

# Aromatic Phenols

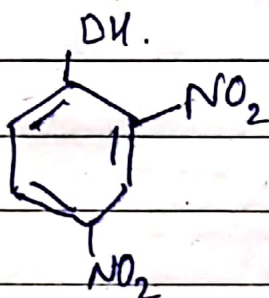


(Phenol)

Hydroxy Benzene

Phenols are the compounds containing an OH group attached directly to Benzene Ring. They are mono-hydric or Poly-hydric, acc. to the no. of OH groups that they contain.

Derivatives

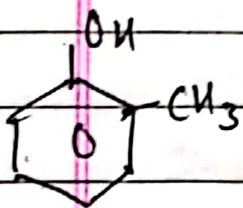


(2,4, Dinitrophenol)

(4-Nitrophenol)

or

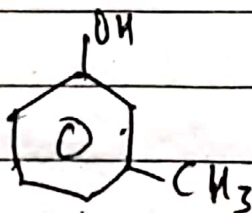
Para-Nitrophenol



2-methyl phenol

or

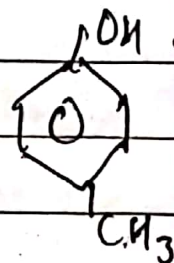
(o-Cresol)



3-methyl phenol

or

(m-Cresol)

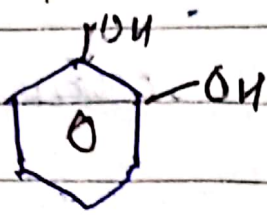


4-methyl phenol

(p-Cresol)

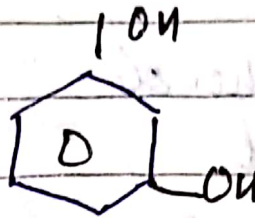
All are monohydric Phenols

## Polyhydric Phenols :-



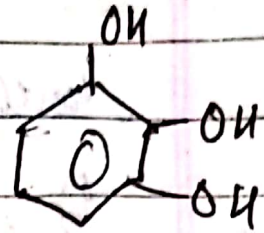
1, 2 benzene di-ol.  
or

Catechol



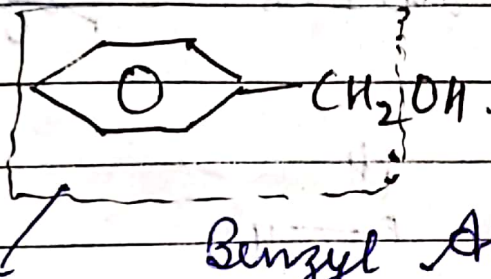
1, 3 benzene diol.  
or

Resorcinol



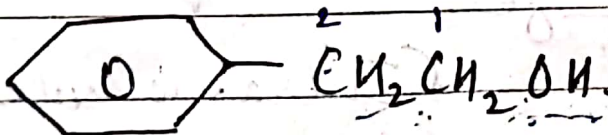
1, 2, 3 benzene triol.  
or

Pyrogallol



Benzyl Alcohol.

It is not a phenol because OH grp is not directly attached to the Benzene ring.



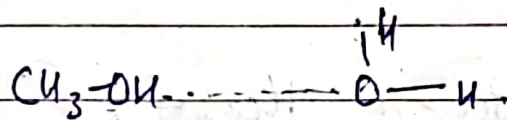
2-Phenylethanol.

→ Compounds that contains an OH grp in a side chain attached to an aromatic ring are not Phenols. They are c/d as Aromatic alcohols.

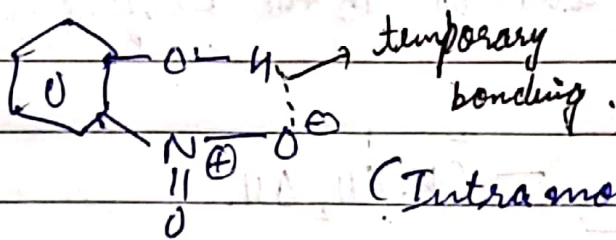
# Physical Properties of Phenol

1. Mostly phenols are colourless liquids or solid.
2. Phenols have a characteristic Carbolic odour which is toxic in nature.

• Q: B.P. of phenols are higher than aliphatic alcohols of comparable M.Wt.?



Intermolecular H-B

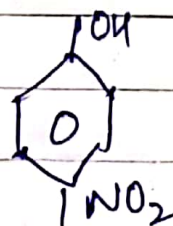
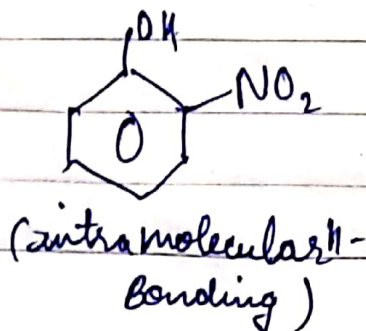
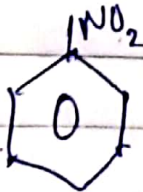


(Intramolecular H-B)

Ans → This is due to stronger intermolecular H-B in phenols.

• Q: The "introduction" of hydroxy<sup>grp.</sup> into an already substituted aromatic ring ~~reduces~~ its B.P.

Ans: →

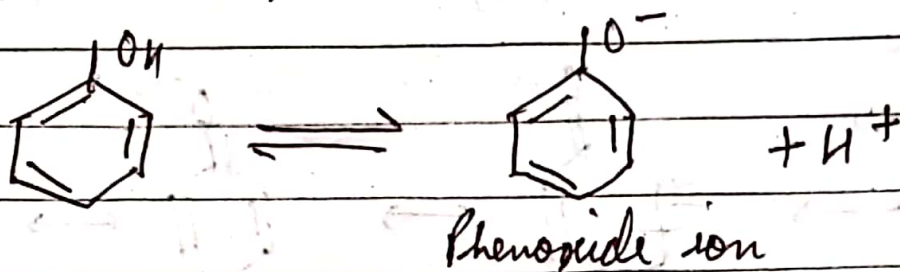


(intermolecular H-Bonding)

In para position due to intermolecular H-Bonding the B.P. ↑.

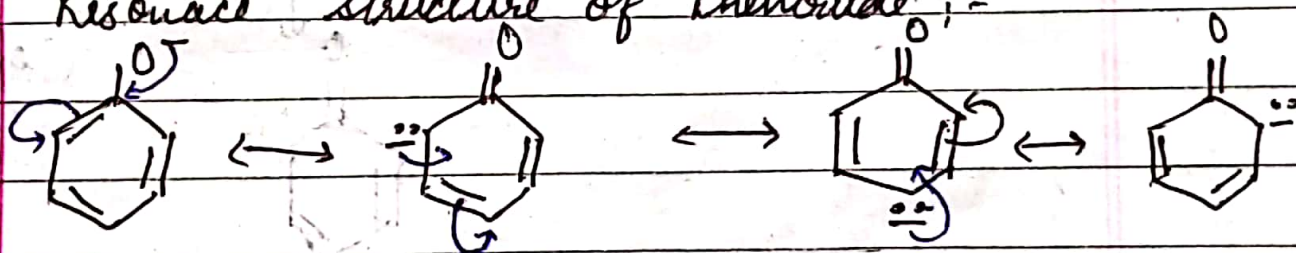
### Acidic Nature of Phenol :-

Phenols are more acidic than alcohol but less acidic than Carboxylic acid. Phenols are acidic due to format<sup>n</sup> of stable phenoxide ions in aqueous sol<sup>n</sup>.



It is stable due to its resonance structure.

### Resonance structure of Phenoxide :-

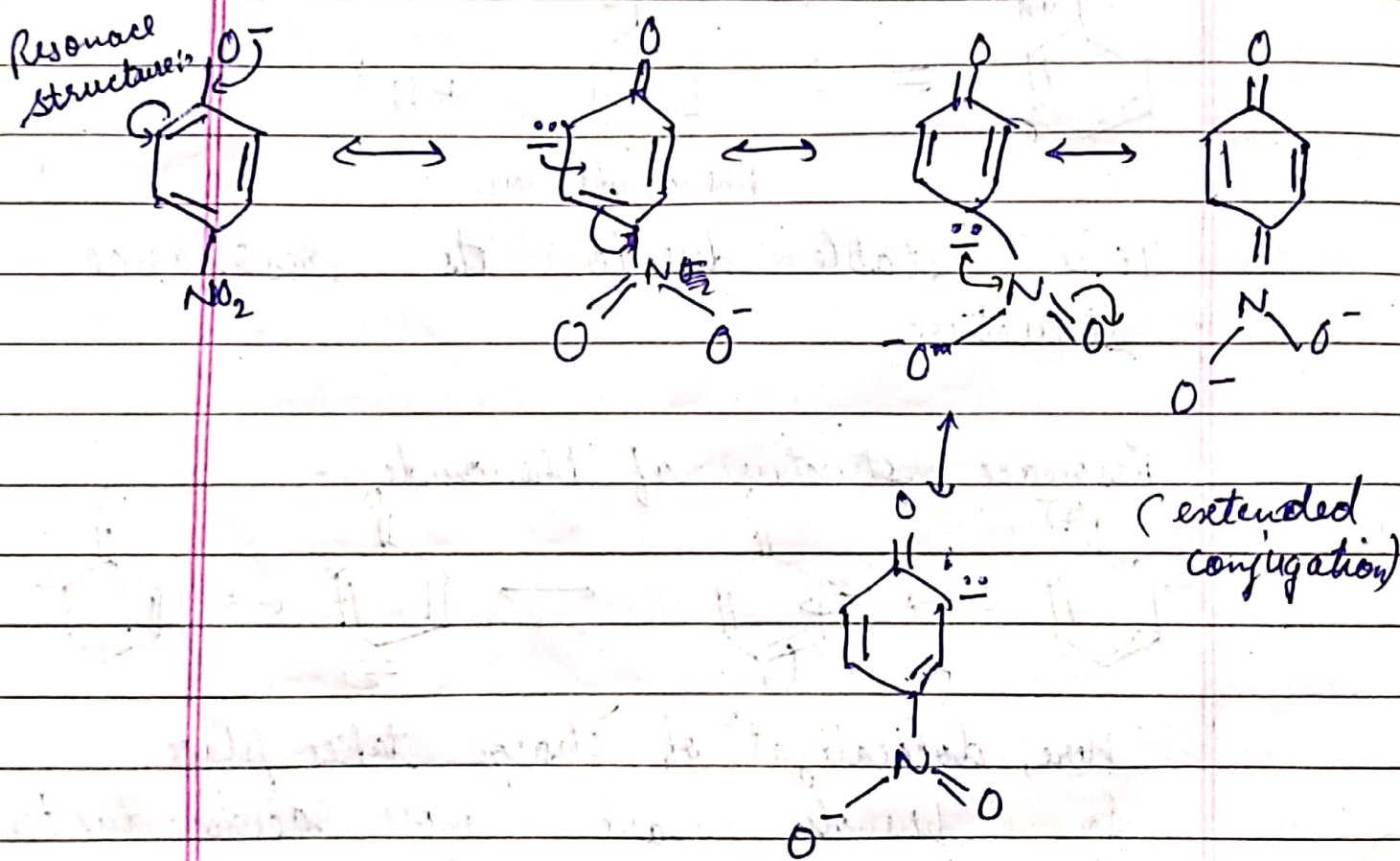
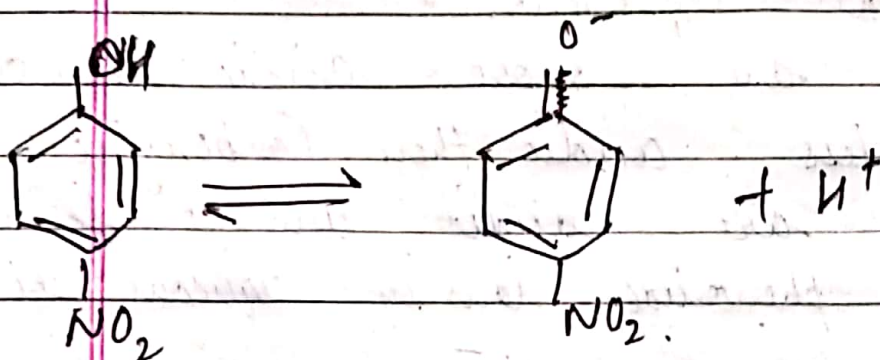


Here, delocalizat<sup>n</sup> of charge takes place. So, phenols are more acidic due to their resonance structures.

Phenols are more acidic than cyclohexanol which is having no resonance structure.

# Effect of substituent on Acidity :-

i) Electron withdrawing substituents :-  
[ $-\text{NO}_2$ ,  $-\text{Cl}$ ,  $-\text{CHO}$ ,  $-\text{CN}$ ,  $-\text{COOH}$ ].



- $e^-$  withdrawing groups on aromatic rings are acid strengthening. It enables the ring to withdraw more  $e^-$  from phenoxide ion [phenoxy oxygen]. This stabilizes the phenoxide ion and results in strong acid.

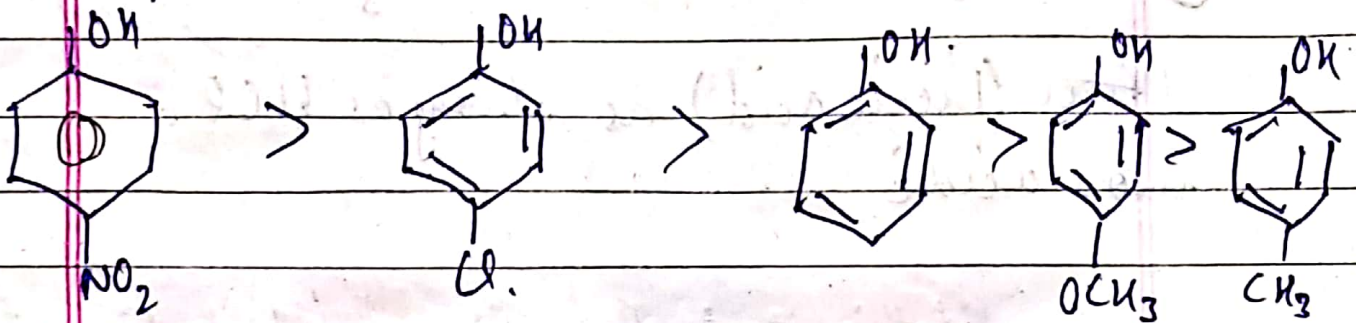
e.g. → para-nitrophenol is more acidic than phenol & alcohol.

