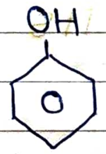
Unit-II
chapter-1

Phenols

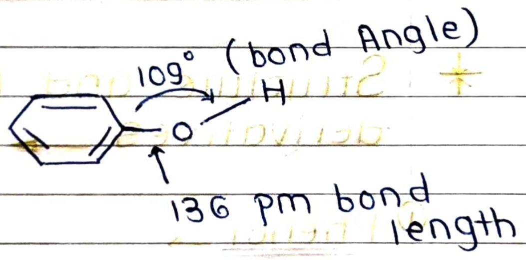
Phenols →
phenols are molecules that have a hydroxyl group (-OH) attached to a carbon atom of an aromatic ring

In phenol, hydroxyl functional group is directly attached to the Sp^2 hybridised carbon atom of benzene ring.

phenol is also known as phenic acid or a phenylic acid.
Its IUPAC name is benzenol with the formula C_6H_6O and it occures as transparant crystalline solid.



phenol (Phenic acid)
IUPAC name - Benenol



* Qualitative test for phenol →

Test	Observation	Inference
① Solubility test → O.C + ether/water	Soluble in ether and water	phenol group is present
② Feric Cl. Test → O.C + aq $FeCl_3$· Sol^n	blue/violet/purple color develp	phenol group is present.

③ libermann Test → O.C + $NaNO_2$, heat and Cool. Add conc. H_2SO_4, shake.	Deep green colour.	phenol group is present.
④ Pthalein test → O.C + pthaleic anhydride + conc. H_2SO_4, heat & Cool. Add dil NaOH and pour in water.	① pink colour	phenol, O-cresol
	② blue colour	Catechol, M-~
	③ flurocent greenc	Resorcinol
	④ No colour.	P-cresol.

* Structure and uses of phenols & its derivatives →

① Phenol →

Structure →

Uses →

① It is used to prepare reagents in plastic manufacturing industries.

② It is used to prepare phenolic resins.

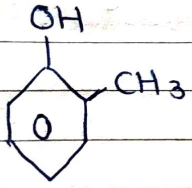
③ It is a precursor to many drugs.

④ It is used in cosmetic industory to prepare

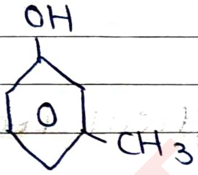
Sunscream, skin lightning cream, and hair colouring solution.

② Cresol → Hydroxytoluene / methyl phenol.

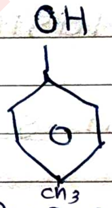
Structure →



O-Cresol



M-cresol



P-cresol

Uses →

① mixed cresols are used as disfectant and preservatives.

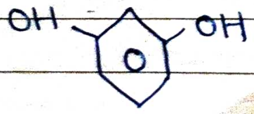
② O-cresol is used as solvent, disinfectant and chemical intermediate.

③ m-cresol is used to produce certain harbis-cides and antioxidant.

④ P-cresol is used to prepare antioxidant and in fragrance and dye industries

③ Resorcinol → benzen di-ol.

Structure →



Uses →

① It is used as antiseptic and disinfectant.

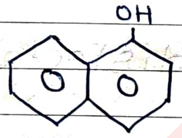
② It is a skin protectant & topical analgesic.

③ It is used in the production of dyes and plasticizer.

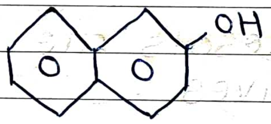
④ It is an analytical reagent.

④ Napthols →

Structure →



1-Naphthol



2-Naphthol.

Uses →

① 1-Naphthol is a precursor to variety of insectiscide and pharmaceuticals.

② It is used as molish reagent.

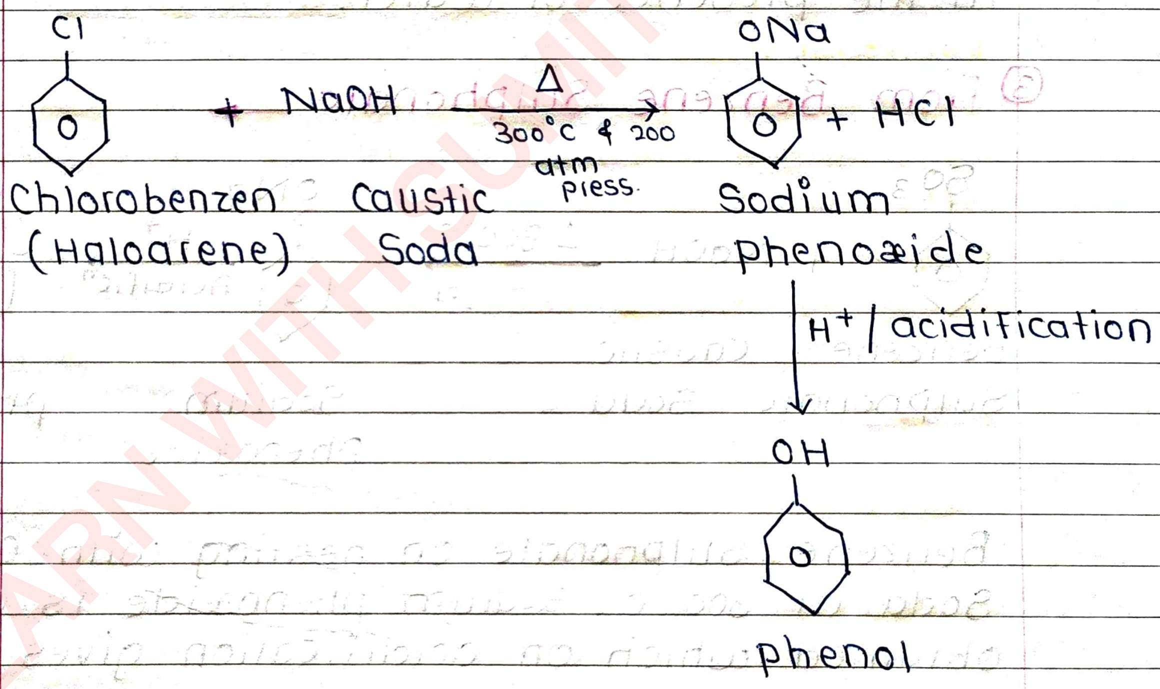
③ In Sakaguchi test, 1-Naphthol with Sodium hypobromite to detect presence of arginine in proteins.

