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PART- 2

PHARMACEUTICAL ORGANIC CHEMISTRY II

PHENOLS

CHEMICAL PROPERTIES OF PHENOLS

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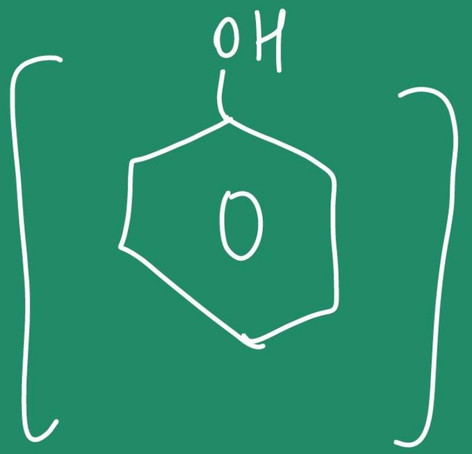
TOPIC: Chemical Properties of Phenol

Phenol



One H-atom is being replaced by a hydroxyl group (-OH).

[Aromatic compound.]

Molecular Formula : C_6H_5OH

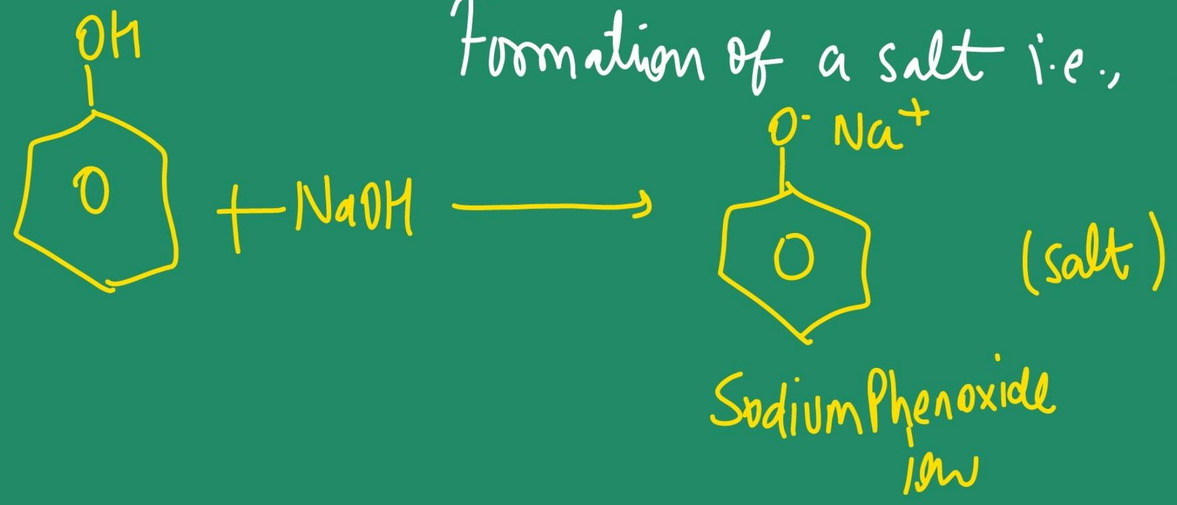
MOP

1. Benzene sulfonic acid
2. Dow's Process
3. Benzene diazonium salt
4. From Cumene.

Chemical Reactions of Phenol :—

Phenol undergoes various chemical reactions.

1. **Salt formation :** Phenol reacts with a base (NaOH) for the formation of a salt i.e., Sodium Phenoxide.

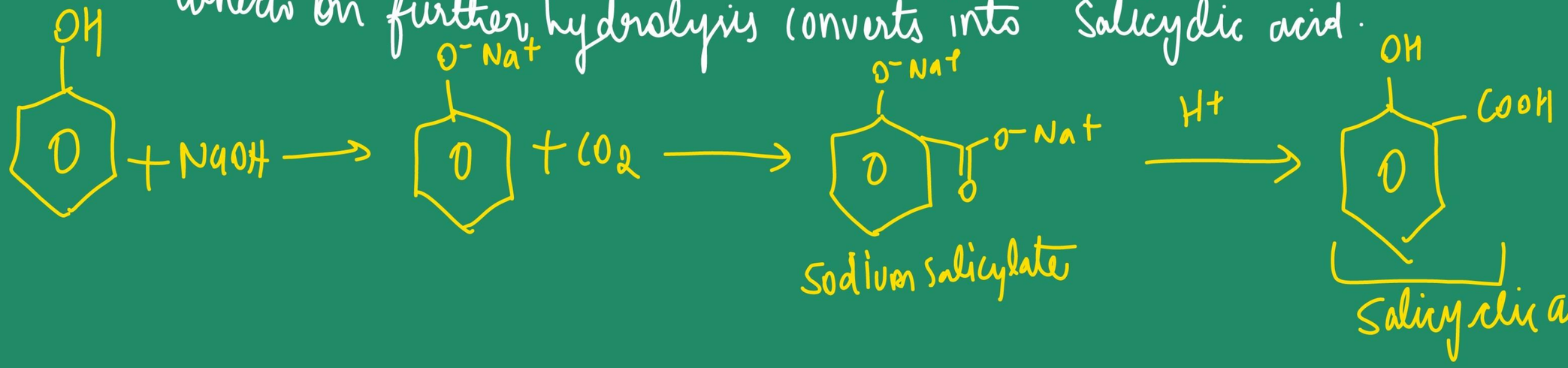


2. ***

Kolbe's Reaction

In this reaction, Phenol reacts with a Base (NaOH) for the formation of a salt.

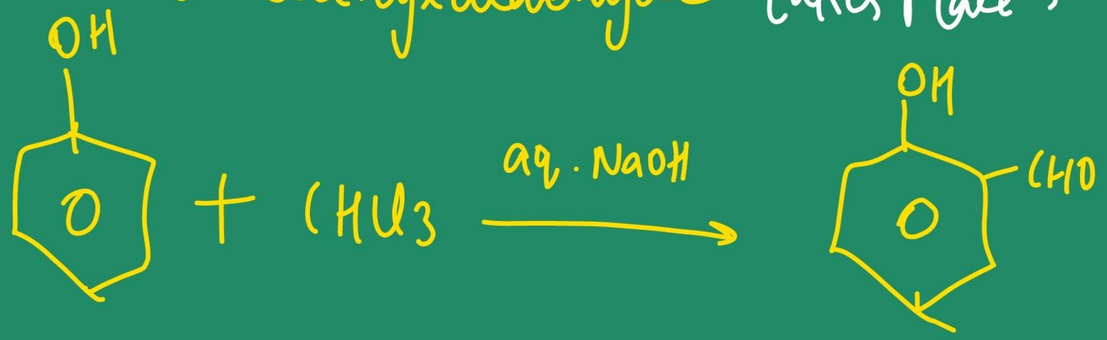
Sodium Phenoxide reacts with CO_2 to form sodium Salicylate which on further hydrolysis converts into Salicylic acid.



3. MM Imp.

Reimer–Tiemann Reaction

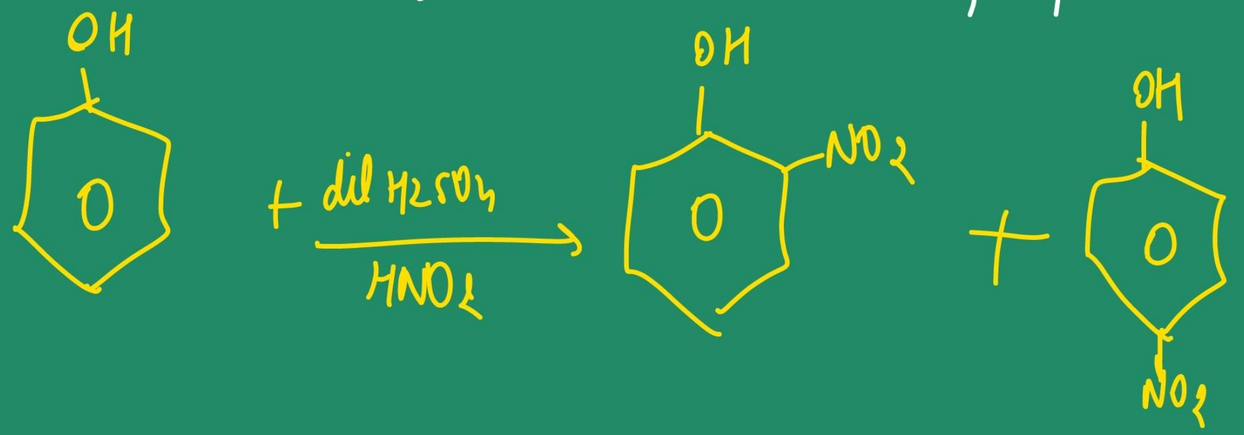
In this reaction, Phenol reacts with Chloroform ($CHCl_3$) in the Presence of a Base, formation of O-Salicylaldehyde takes Place.



4. Nitration

In this reaction, Phenol reacts with dil HNO_2 in the presence of H_2SO_4.

The formation of O-nitrophenol & p-nitro Phenol takes Place.



5. Reduction

Phenol shows reduction reactions as well.

Benzene (Zinc oxide)