(ii) Electron Releasing Substituents:

$[-CH_3, -OCH_3, -NH_2]$

$e^-$  releasing grps on aromatic ring are acid weakening.

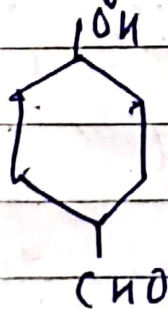
It strengthens the st. (-) ve charge on phenoxy oxygen & inhibits the charge delocalization due to resonance which destabilize the phenoxide ion & results in weaker acid



← Acidic Nature.

[  $e^-$  withdrawing → ↑ acidity of phenol ]  
 [  $e^-$  Releasing → ↓ acidity ]

⇒ p-hydroxy benzaldehyde.



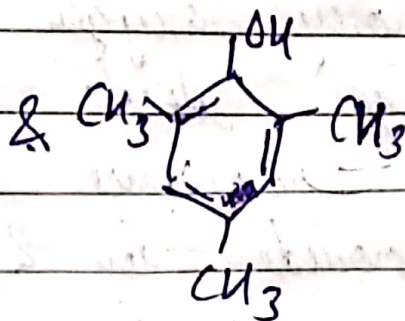
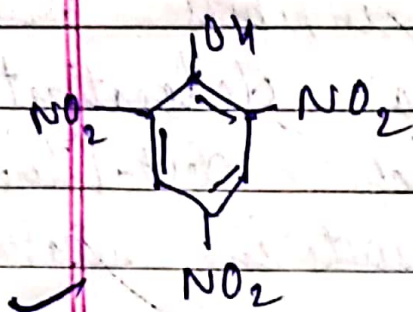
⇒ m-hydroxy benzaldehyde →

#9. 4-cyano phenol, & then Phenol.



More acid than phenol  
due to  $e^-$  withdrawing grp.

# 2,4,6 trinitrophenol, & 2,4,6 trimethylphenol



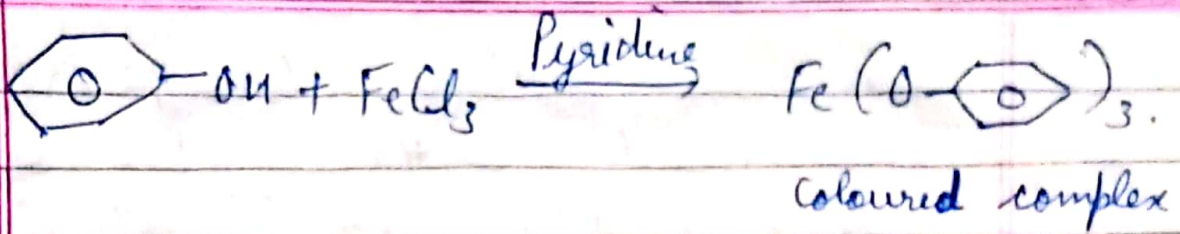
1 part (Picric acid) as strong as HCl.  
more acidic

Qualitative test for Phenol / Identification test  
of phenol :-

① Ferric Chloride test :-

Compounds with phenolic group will form a blue, violet, purple, green, brown & coloured complex on addition of aqueous  $FeCl_3$ .

This react<sup>n</sup> is used for the identification of phenolic group.



(i) for water soluble phenol :-  
 dissolving 15 mg of unknown compound  
 + 0.5 ml of water + 2-3 drops of  $\text{FeCl}_3$   
 ↓ in Pyridine.

red, blue, violet, Brown coloured complex.

#  
 (ii) for water insoluble phenol :-  
 15 mg of unknown compound + 0.5 ml of methylene  
 chloride + 2-3 drops of  $\text{FeCl}_3$ .  
 ↓ Pyridine

Red, blue, violet, brown coloured complex.

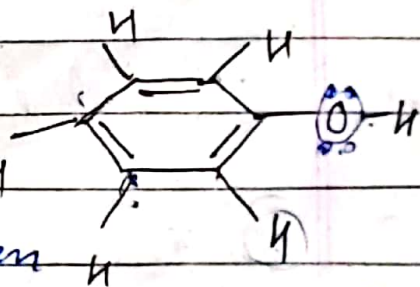
Structure & uses of phenol & its derivatives :-

⇒ structure

⇒ Phenol (Hydroxy Benzene)  
 structure :-

In phenol all ring  
 carbon atoms are

$sp^2$  hybridized & the oxygen  
 atom of OH grp is  $sp^3$  hybridized. All

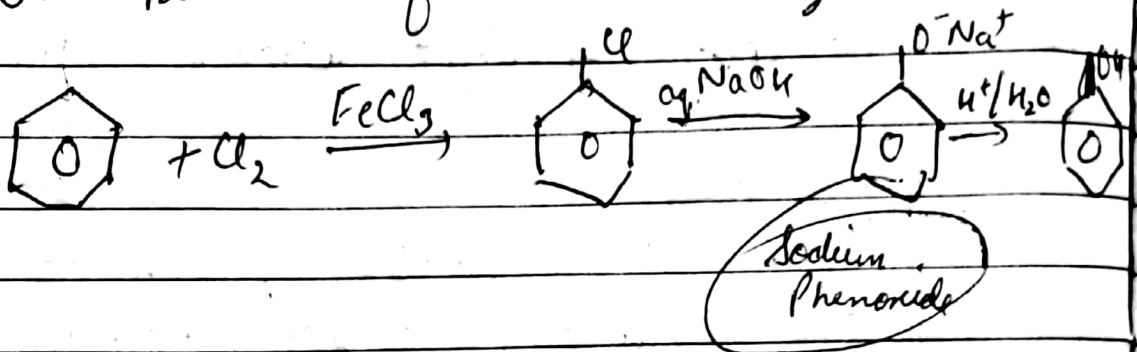


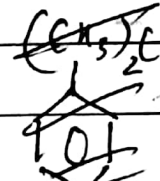



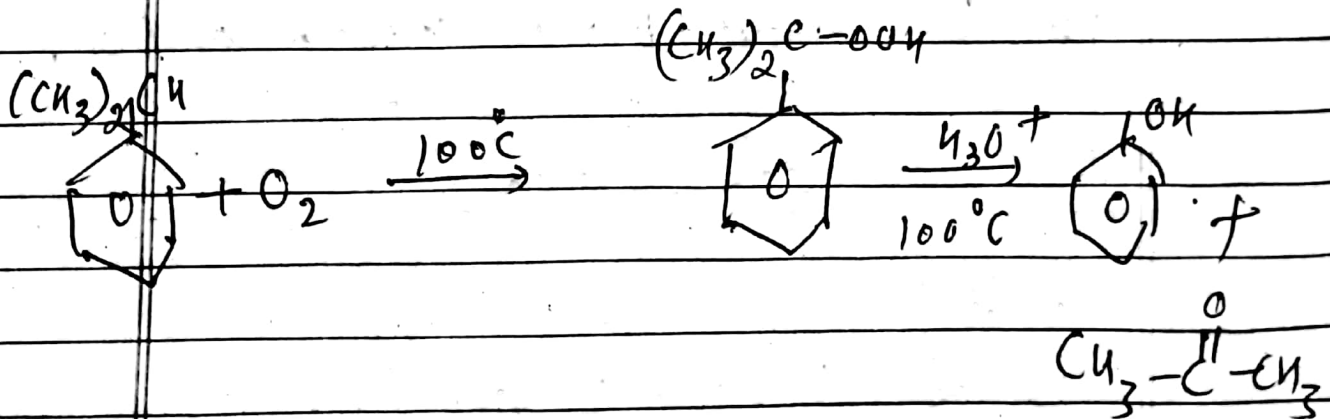
ring carbon atoms have p-orbital & these are  $\perp$  to the plane of  $\sigma$  bond (sigma bond). The lateral overlap of these p-orbital produces a delocalized  $\pi$ -molecular orbital.

### Preparat<sup>n</sup> of Phenol $\rightarrow$

(1) Dow's Process  $\rightarrow$  from chlorobenzene.

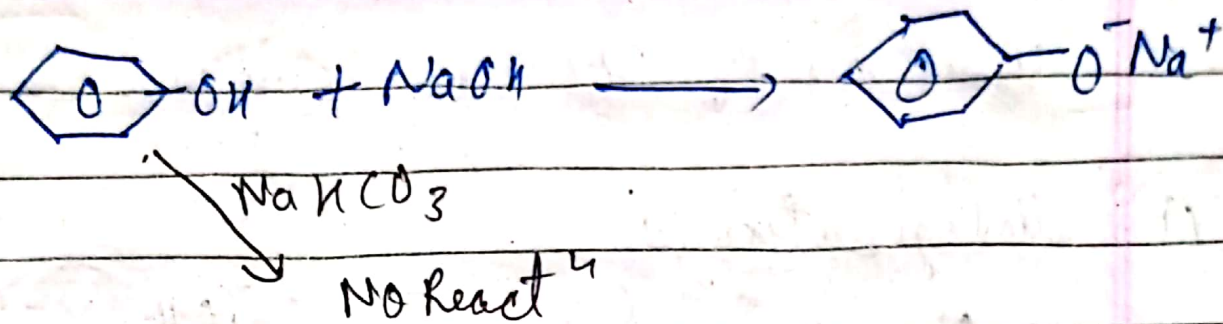


(2) Cumene Process  $\rightarrow$  [   ]

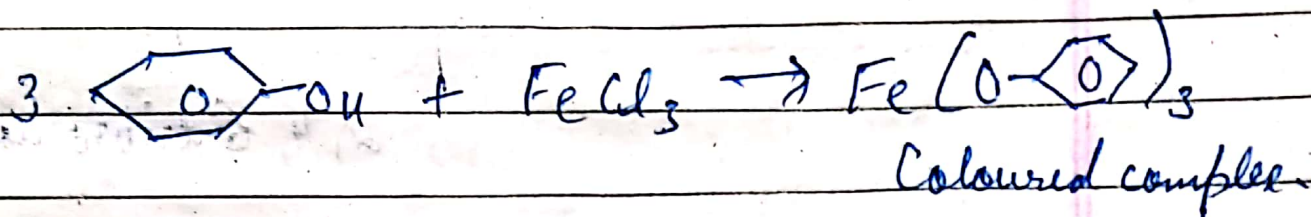


### Chemical Properties $\rightarrow$

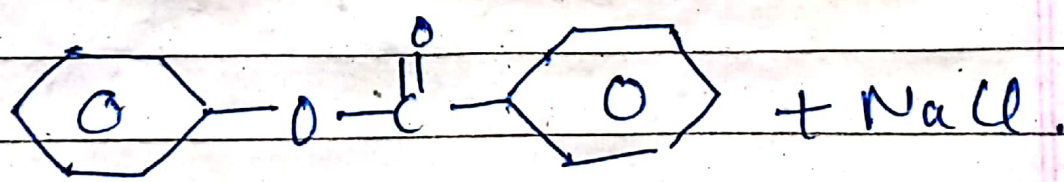
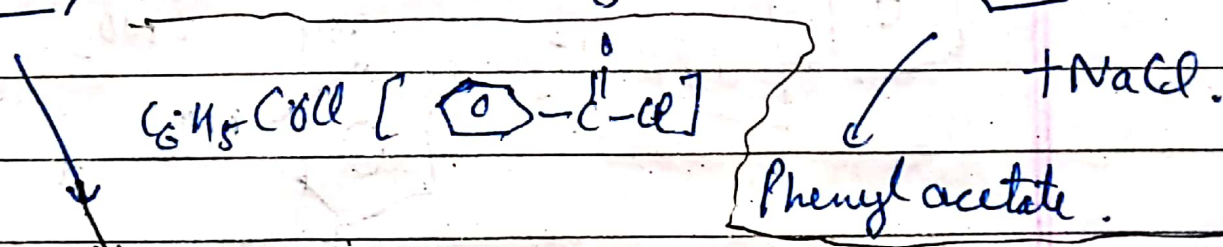
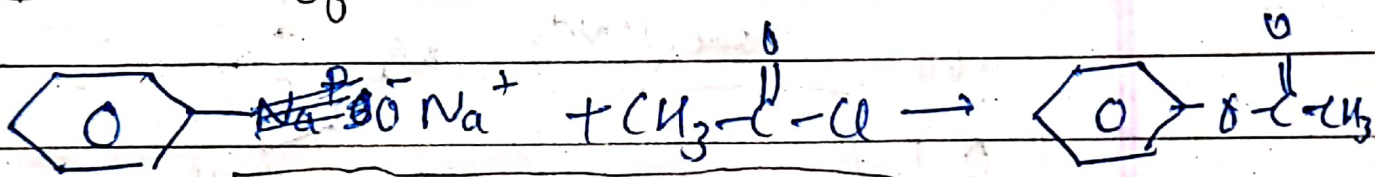
- (1) Reaction due to phenolic/OH group  $\rightarrow$
- (2) Formation of salts  $\rightarrow$



