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B.PHARMA SEM-3

UNIT - 1

PART-1

PHARMACEUTICAL ORGANIC CHEMISTRY II

BENZENE& ITS IT'S DERIVATIVES

INTRODUCTION

STRUCTURE OF BENZENE
HUCKLE'S RULE

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TOPIC: Aromatic compounds, Benzene
structures of Benzene

Organic Compounds

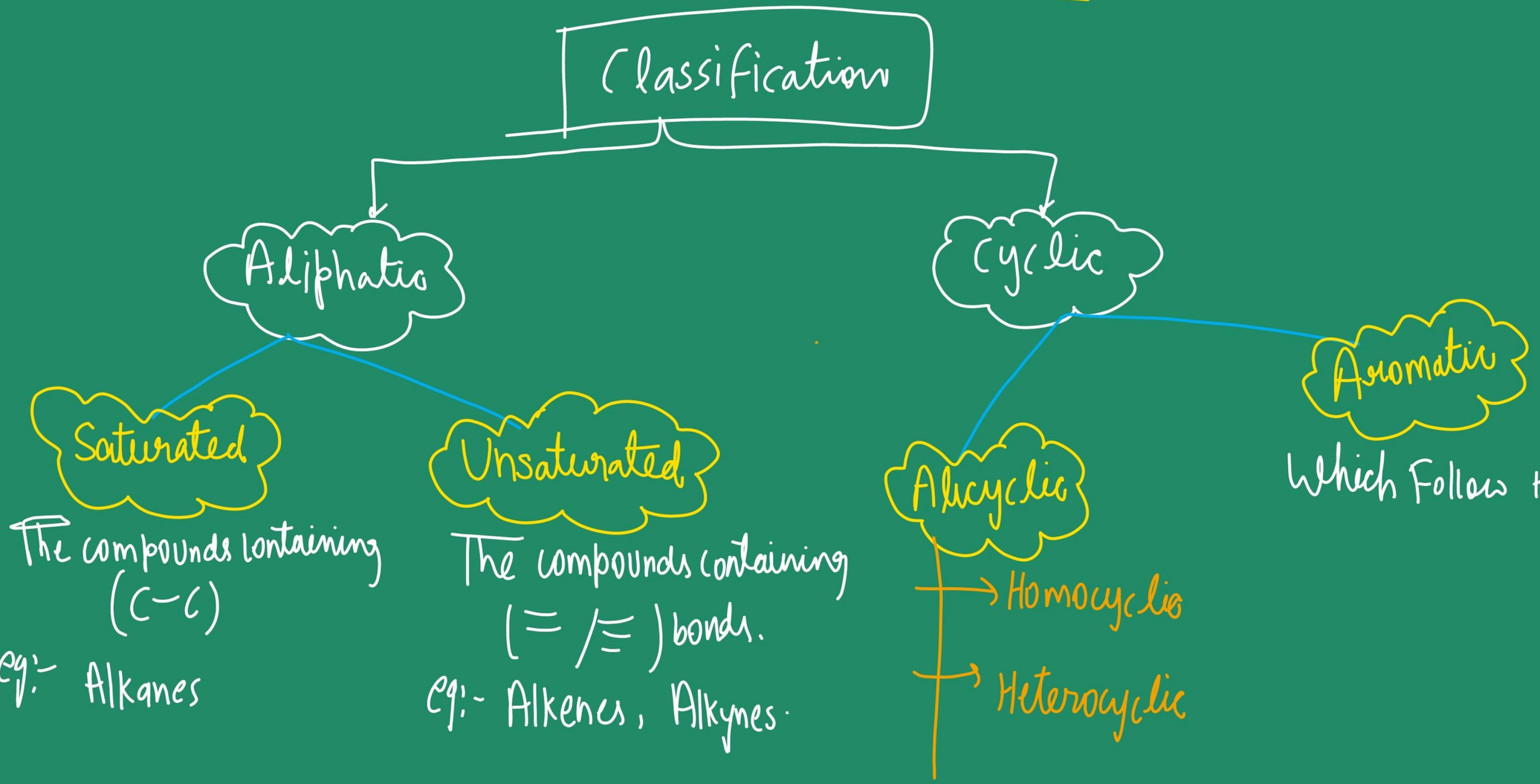
These are the chemical compounds which are made up of Carbon & Hydrogen.

These compounds are often known as "Hydrocarbons"

Hydrocarbons = Hydrogen + Carbon.

Eg:- CH_4, C_2H_6, etc.

Classification of Organic compounds



Aromatic Compounds:—

These are the organic compounds which Follows Huckel rule.

If any compound wants to be aromatic, it must fulfill some conditions.