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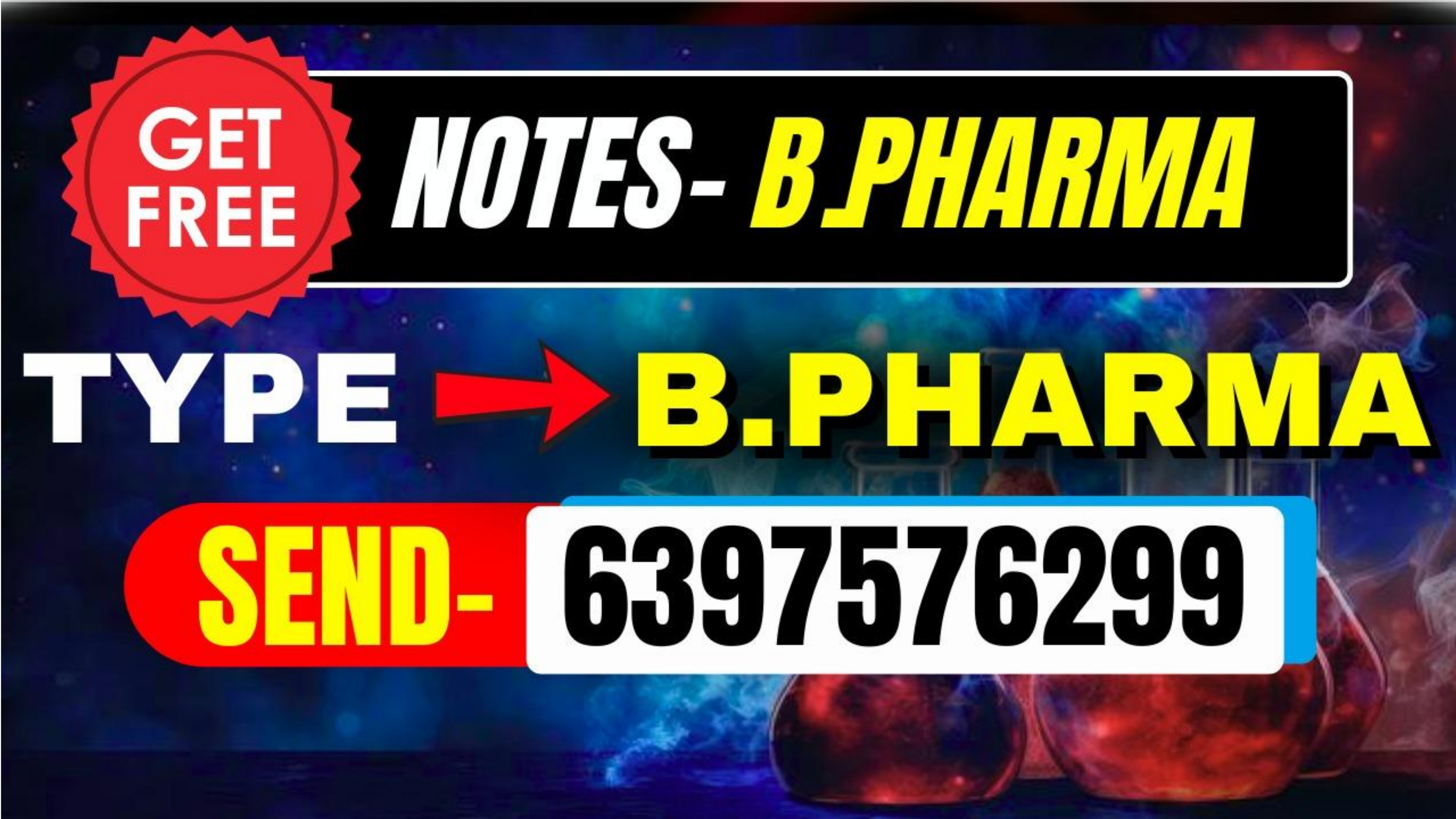
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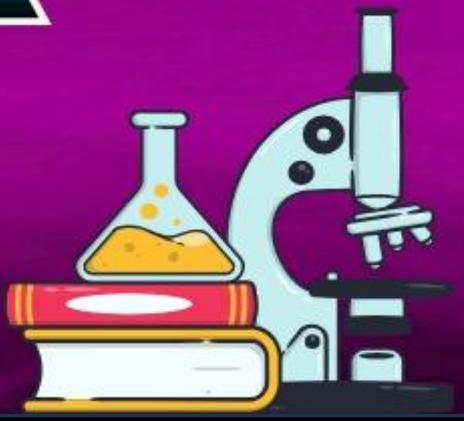
PHENOLS

ACIDITY OF PHENOLS
EFFECT OF SUBSTITUENTS ON ACIDITY STRUCTURE & USES



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TOPIC: Acidity, Effect of substituents

Qualitative Tests

Str & Uses.

✓ Phenol

Aromatic amine

Aromatic acid

Acidity of Phenol

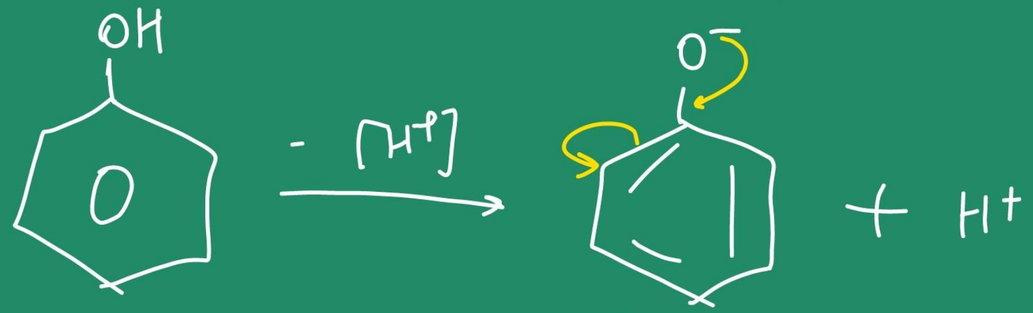
Phenol is an aromatic compound which contains Hydroxy group ($-OH$) attached to a benzene ring.

Phenols are acidic in nature. They donate a Proton & makes a Conjugate Base ($C_6H_5O^-$)

[Stability of conjugate Base $\propto$ Acidic strength]

Phenoxide ion is the conjugate base.

Phenol will be more acidic if Phenoxide ion is stability.



Phenol

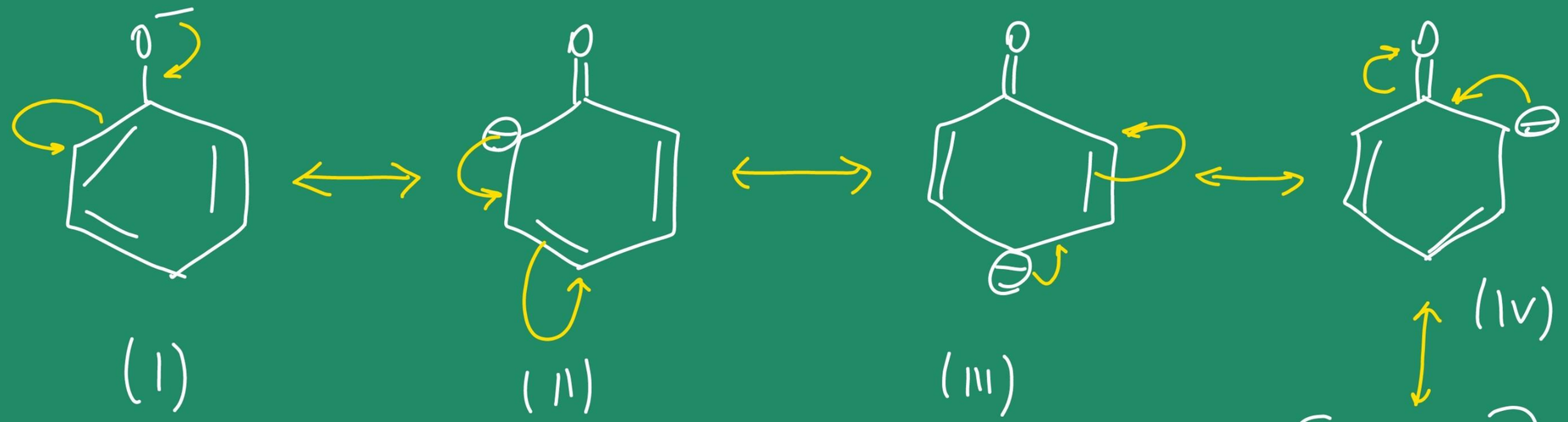
Phenoxide ion

Resonance stabilization

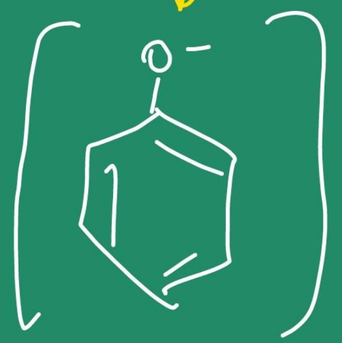
A/C to Arrhenius, Those substances which release H^+ ion on dissociation with any acid and makes a stable conjugate Base.

More the Phenoxide ion will be stable, more acidic Phenol will be.

Resonance



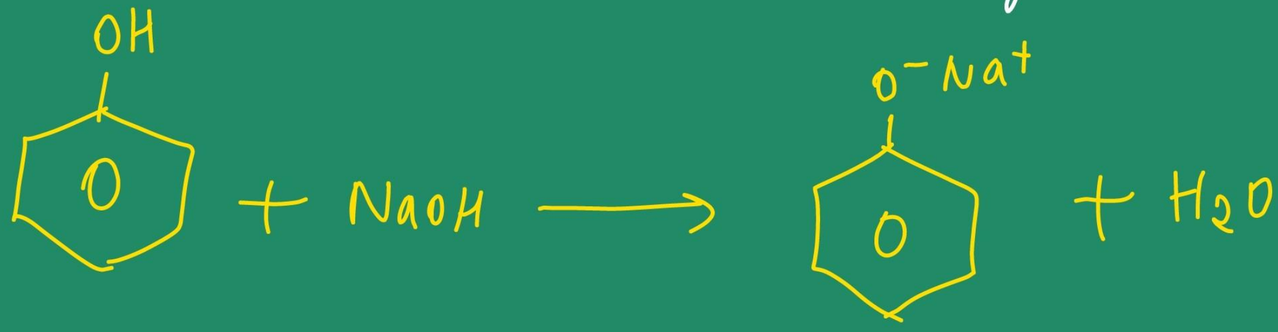
(I) (II) (III) (IV)



(V)

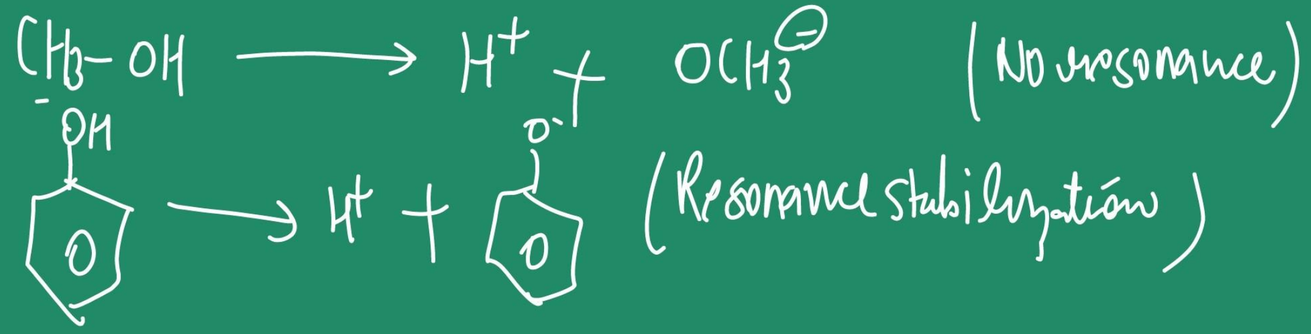
Phenoxide ion is resonance stabilized.

→ Phenol reacts with a base, it will from a salt.
Which indicates its acidic strength.



Sodium Phenoxide

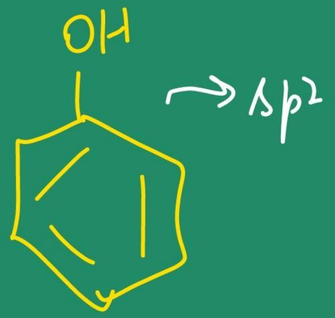
ie. "Phenols are more acidic than alcohol", in Phenol, Phenoxide ion is there which is resonance stabilized unlike alcohol.



% S-character

[Acidic strength ∝ % S-character]

% S-character : [sp > sp^2 > sp^3]



As we know, Phenol is sp^2 hybridized which makes it a compound having more % S.