② React<sup>n</sup> with  $\text{FeCl}_3 \rightarrow$



③ Formation of esters  $\rightarrow$



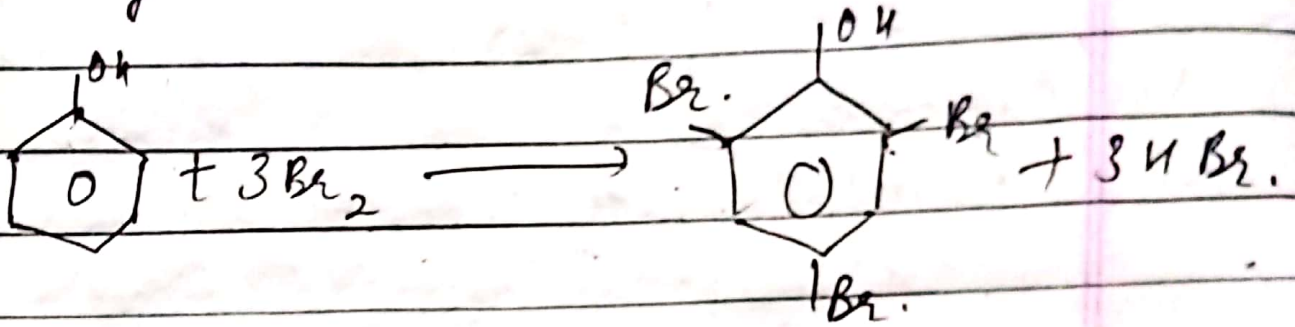
$\checkmark$  this rxn is called Schotten-Baumann React<sup>n</sup>

④ React<sup>n</sup> with Zn dust  $\rightarrow$



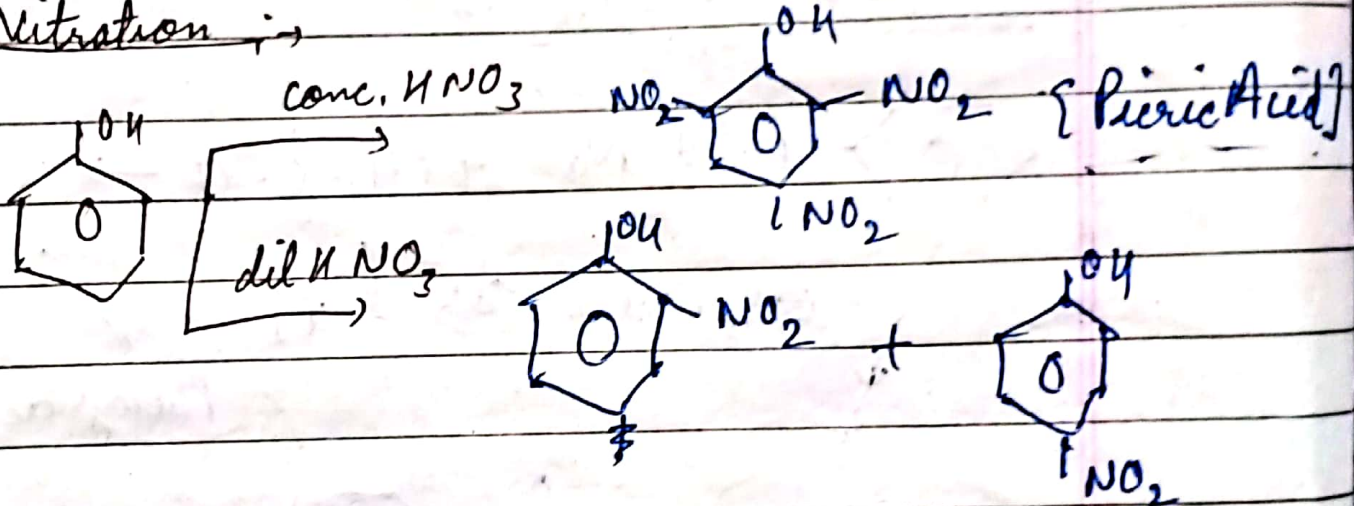
# Reactions of Benzene Ring:

(1) Halogenation:  $\rightarrow$

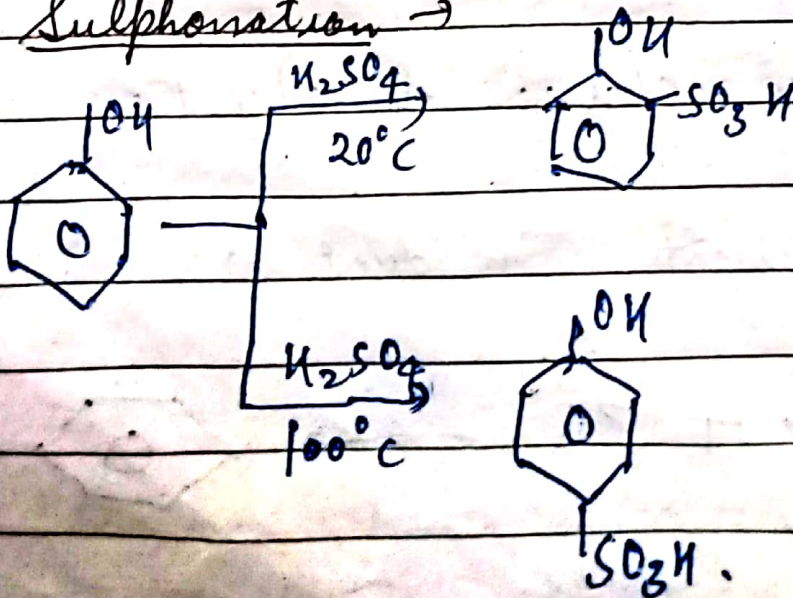


2, 4, 6 tribromophenol

2. Nitration:  $\rightarrow$

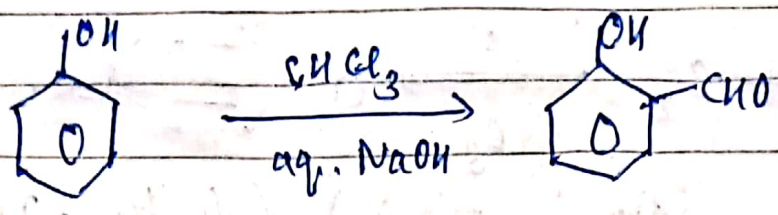


3. Sulphonation  $\rightarrow$

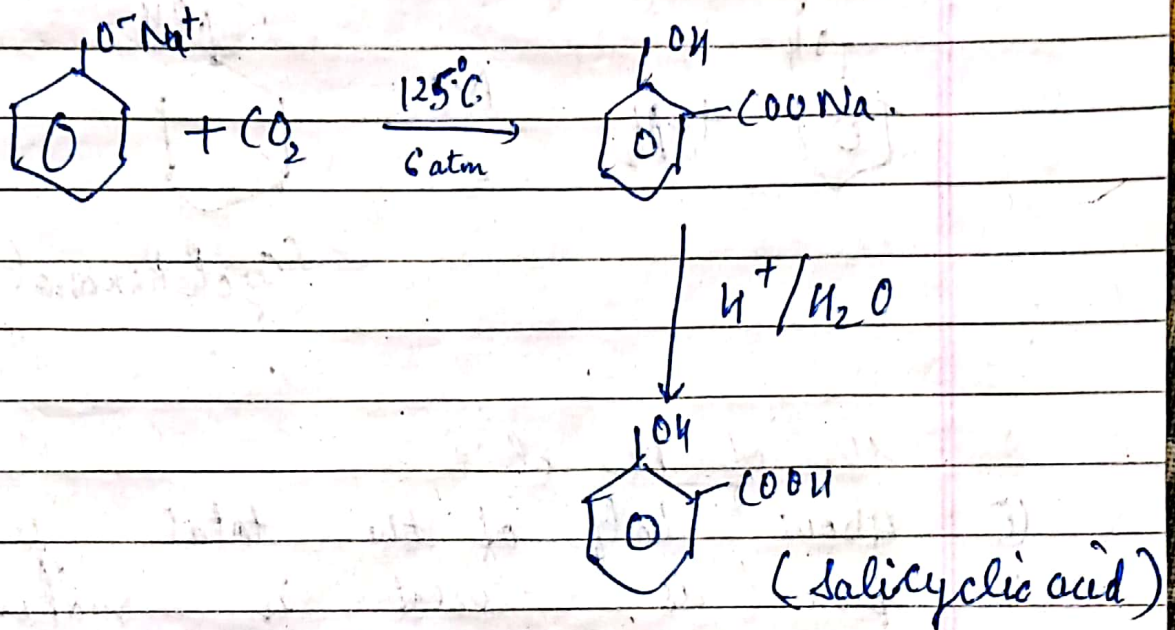


Imp :-

4. Reimer Tiemann React<sup>n</sup> :-

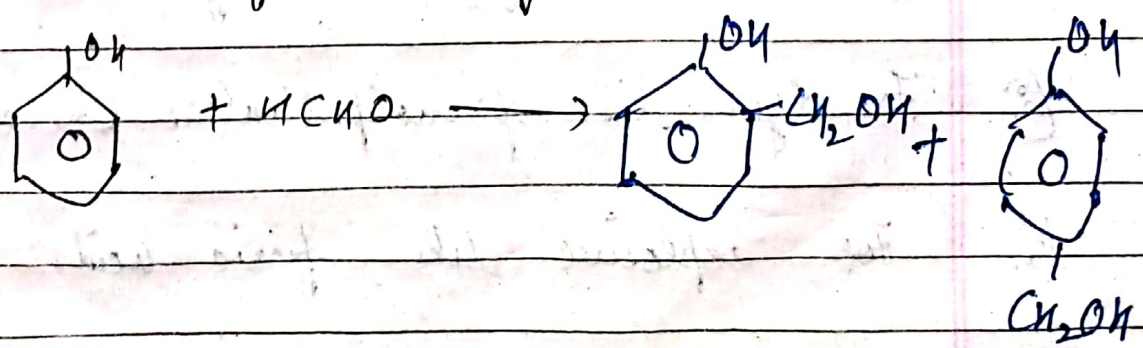


5. Kolbe React<sup>n</sup> :-



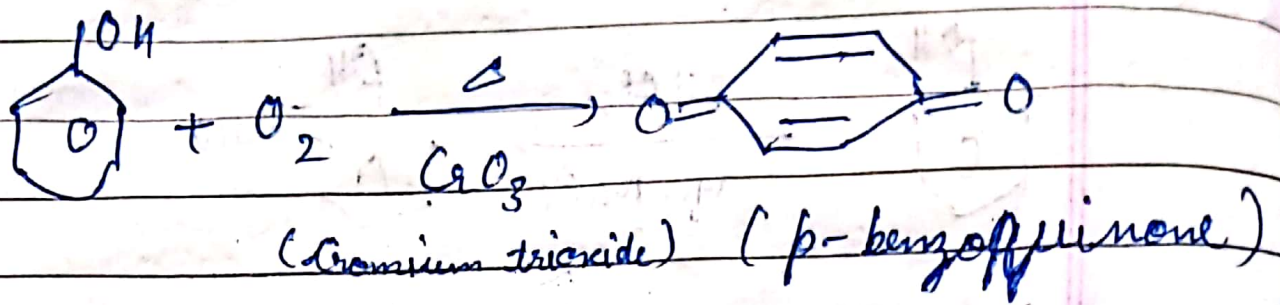
6. React<sup>n</sup> with Formaldehyde :-

Phenol formaldehyde Resin → Bakelite.

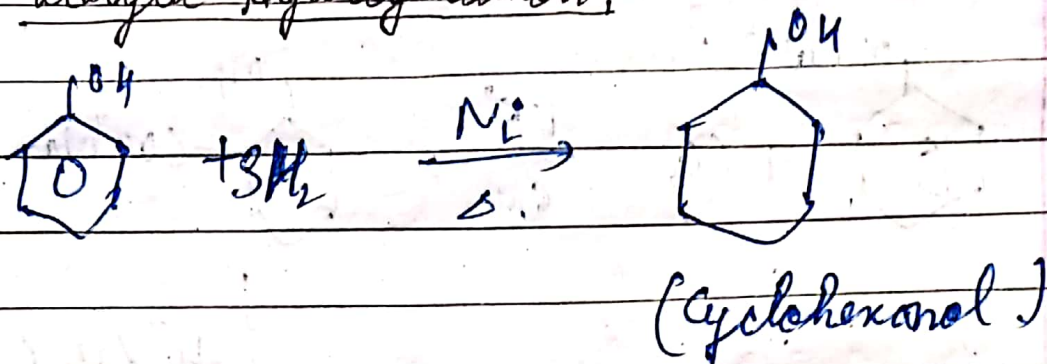


In, this react<sup>n</sup> at high temp. & excess of formaldehyde hard thermosetting plastic bakelite is formed.

## 7. Oxidation :-



## 8. Catalytic Hydrogenation :-

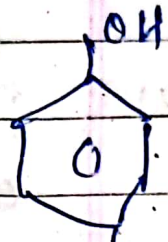
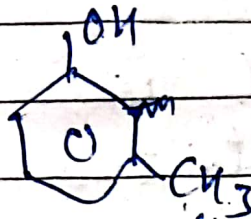
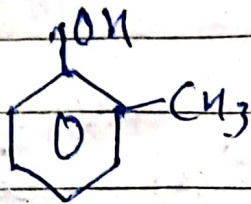


## ⇒ Uses of Phenol :-

- ① About half of the total product<sup>n</sup> of phenol is used in making phenol formaldehyde Resin (PF Resin) i.e. Bakelite.
- ② Phenol is used as a starting material for drugs like aspirin.
- ③ For dyes like phenolphthalein, phenolphthalin.
- ④ For explosives like picric acid.
- ⑤ For valuable products like wood preservative, lignin, herbicides, antiseptic, etc.

# Structure & Uses of Cresol :-

Cresol ( $C_7H_8O$ )



Common Name of Cresol

Synthetic → 2-methyl phenol

o-cresol

3-methyl phenol

p-cresol

4-methyl phenol

→ Cresols are organic compounds which are methyl phenols. Depending on temp, cresols can be solid or liquid, because they have M.P. not far from room temp.

→ They are slowly oxidized by long exposure to air & the impurities gives a yellowish or brownish colour.

