amine.



4) **Reduction of azo compounds:** Azo compounds when reduced with hydrogen in presence of nickel as catalyst, give arylamines.

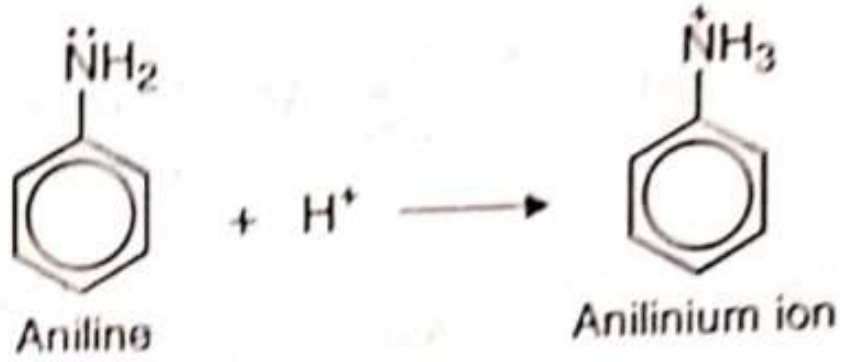


Physical properties

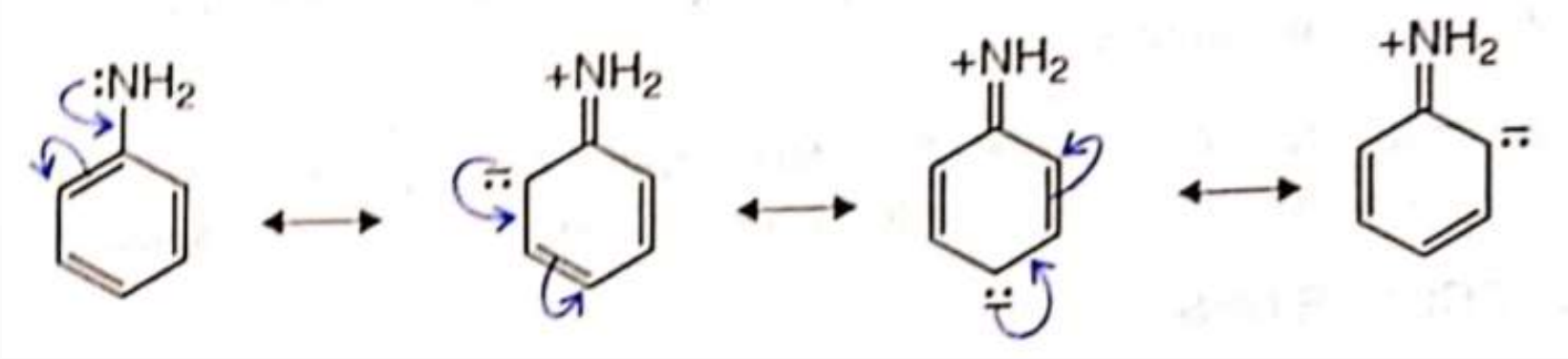
1. Aromatic amines are generally colourless liquids or solids, having a characteristic odour which is not pleasant. They turn brown in air due to oxidation.
2. Boiling points are relatively high due to their high molecular wt and intermolecular hydrogen bonding ability.
3. They are sparingly soluble in water but dissolve in benzene and other organic solvents.
4. They are steam-volatile
5. They are highly toxic. Some of them are carcinogens.

Basicity of Aromatic Amines

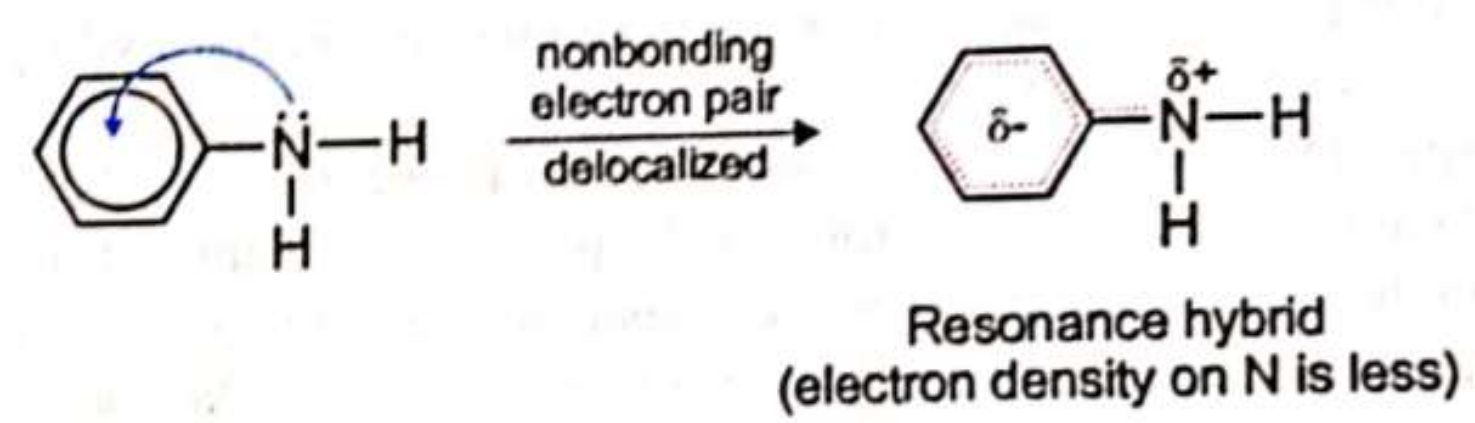
The basicity of amines is a measure of a compound's ability to accept a proton. Aniline accepts a proton as follows:



In aromatic amines, the nonbonding electron pair is delocalized into the benzene ring by resonance and hence is not available of coordination with a proton.