Which are as follows;

1. Compound must be cyclic.
2. Compound must be Planar. (C-atoms sp/sp^2)
3. Compound must be delocalized.
4. Compound must follow Huckel's rule.
   $(4n+2)\pi e^-$.

$4n+2$ πe^-

$n = 0, 1, 2, 3 - - -$

$2\pi e^-, 6\pi e^-, 10\pi e^- - - -$

eg:-

= 2πe⁻

Delocalization of πe⁻

Cyclic ✓

C – sp^2 (Planar) ✓

Del. ✓

6 πe⁻

Follows Huckel rule.

Aromatic

Delocalized

Benzene

It is an aromatic organic compound which contains 6 C-atom and 6 H-atoms connected through an alternate π-bond.

It is cyclic, resonance available

Delocalization of π-bonds.

Molecular Formula: C_6H_6

Structure

Properties

1. Benzene is colourless, flammable and sweet aroma ring.
2. Boiling Point :- 80°C M.P. = 5.5°C
3. It is insoluble in water but completely soluble in organic compounds.

Structure of Benzene

There are 4 types of structures are given for Benzene which are as follows;

- Kekule Structure
- Chemical structure
- Resonance Structure
- Molecular Orbital structure

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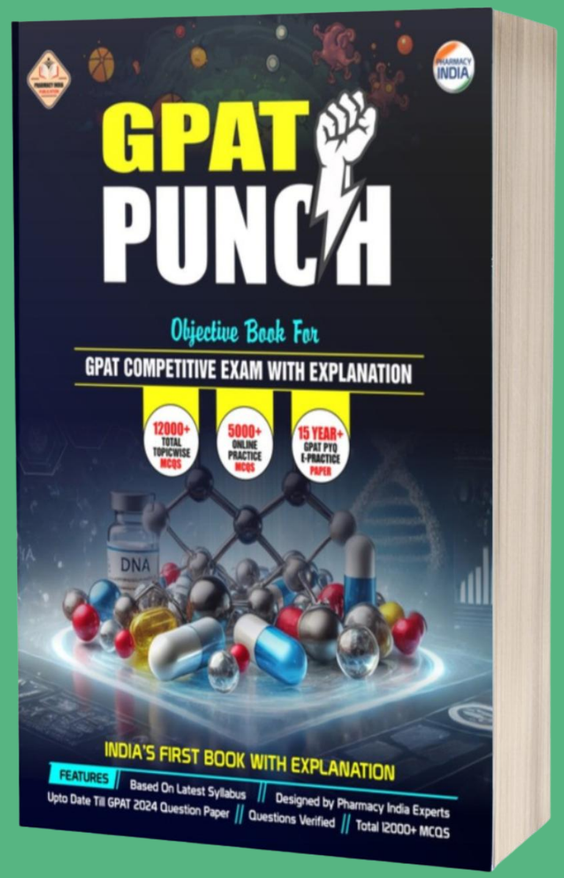

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Unit-I

Topic: - structure of Benzene & it's Evidences (Short + long)

Structure of Benzene

It follows 4 type of structure;

1. Kekule Structure
2. Chemical Structure
3. ** Molecular Orbital Structure
4. Resonance Structure.

Kekule Structure

In 1865, Kekule proposed a structure a Benzene.

which is cyclic in nature and still widely used.