→ In its chemical str. a cresol molecule has a methyl grp substituted on to the ring of phenol

Appearance →

o-cresol  
colourless crystalline

m-cresol  
thicker liquid

p-cresol  
greeny looking solid

Molar Mass is same of all cresol

⇒ 108g/mol

uses of cresols :-

1. Mixed cresols are used for wood preservative & disinfectant

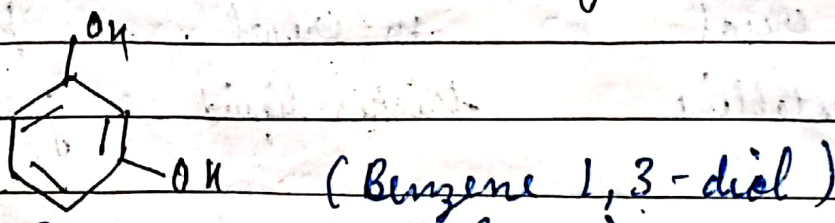
(a) o-cresol is used as a solvent, disinfectant & chemical intermediate

(b) m-cresol is used to produce certain herbicides & to produce anti-oxidant.

(c) p-cresol is used largely in the form of anti-oxidants in fragrance & dye industries.

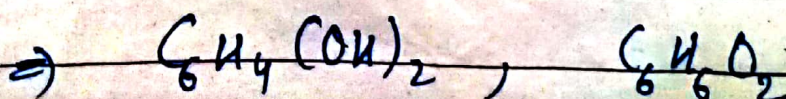
Acute inhalation exposure by humans to mixed-cresols (Respiratory tract problem)  
Mixed-cresols results in respiratory tract irritation.

Structure & uses of Resorcinol :-

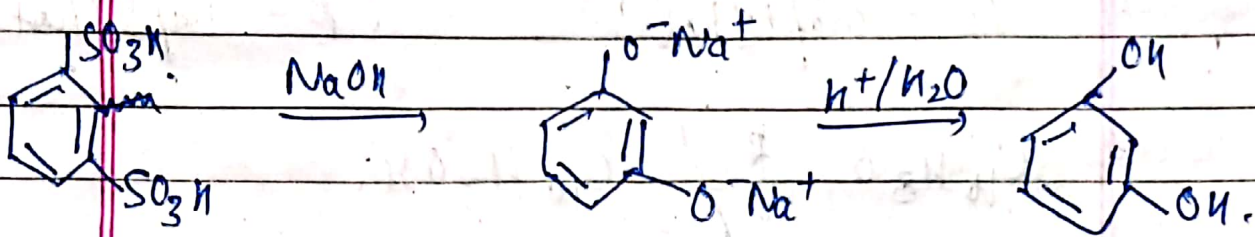


Common name → Resorcin.

m-dihydroxy benzene.



- Resorcinol is 1,3 isomer of benzenediol with a chemical formula  $C_6H_4(OH)_2$
- It is white solid soluble in water.
- It does not occur naturally in free state
- It is obtained by m-benzene sulphonic acid.



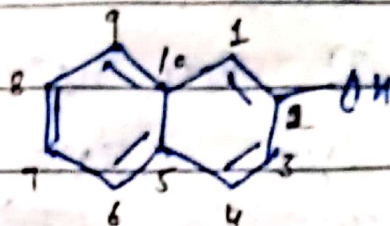
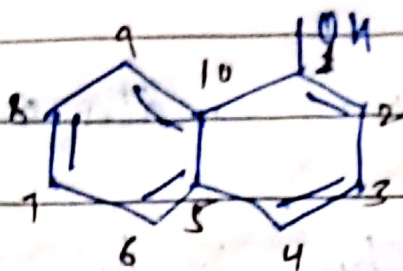
Uses :-

- It is an antiseptic disinfectant & it is used 5% - 10% in ointments in the treatment of chronic skin diseases.
- Used in the treatment of gastric ulcers.
- It is used as a skin-protectant
- Used in the preparation of product of azodye & as a UV absorber.
- Resorcinol reacts with formaldehyde



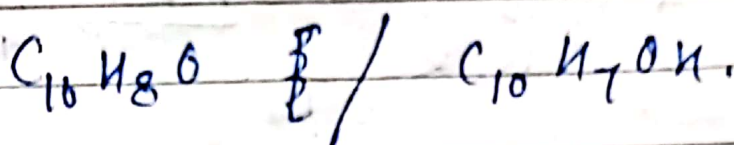
& form the thermosetting resin.

Structure & uses of Naphthol is



1-naphthol  
( $\alpha$ -naphthol)

2-naphthol  
( $\beta$ -naphthol)



- Naphthol is a <sup>shiny</sup> fluorescent colourless crystalline solid with the formula  $C_{10}H_7OH$ .
- It is derived from naphthalene & belonging to phenol family.
- It exists in 2 isomers i.e.  
1-naphthol & 2-naphthol  
differing by location of hydroxyl group on the naphthalene ring.

1-naphthol

2-naphthol

Appearance  $\rightarrow$  Colourless / white solid.

Colourless crystalline solid.

• Naphthol contains naphthyl hydroxyl group, it is highly polar molecules. with the oxygen atom attracting  $e^-$  density through the bonds towards itself.

• Naphthol is soluble in solvents like ethanol, methanol due to the ability to form H bond with alcohol.

Uses :-

→ Both isomers are used for dyes, pigments, insecticides, perfumes, antiseptics, etc.

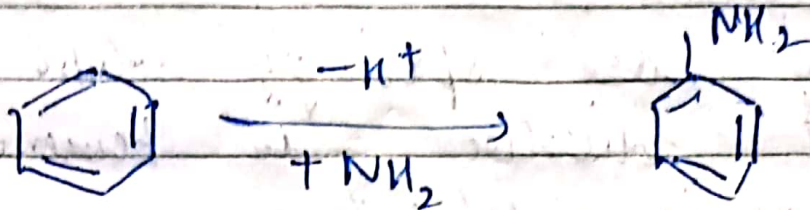
→ 1-naphthol is precursor to a variety of insecticides, it undergoes azo-coupling to give azo-dye.

Imp → In Molisch test, as molisch reagent for detecting the presence of carbohydrates

→ In Sakaguchi test, 1-naphthol + sodium hypobromide for detecting the presence of arginine in proteins.

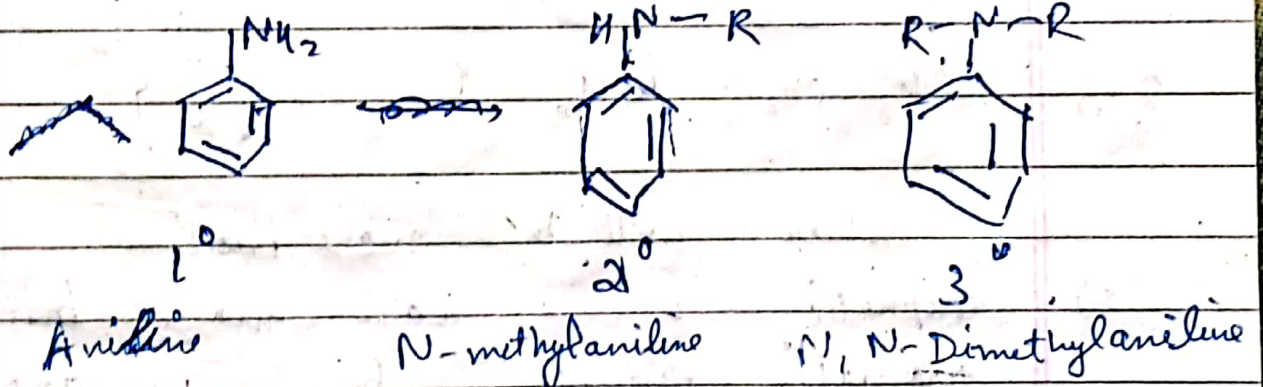
# Aromatic Amines :-

The derivatives in which Hydrogen of Benzene ring has been replaced by amino grp.

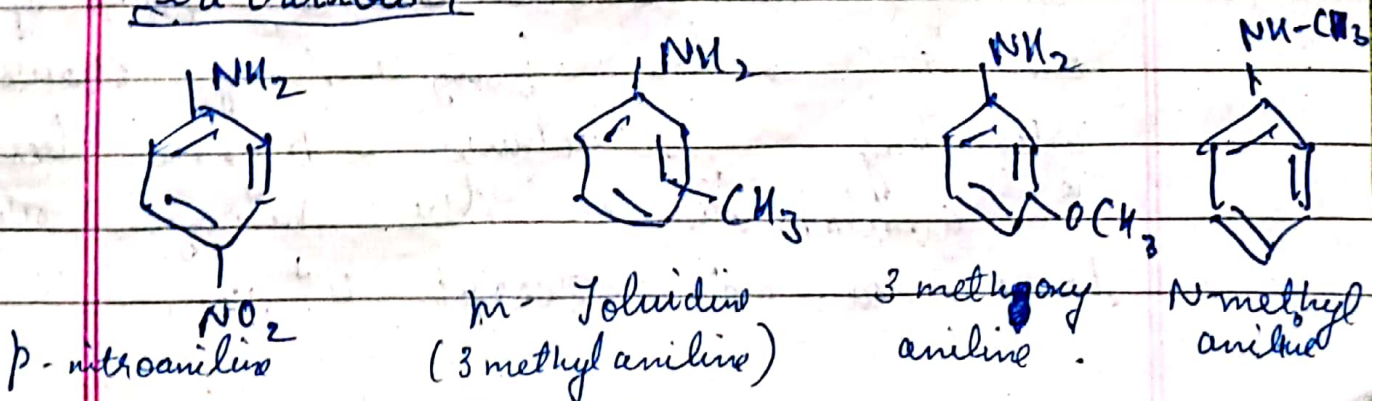


All the compounds in which amino or substituted amino grp is bonded directly to the benzene ring are c/d as aromatic amines.

Aromatic amines could be ~~des~~ represented as  $1^\circ$ ,  $2^\circ$ , &  $3^\circ$  amines.



## Derivatives :-

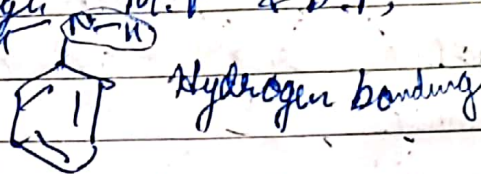


Anilines is less basic than ethylamine

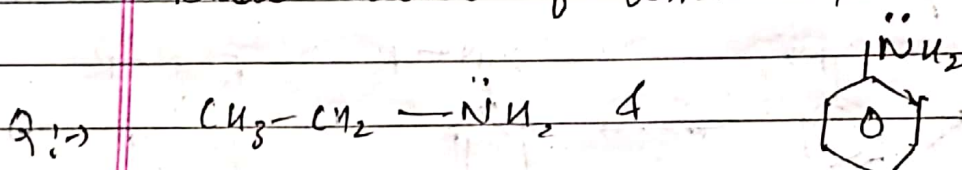
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Physical properties of amines: ->

- > Colourless liquid or solid having a characteristic odour which is not pleasant
- > They turn brown in air due to oxidation.
- > They are sparingly soluble in water but dissolve in benzene & other organic solvents.
- > The polar nature of NH bond results in formation of hydrogen bond with other amine molecules having high M.P & B.P, than alkanes



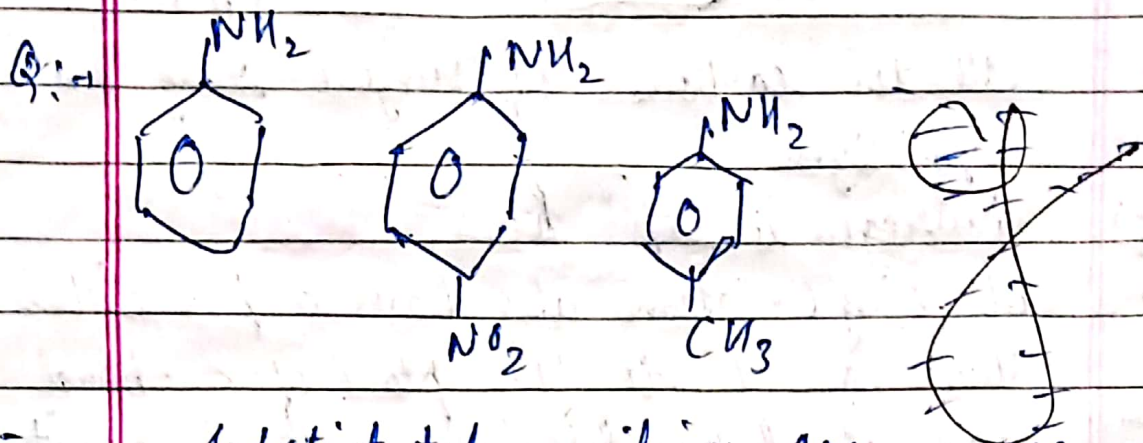
Basic Nature of Amines: ->



which will be more basic.

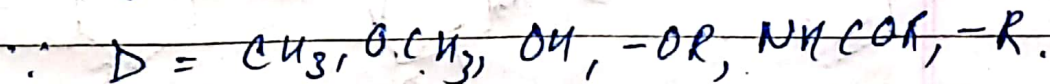
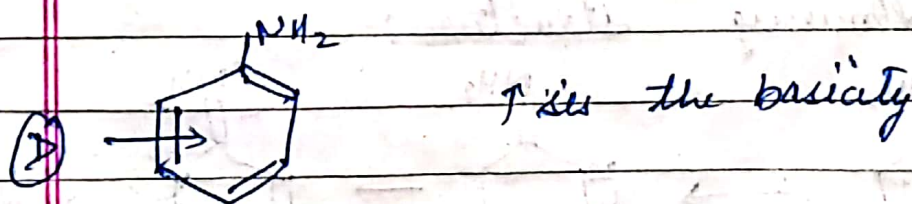
- => Aliphatic amines are more basic than aromatic amines because in aromatic amines there is delocalisation of l.p. of  $e^-$  due to which benzene ring shows resonating structures & become less  $e^-$  availability in the nitrogen atom hence, can not accept  $\text{H}^+$  ion,

where as in aliphatic amine due to inductive effect nitrogen accepts  $H^+$  ion & becomes more basic as compared to the aromatic amines.