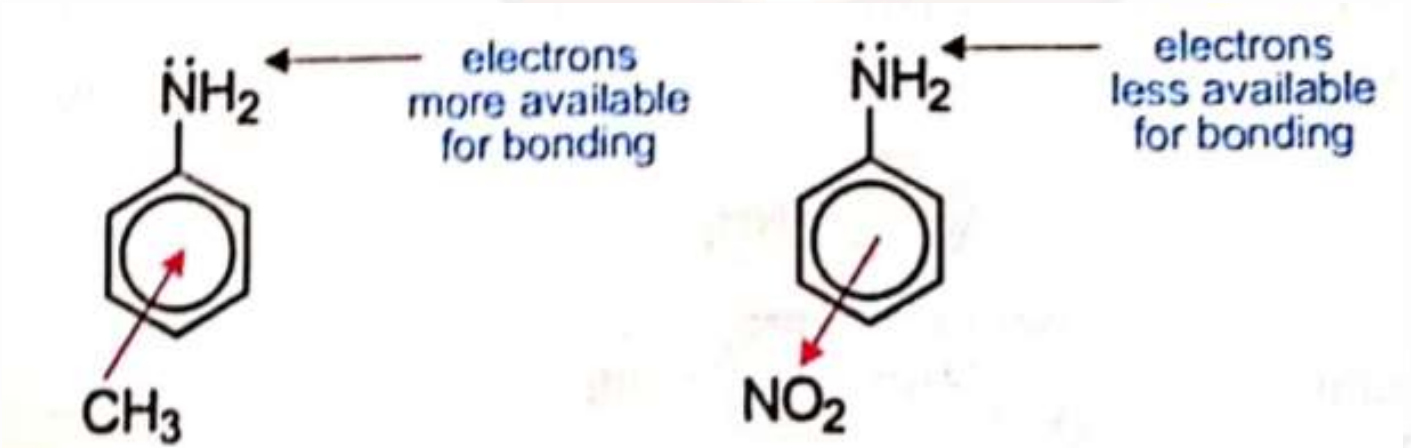


Thus we have,



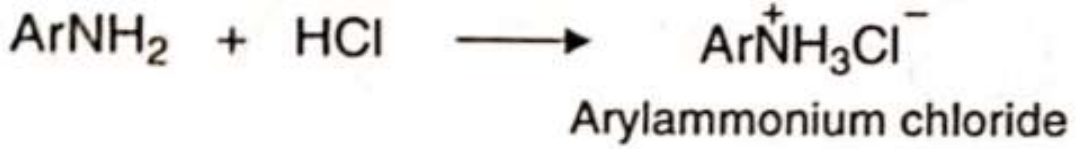
The nonbonding electron pair in the hybrid being dispersed over the benzene ring and also Nitrogen atom, is less available for protonation.
Hence aromatic amines are less basic than aliphatic amines which show no resonance.

- o-Nitroaniline is even more weakly basic than aniline because the electron-withdrawing effect on the ring lowers the electron density on N atom, making the electron pair even less available for protonation.
- In p-toluidine the CH3 group is electron-donating and increases the electron density on the N atom, making the electrons available for protonation more than in aniline. Hence, toluidine is more basic relative to aniline