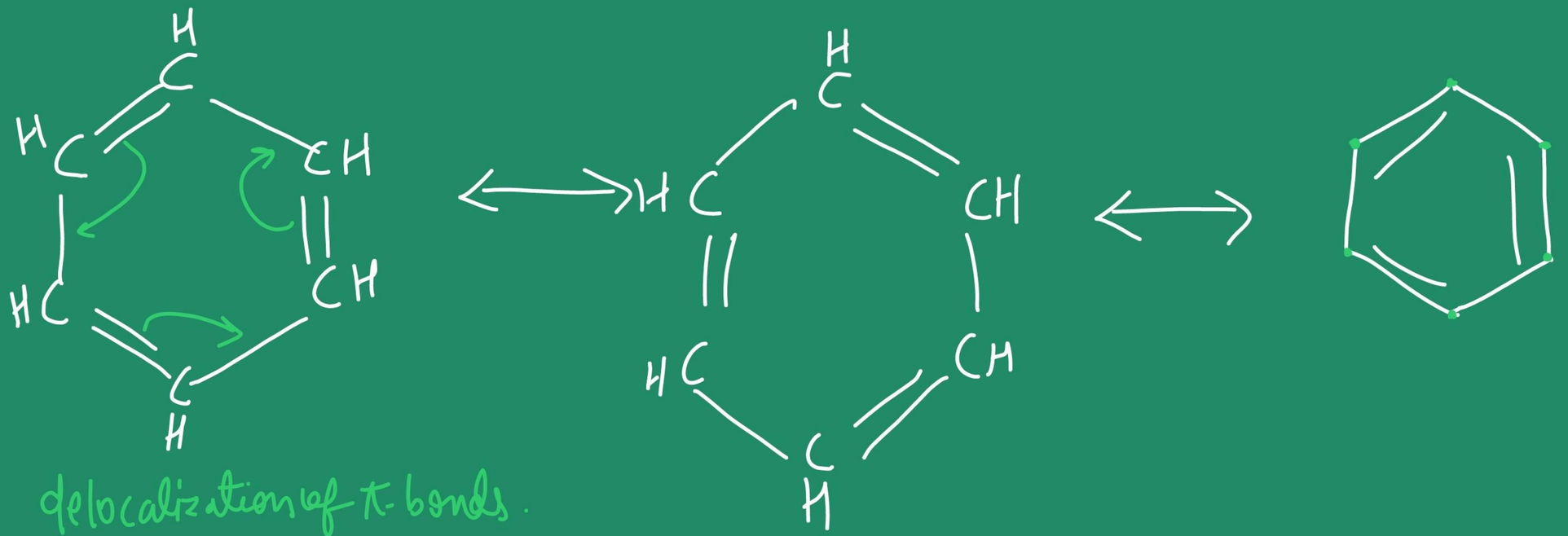
According to Kekule,

Benzene is a cyclic compound having a ring-like Structure

In Benzene, there are alternate π-bonds which are in conjugation with each other.

Molecular Formula: C_6H_6

There are six C-atoms attached with 6 H-atoms.



delocalization of π-bonds.

Hexagon → 6

Chemical Structure :

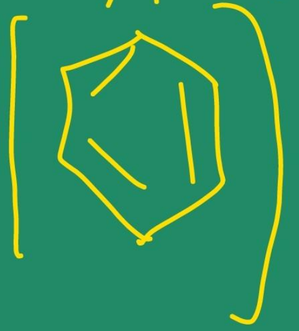
According to the chemical structure. Benzene consists of a hexagonal ring (6-mem cyclic ring).

∴ Alternate double bonds are Present here.

Molecular Weight : 78 g/mol ; Molecular Formula : C_6H_6

Hybridization : sp^2 ($C=C$ → sp^2)

Bond angle : 120°

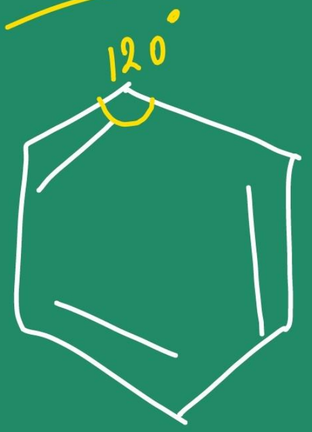


Bond length :

C–C ; C=C : → ~1.40 Å

C–H ⇒ ~1.09 Å

Bond Angle



Benzene

$C=C$: sp^2

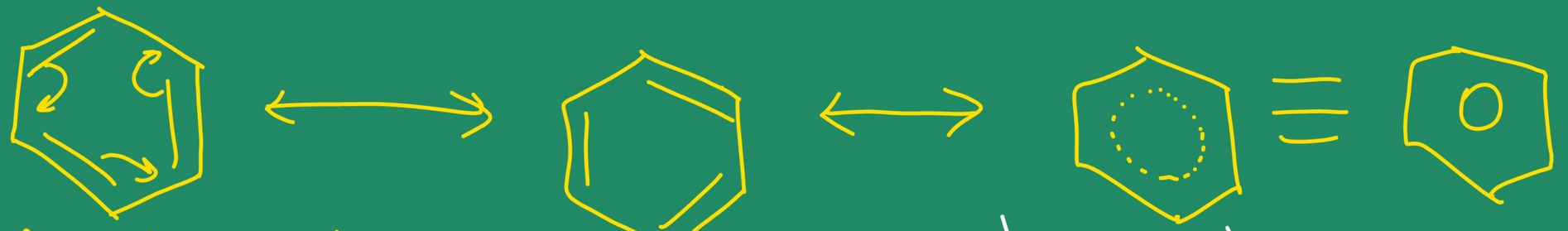
$C-C$: sp^3

$C\equiv C$; sp

Resonance Structure :—

In Benzene, There's a delocalization of Alternate π-bonds.

So it will form resonating structure.



Alternate π-bonds delocalization

Resonating structures.

Resonance hybrid.

This circle represents the deloc^ of π-bonds in complete ring.

All the resonating structures and resonance hybrid explains the stability & reactivity of Benzene.

Molecular Orbital Structure :—

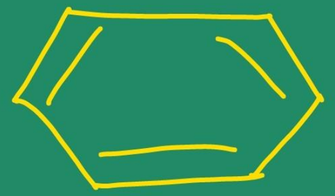
These structures are more advanced & Precise.