[High % S ∝ More acidic strength]

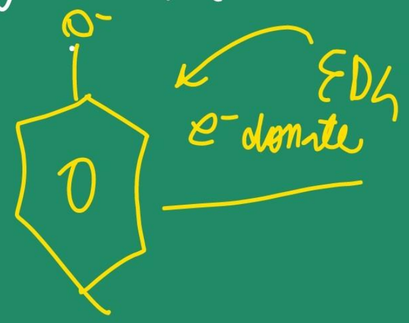
Effect of Substituents

Electron withdrawing group (EWG)

Electron Donating group (EDG)

$$A:S \propto \frac{EWG}{EDG}$$

Those groups which donate e^- to the Phenoxide ion, increases the e-density destabilize the Phenoxide ion.



destabilize.

Due to EDG, Acidic strength of Phenol decreases.

because Phenoxide ion is destabilized.

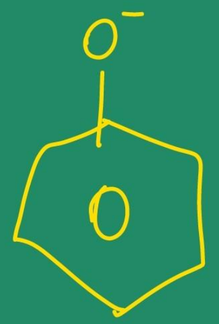
eg :- Alkyl ($-CH_3$, $-C_6H_5$ etc.)

$-\ddot{N}H_2$

$-OH$ etc.

These are the groups, which withdraws electron from Phenoxide ion & makes it more stabilize.

∴ Phenol will become more acidic



← more stable.

→ e^- withdraw

eg:- → X (F, Cl, Br, I)

NO_2, CHO, COOH etc.

Qualitative Tests

① **Litmus Test :-** It turns blue litmus Paper into Red. This shows that Phenols are acidic in nature.

② **Ferric chloride ($FeCl_3$) Test :** 1-2 drops of 5% $FeCl_3$ solution to Phenol, the Purple, green & blue colour indicates the Presence of Phenol.

③ **Bromine water**

1-2 drops of bromine water to Phenol, decolourization of Br_2/H_2O takes Place.

(4) **Sodium Nitrite Test :-** 1-2 drops of 10% $NaNO_2$ solution

Red/Pink colour indicates the Presence of Phenol.

(5) **Solubility Test :-** Phenols are acidic in nature so it easily dissolved in NaOH solution.

Phenol + Base ⟶ salt .

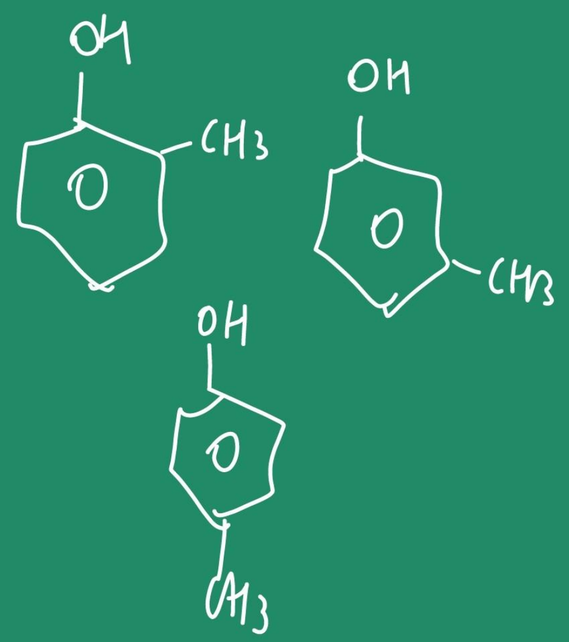
Structure & Uses

1. Phenol

or C_6H_5OH

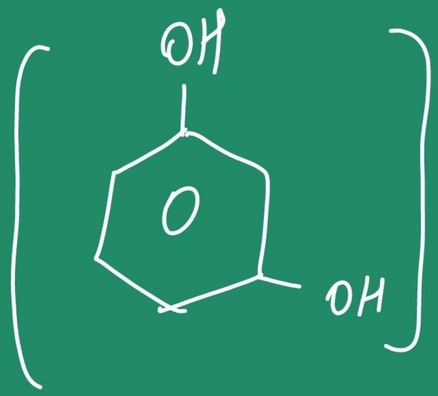
Production of Plastic, resin etc.
Antiseptic, disinfectants etc.
used in Pain killer etc.

2. CRESOL



Wood Preservatives.
Strong Germicides, Dis-infectants etc.

Resorcinol



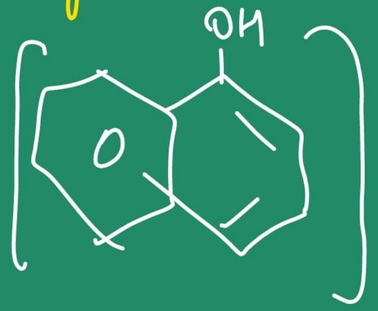
→ Used as an antiseptic disinfectant, etc.

→ Wound cleaning, Anti-inflammatory.

→ Used in the treatment of acne & Pigmentation.

Napthols

- dyes, Pigments, Colouring agent.
  Antiseptic, Antiinflammatory.



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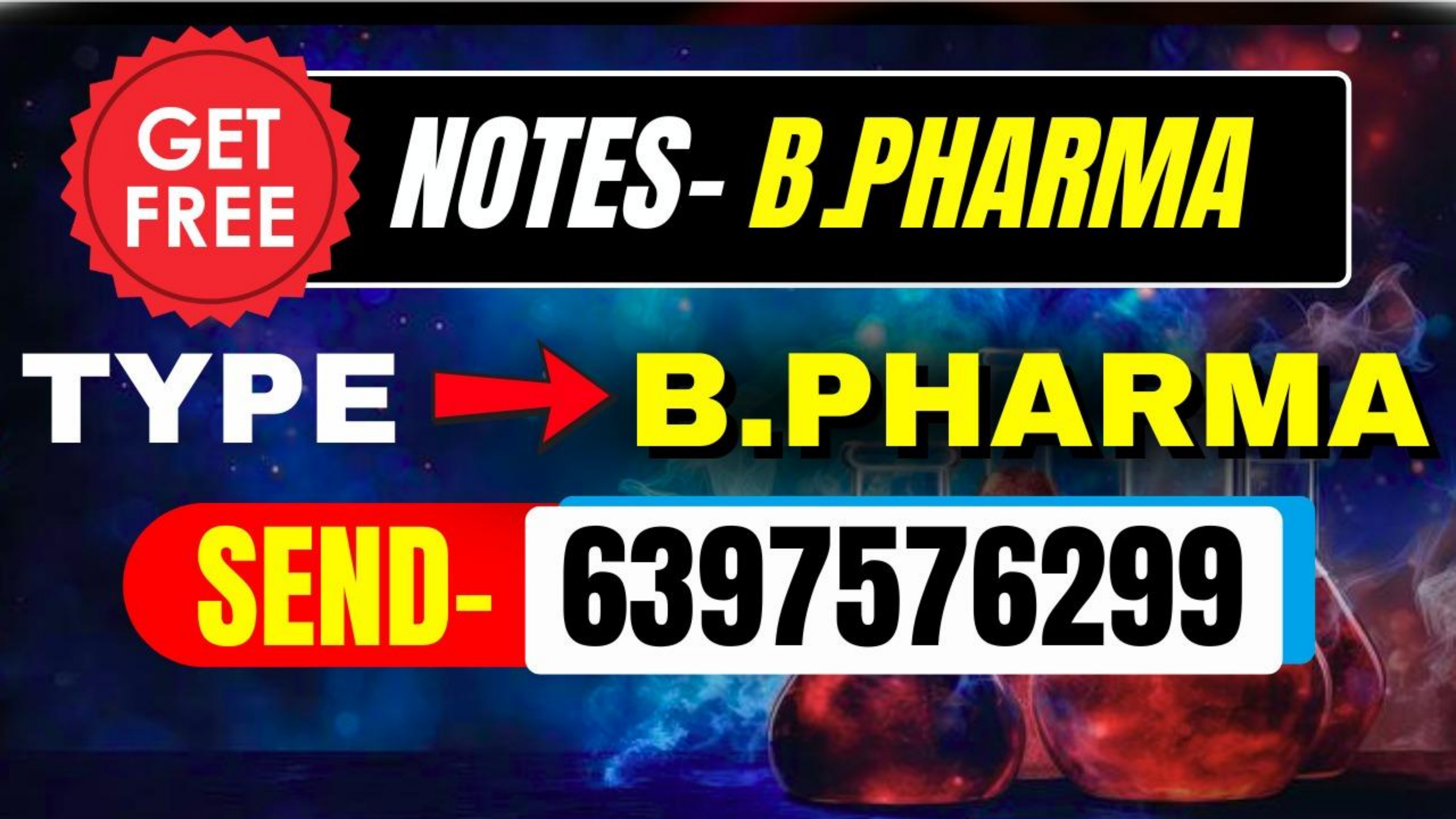
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PHARMACEUTICAL ORGANIC CHEMISTRY II