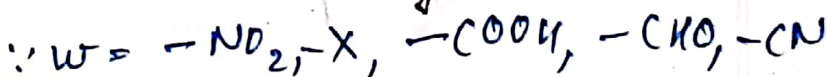
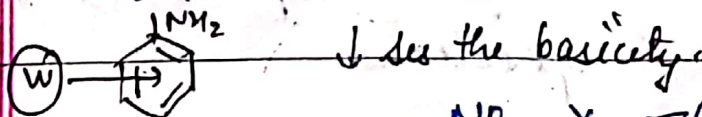


Substituted anilines are more or less basic than aniline depending on the nature of substituents.

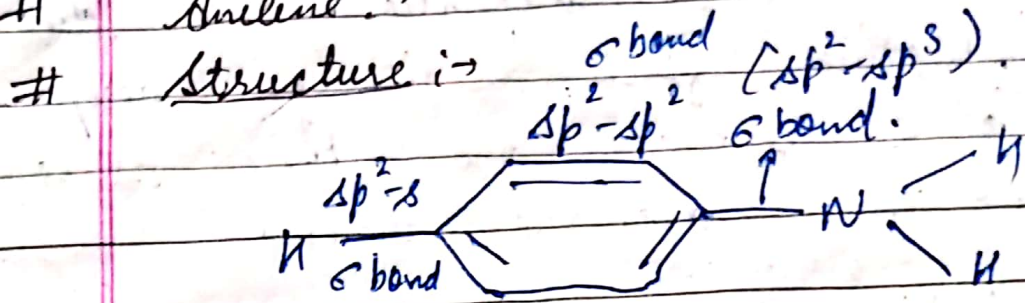
(1)  $e^-$  donating groups -  
 $e^-$  donating grps adds  $e^-$  density at benzene ring making the aryl amine more basic than the aniline.



(2)  $e^-$  withdrawing grps  $\rightarrow$  removes the  $e^-$  density from the benzene ring making the aryl amine less basic than aniline.



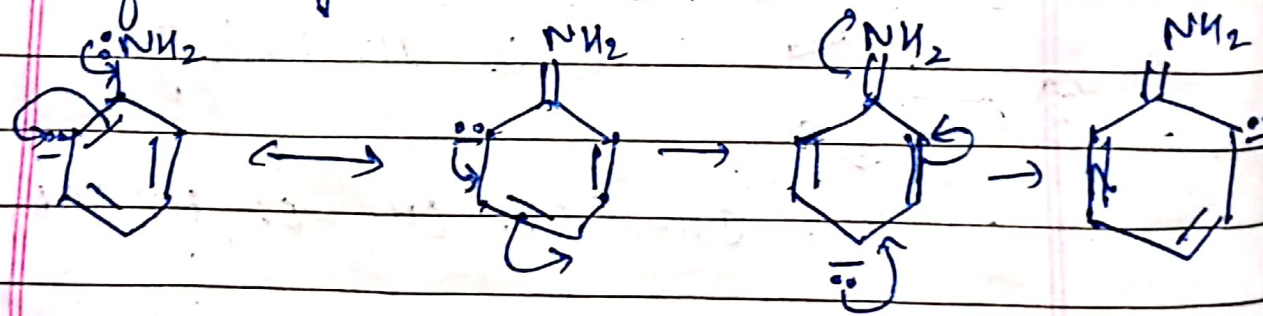
# Aniline: ?



- $\rightarrow$  All the carbons of benzene ring are  $sp^2$  hybridized.
- $\rightarrow$  Nitrogen is  $sp^3$  hbr.
- $\rightarrow$  All ring C-atoms also have a p-orbitals & these are  $\perp$  to the plane of  $\sigma$ -bond.
- the lateral overlapping of these orbitals produces  $\pi$ -Molecular orbitals.
- the l.p. e<sup>-</sup> on Nitrogen atom exist in  $sp^3$  hybrid orbitals.

Resonating Structure  $\rightarrow$

$\rightarrow$  Acc to resonance theory Aniline is considered to be the resonance hybrid of following structure:-



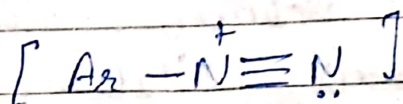
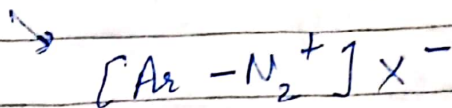
$E^+$  will attack at o & p positions.

- Ortho & para positions carry negative charge. So electrophile will attack on the positions.

# Arene/Aromatic / Aryl gp.



Arene Diazonium salt :-

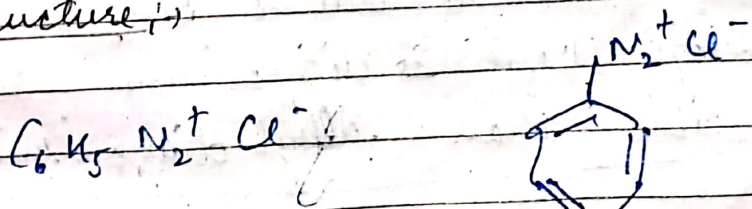


Arene diazonium ion

$[R - N_2^+] X^- \rightarrow$  Alkyl diazonium salt

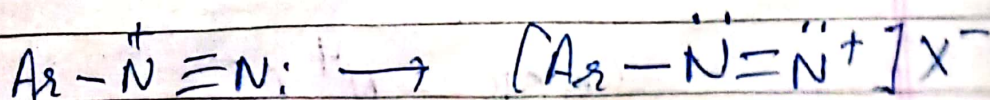
The compounds are characterised by the presence of functional gp  $[-N^+ \equiv N:]$  directly bonded to Aryl gp, the arene diazonium ion forms salt with anions such as  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $HSO_4^-$ ,  $BF_4^-$ , these are called as arene diazonium salt.

Structure :-



(Benzene diazonium chloride)

The electronic str. of diazonium salt is written as

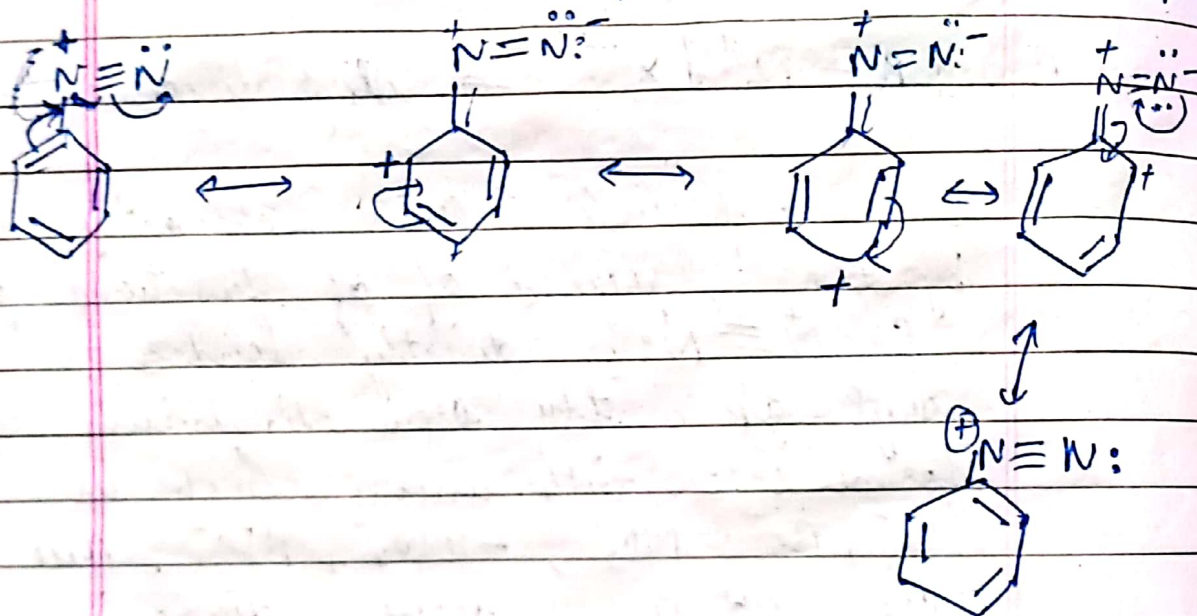


$R Mg X \rightarrow$  Grignard reagent.

$e^-$  deficient

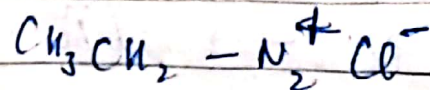
Date \_\_\_\_\_  
Page \_\_\_\_\_

The diazonium ion is resonance stabilized the (+) or charge being distributed over the two Nitrogen atoms. The stability of arene diazonium salt relative to alkyl diazonium salt is also due to resonance involving the benzene ring.



more resonance due to benzene ring, so ~~alkyl~~ Arene diazonium salt is more stable than Alkyl diazonium salt.

Thus, the Carbon-Nitrogen bond acquires partial double bond character & is stronger than C-N bond in alkyl diazonium salts.



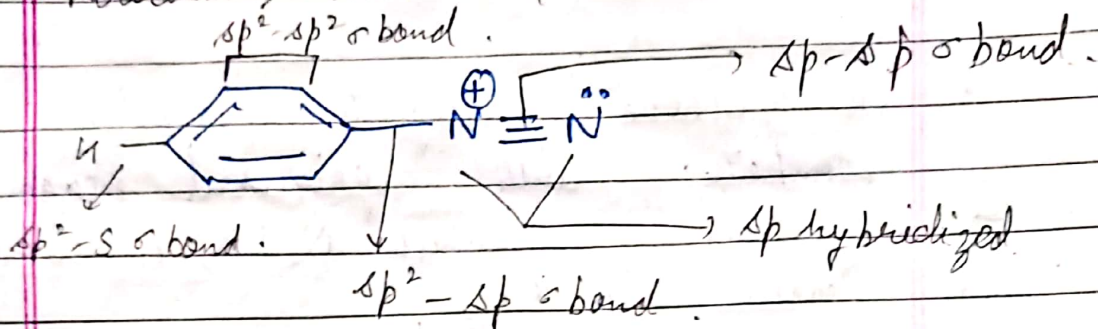


H.C  $\equiv$  CH ( $sp-sp$ ) hybridized.

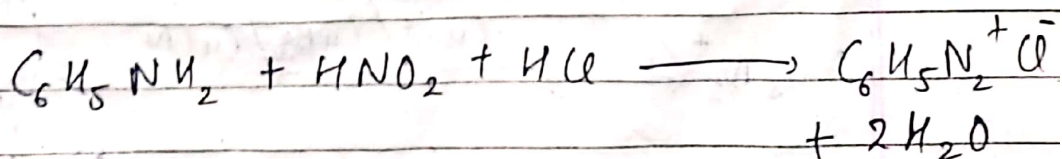
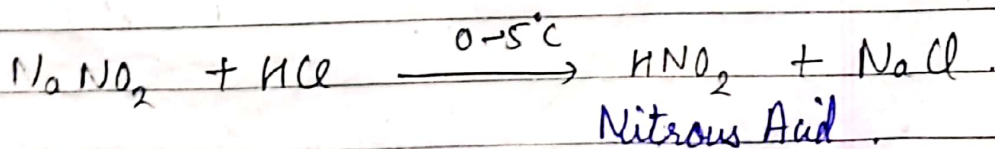
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The aliphatic diazonium salts are unstable because alkyl grp is incapable of participating in resonance.

Molecular structure :-



Preparation of Arene Diazonium salts :-  
Arene diazonium salts are prepared by the act<sup>n</sup> of an aromatic primary amine with nitrous acid at  $0-5^{\circ}\text{C}$ . The nitrous acid is obtained by taking sod. Nitrite & a more mineral acid in reaction mixture.



(Benzyl diazonium chloride)

The process of converting an amine into diazonium salt is called as Diazotization.

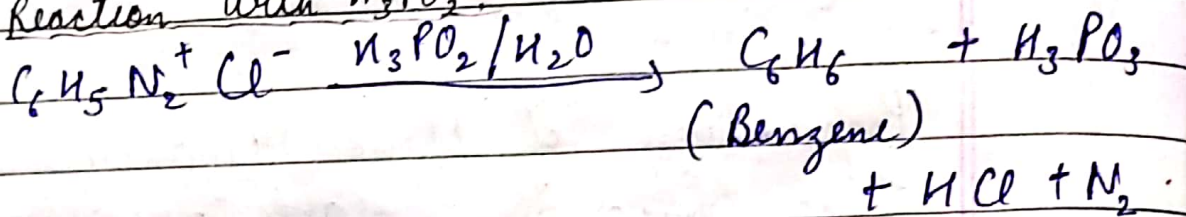
## Chemical Reactions :-

• Aromatic diazonium salts are highly reactive & undergo many useful applications.

• As synthetic reagents diazonium salts compete with Grignard reagents.

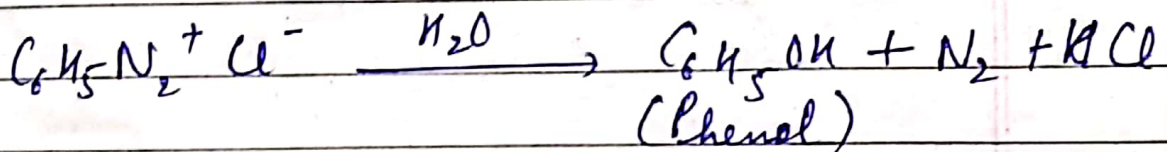
→ Reactions in which  $N_2^+ X^-$  involved -

• Reaction with  $H_3PO_2$  :-

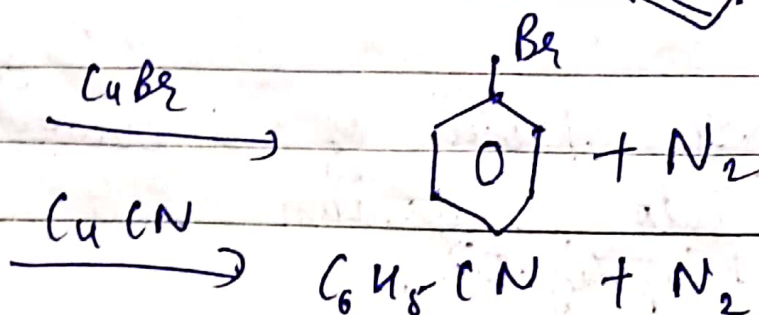
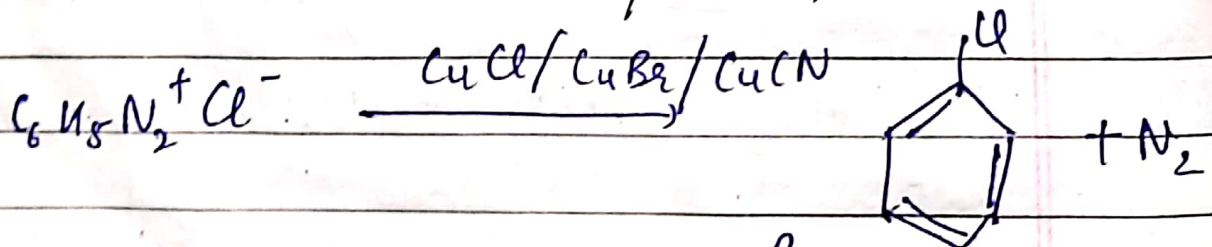


This react<sup>n</sup> is used for the preparation of Benzene.