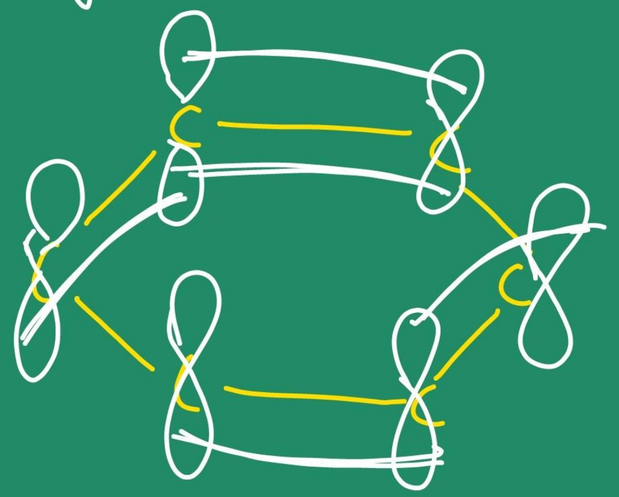
Atomic orbital Combine togethes for the formation of Molecular O's.

Benzene is having both σ & π Molecular O's.

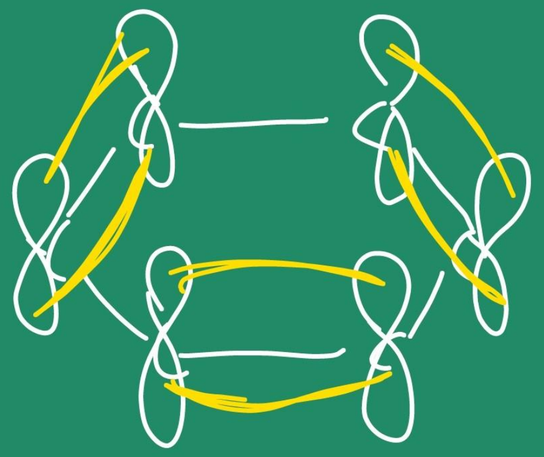
All the 6 C-atoms of Benzene are sp^2-hybridized which Produces sp^2 Hybrid Orbitals

In Benzene, one unhybrid orbital is also Present.





All C-atoms are sp^2 hybridization.



Molecular Orbital Structure.

Overlapping of Atomic orbitals.

Evidences

Analytical Evidence

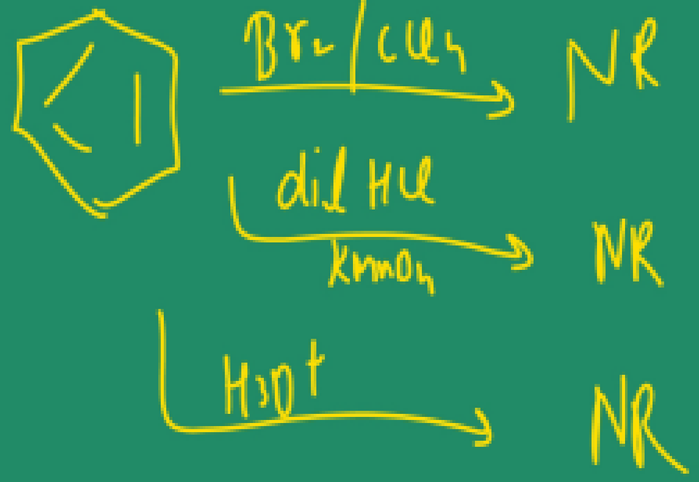
Synthetic Evidence

Other Evidences

Synthetic Evidences

Since we know that, Benzene has unsaturation so it could be constructed into a ring component.

But it does not behave like Alkene/Alkyne because it shows different Chemical Properties.



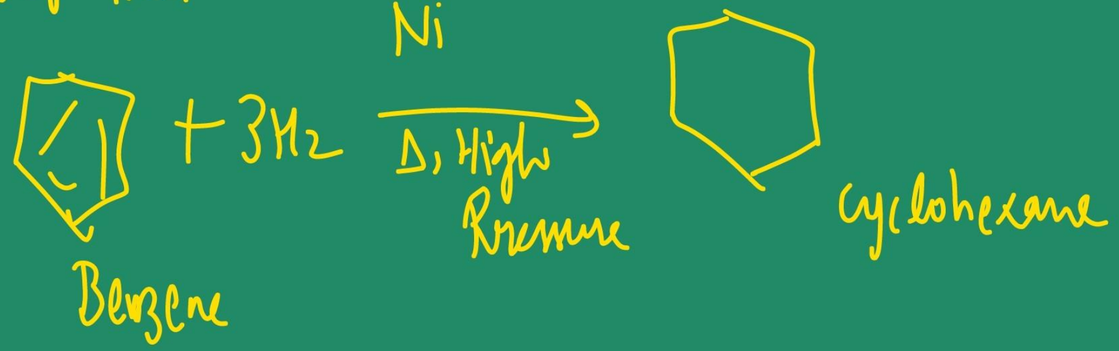
Benzene easily shows Electrophilic Aromatic Substitution reaction Unlike Alkene & Alkyne.