AROMATIC AMINES

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TOPIC: Aromatic amine

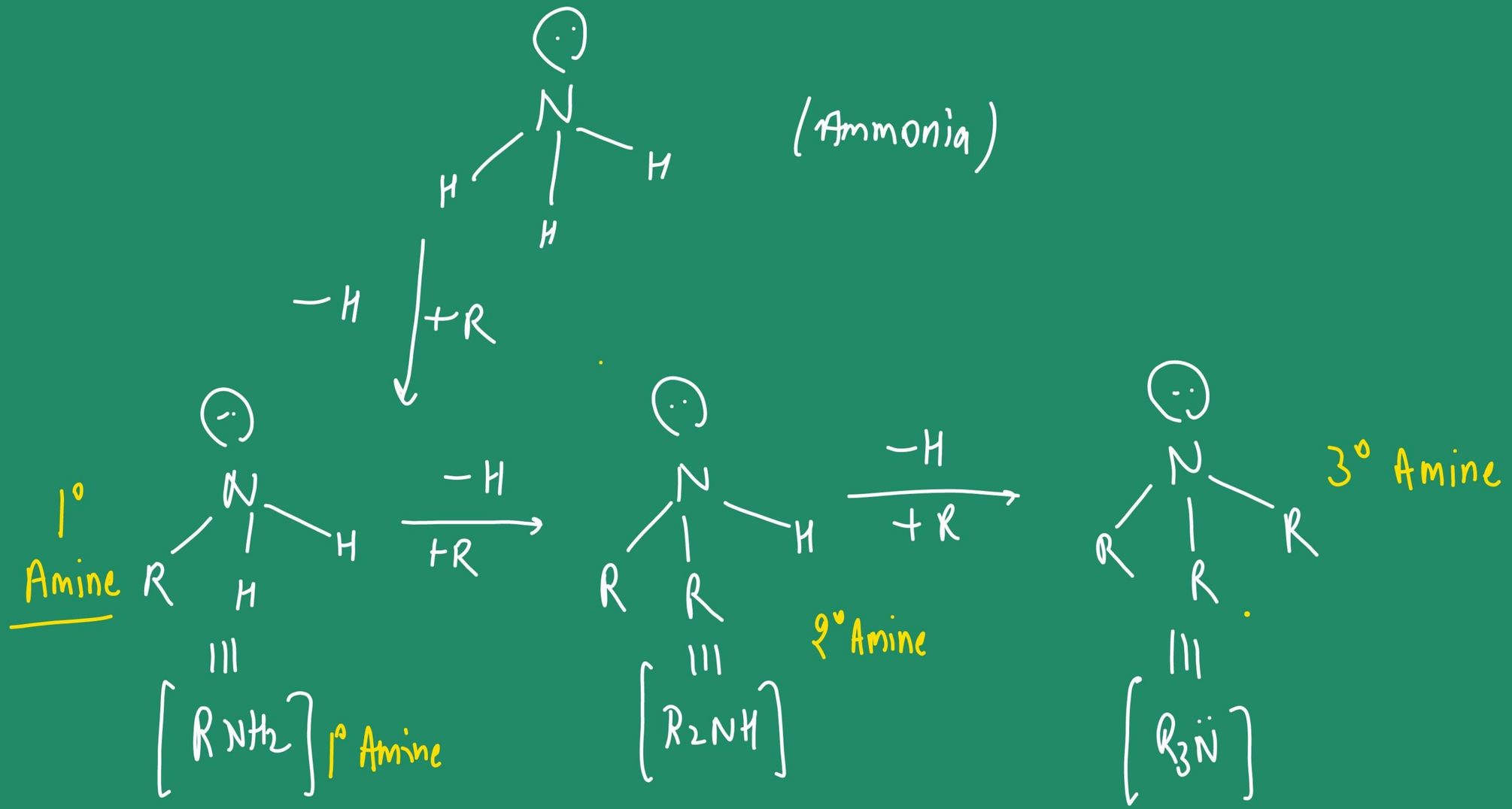
Aromatic Amine

These are the organic compounds where $-NH_2$ group is attached to the benzene ring.

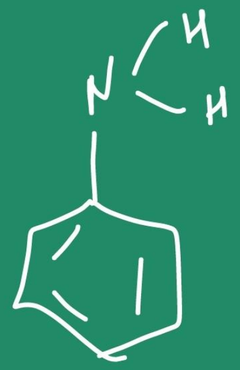
These are the organic compounds in which $-NH_2$ group replaces $-H$ group from benzene ring.

Aniline (Aromatic amine)

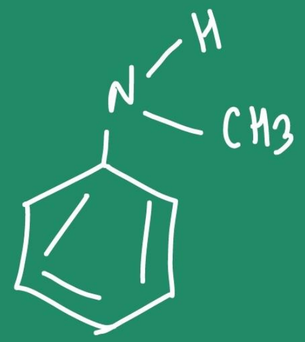
Amine groups are classified into three types ;



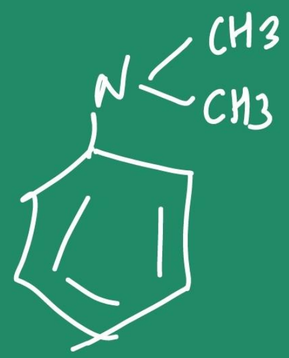
eg:-



Primary Amine



Secondary Amine



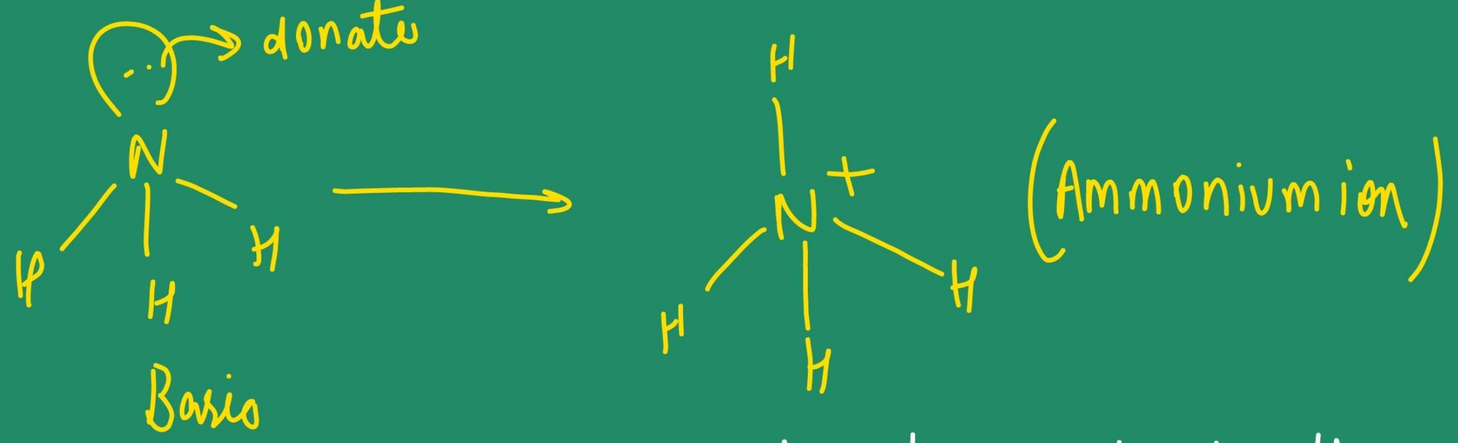
Tertiary Amine

Properties

1. These are colourless / yellowish solids or liquids.
2. It has an unpleasant odour : B.P :- 200 - 300°C M.P :- 50 - 150°C
3. They are moderately soluble in water but highly soluble in Organic solvents.

Basicity of Amines

Amines are derived from NH_3, i.e., basic in nature that donate a lone pair



Aromatic amines are basic in nature because they're the derivative of NH_3.

Which contains lone pair & after donating these lone pairs it becomes basic.

→ lone Pair (donate)

∴ Basic nature

Acc. to lewis concept,

Those substance which donate lone pairs are Bases.

Those substances which accept lone pair are Acids:

Substi:/ Factors affecting Basicity :—

The basicity of aromatic amine depends on many factors.

∴ lone pair ↑ ∝ e⁻ density ↑ ∝ Basicity

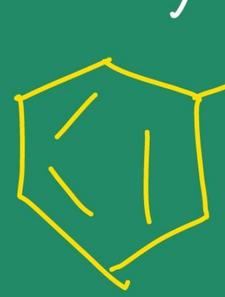
Basicity ∝ localized lone Pair

Basic strength ∝ EDG / EWG

We have two types of substituents;

1. Electron donating groups (EDG's)
2. Electron Withdrawing group (EWG's)

(Alkyl groups, NH_2, CH_3 etc.) — EDG



NH_2

e⁻ rich

EWG — ($-X$, NO_2, CHO, COOH etc.)

These are the groups which donate e^- & increases the e^- density.

→ e^- density ∝ Basicity

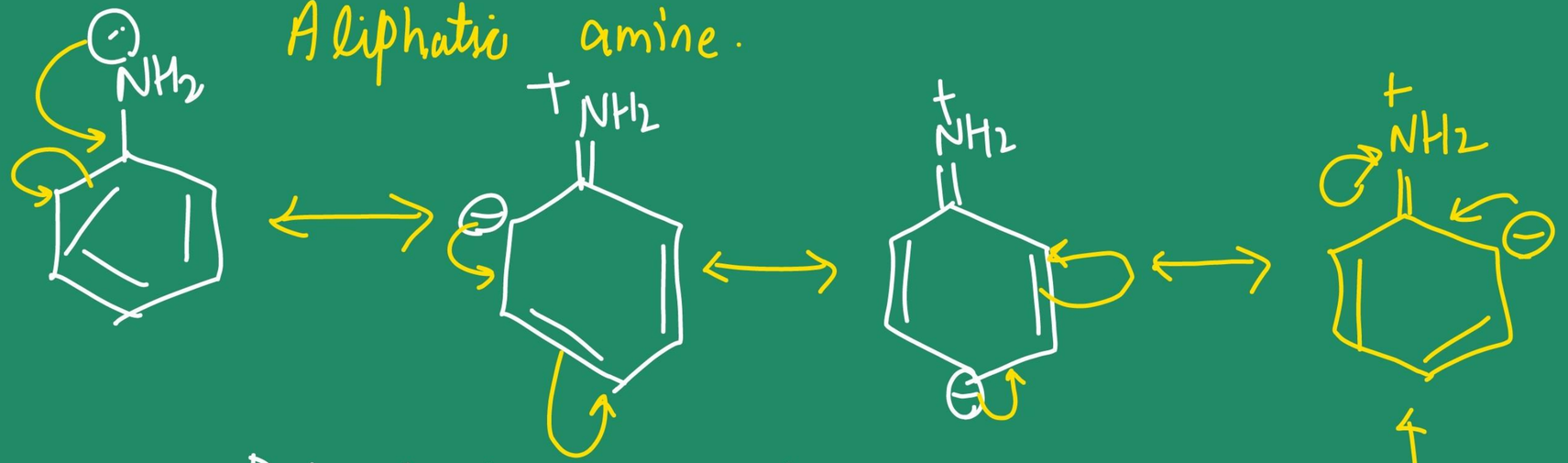
→ These are the groups which withdraws e^-.

→ decreases the e^- density.

→ e^- density ↓ Basicity ↓

→ Aromatic amines are Weakly/Mildly Basic in nature.

They are having a Weak basic strength as compared its Aliphatic amine.



Delocalization of e^- is Proceeding.

"Due to resonance, Aromatic amine are less basic as compared to aliphatic amine."

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AROMATIC AMINES

ARYL DI- AZONIUM SALTS

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TOPIC: Aryl Di-azonium Salt

Amines (Introduction)

Basics

Classification

Basicity of Aromatic amines.

Factors affecting.

(Basic) Aliphatic amine >> Aromatic amine

pKa Values

- Aromatic amine – 4-7
- Aliphatic amine – 8-11

- Acidic strength $\propto \frac{1}{pK_a}$
- Basic strength $\propto \frac{1}{pK_b}$

Stability of Amines

We have different type of Amines;

1° Amine — RNH_2

2° Amine — R_2NH

3° Amine — R_3N

Stability → [3° > 2° > 1°]

In 3° Amine, Steanic Hindrance is Present due to three alkyl groups. which decreases its stability

Stability Order :-

$$\underbrace{\left[2^{\circ}\ \text{Amine} > 3^{\circ}\ \text{Amine} > 1^{\circ}\ \text{Amine}\right]}_{\text{Aliphatic amine}} > \text{Aromatic amine}$$

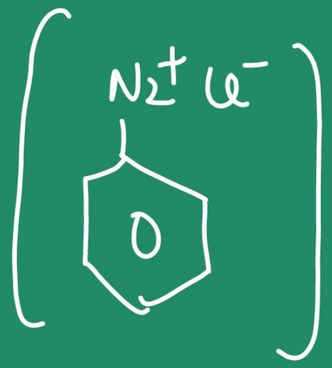
(due to Resonance)

Aryl-Diazonium Salt

It is an organic compound which contains two azo groups

Here, diazo group is directly attached with benzene ring.