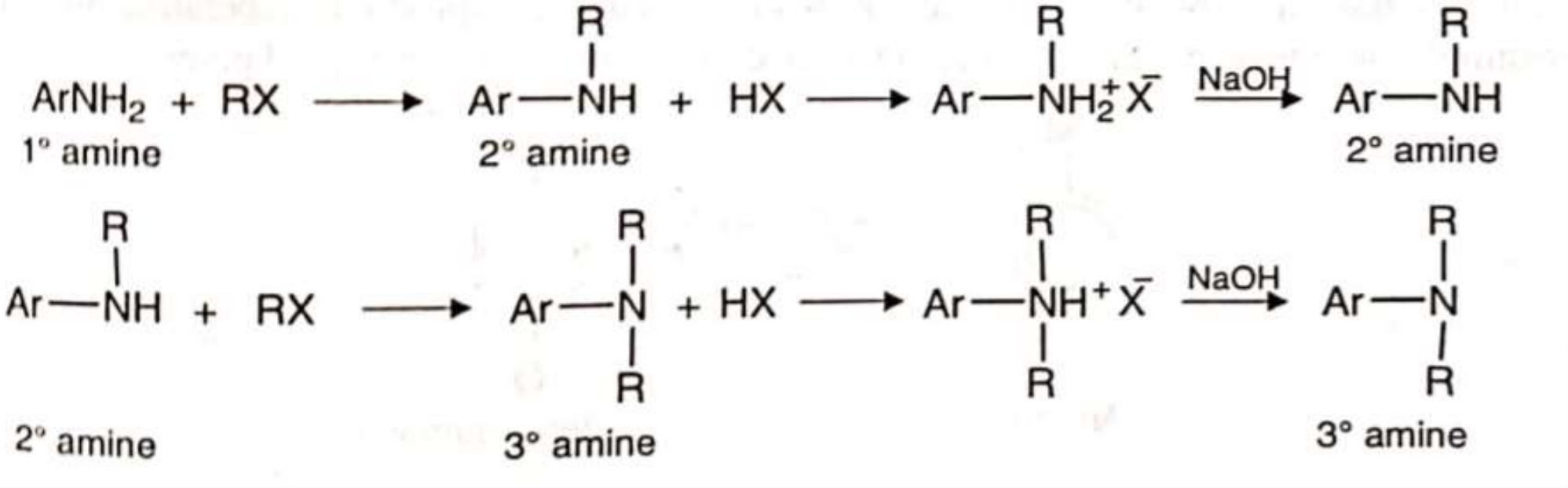


Chemical Properties

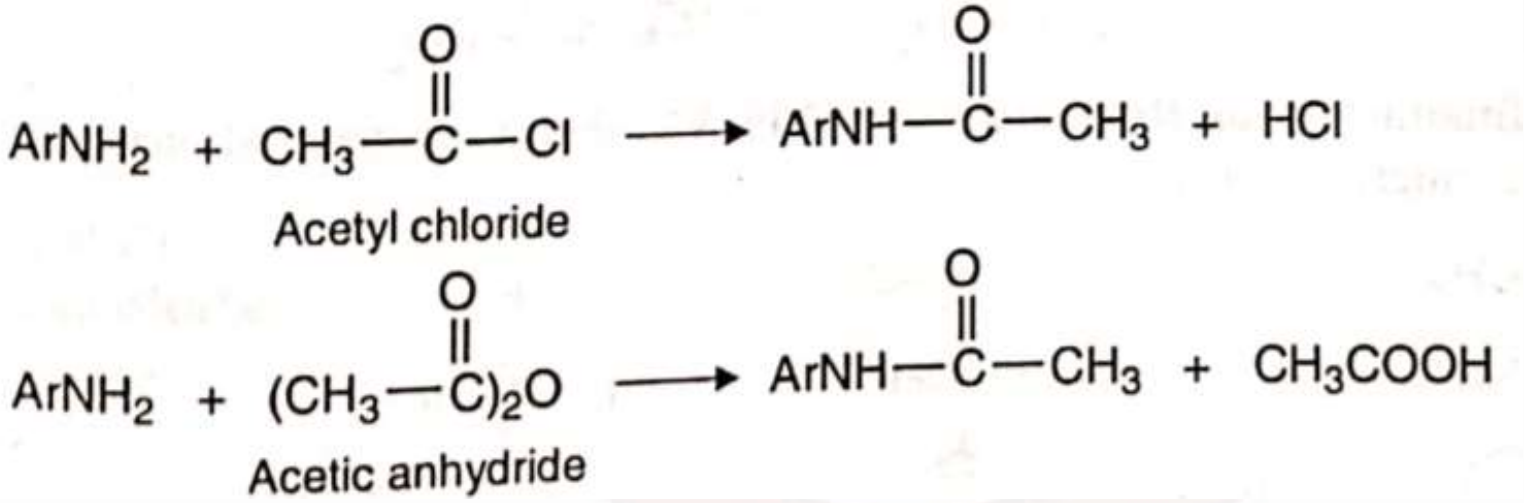
1. **Salt formation:** Aromatic amines form crystalline salts with strong mineral acids



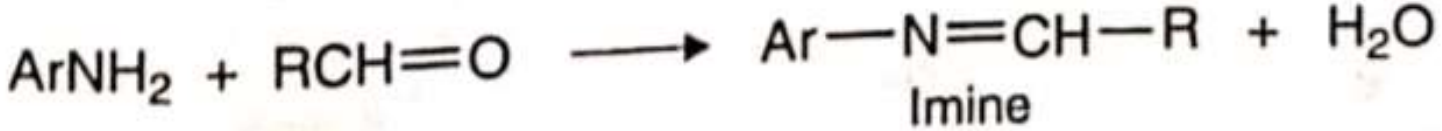
2. **Alkylation:** They react with alkyl halides to form 2^0 and 3^0 amines. These amines react with HX to form salts. These salts can be treated with aq.NaOH to give free 2^0 and 3^0 amines.



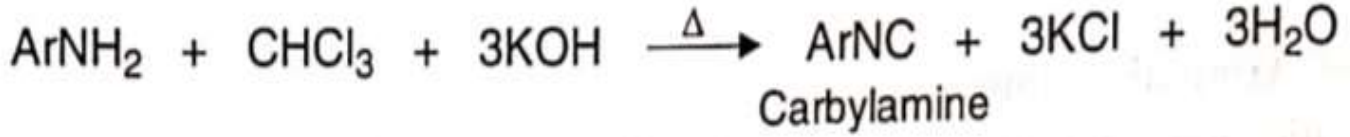
3. **Acylation:** With acid halides and anhydrides, they form N-arylamide.



4. **Reaction with aldehydes:** They react with aldehydes to form imines

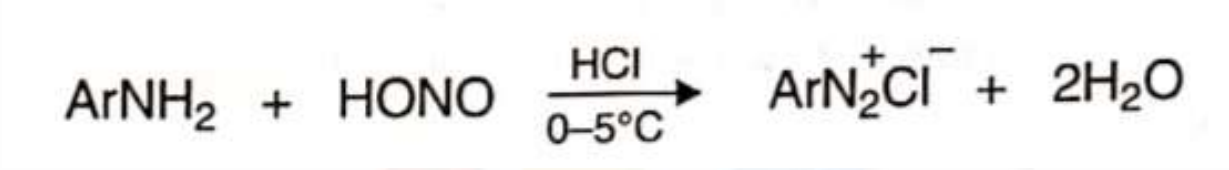


5. **Carbylamine reaction:** Primary aromatic amines react with ethanolic potassium hydroxide and chloroform to form carbylamines or isonitriles which have a disagreeable odour.

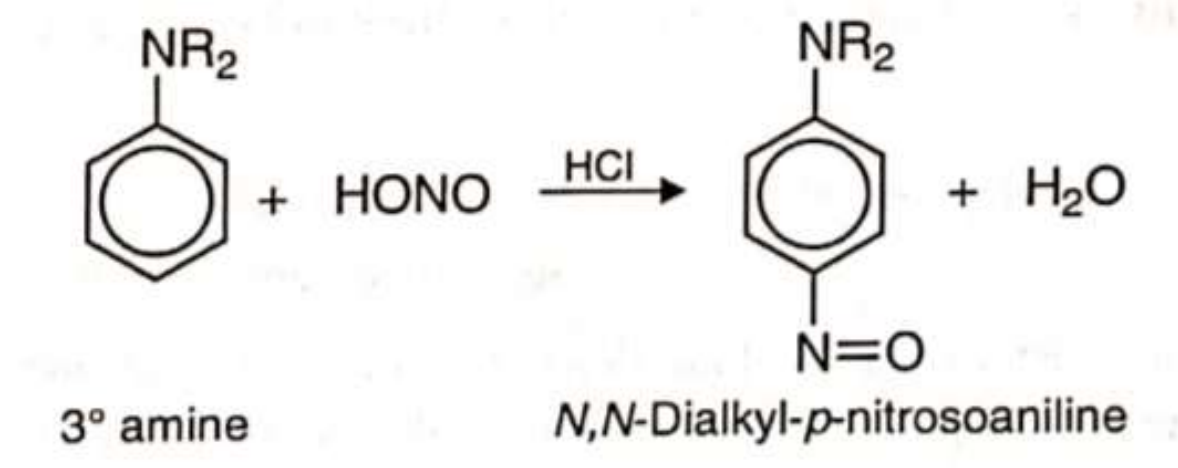


6. Reaction with nitrous acid

Primary aromatic amines undergo diazotization to give diazonium salts.