Other Evidences

Benzene is not an aliphatic compound because it shows different Chemical Properties.

So definitely, it a cyclic compounds.

Addition of H_2:



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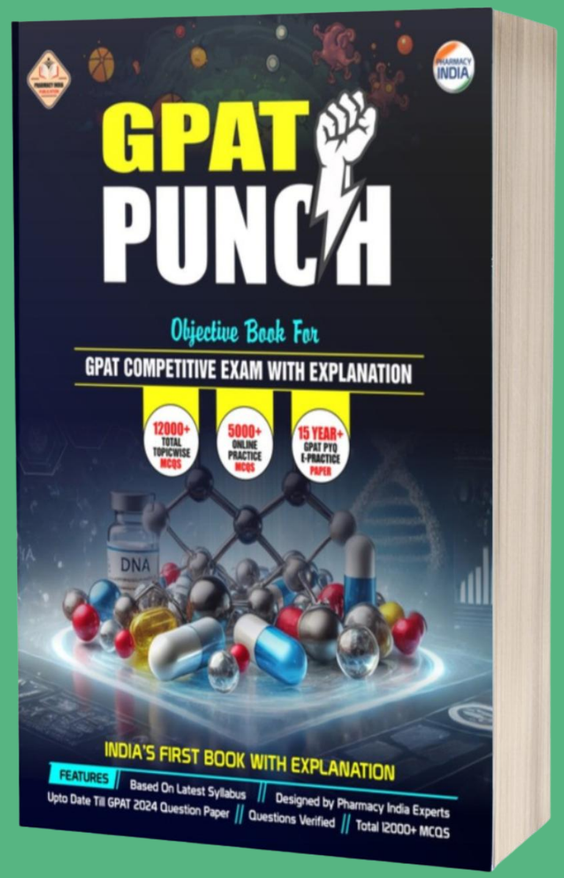

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BENZENE & IT'S DERIVATIVES

CHEMICAL REACTION OF BENZENE
DERIVATIVES OF BENZENE

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TOPIC: Chemical Reactions of Benzene

Chemical Reactions of Benzene

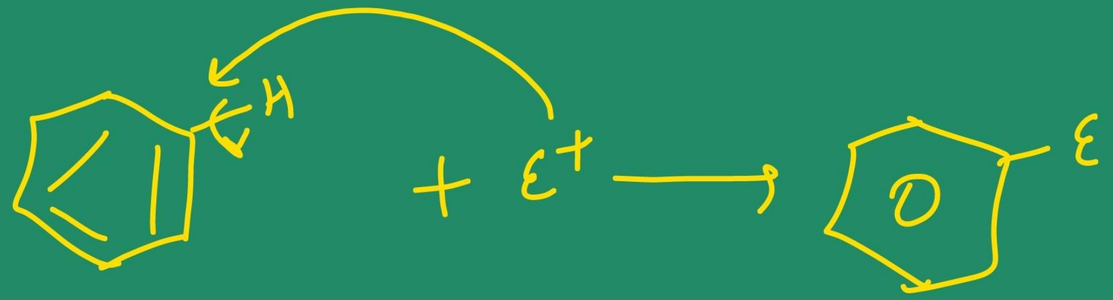
Benzene shows many types of chemical reactions.
due to delocalization it undergoes various reactions as follows;

1. Friedel Craft Alkylation
2. Friedel Craft Acylation
3. Halogenation (F, Cl, Br, I)

(1, 2, 3 ★★★)

4. Nitration
5. Sulphonation

Electrophilic substitution Reactions



E+ sub" reaction (ESR)

Replacement of a H-atoms with any electrophile (e^- deficient species) at Benzene ring.

अरिरागी	आगंतुक
E^+	Nu^-
e^- density ↓	e^- density ↑
e^- deficient	e^- rich

Friedel Craft Alkylation

In this reaction, an alkyl group (CH_3, C_2H_5 etc.) is substituted in the Place of Hydrogen at Benzene ring.

This rxn Proceeds in the Presence of a lewis acid ($AlCl_3$).

Benzene ring reacts with CH_3Cl (Alkyl halide) in the Presence of Anhy. $AlCl_3$ to form alkyl benzene.