General Formula: $ArN_2^+X^-$

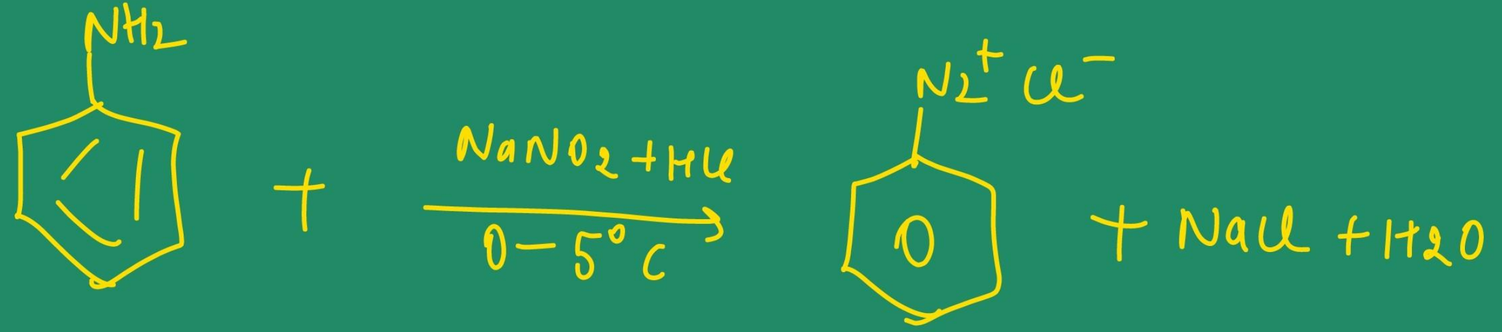


Benzene diazonium chloride.

Methods of Preparation

When aniline reacts with Sodium Nitrite & HCl.

it Produces the desired Product.



Synthetic Uses

1. They are very versatile and used as an intermediate in many organic synthesis.
2. They're used for the formation of dyes & Pigments.
3. Used in formation of drugs. (eg. Anti-biotics etc.)
4. Pesticides formation.

Chemical Reactions

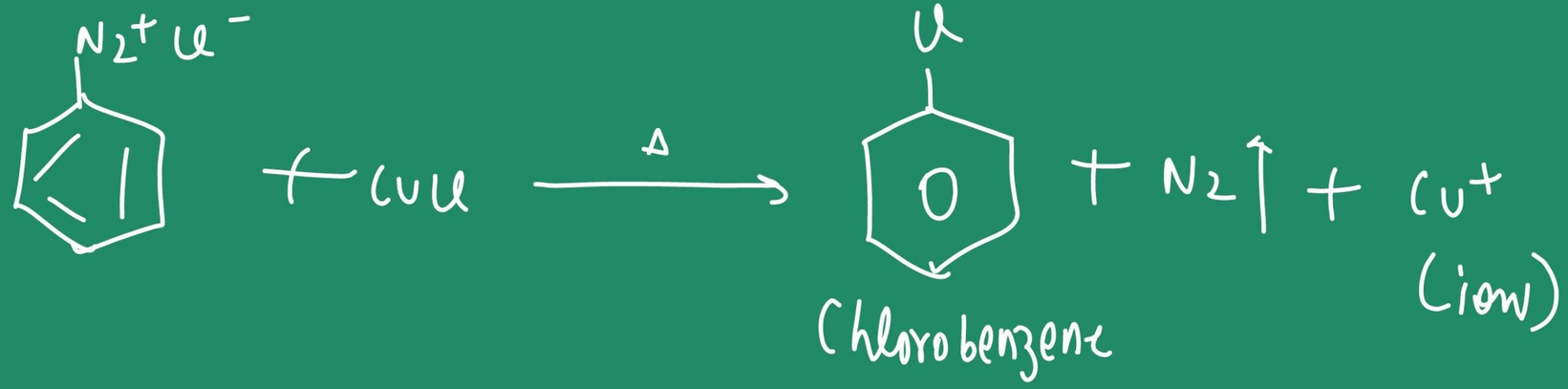
1. Azo coupling

Aryl diazonium salt reacts with aniline for the formation of Synthetic dye.

(Yellow dye)

2. Halogenation

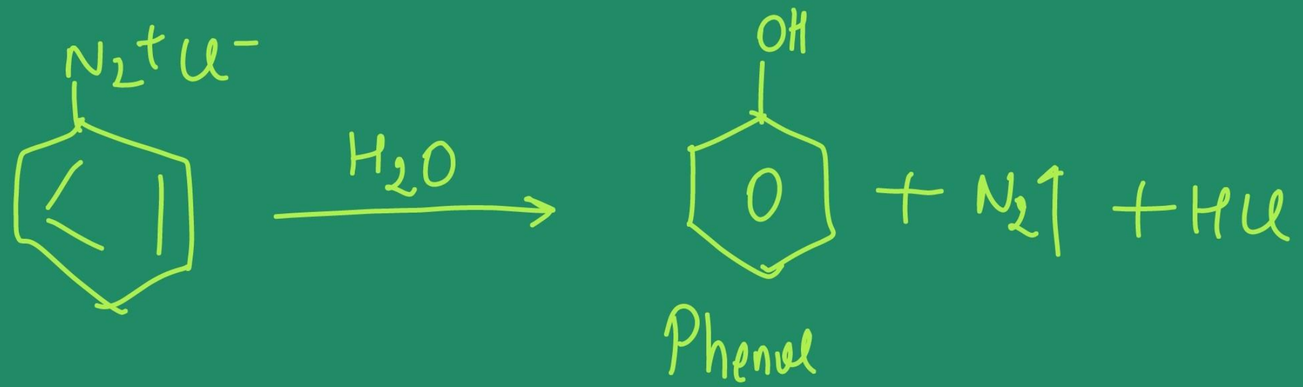
Aryl diazonium salts react with cuprous chloride in the Present of Heat.



3. Phenol Preparation

Aryl diazonium salt reacts with H_2O, in the presence of Heat.

Phenol, forms.



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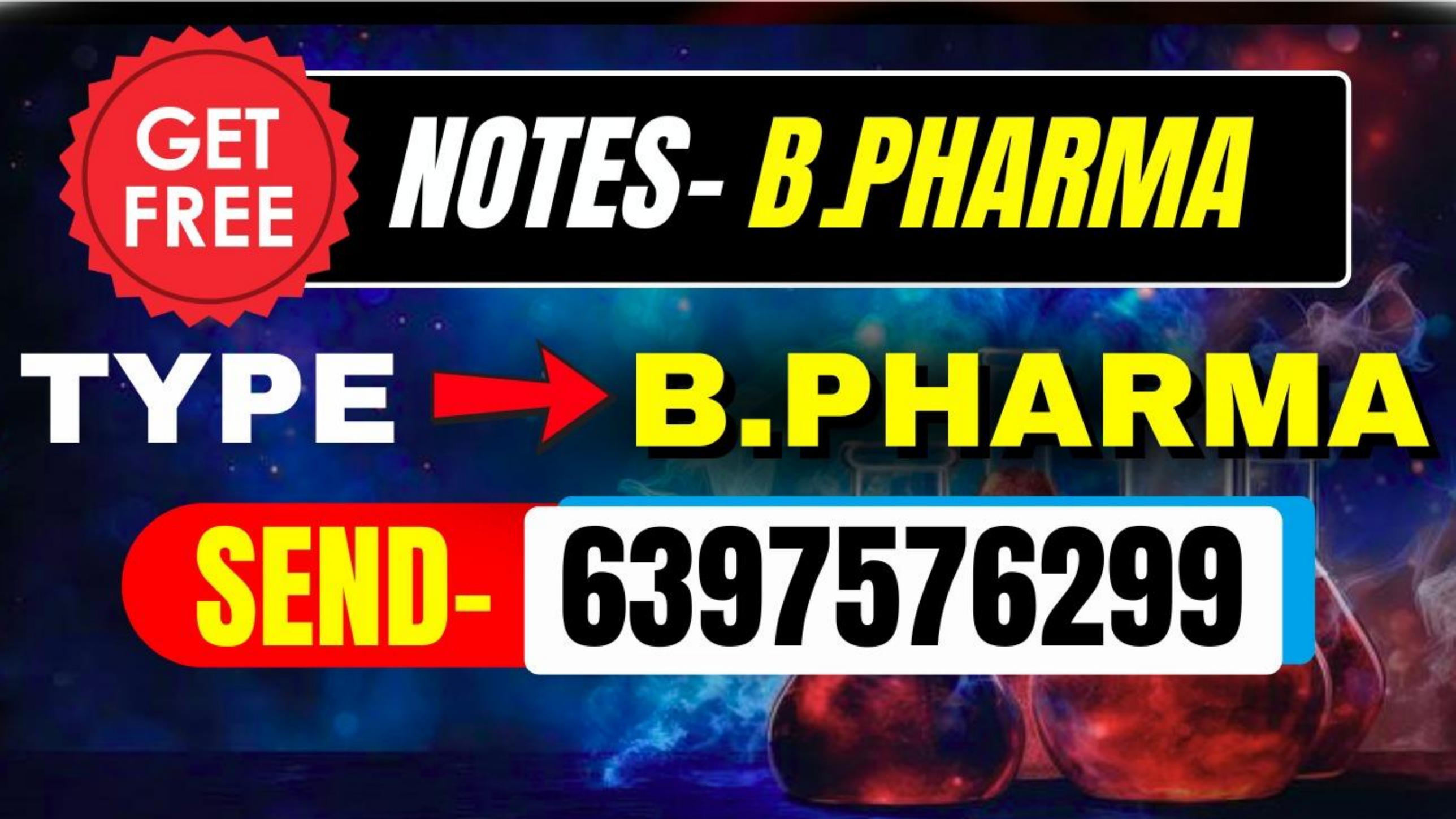
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AROMATIC ACIDS

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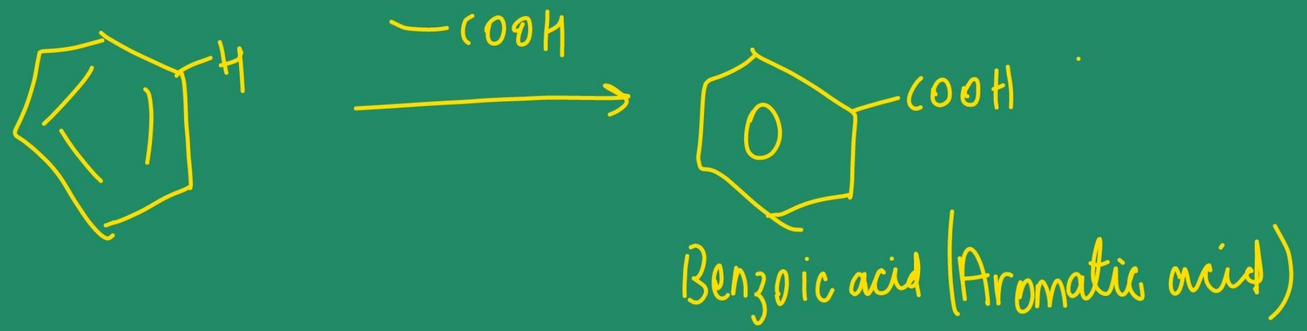
Topic: Aromatic acids

Aromatic Acids

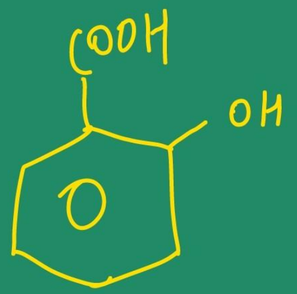
Aromatic acids are the Organic compounds in which a $-COOH$ group is directly attached Benzene ring.