* Methods of preparation of phenols →

The methods of preparation of phenol are as follows →

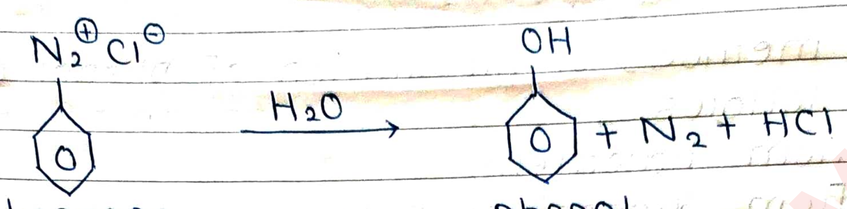
① From haloarens
② From diazonium salt
③ From benzene sulphonate
④ By decarboxylation of Salicylic acid

① From haloarens →



Chlorobenzen on heating with caustic soda at 300°c under 200 atm pressure gives Sodium phenoxide which on acidification gives phenol.

② From Diazonium Salt →

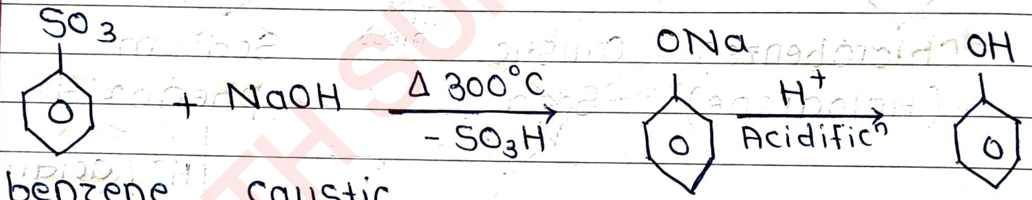


benzene diazonium Chloride

phenol.

A diazonium Salt gives phenol when warm in the presence of water.

③ From Benzene Sulphonate →



benzene Sulphonate

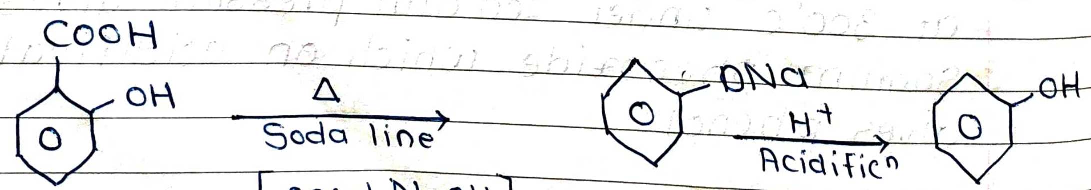
caustic Soda

Sodium phenoxide

phenol

Benzene sulphonate on heating with caustic Soda at 300 °c, sodium phenoxide is a obtained which on acidification gives phenol.

④ By decarboxylation of Salicylic acid →



Salicylic acid

[COO + NaOH]

Sodium phenoxide

phenol

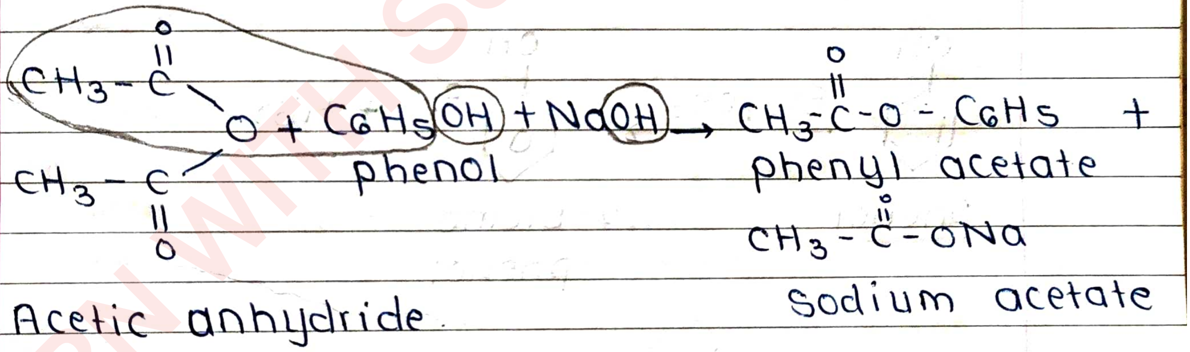
Salicylic acid on heating with Soda lime (it is mixture of Coo & NaOH) undergoes decarboxylation to give Sodium phenoxide which on acidification gives phenol.

* Reactions of Phenols →

Phenol undergoes following reactions –

a) formation of ester
b) Hydrogenation
c) Oxidation
d) Halogenation.

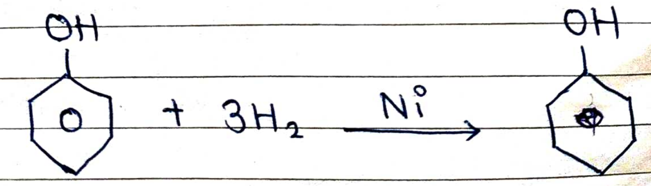
ⓐ Formation of ester →



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 + C_6H_5OH + NaOH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-C_6H_5 + CH_3-\overset{\overset{O}{\|}}{C}-ONa$$

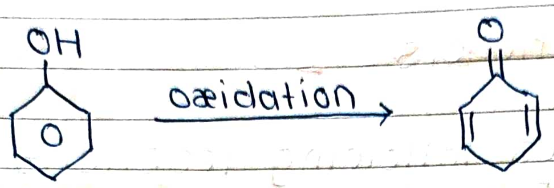
Acetic anhydride reacts with phenol in the presence of caustic soda to give phenyl acetate and sodium acetate.

ⓑ Hydrogenation reaction →



Hydrogenation of phenol in the presence of nickel form cyclohexanol.

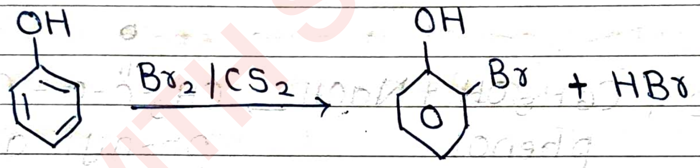
ⓒ Oxidation →



phenol → benzo-1,4 quinone

phenol gets easily oxidised to benzo-1,4 quinone.