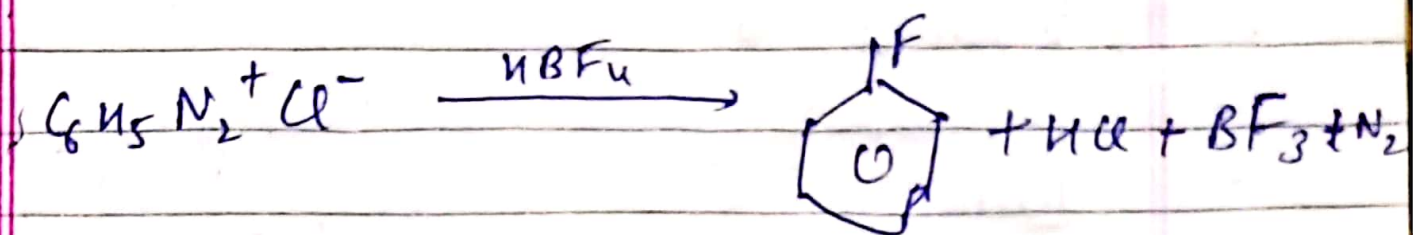
• React<sup>n</sup> with water :-



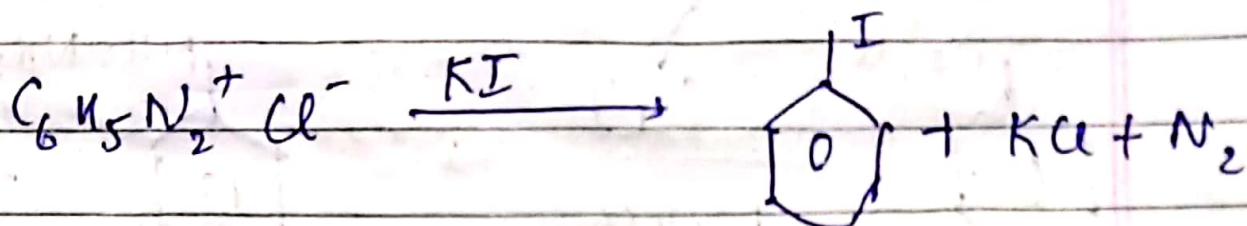
• React<sup>n</sup> with  $CuCl / CuBr / CuCN$  :-



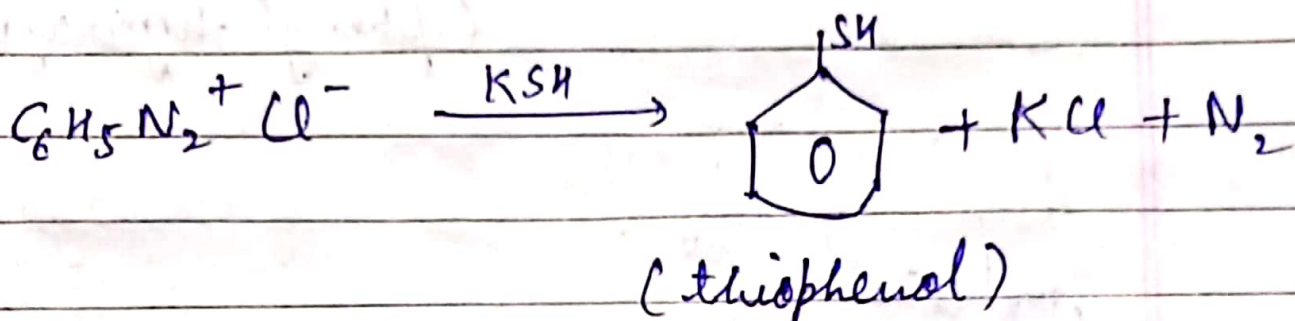
• React<sup>n</sup> with ~~HBr~~  $\text{HBF}_4$  :-



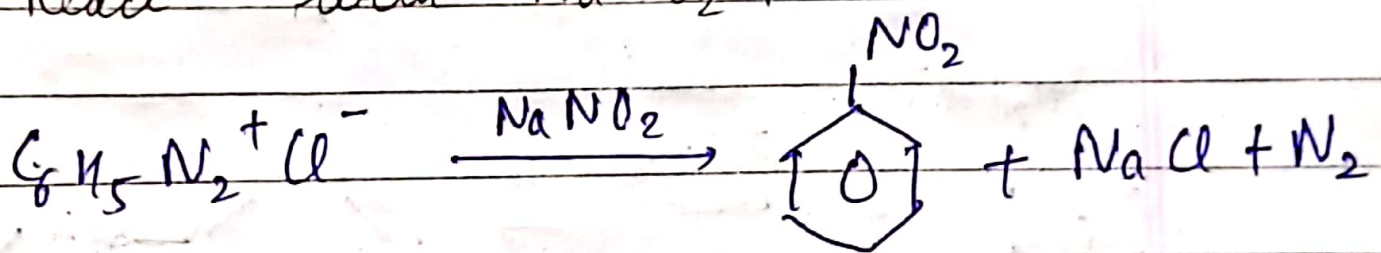
• React<sup>n</sup> with Potassium Iodide :-



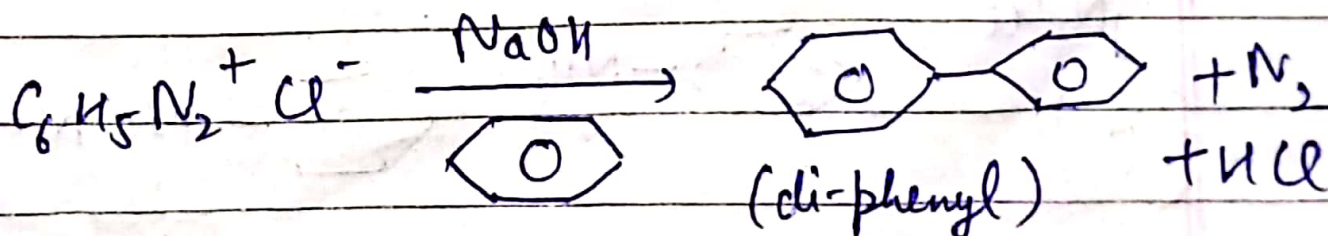
• React<sup>n</sup> with  $\text{KSH}$  (thiophenol) :-



• React<sup>n</sup> with  $\text{NaNO}_2$  :-

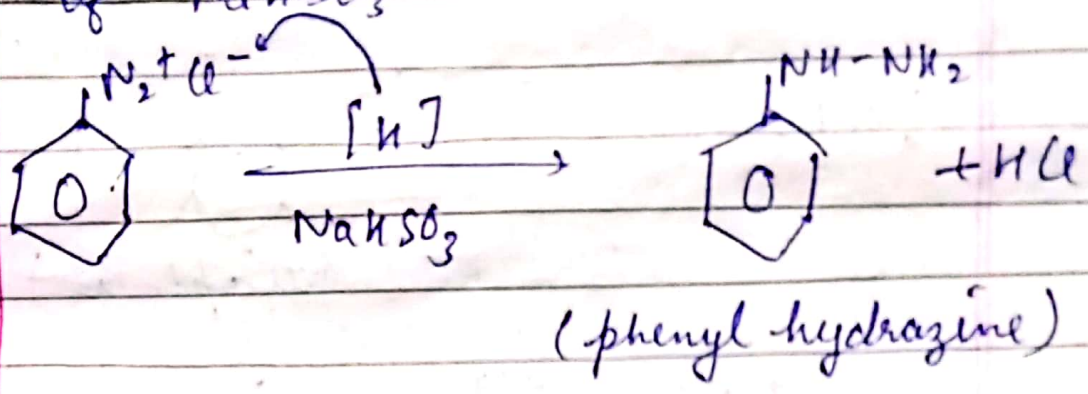


• React<sup>n</sup> with Benzene in the presence of base :-

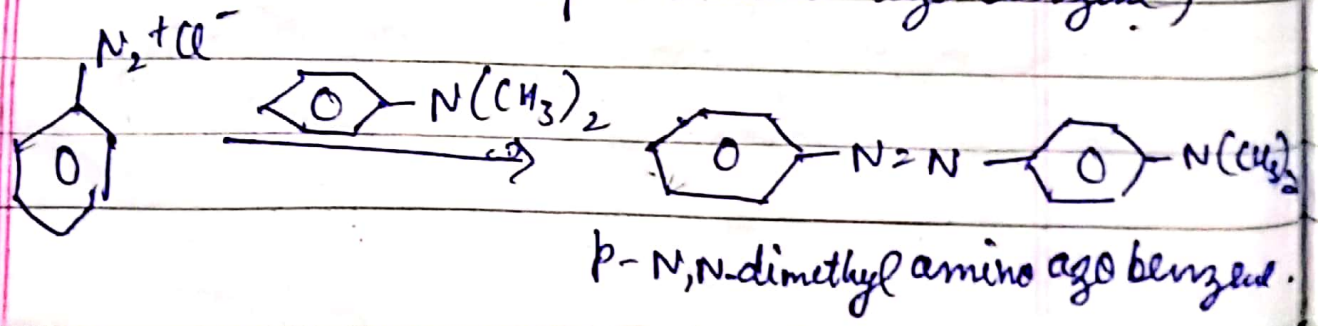
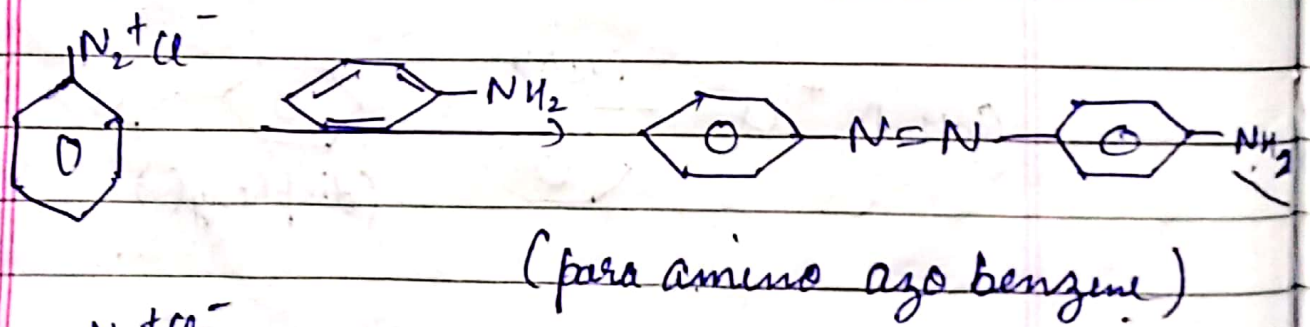
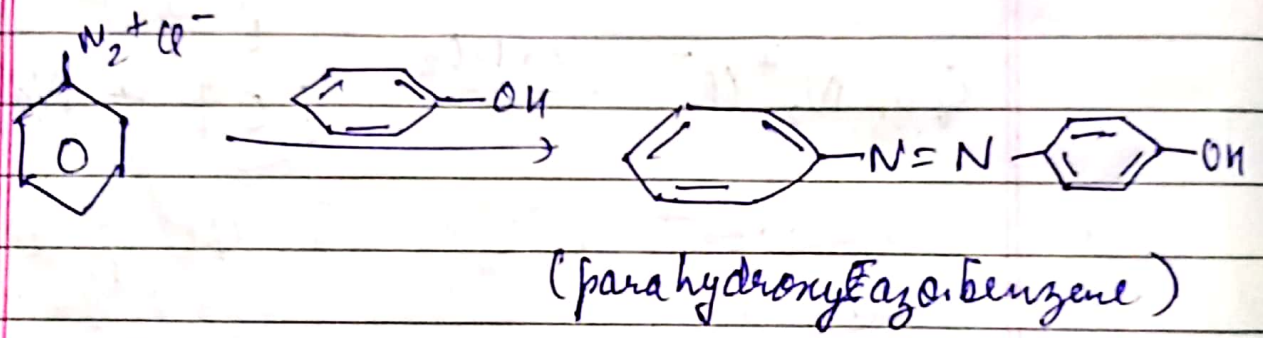
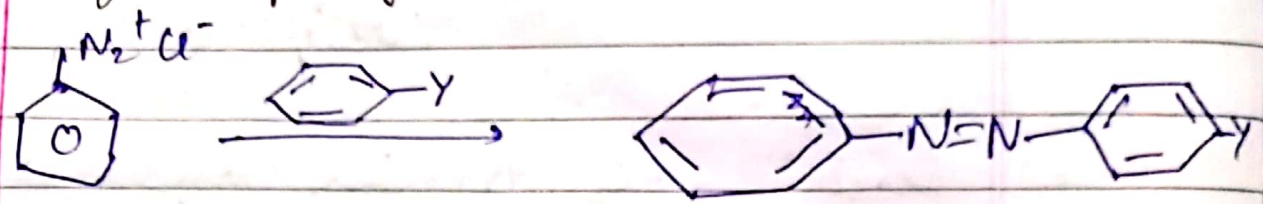


→ Reactions in which nitrogen atoms are retained :-

Reduction :-  
Addition of Hydrogen in the presence of  $\text{NaHSO}_3$



Azo-coupling :-



# Aromatic Carboxylic Acids :-



COOH

R-COOH

Aliphatic,

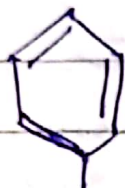
Aromatic

(Benzoic Acid)  $\rightarrow$  1<sup>st</sup> compound.