In such compounds one H-atom is being replaced by $-COOH$ groups i.e., Benzoic acid.

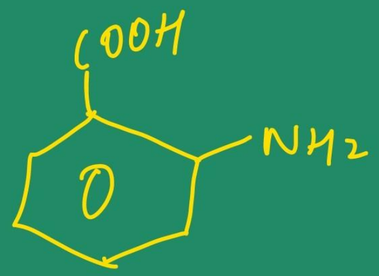


Benzoic acid (Aromatic acid)

eg:-



Salicylic acid

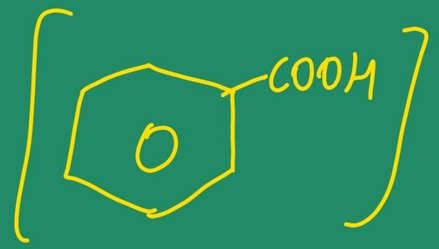


etc.

Properties

1. These compounds are soluble in Organic compounds but weakly soluble in water.
2. Aromatic acids are stronger than aliphatic acids due to resonance stabilization.
3. These are white / colourless solids.

Benzoic acid

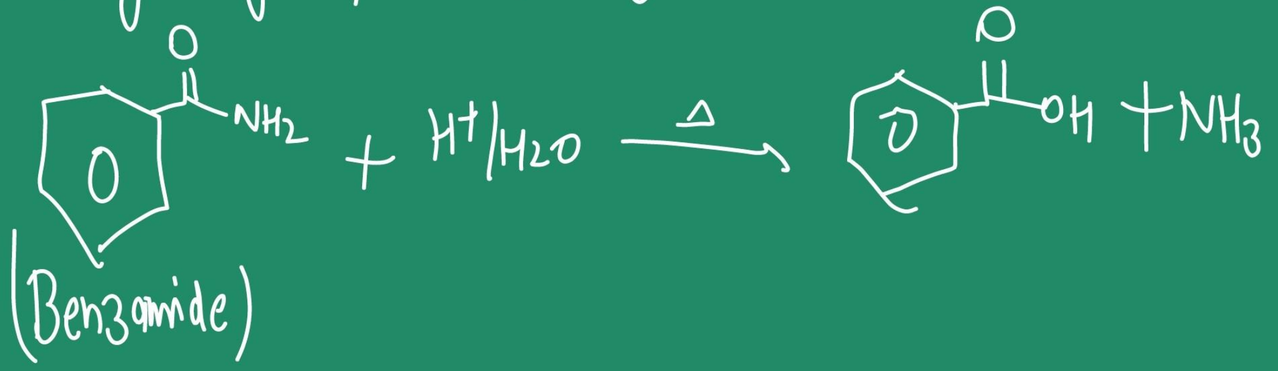


This is a colourless crystalline white organic compound. which contains a —COOH group.

This acid also known as Benzene carboxylic acid.

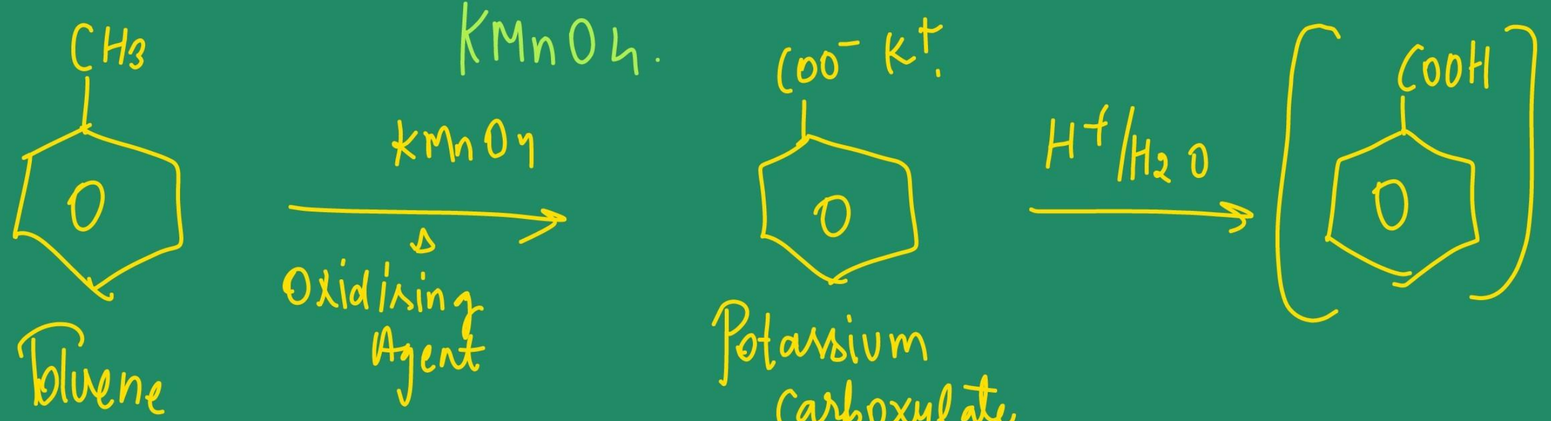
Methods of Preparation :—

Amides on hydrolysis Produces benzoic acid.

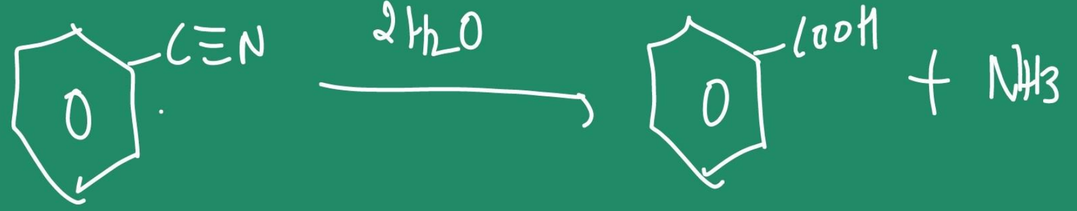


(Benzamide)

2. **Oxidation** It can be prepared by the oxidation of 1° & 2° alkyl benzene by using reagents like alkaline / acidic



3. **From Benzonitrile :** Benzonitrile on hydrolysis gives benzoic acid.

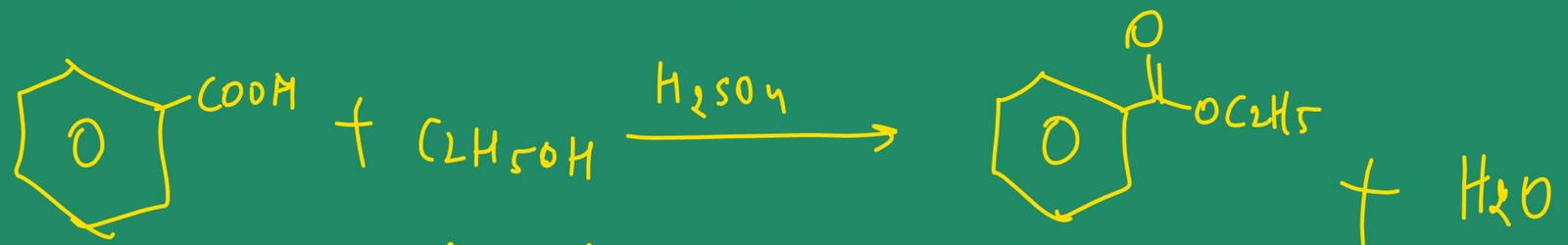


Chemical Reactions

1. Esterification :- Benzoic acid reacts with an alcohol

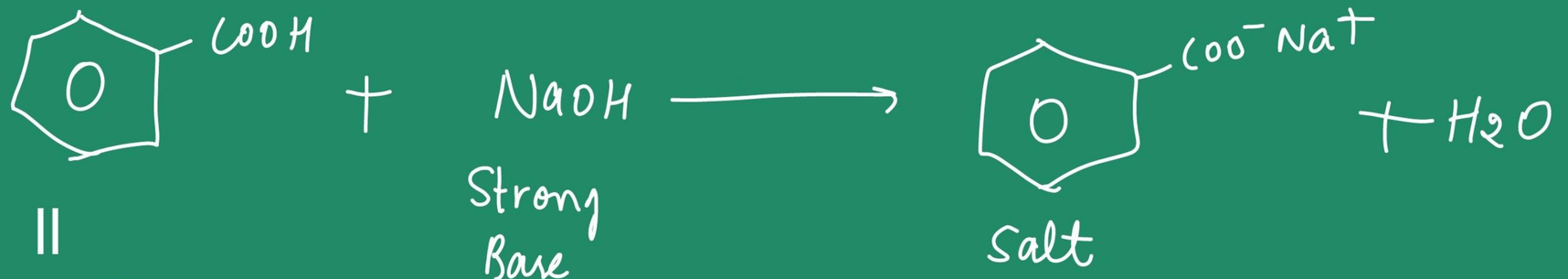
In the Presence of any acid i.e., Conc. H_2SO_4

For the formation of Ester.



Acid Alcohol Ester

2. **Salt formation** Benzoic acid reacts with a base to form salt.



3. **Formation of acyl halide**

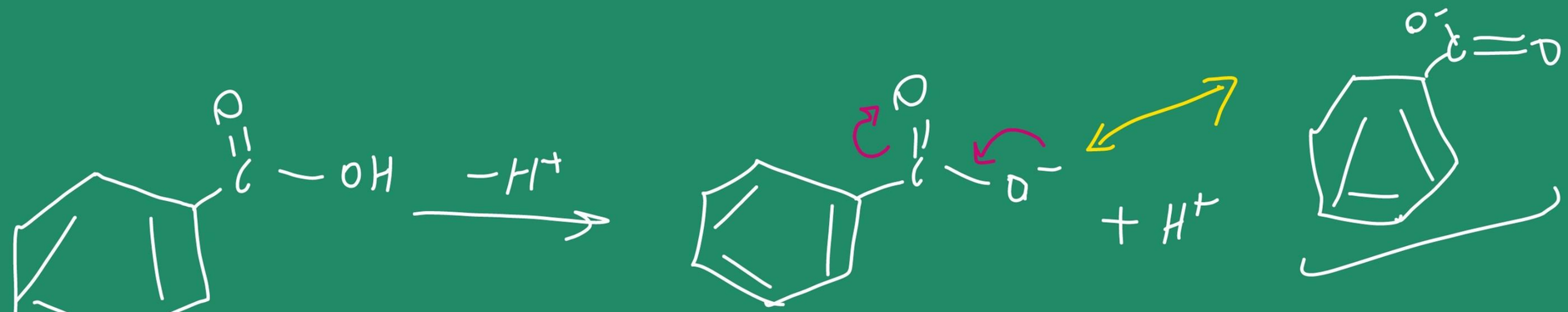
When benzoic acid reacts with PCl_5 it form benzoyl halide.