ⓓ Halogenation →

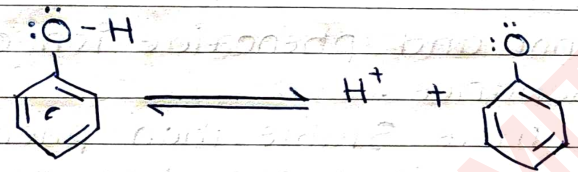


phenol → 2-bromo-phenol

phenol on treatment with bromide in presence of Solvent like carbon disulphite at low temp^{e}. given 2-bromo phenol.

* Acidity of phenols →

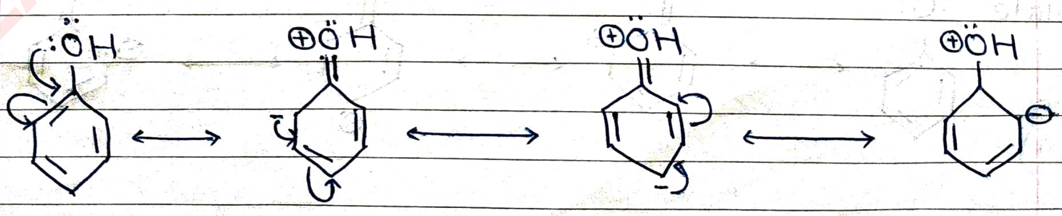
Phenols are stronger acids as compaired to alcohols because pKa value for phenol is 10. because of acidic nature, phenols can turn blue litmus into red and react with aq alkali to form phenate. As compaired to carboxylic acids, phenols are weak acid.



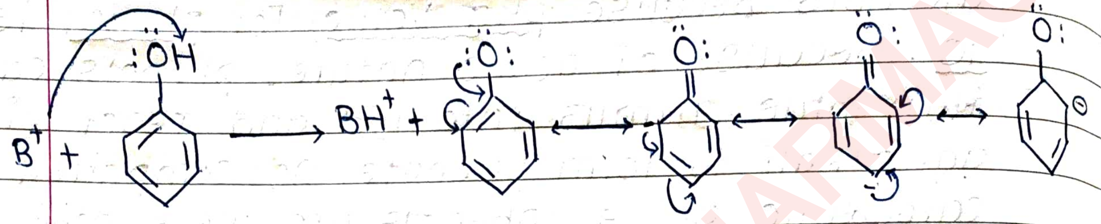
Phenol
PKa = 10

Hydroxyl group bonded to benzene ring is much more acidic that hydroxyl group in alcohol. Due to the resonance in phenol, O-atom acquires negative charge -ve which weakens -OH bond and facility release of proton.

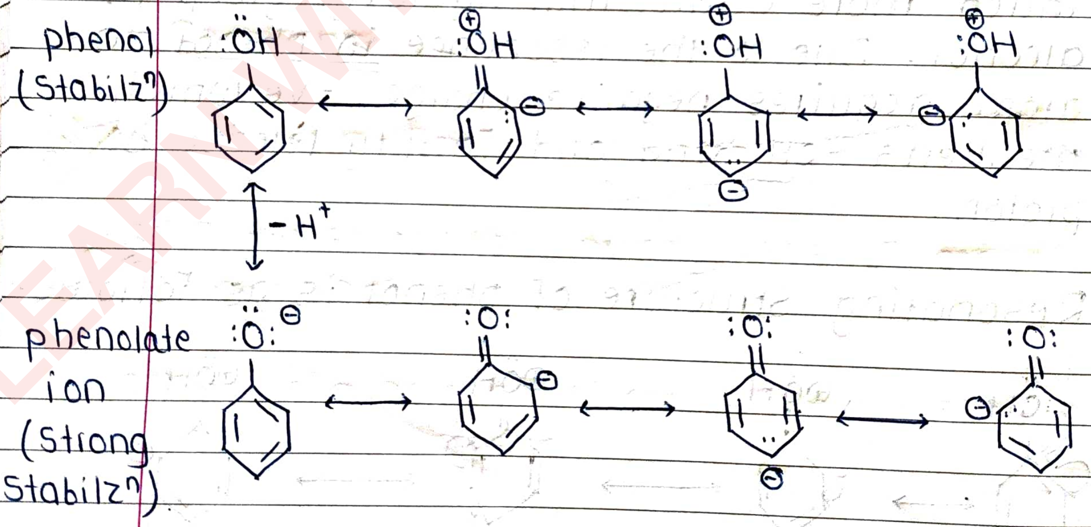
Resonating structure of phenol is as follows–



Depiotonation of phenol forms phenoxide ion (Phenate ion) which also exist as a resonance.



Hence, both phenol and phenoxide ion are Stabilised by resonance.
phenoxide ion is more Stable than phenol as -ve charge gets delocalised over benzene ring but resonating structure of phenol involves separation of +ve & -ve charges. There fore phenol has greater tendancy to form phenate ion by releasing proton.

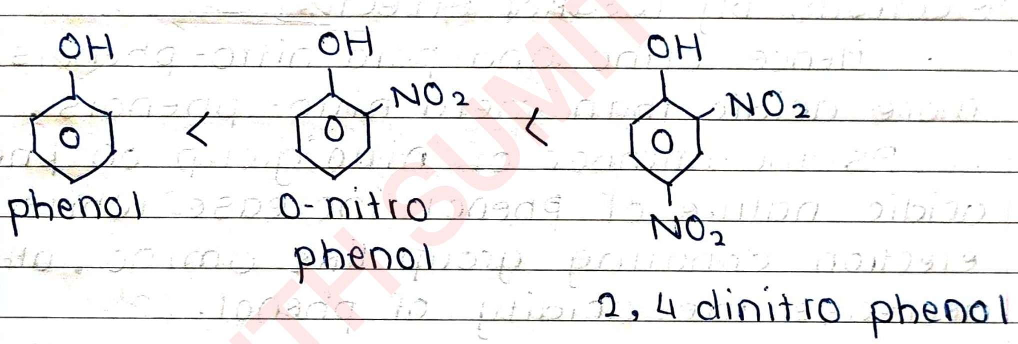


* Effect of substituent on acidity of phenol

When a phenol has electron withdrawing substituent group, acidity of phenol is increased.