Aromatic acids are compounds in which one or more Carboxyl groups (-COOH) are attached directly to the aromatic ring.

e.g.  $\rightarrow$

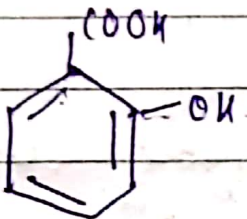
(a)



COOH

(Benzoic acid)

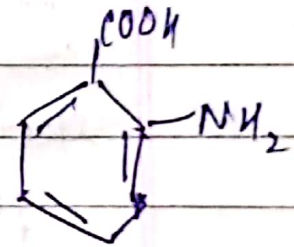
(b)



o-hydroxy benzoic acid

2- " " "  
(Salicylic acid)

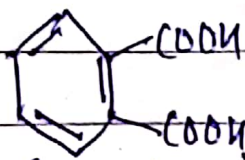
(c)



o-ty amino benzoic acid

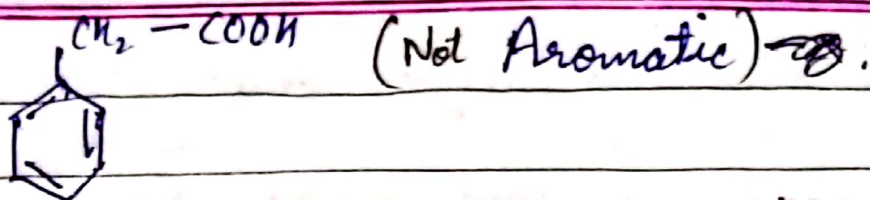
(Anthranilic acid)

(d)



(Phthalic acid)

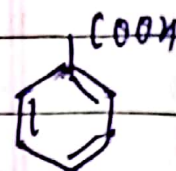
Benzene 1,2 dicarboxylic acid.



2-phenyl-ethanoic acid.

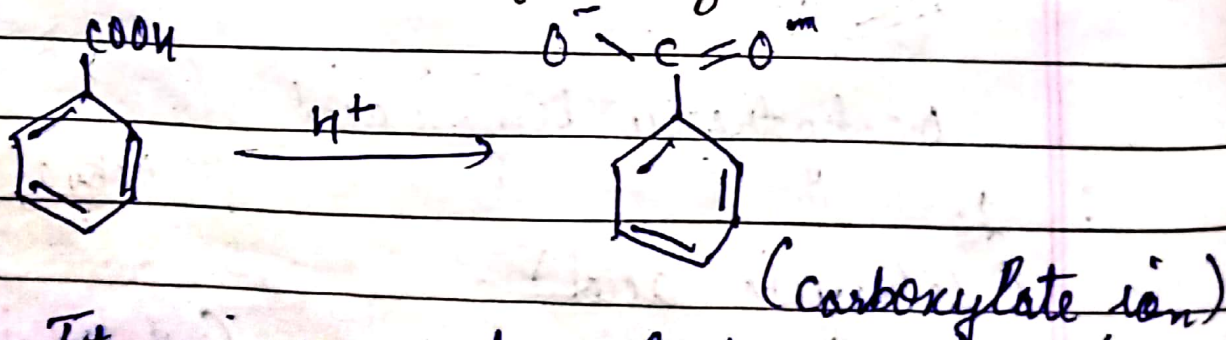
$\Rightarrow$  The compounds in which carbonyl group is not attached directly to the aromatic ring are called side chain aromatic acid.

Physical properties:

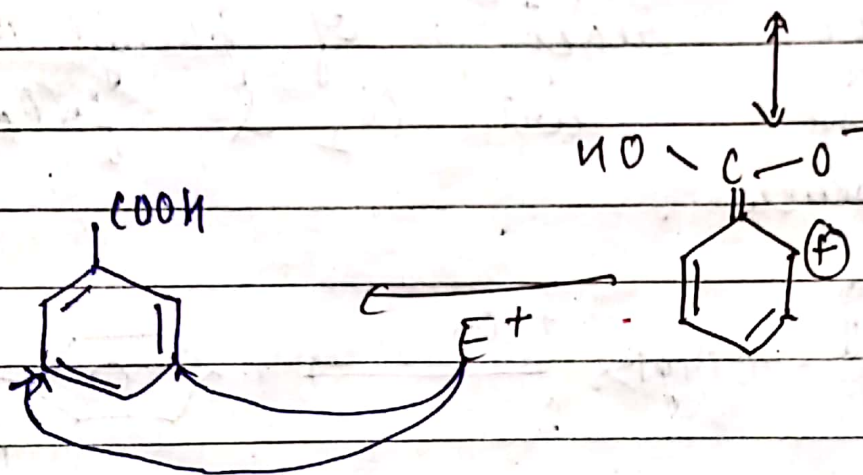
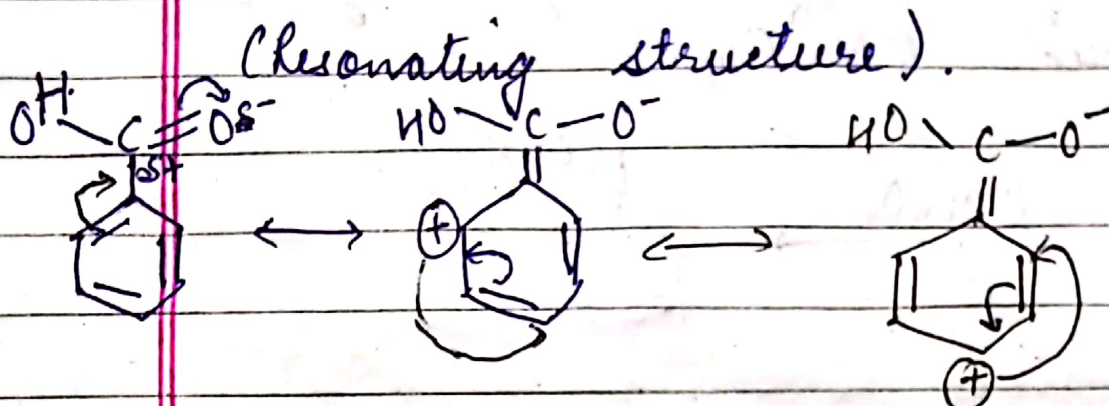
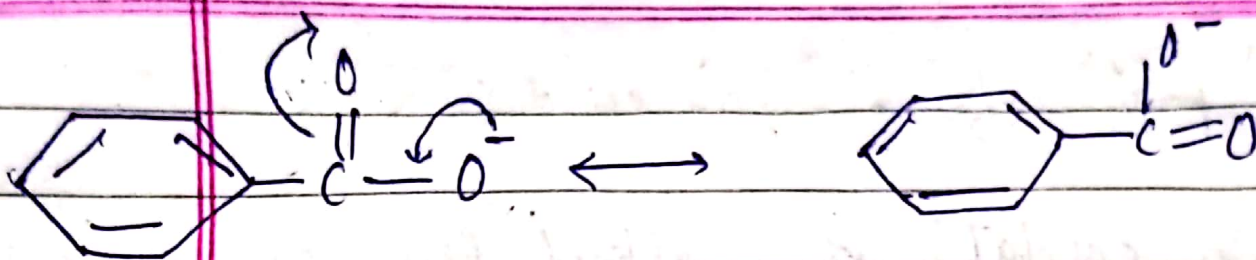


- $\rightarrow$  Benzoic acid is colourless solid. M.P is  $122^\circ\text{C}$
- $\rightarrow$  Soluble in water, diethyl ether, ethanol & benzene.
- $\rightarrow$  Benzoic acid is stronger acid than acetic acid.

Acidic Nature of Benzoic Acid:



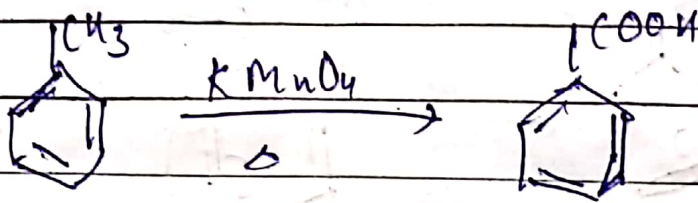
It gives carboxylate ion due to which benzoic acid is acidic.



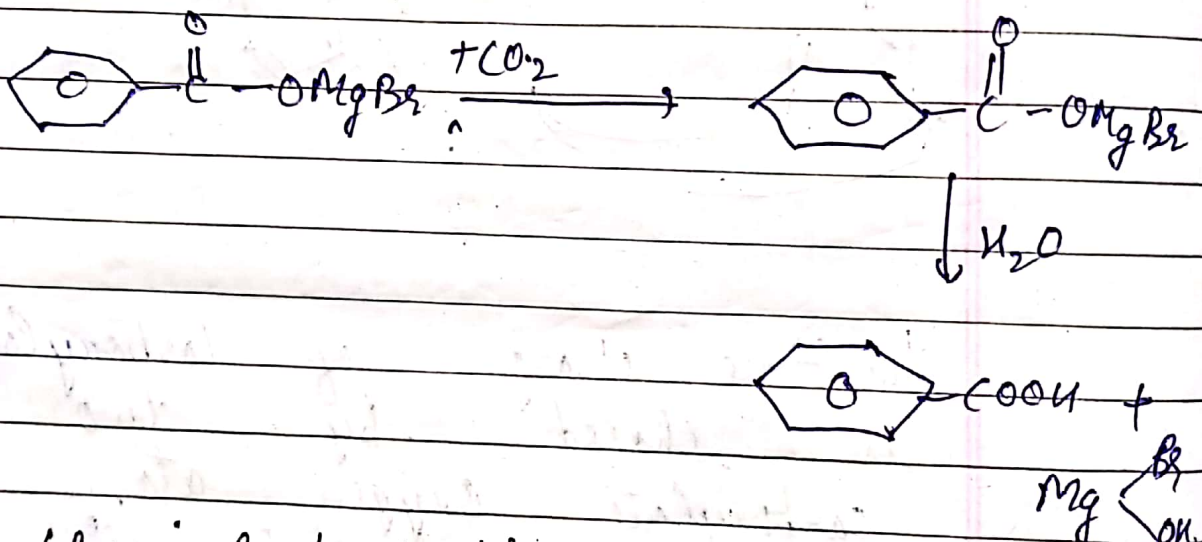
The (-)ve charge of carboxylate ion is shared by two carboxylate oxygen atoms but can not effectively delocalized by the aromatic ring. This is because the oxygen atom of carboxylate ion are not attached directly to the aromatic ring.

# Preparat<sup>n</sup> of Benzoic Acid (→)

1. By oxidat<sup>n</sup> of Alkyl Benzenes with acidic  $KMnO_4$ .



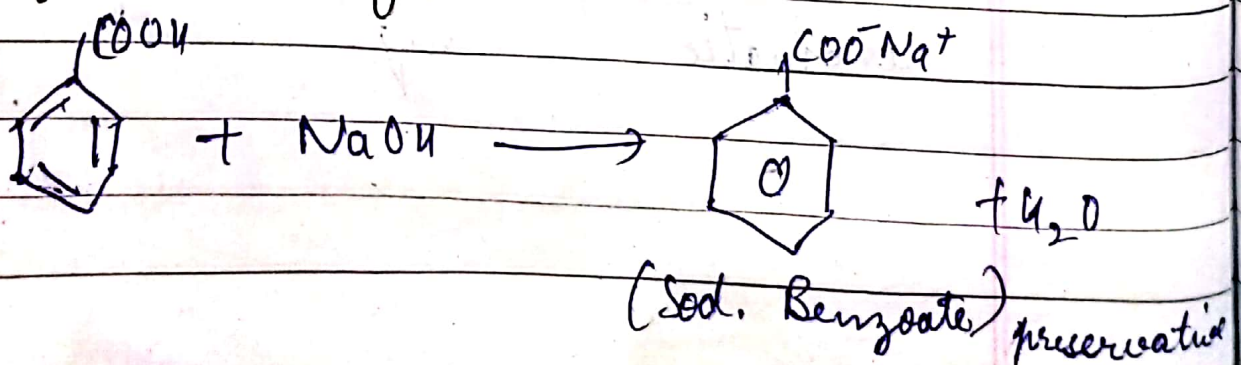
- (2) By the react<sup>n</sup> of phenyl Magnesium Bromide with  $CO_2$  & followed by hydrolysis.