Acidity of Aromatic Acids

Aromatic acids are strong acids.

On donating a Proton, They are highly resonance stabilized which makes its conjugate Base even more stronger.

(Acidic Strength $\propto$ Stability of Conjugate Base)



Benzoic acid

Resonance stabilization
C.B stable.

→  ion is having a negative charge & for stability it delocalises this Charge. (Resonance stabilization)

due to resonating structure, it more stable & acidic.

Aromatic acids are more acidic than aliphatic due to,

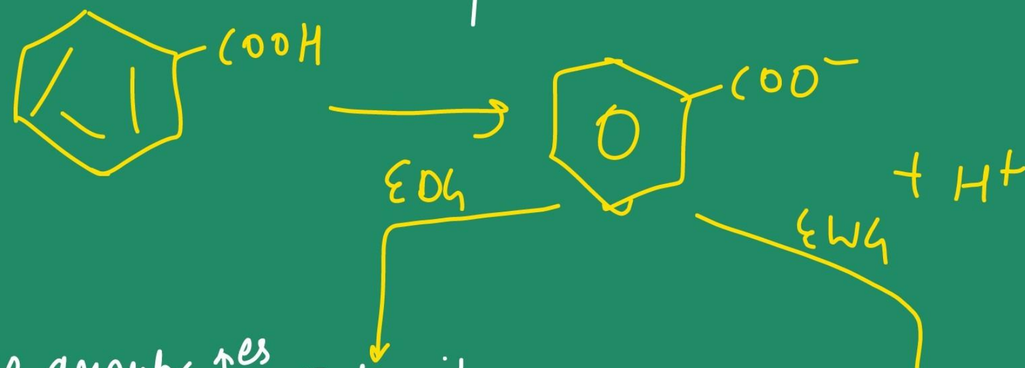
→ Contain lone pair / Resonance Stabilization.

→ % S-Characters ∝ Acidic Strength.

Effect of Substituents

Electron donating group (EDG)

Electron Withdrawing group (EWG)



These groups ↑es e⁻ density

Acidic str: ↓

These group decreases the e⁻ density.

Acidic strength ↑

$$\text{Acidic strength} \propto \frac{\text{EWG}}{\text{EDG}}$$

EWG

- $-X$ (F, Cl, Br, I)
- $-CHO$
- $-NO_2$
- $-COOH$ etc.

EDG

- Alkyl groups
- $-\ddot{N}R_2$
- $-\ddot{N}H_2$ etc.

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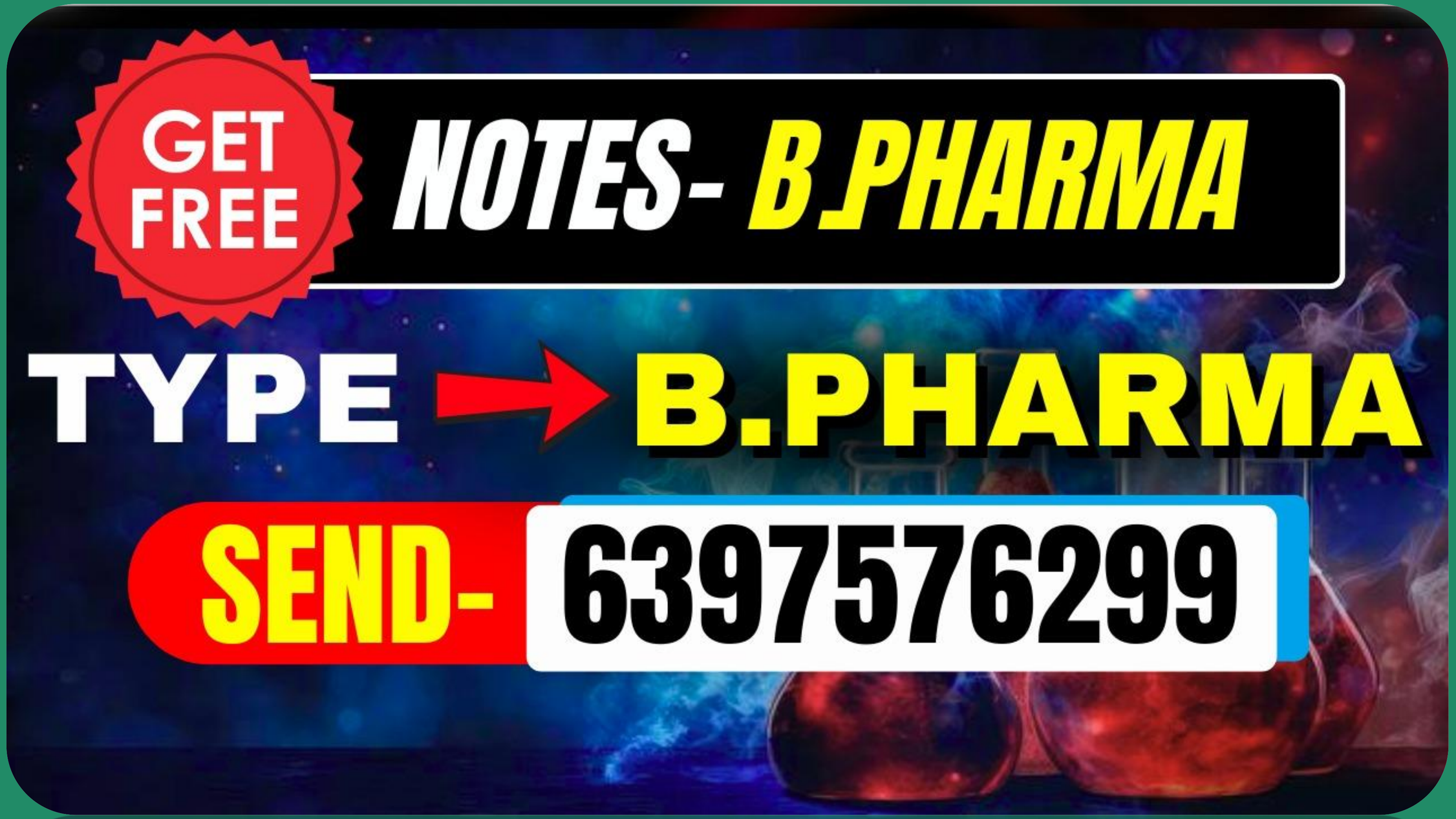
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UNIT - 2

PART-1

PHARMACEUTICAL ORGANIC CHEMISTRY II

PHENOLS

PHENOL & IT'S METHODS OF PREPARATION

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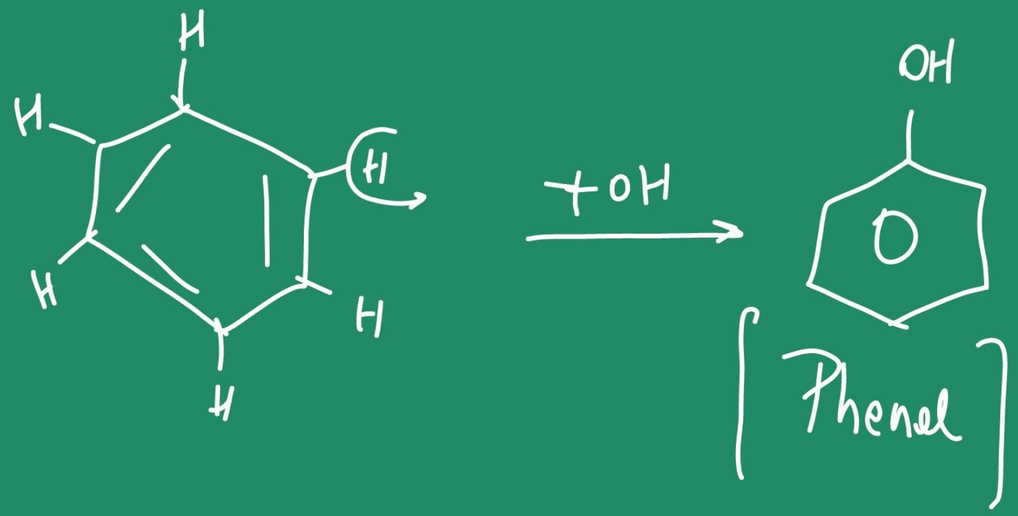
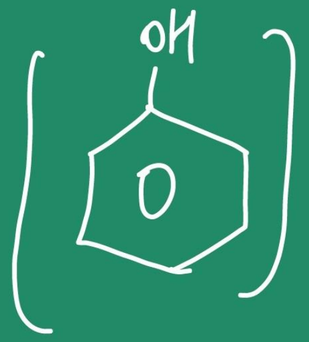
POC

SEM-3
UNIT-2
TOPIC:- Phenol & It's Methods of Preparation

- Phenol
- Aromatic amine
- Aromatic acid

Phenols





Phenol

Molecular Formula :- $[C_6H_5OH]$

Phenols are also known as 'Carbolic acid'.

This is an aromatic compound in which one H-atom is replaced by Hydroxyl group ($-OH$).

[Molecular Formula : C_6H_5-OH] [Molecular Weight : 94.11 g/mol]

Properties of Phenol

→ Phenol is colourless. (Sometime Yellowish compound).

→ Phenol is having a Pungent odour.

→ Phenol is mildly / weakly soluble in water but completely Soluble with organic solvents.

Melting Point :- [40.5°C] Density = 1.07

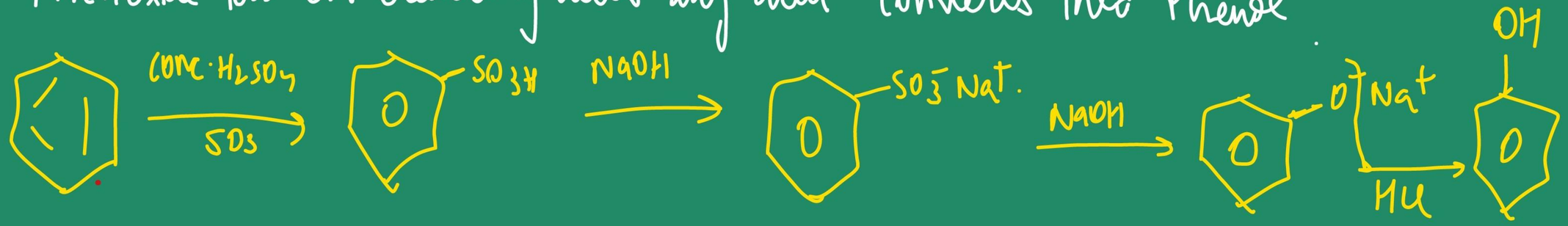
Boiling Point : 181.7°

Methods of Preparation of Phenol

1. From Benzene sulfonic acid:

When sodium salts of aromatic sulfonic acid reacts with NaOH, Sodium benzene sulfonate forms which further reacts with Base NaOH for the formation of Sodium Phenoxide.