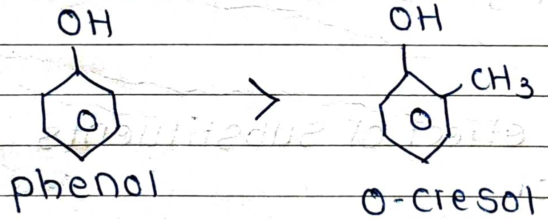
Increase in electron withdrawing group ability to delocates negative charge, more than the phenoxide ion.

Hence 2,4 dinitrophenol is more acidic than o-nitro phenol which is more acidic than phenol.



Election donating decreases acidity of phenol e.g..

phenol is more acidic as compared to o-cresol.



presence of electron withdrawing group on benzene ring in phenol increase acidity of phenol while electron releasing group / donating will decrease the acidity of phenol.

If there is a nitro group substituted on phenol, it will increase acidic nature of phenol.
Hence nitro phenol will be more acidic than phenol.

position of nitro group an phenol will affect acidity of phenol.
A nitro group at 'O' and 'P' position withdraws electrons by stronger effect while nitro group at 'm' position withdraws electrons by weaker effect.
Hence ortho and para nitro-phenols are more acidic than meta nitro-phenols.
As the number of nitro group on phenol acidic nature of phenol increase while electron donating group like amino, alkyl decrease the acidity of phenol.

* Questions →

2 mark Q1) Write a Short notes on acidity of phenol.

2 mark Q2) Draw Structure & given uses of cresol and recorcinol.

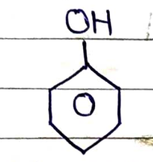
Q3) Write a note on effect of substituents on acidity of phenol.

Q4) Write qualitative test for phenol.

Q5) Give method of preparation of phenol.
Q6) Explain reaction of phenol.

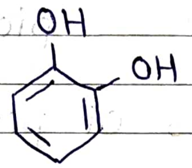
* Nomenclature Of Phenols →

- In IUPAC -OH group is represented as hydroxyl. It is used as prefix, while benzene part of the molecule is used as suffix.



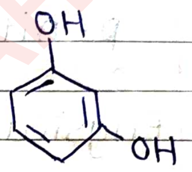
phenol

Imp



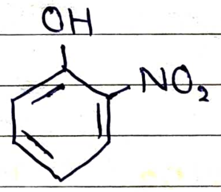
1,2 dihydroxy benzene
o- hydroxyl phenol
(Catechol)

Imp

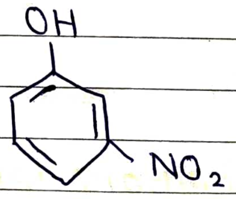


1,3 dihydroxy benzene
m- hydroxyl phenol
(Resorcinol)

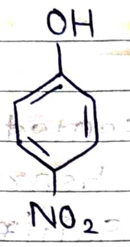
1,4 dihydroxy benzene
(Hydroquinone)



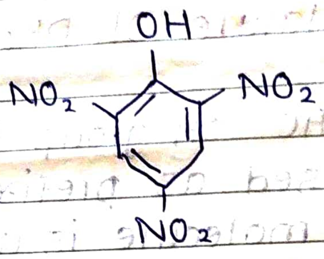
2- nitrophenol
o- nitrophenol



3- nitrophenol
m- nitrophenol



4-nitrophenol
p-nitrophenol



2,4,6-trinitrophenol
picric acid

* Physical properties of phenol →

- Colourless, crystalline, poisonous solid with phenolic odor.
- Melting point 41°c and boiling point 182°c.
- Sparingly soluble in water forming pink Sol^n of room temperature.
- Completely soluble above 68.5°C
- Used as disinfectants and in washrooms.
- Causes blisters on skin.

* Difference bet^n Alcohols and ~~be~~phenols

Alcohol	Phenol.
① OH group is attached to an alkyl group.	OH group is attached to an aryl group.
② Hydroxyl derivatives of alkene.	Hydroxyl derivatives of benzene
③ lower alcohols are colourless liquids	Colourless crystalline deliquescent Solid.
④ They characteristics Sweet smell and burning taste	They have a characteristic phenolic odor.
⑤ General Formula is R-OH.	General formula is C_6H_5OH.

V.IMP Phenols are less acidic than carboxylic acid.

IUPAC nomenclature of phenol is → 1-Hydroxybenzene

Phenol heated with zn dust product → Benzene

Aniline converted into phenol by → Diazotization

Unit - 2
Chapter - 2

* Aromatic Amines *

IMP 2 mark

Definition →

Amines it means no. of alkyl or aryl substituents bonded to the nitrogen atom.

~~eg~~..:

There are of two types :-

① Aliphatic Amines
② Aromatic Amines

Aromatic amines are weaker than aliphatic amines.

① Aliphatic Amines →

It means no. of alkyl substituents bonded to the nitrogen to the nitrogen atom

e.g...

Methyl amine :- CH_3-NH_2
Dimethyl amine - $CH_3-NH-CH_3$

② Aromatics Amines →

It means no. of aryl substituents bonded to the nitrogen atom.

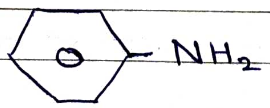
It is subclassified into four types →

① Primary Aromatic Amines →

In this type, only one hydrogen atom in ammonia has been replaced.

e.g....

$Ar-NH_2$

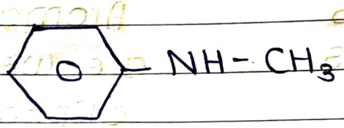


Aniline

(ii) Secondary Aromatic Amines →

In this type, two of hydrogen atoms in ammonia has been replaced by aryl, alkyl or both.

e.g...

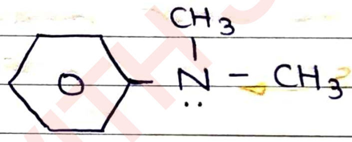


N - methyl aniline

(iii) Tertiory Aromatic Amines →

In this type, all of the hydrogen atoms in ammonia has been replaced by aryl, alkyl or both.

e.g...