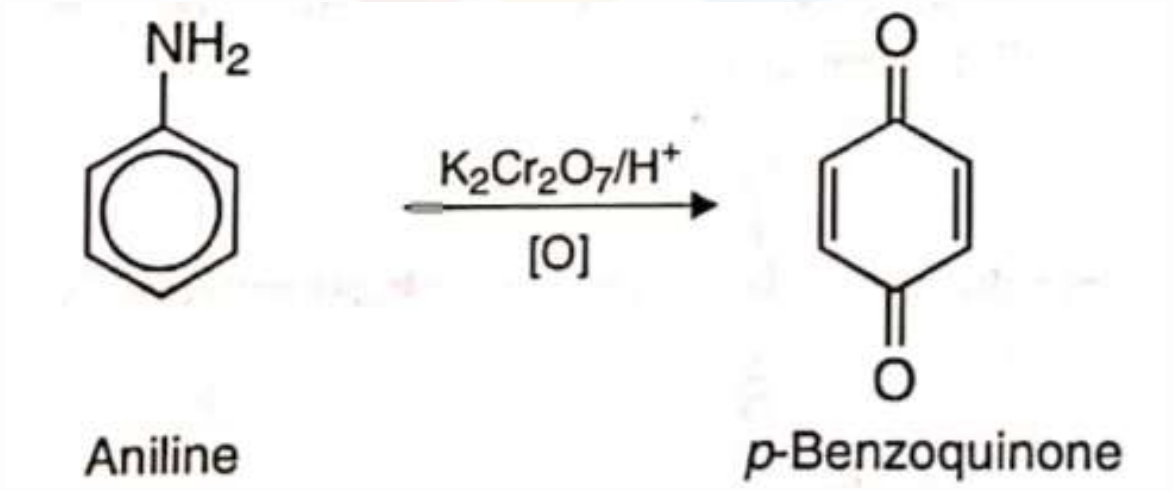


Tertiary amines undergo C-nitrosation.

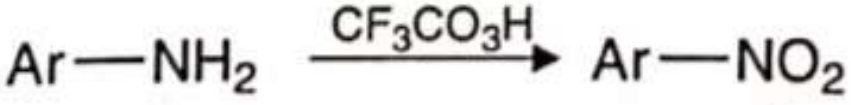


7. **Oxidation:** Aromatic amines are readily oxidized to give products depending on conditions.

For example, aniline on oxidation with potassium dichromate and sulphuric acid gives p-benzoquinone.



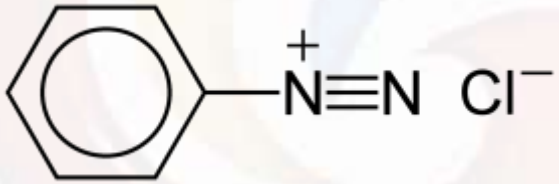
Pertrifluoroacetic acid oxidizes the –NH2 group to –NO2 group.



Aryl diazonium salts

Aryl diazonium salts are the class of organic compounds with general formula $R–N_2^+X^-$

where X is an organic or inorganic anion (for example, Cl^-, Br^-, BF_4^-, etc.) and R is an alkyl or aryl group.



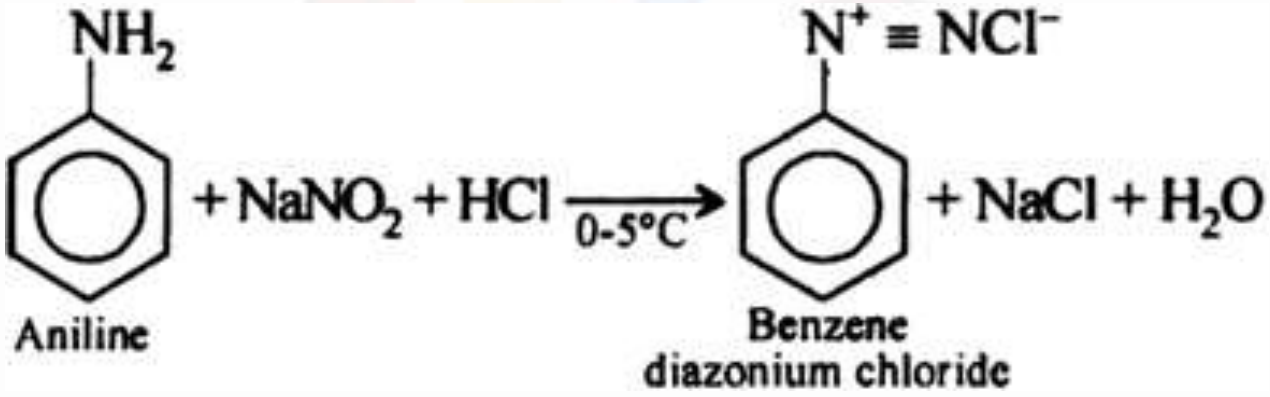
Hence, they have two nitrogen atoms with one being charged.

•Generally, diazonium salts have Cl^-, Br^-, BF^{-4}, as X. The name of these salts is based on the presence of the N^{+2} group or the diazonium group.

•The naming of these salts is done by adding the suffix diazonium to the parent hydrocarbon from which they are derived and then it is followed by the anion X such as bromide.

Preparation

By reacting nitrous acid with aromatic amines. The reaction of aniline (aromatic amine) with nitrous acid results in the diazonium salt formation that is benzene diazonium chloride.