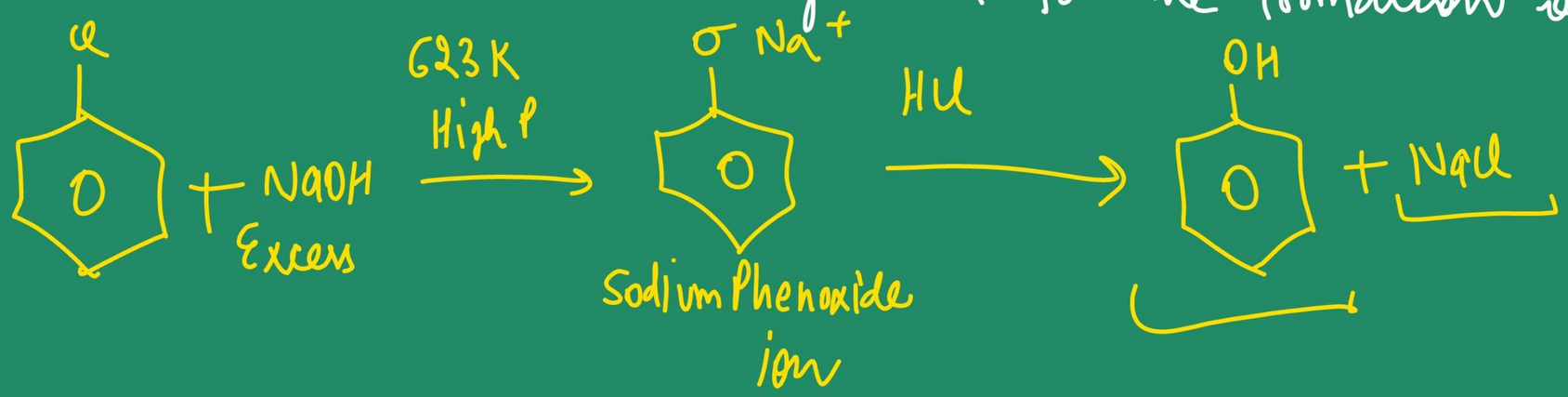
Phenoxide ion on reacting with any acid converts into Phenol.



2. DOW's Process

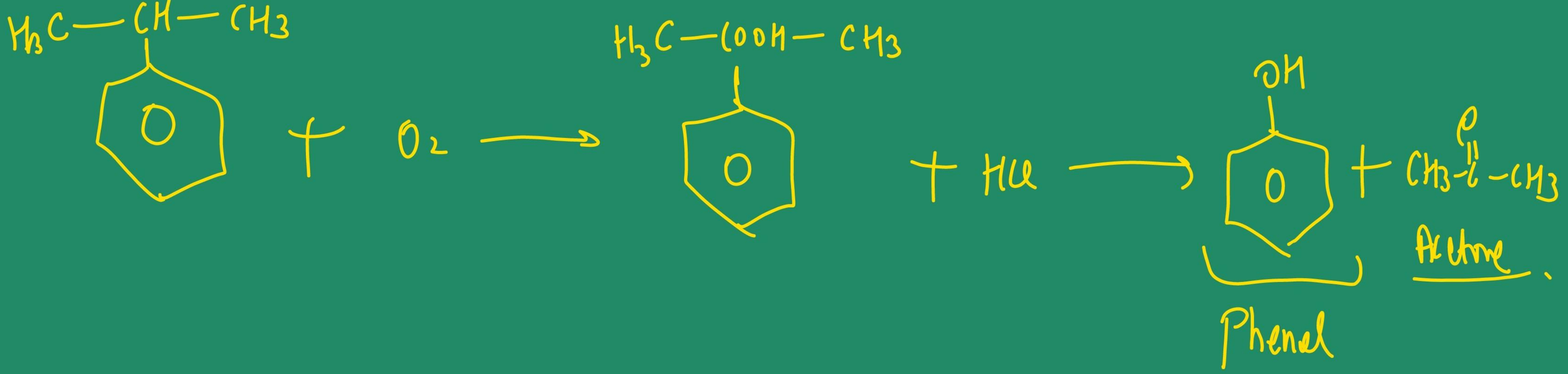
When chlorobenzene is heated in the presence of excess NaOH at a high Temp. & Pressure, it forms Sodium Phenoxide ion

It further reacts with any acid for the formation of Phenol.



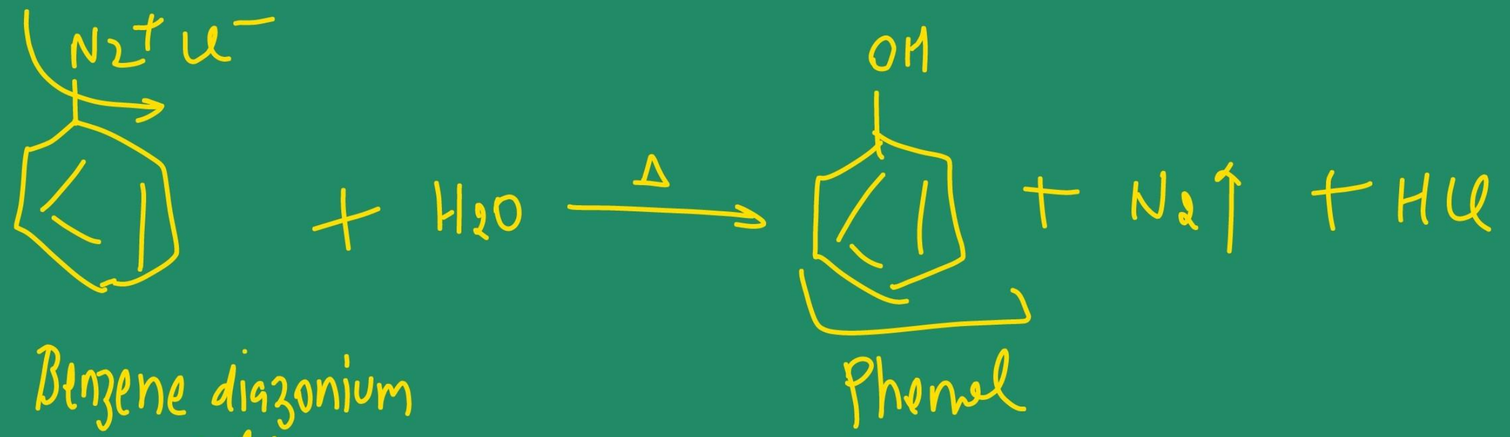
3. From Cumene :—

In this method, cumene is oxidised to give cumene peroxide which on further acidification gives Phenol.



4. From Benzene diazonium salt

When benzene diazonium salt is heated with H_2O, Phenol obtained.



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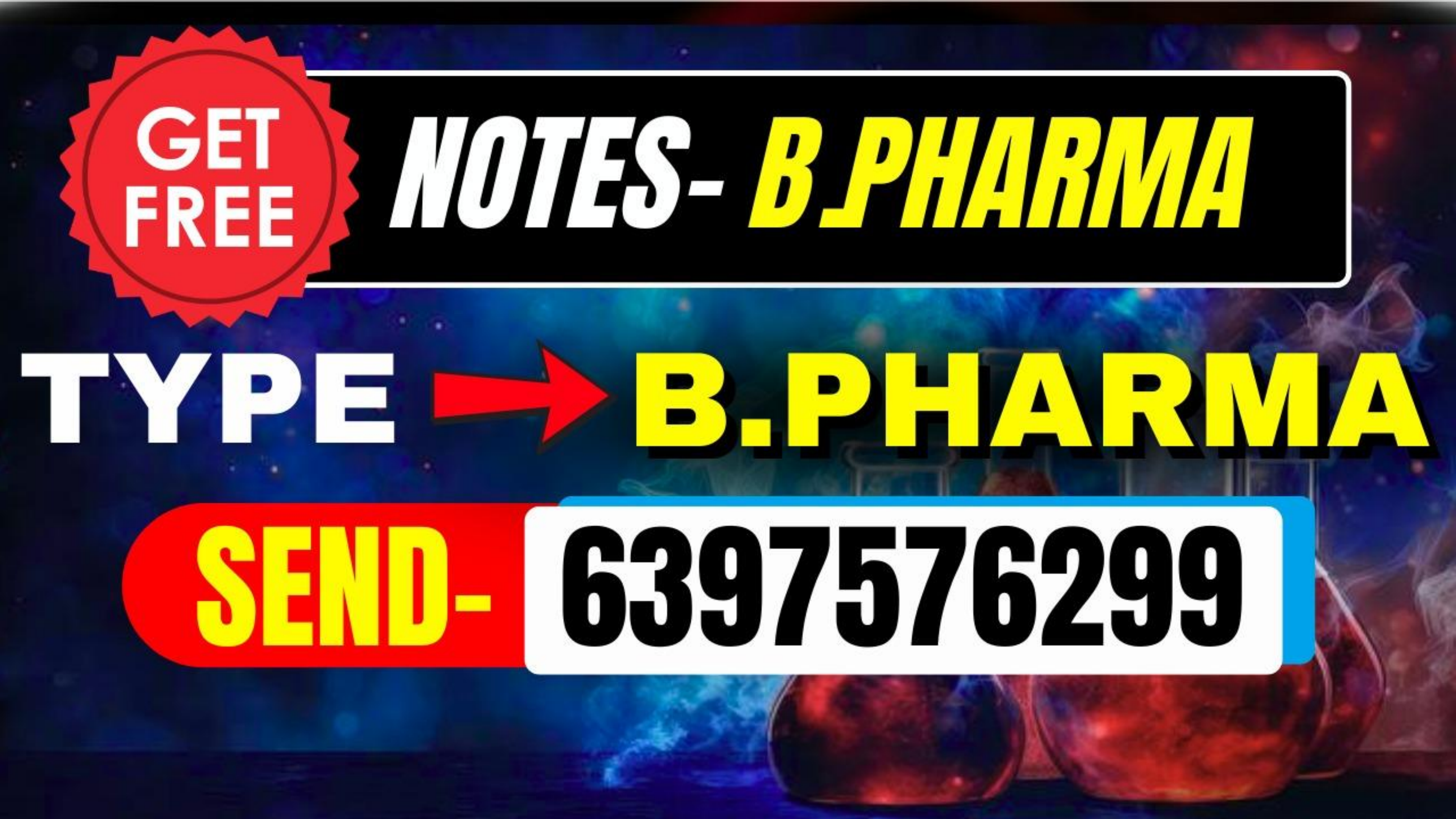
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