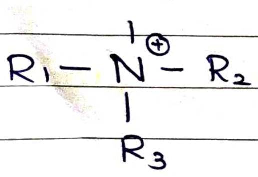


N, N dimethyl aniline

(iv) Quaternary Amines →

They are also known as Quates and are positively charged polyatomic ion of Structure

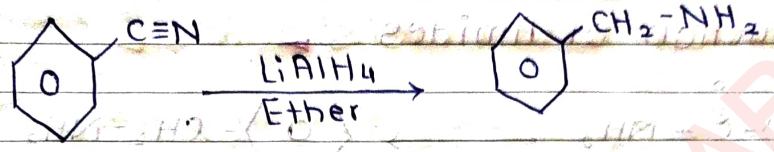
e.g...



V.IMP
5mark

* Methods of preparation of aromatic amines →

① Reduction of nitrile →

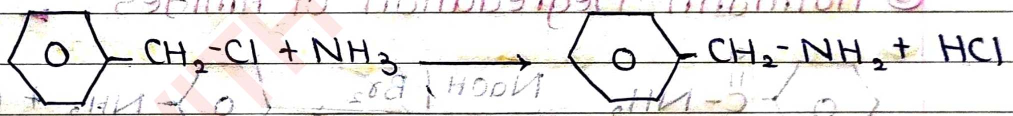


Aromatic nitrile

Primary aromatic amine | Benzyl amine

Nitriles can be reduced by lithium aluminium hydride to the primary aromatic amines in the presence of ether solvent.

② Reaction with Ammonia →

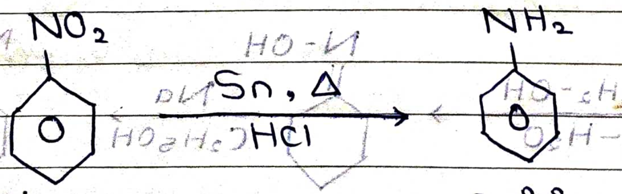


Benzyl chloride

1° aromatic amine | Benzyl amine

Benzyl chloride reacts with ammonia to give benzyl amine. (Primary Amine)

③ Reduction of nitro compound →

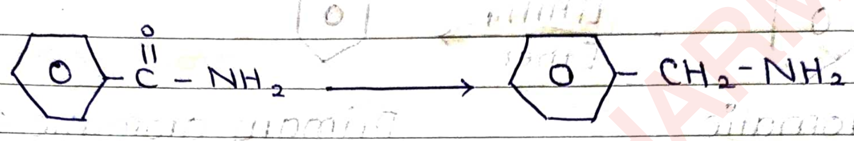


nitro benzene

Aniline

Nitro benzene on heating within in the presence of HCl undergoes reduction to give Aniline (Primary amine)

④ Reduction of Amides →

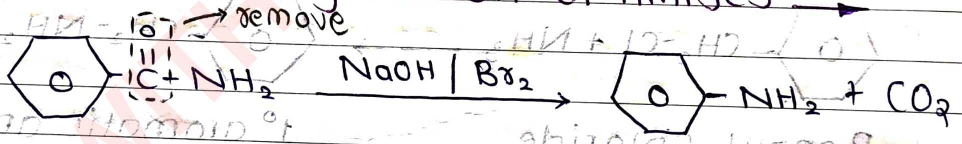


Aryl carboxamide/ Benzamide

benzyl amine

Benzamide undergoes reduction to give primary amine i.e benzyl amine

⑤ Hofmann Degredation of Amides →

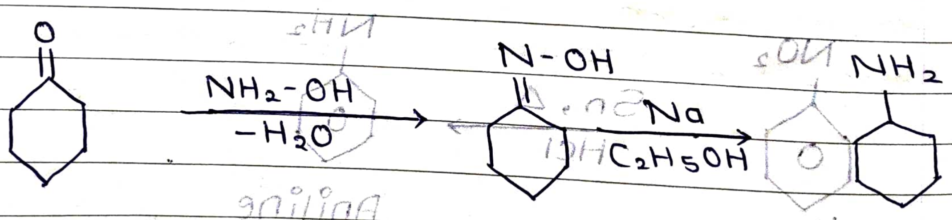


Benzamide

Aniline

Benzamide on heating with bromine in the presence of NaOH, it will change into aniline
i.e. primary amine

⑥



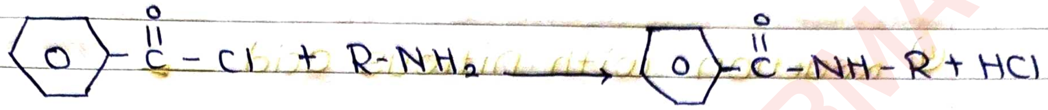
Cyclohexanone

cyclo-hexanoamine

cyclo hexyl-amine

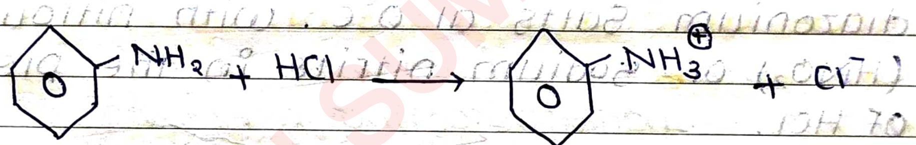
* Reactions of Aromatic Amines

① Formation of Amides →



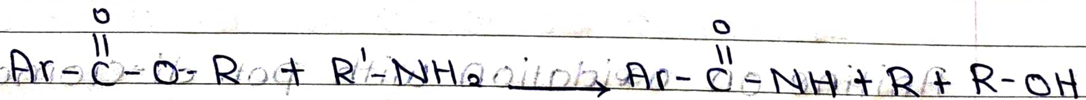
Addition of 1° or 2° amine into acyl chloride results into respective amides.

② Formation of Quaternary Salt →



Reaction of aromatic amines (Aniline) with the acid will give quaternary salt or ammonium salt.

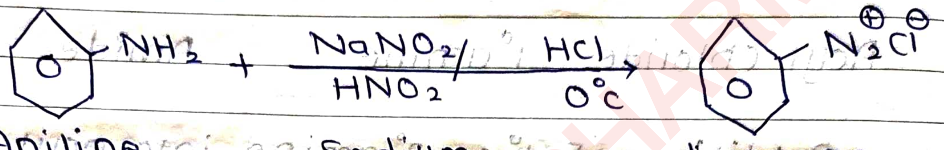
③ Formation of Amides from ester →



$$Ar-\overset{O}{\overset{\|}{C}}-O-R + R'-NH_2 \longrightarrow Ar-\overset{O}{\overset{\|}{C}}-NH-R + R-OH$$

Aromatic esters reacts with primary amine to give Secondary Aromatic amide and alcohol.