Benzene Toluene

Mechanism

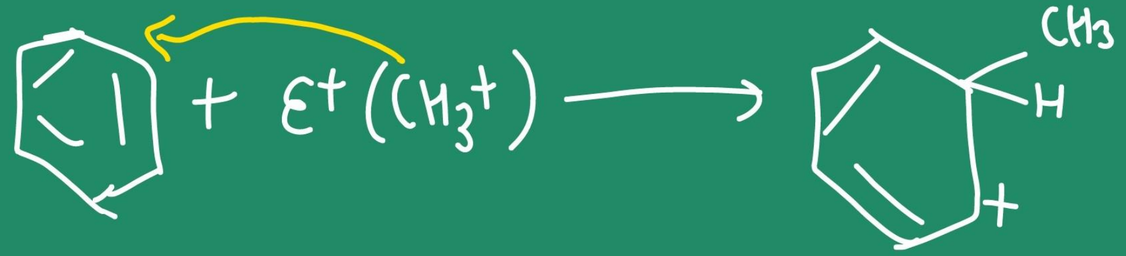
This reaction proceeds in 3-steps.

1. **Formation of an electrophile**: In this step, $AlCl_3$ reacts with CH_3-Cl for the formation of carbocation (C+)

$$CH_3-Cl + AlCl_3 \longrightarrow \underbrace{CH_3^+}_{E^+} + AlCl_4^-$$

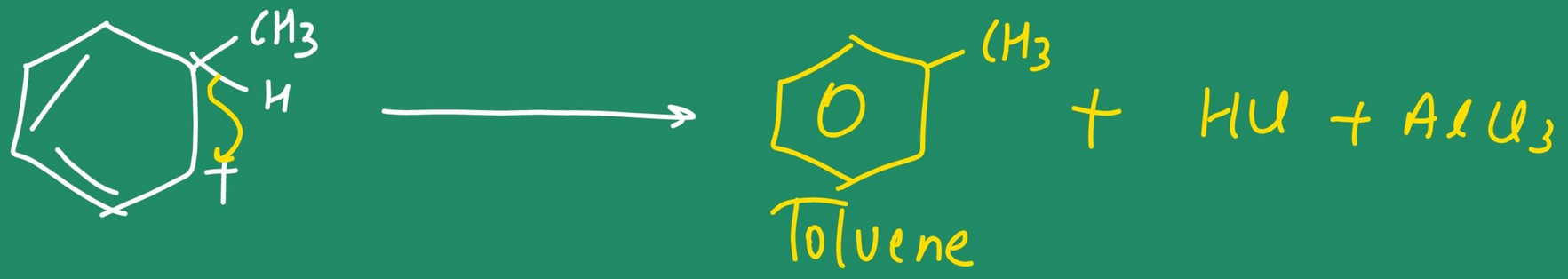
($AlCl_3$: lewis acid)

2. **Attack of E^+ on benzene ring**:



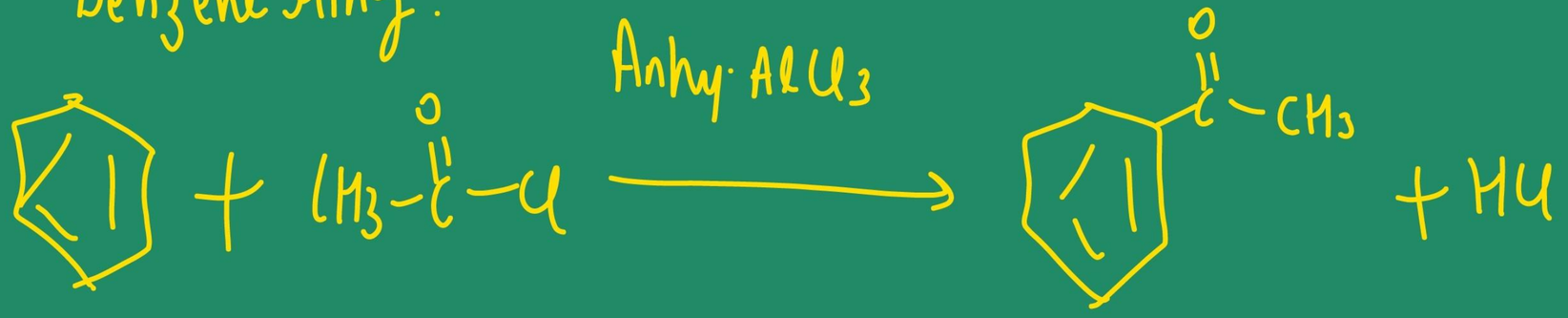
(intermediate)

3. Loss of Proton



Friedel Craft Acylation

It involves the substitution of H-atom with any acyl group in Benzene ring.