Applications of diazonium salts

1. Synthesis of dyes

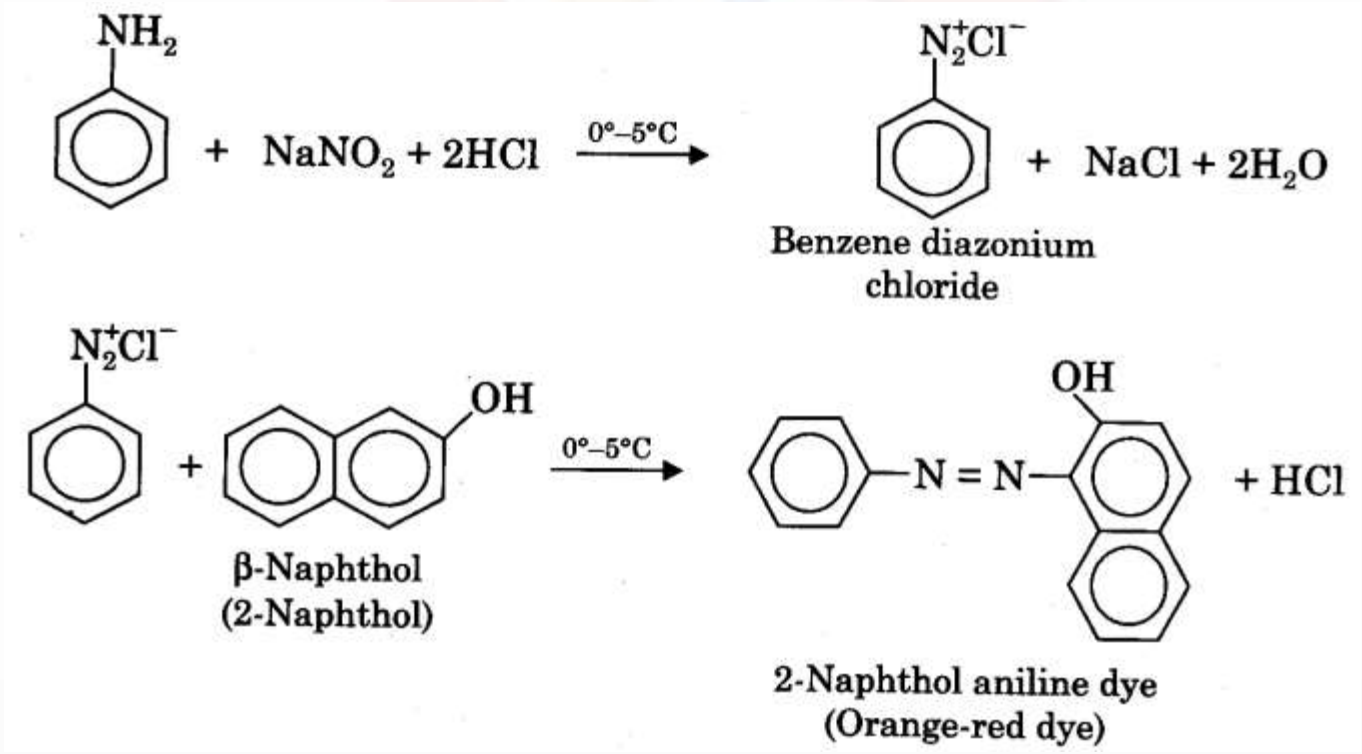
   Aromatic azo compounds are colored.

   They are synthesized by coupling of diazonium salt with suitable coupling reagents.

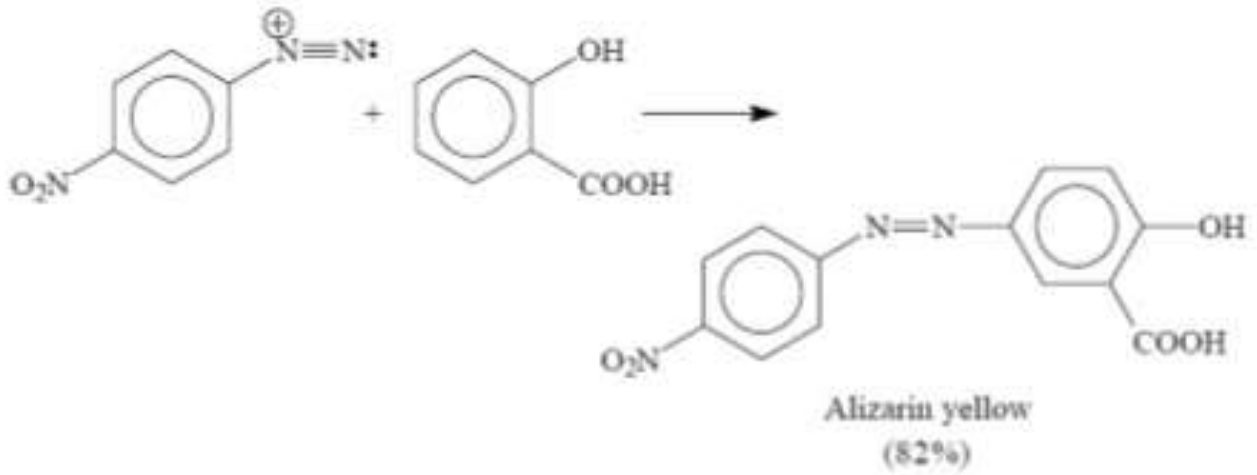
   They are employed as dyestuffs

1. Synthesis of 2-naphthol

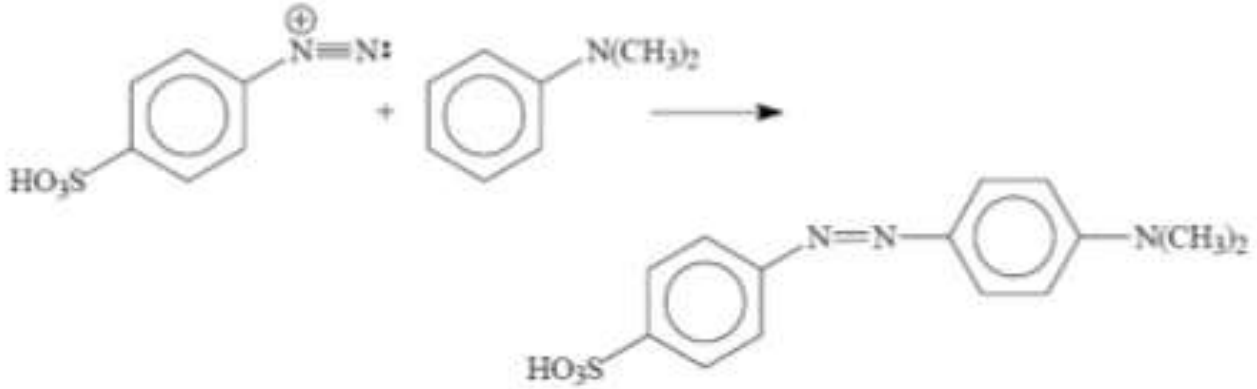
2- Naphthol aniline dye is a scarlet dye can be prepared by coupling reaction. Aniline reacts with sodium nitrite in the presence of hydrochloric acid forms benzene diazonium chloride. Further benzene diazonium chloride reacts with 2-naphthol forms a bright orange colour 2-naphthol aniline dye.