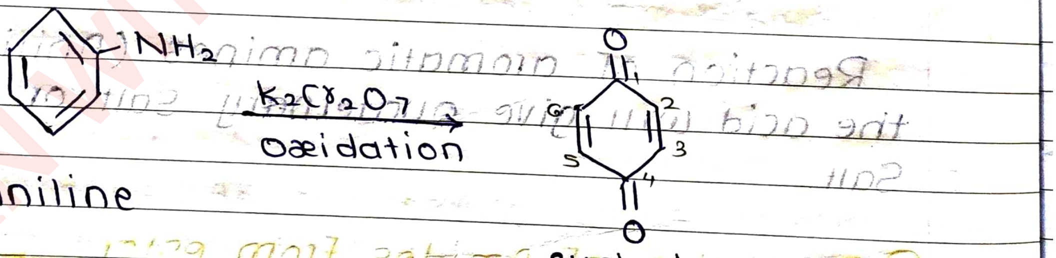
④ Reaction with nitrous acid →



Aniline Sodium nitrite benzene diazonium Salt.

primary aromatic amines form stable diazonium salts at 0°c. with nitrous acid (HNO$_2$) or sodium nitrite in the presence of HCl.

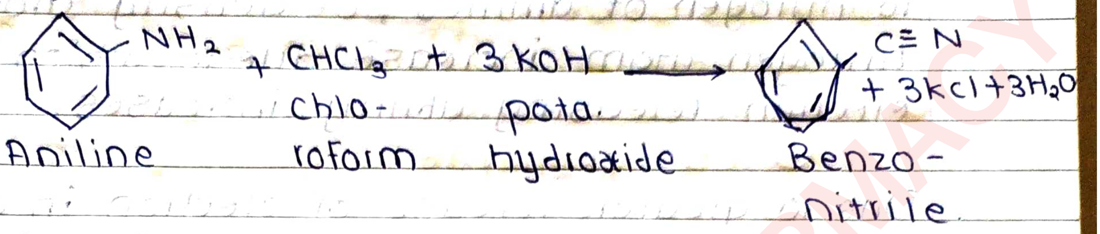
⑤ Oxidation reaction →



Aniline cyclo-hexa-2,5 diene 1,4- dione

Aniline on oxidation with pot. di-cromate (K$_2$Cr$_2$O$_7$) gives cyclohexa-2,5 diene-1,4 dione.

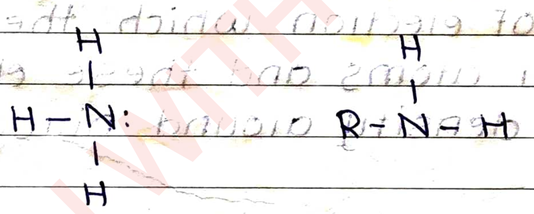
⑥ Formation of Nitrile → ($C\equiv N$)



Aniline reacts with chloroform in the presence of alkaline ~~chloro~~ media i,e. KOH to give benzonitrile with the elemination of KCl and H_2O molecule.

* Basicity of Aromatic Amine →

Amines are basic in nature because they posses a pair of unsheared electrons electrons which they shear with other atoms.



unsheared / lone pair of electron create electron density around nitrogen atom.

Greater the e- density around nitrogen atom, the more basic is the molecule.

Groups that donate electrons will increase the basisity of amines while group that decrease electron density around nitrogen atom will ↓se the basisity of amines.

Due to this property of alkyl groups attached to nitrogen of amines, e- density around nitrogen atom increase due to which its electron releasing ability increases.

Due to greater release of electron in alkyl amine, molecules become more basic than ammonia because in ammonia no electron releasing group is attached while in alkyl amine electron releasing group is available.

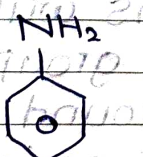
3° > 2° > 1° > ammonia.

* Effects of Substituents on basicity of Amine

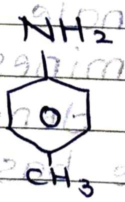
Amines are basic in nature as they have loan pair of electron which they shair with other atoms and these electron create electron density around nitrogen atom.

Greater the electron density, more basic is the molecule while lesser the electron density, less basic is the molecules.

Electron donating groups added e⊖ density to benzen ring making aromatic amines more basic than aniline.



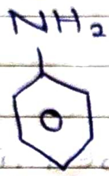
Aniline



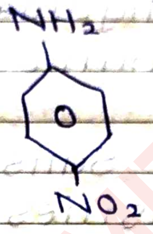
4- methyl aniline

4-methyl aniline is more basic than aniline because it contains $e^{\ominus}$ donating group like methyl.

Electron withdrawing group removes $e^{\ominus}$-density from benzene ring & hence 4 nitro aniline is less basic than aniline.