Mechanism

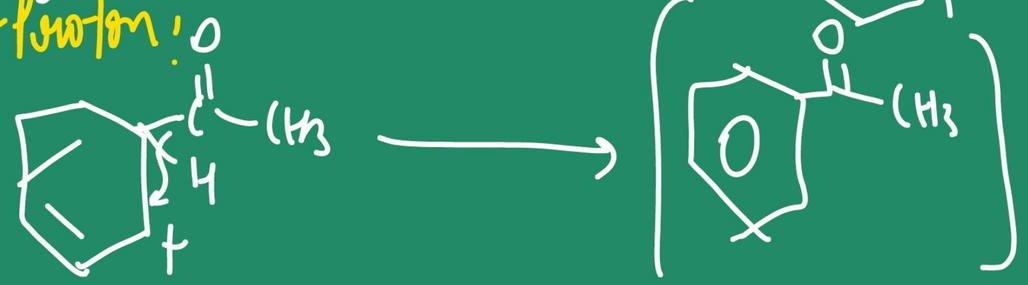
It follows 3-step mechanism;

1. Formation of E^+ :-

CH_3COCl, reacts with Anhy $AlCl_3$ for the formation of E^+.

2. Attack of E^+ on Benzene ring:

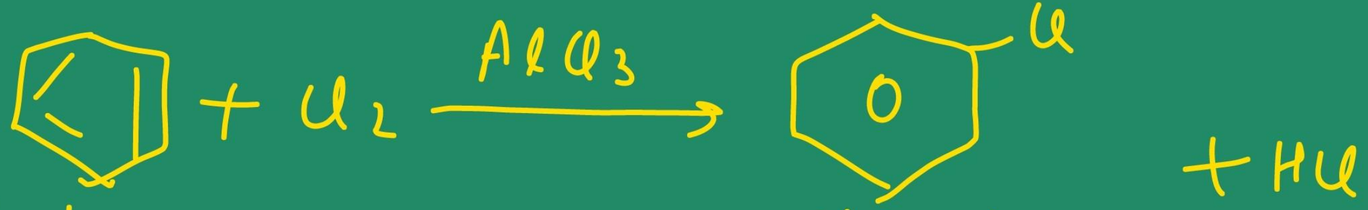
3. Loss of proton:



Halogenation

Addition of Halogen takes Place to a benzene ring.

eg: Chlorination



Chlorobenzene

Mechamsm

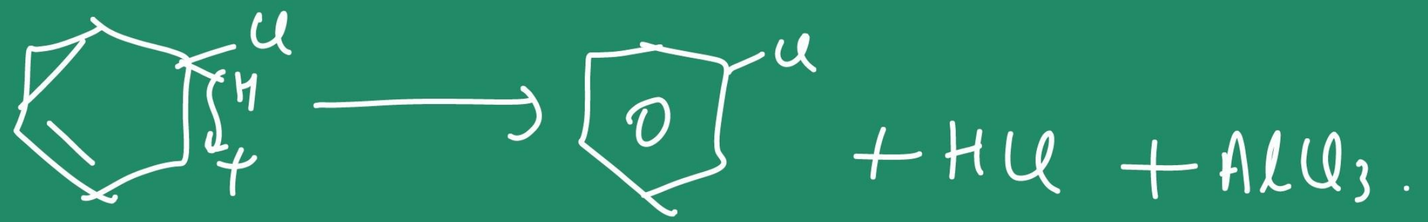
. It follows Et radical Mechanism.
. It complete in 3- steps.

1. Formation of Radicals:

$$Cl-Cl \xrightarrow{AlCl_3} Cl^{\bullet} + Cl^{\bullet} \quad \text{(Formation of Radical)}$$