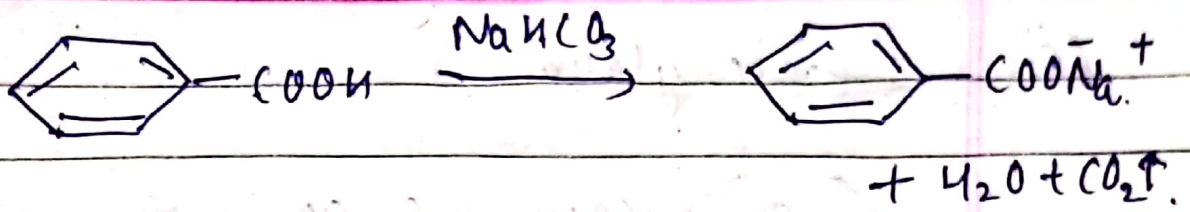
## Chemical properties (→)

- (A) Reactions of  $-COOH$  group (→)

- (i) formation of salt (→)

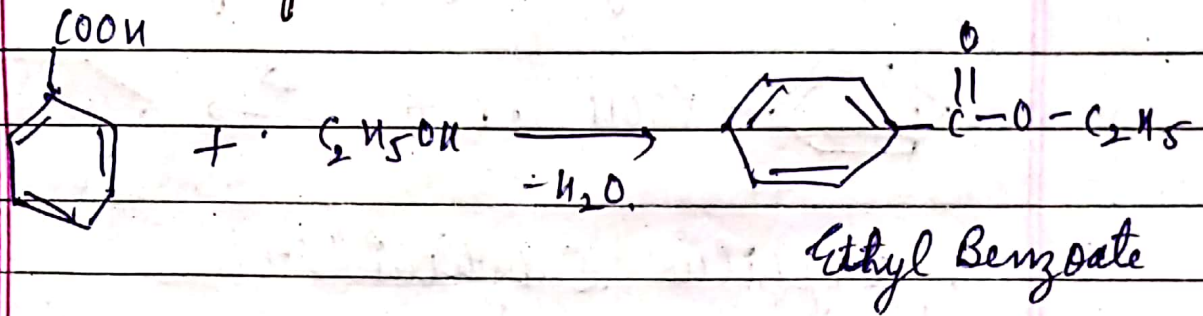




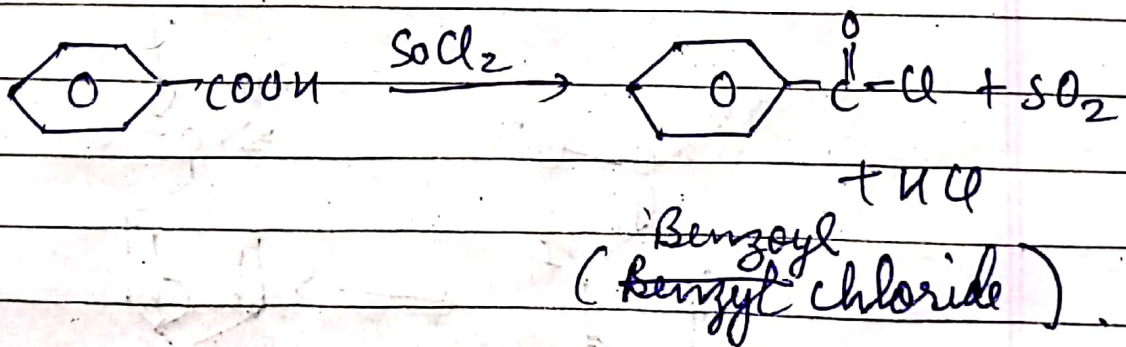
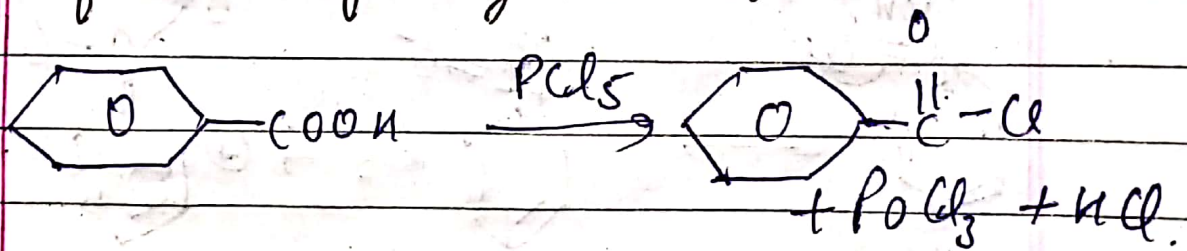


Sod. Benzoate use:  $\rightarrow$   
 It is used for preserving pickles, tomato ketchup, & fruit juices.

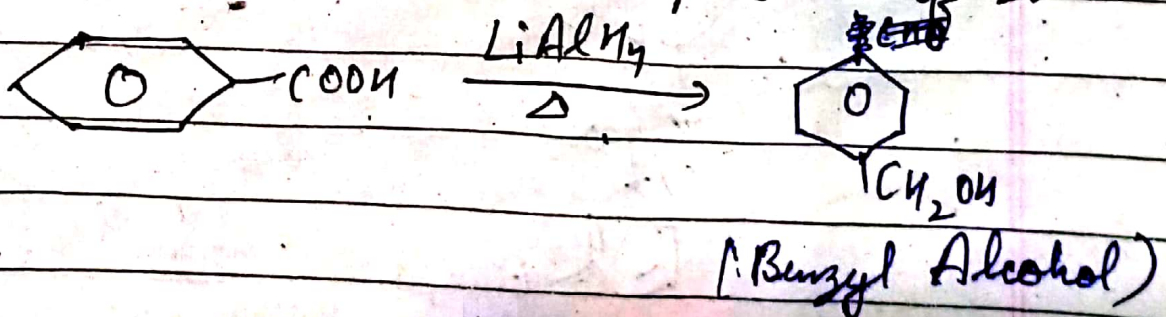
(2) Ester formation:



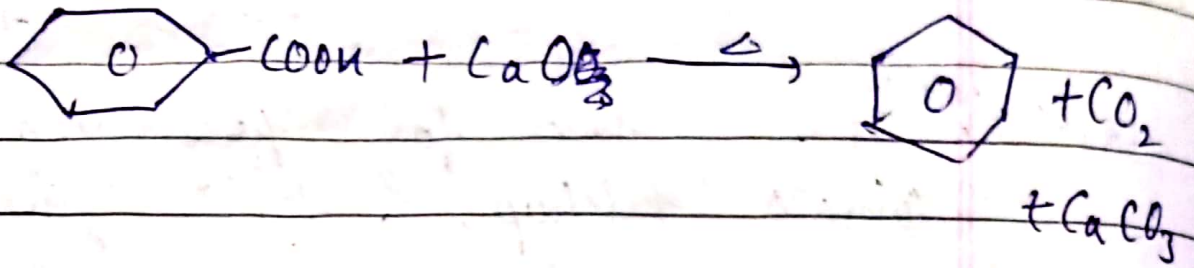
(3) format<sup>n</sup> of acyl halides:



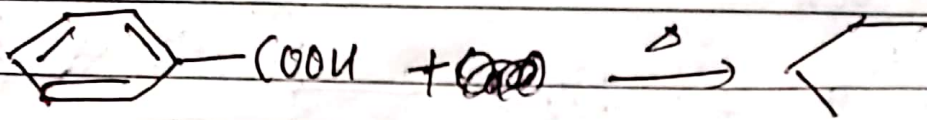
(4) Reduct<sup>n</sup> in the presence of  $\text{LiAlH}_4$



(5) Decarboxylation :->

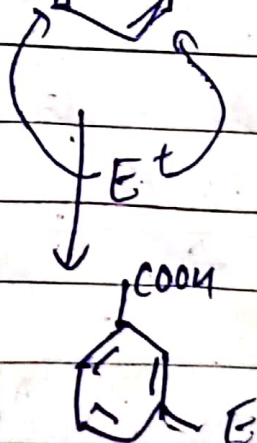
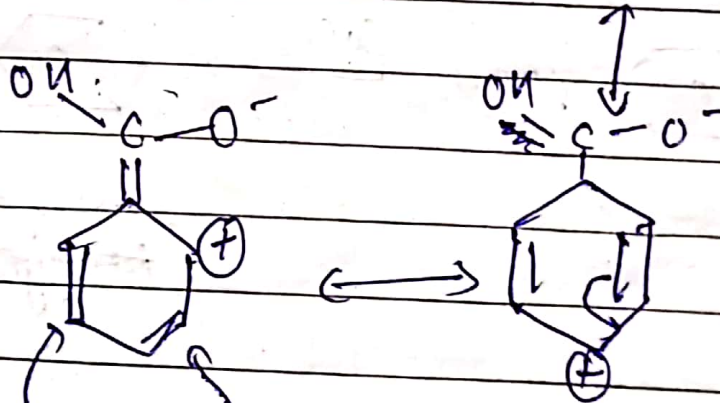
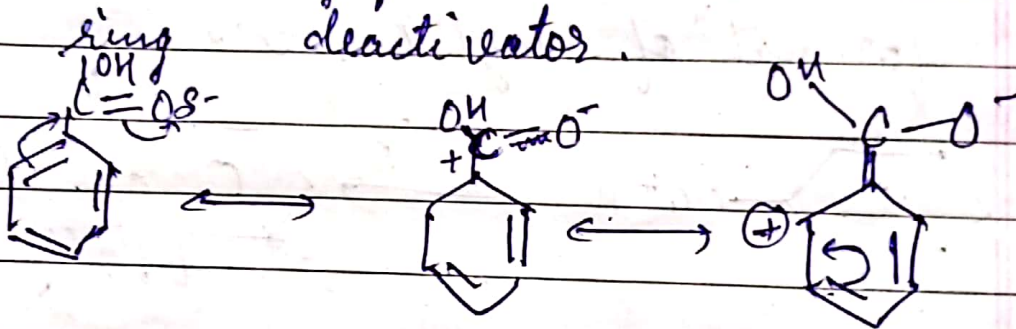


(6) Reactions of Benzene Ring :->



Electrophilic Substitution :->

Acidic grp is meta directing & deactivator.



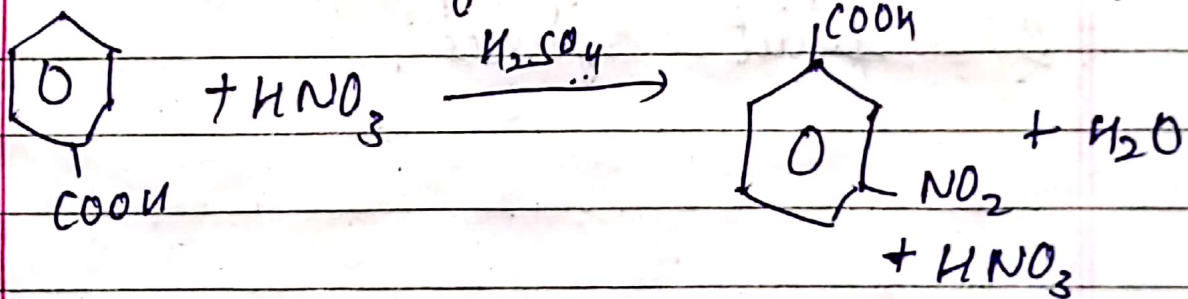
O & p positions carry (+)ve charge  
 So  $E^+$  can not attack on these positions.

It will attack on meta which is relatively  $e^-$  rich.

So, the Carboxyl grp directs the  $E^+$  towards the m-position.

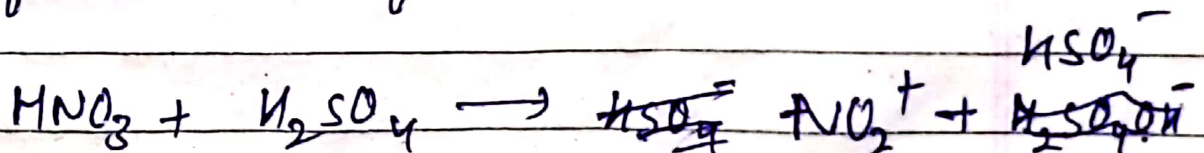
The Carboxyl grp is ring deactivator  
 It means that the Benzoic acid undergoes  $E^+$  substitution slowly.

e.g.  $\rightarrow$  Nitration of Benzoic acid with a mixture of conc.  $HNO_3$  &  $H_2SO_4$ .

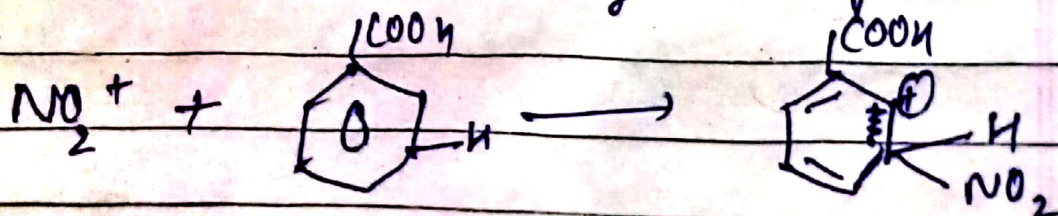


Mechanism  $\rightarrow$

① formation of  $E^+$   $\rightarrow$

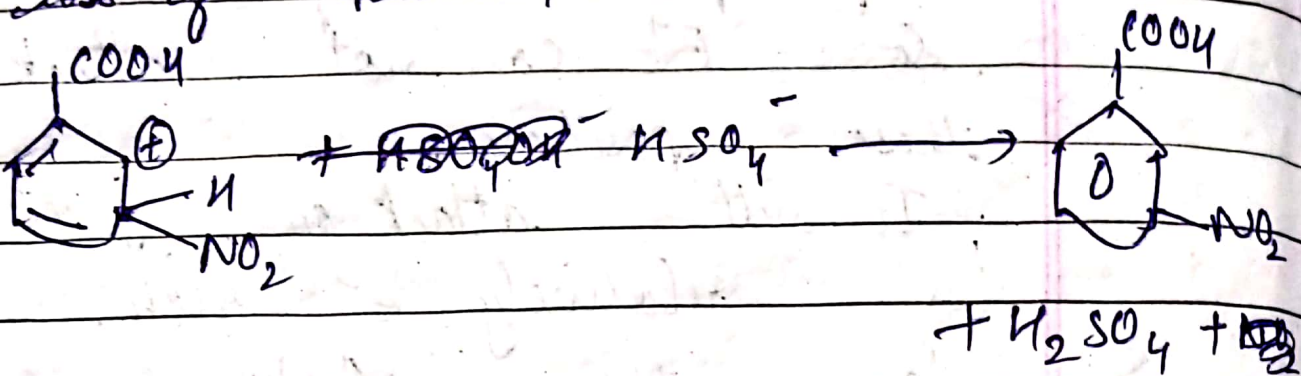


②  $E^+$  attack on benzoic ring  $\rightarrow$



(8)

loss of proton  $\rightarrow$



(m-nitrobenzoic acid)

Uses of Benzoic Acid  $\rightarrow$

- $\rightarrow$  It is used as germicides in medicines for urinary infection & in vapour form for disinfectant brochi tube
- $\rightarrow$  As food preservative sodium Benzoate is used for preserving pickles, tomato ketchup & fruit juices.