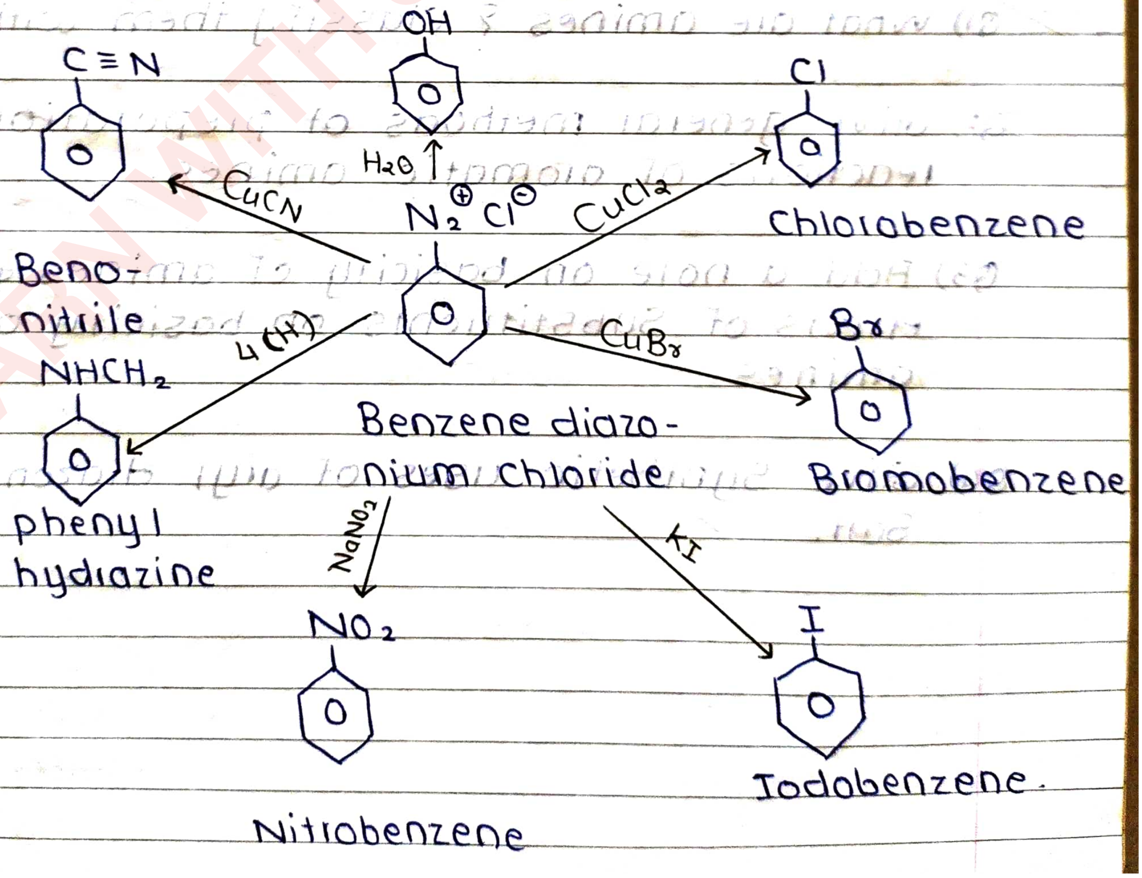


Aniline



4-nitro aniline

* Synthetic Uses of aryl diazonium Salt →



① Benzene diazonium Salt is used in a synthesis of organic compounds like :-

- ⓘ Phenol
- ⓘⓘ chlorobenzene
- ⓘⓘⓘ Bromobenzene
- ⓘⓥ Iodobenzene
- ⓥ Nitrobenzene
- ⓥⓘ Phenyl hydrazine
- ⓥⓘⓘ Benzo nitrile.

② Aryl diazonium Salts are used in dye, pigment industries.

Questions :-

2 mark Q1) What are amines ? classify them with.

5 mark Q2) Give general methods of preparations & reactions of aromatic amines.

Q3) Add a note on basicity of amines & effects of substituents on basicity of amines.

Q4) Give synthetic uses of aryl diazonium salt.

Unit-2

Chapter-3

✱ Aromatic Acids ✱

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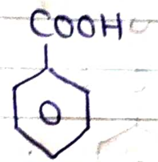
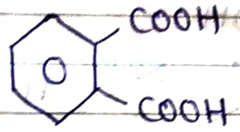
Aromatic acids are the compounds, in which one or more carboxylic acid groups are attached directly to the aromatic ring.

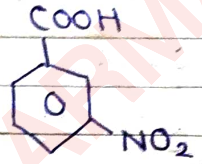
e.g...



benzoic acid



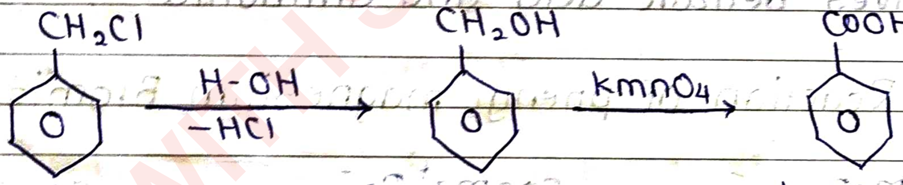
pthalic acid



3-nitro benzoic acid

✱ Methods of preparation of aromatic Acids →

① Oxidation of Benzyl chloride →

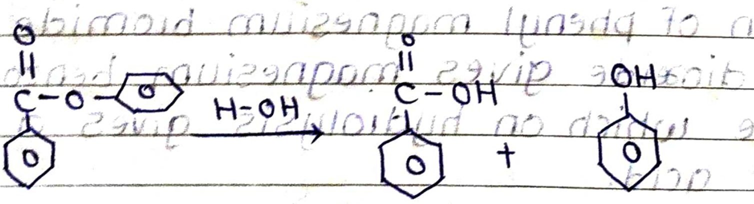


Benzyl

benzoic acid

benzyl chloride undergoes hydrolysis to give benzyl alcohol which upon oxidation with $KMnO_4$ gives benzoic acids.

② Hydrolysis of phenyl Benzoate →



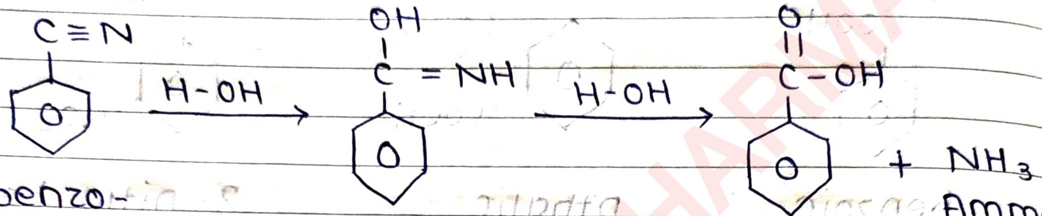
phenyl benzoate

Benzoic acid

phenol

phenyl benzoate undergoes hydrolysis to yield a mixture of benzoic acid and phenol.

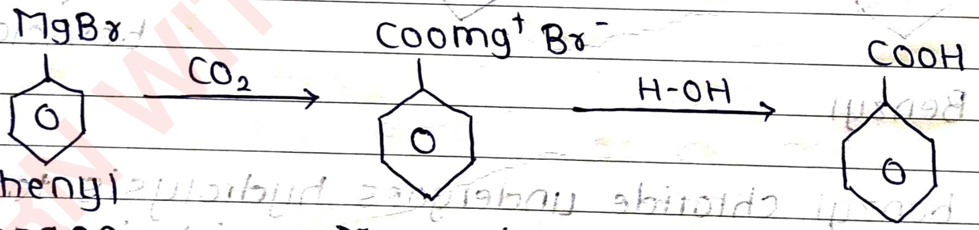
③ Hydrolysis of benzonitrile →



benzonitrile — Intermediate — Benzoic acid — Ammonia

Benzonitrile undergoes hydrolysis to give an intermediate which on furthers hydrolysis gives benzoic acid and ammonia.