1. Synthesis of Alizarin yellow and methyl orange



Alizarin yellow
(82%)



Methyl orange
(70%)

UNIT II

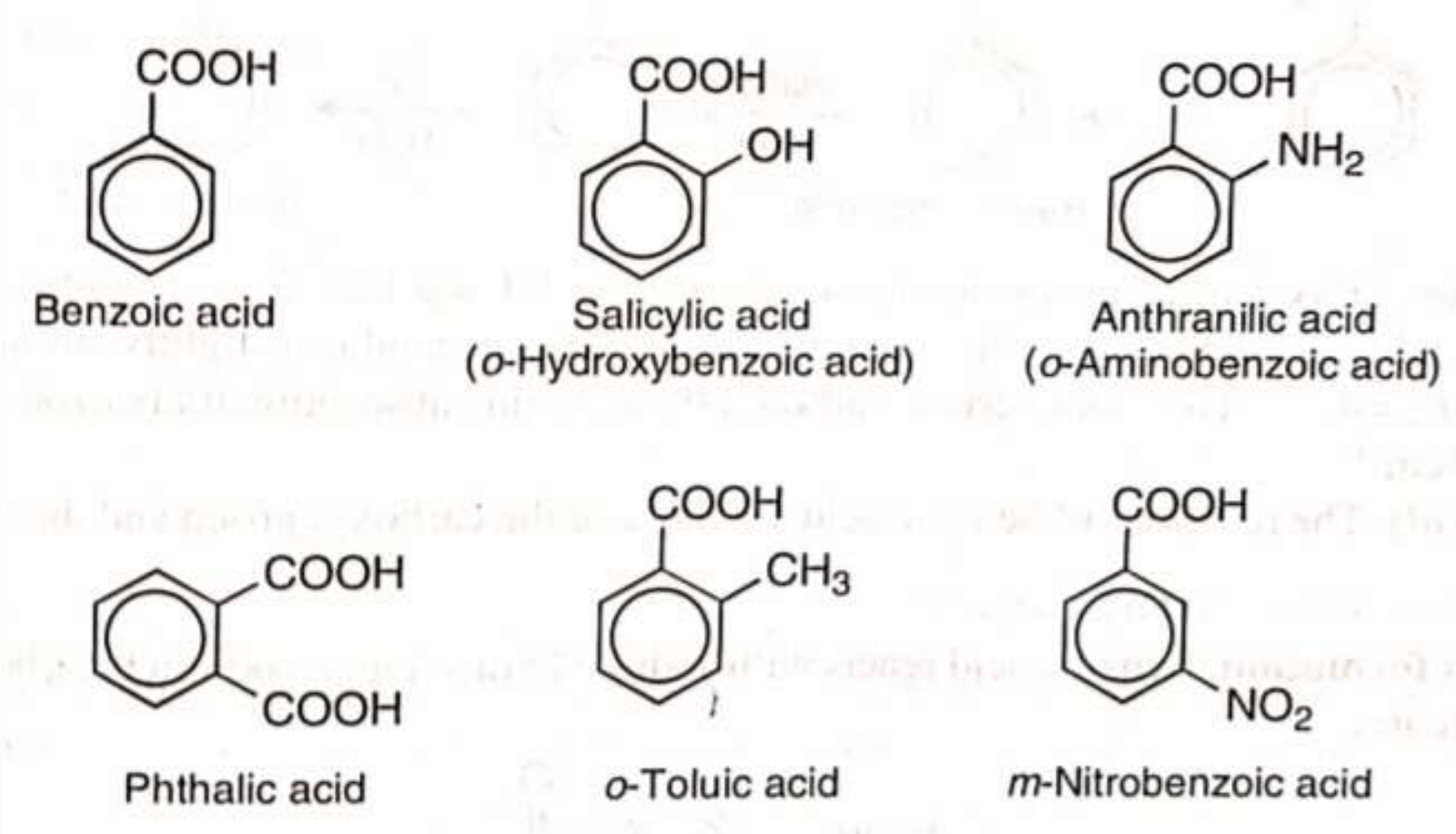
Phenols

Aromatic amines

Aromatic acids

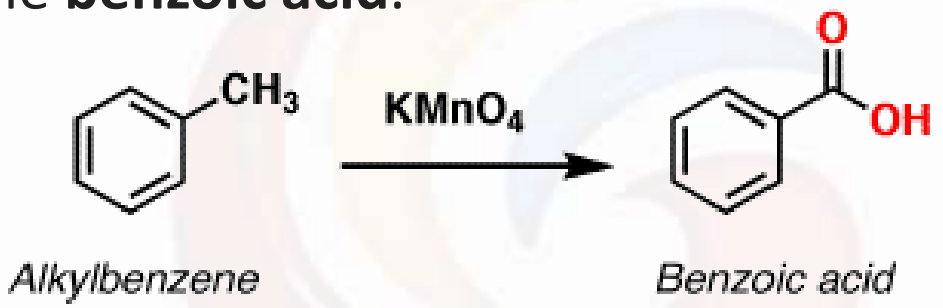
Aromatic carboxylic acids

- Aromatic acids are compounds in which one or more carboxyl groups are attached directly to the aromatic ring.

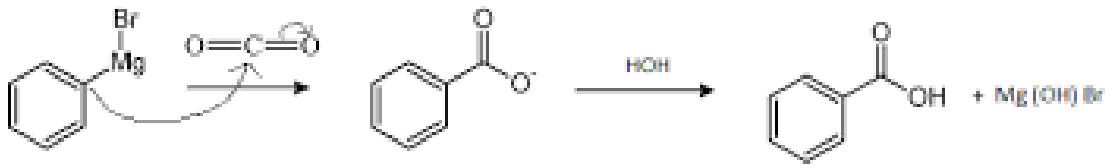


Prepararion

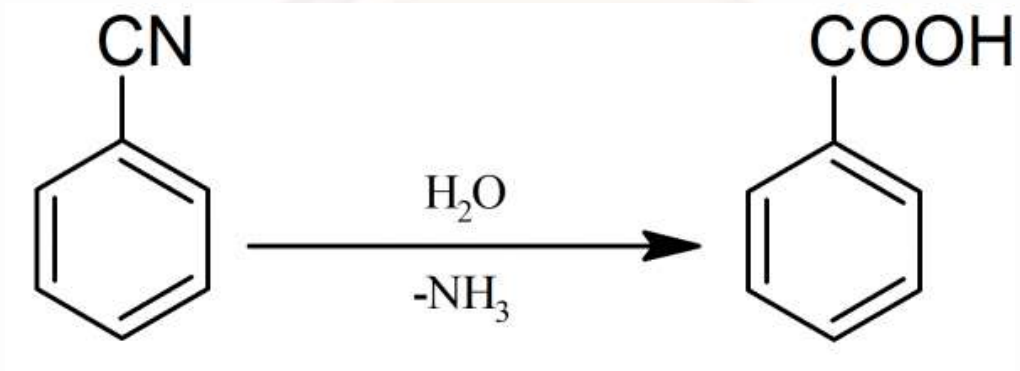
1. Oxidation: Treatment of an **alkylbenzene** with **potassium permanganate** results in **oxidation** to give the **benzoic acid**.