④ Reaction of phenyl magnesium Bromide →

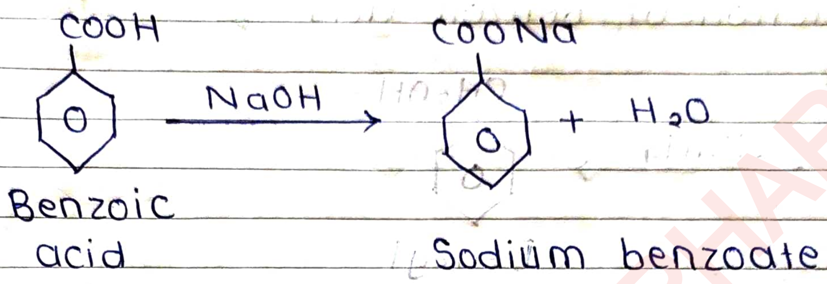


phenyl magne. bromide — Magnesium benzoate bromide — benzoic acid.

Reaction of phenyl magnesium bromide with carbon dioxide gives magnesium benzoate bromide which on hydrolysis gives a benzoic acid.

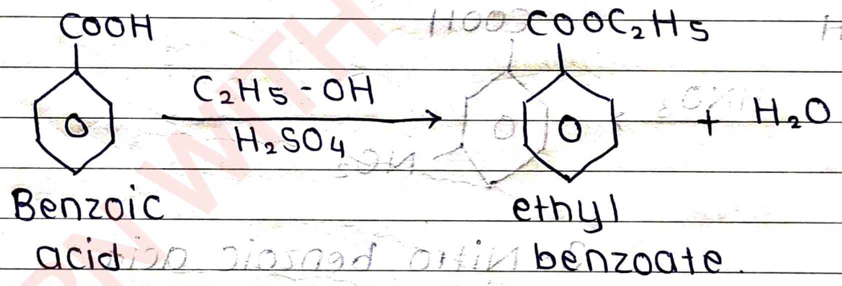
* Reactions of Aromatic Acids →

① Salt formation →



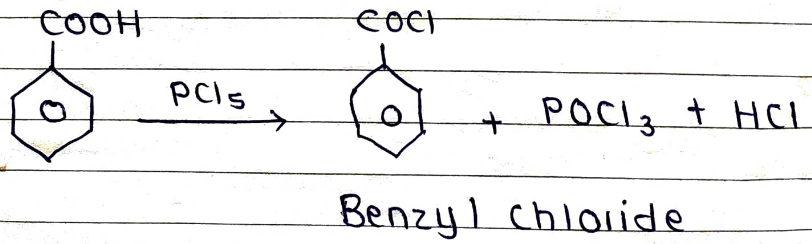
Benzoic acid reacts with sodium hydroxide to give a salt
i,e Sodium benzoate.

② Ester formation →



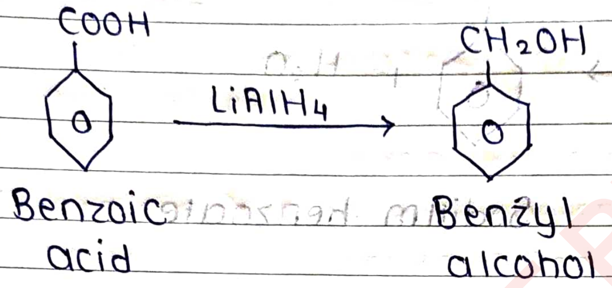
Benzoic acid on treatment with ethyl alcohol in the presence of Conc. H_2SO_4 give ethyl benzoate.

③ Acyl halide formation →



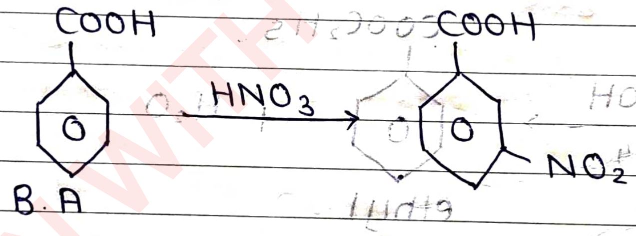
Benzoic acid reacts with phosphorous pentachloride to give benzyol chloride.

④ Reduction of benzoic acid →



Benzoic acid undergoes reduction in presence of $LiAlH_4$ to give benzyl alcohol.

⑤ Electrophilic Substitution Reaction →



3- Nitro benzoic acid.

B.A undergoes electrophilic substitution in presence of nitric acid to give 3 nitro benzoic acid.

* Acidity of Aromatic Acid

① Carboxylic acids are more acidic than phenol and alcohol because hydroxyl group of C.A is readily looses a H^+ ion than phenol and alcohol and its pka (dissociation constant) is greater than phenol and alcohol.

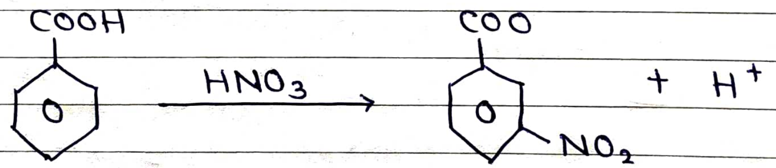
② larger the pka value of carboxylic acid is more as compaired to phenol and alcohol hence it is more acidic than phenol and alcohol.

③ C.A can easily ionized and exist in a dianamic equillibrium between carboxylate ion and hydronium ion.
hence they show acidic nature

$$Ar-COOH + H_2O \rightleftharpoons Ar-COO^- + H_3O^{\oplus}$$

Aromatic acid — Carboxylate ion — hydronium ion.

* Effects of substituents on acidity of aromatic acids →



Benzoic acid

3-nitro benzoate

① Electron withdrawing group increase acidity of benzoic acid because electronegative atom stabilizes anion.

② Electron releasing group on meta and para position decreases acidity of benzoic acid.

③ Ortho substitution by electrophilic or a nucleophilic group increases acidity of benzoic acid due to steric effect.