2. Reaction of phenyl magnesium bromide with carbon dioxide followed by acid hydrolysis.



3. Acid hydrolysis of phenyl cyanide (Benzonitrile).

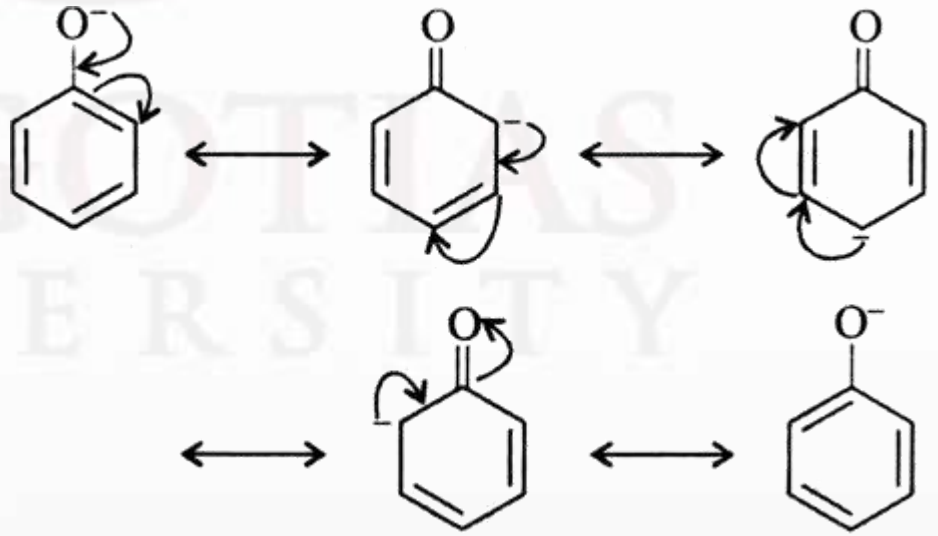


Acidity of benzoic acid

- Aromatic acids are weaker than mineral acids
- Acidity of carboxylic acid is higher than alcohols and phenols
- Benzoate ion formed is stabilized by two equivalent resonance structures in which the negative charge is effectively delocalized between two more electronegative oxygen atoms

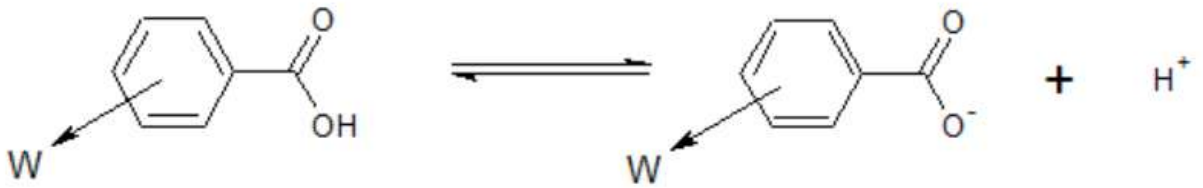
Acidity of benzoic acid

- Oxygens of carboxylate ion are not directly adjacent of the aromatic ring
- Hence resonance stabilization by aromatic π molecular orbital will not take place.
- In phenols, the negative charge is less effectively delocalized over one oxygen atom and less electronegative carbon atoms in phenoxide ion
- Therefore the carboxylate ion exhibits higher stability in comparison to phenoxide ion.
- Hence carboxylic acids are more acidic than phenols



Effect of substituents on acidity

- Because benzene ring does not participate in resonance-stabilization of the carboxylate group, substituents on a benzene ring influence the acidity primarily by the Inductive effect
- **Electron withdrawing group** increases the acidity of a benzoic acid, as it stabilizes the carboxylate ion and destabilizes the acid



W = electron Withdrawing group

The carboxylate anion is stabilized by the electron withdrawing group increasing the acidity of the conjugate acid.

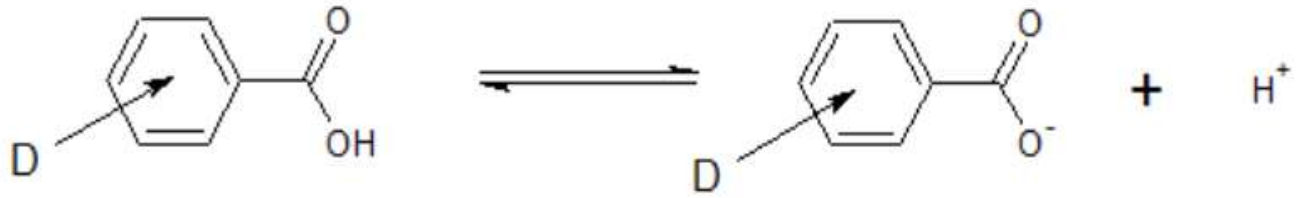
Electron-withdrawing groups deactivate the benzene ring to electrophilic reactions and make benzoic acids more acidic.

- Ex. –X, -CN, -NO2, -COOH, -COOR, -CHO, -COR,

Effect of substituents on acidity

- Because benzene ring does not participate in resonance-stabilization of the carboxylate group, substituents on a benzene ring influence the acidity primarily by the Inductive effect
- **Electron releasing group** (at meta or para) decreases the acidity of a benzoic acid, as it destabilizes the carboxylate ion

The conjugate base of benzoic acid is destabilized by electron-donating groups. This makes the acid less acidic



D = electron Donating group

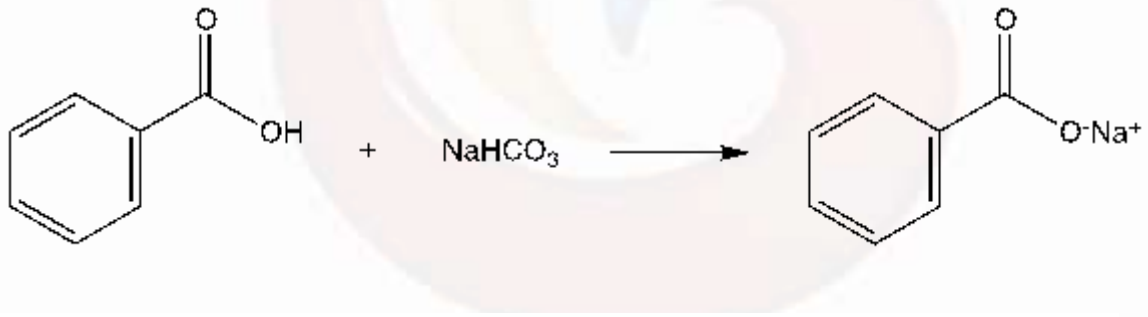
The carboxylate anion is destabilized by the electron withdrawing group decreasing the acidity of the conjugate acid.

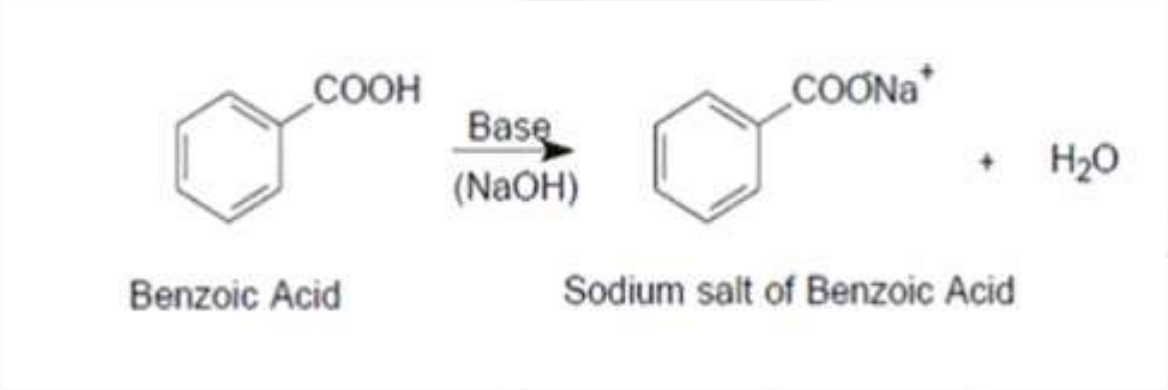
Electron-donating groups activate the benzene ring to electrophilic reactions and make benzoic acids less acidic.

- Ex. –NH2, -RCONH, -OH, -OR, -R

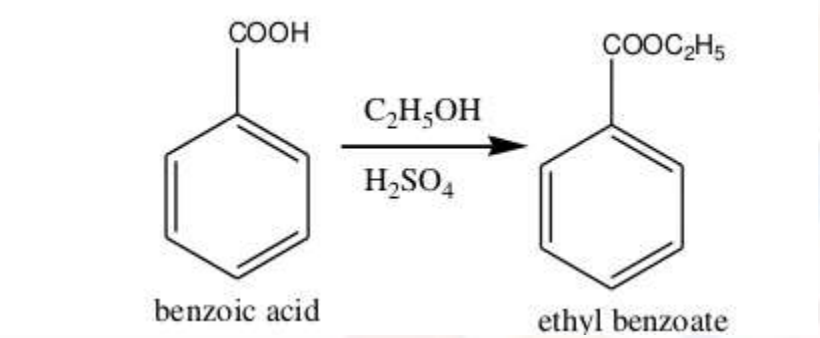
Reactions of aromatic carboxylic acids

1. Benzoic acid reacts with sodium hydroxide of sodium bicarbonate to form sodium benzoate.

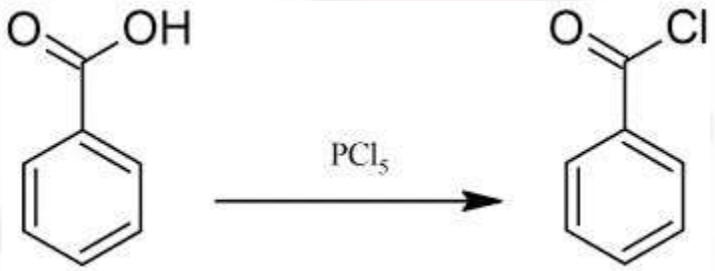




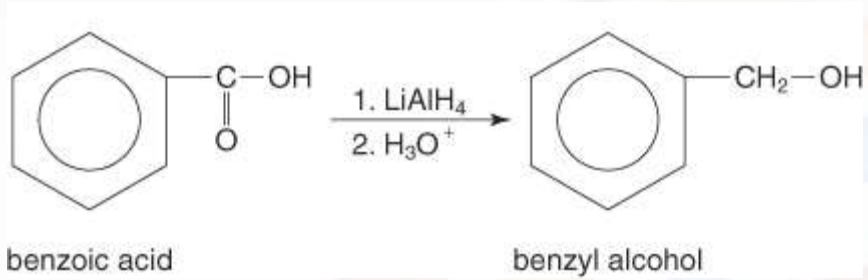
2. Ester formation: Benzoic acid reacts alcohols in the presence of sulphuric acid to form esters.



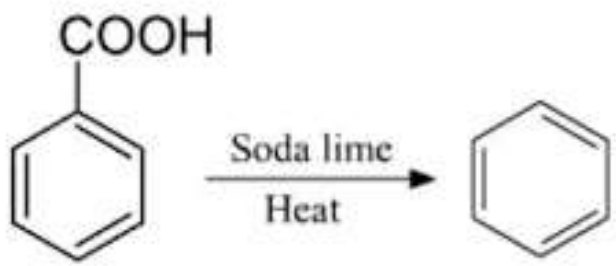
3. Acyl halide formation: Benzoic acid reacts with phosphorous pentachloride or thionyl chloride to form benzoyl chloride.



4. Benzoic acid undergoes reduction with lithium aluminium hydride to give benzyl alcohol.



5. Decarboxylation: When heated with soda lime, benzoic acid looses a molecule of CO2 to give benzene.



Uses of benzoic acid

- Benzoic acid is most commonly found in industrial settings to manufacture a wide variety of products such as perfumes, dyes, topical **medications** and insect repellents.

- Benzoic acid's **salt** (**sodium benzoate**) is commonly used as a pH adjustor and preservative in food, preventing the **growth** of microbes to keep food safe

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