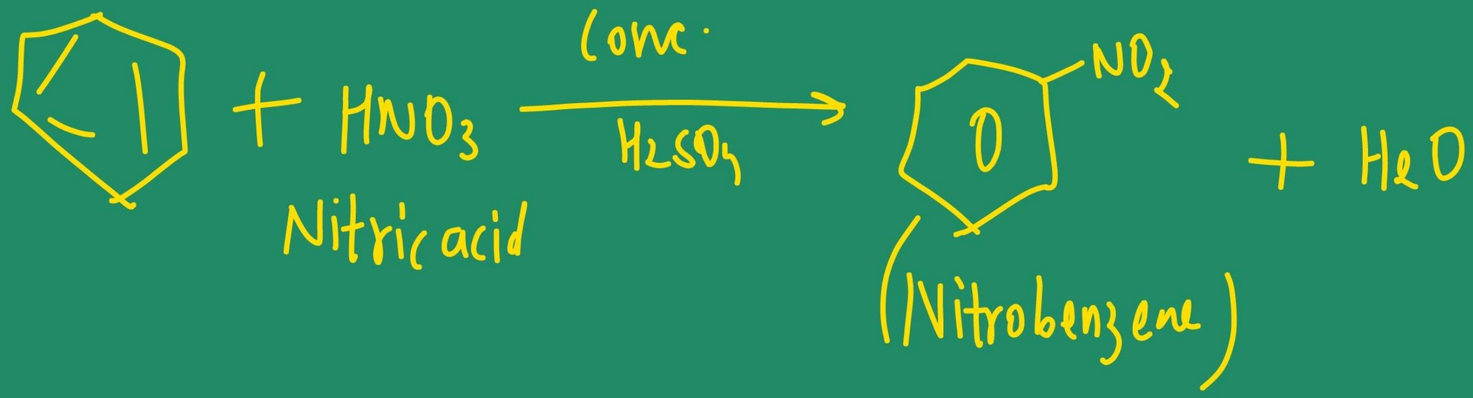
2. Attack on Benzene ring

3. loss of Proton :



Nitration

In this reaction, Benzene ring reacts with conc. HNO_3 in the presence of an acid, conc. H_2SO_4 for the formation of Nitrobenzene.



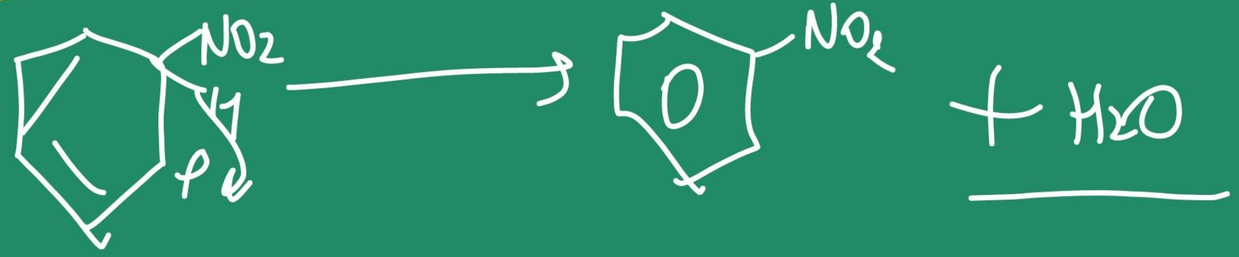
Mechanism

1. Formation of E^+:

$$HNO_3 + H_2SO_4 \longrightarrow HSO_4^- + \underbrace{NO_2^+}_{E^+} + H_2O$$

2. Attack of E^+ on Benzene ring:-

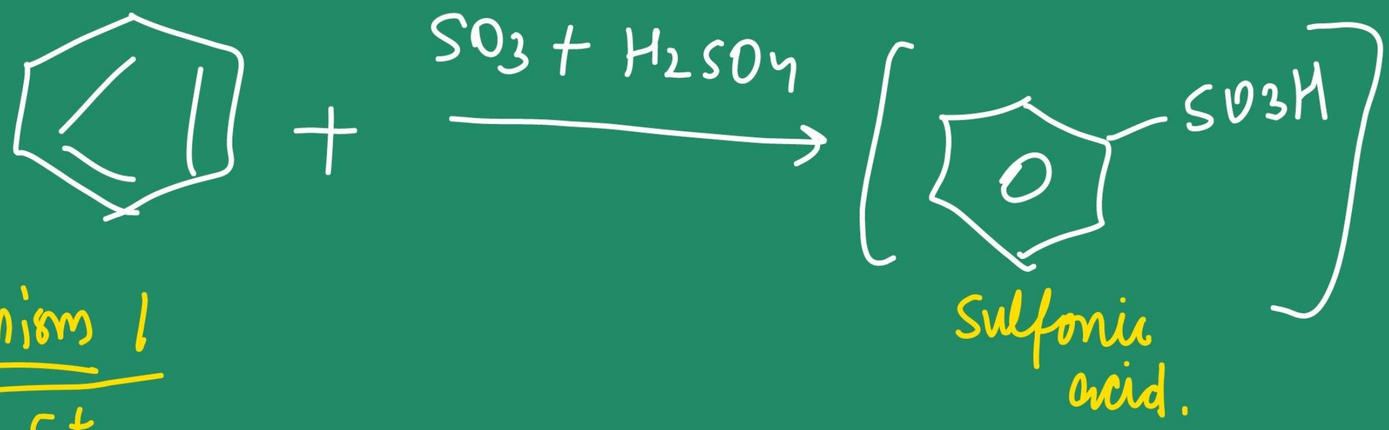
3. Ion of Proton



$+ H_2O$

Sulfonation

Benzene reacts with fuming H_2SO_4 to produce the final product.



Sulfonic acid.

Mechanism :

1. E^+
2. attack on benzene ring
3. loss of H^+

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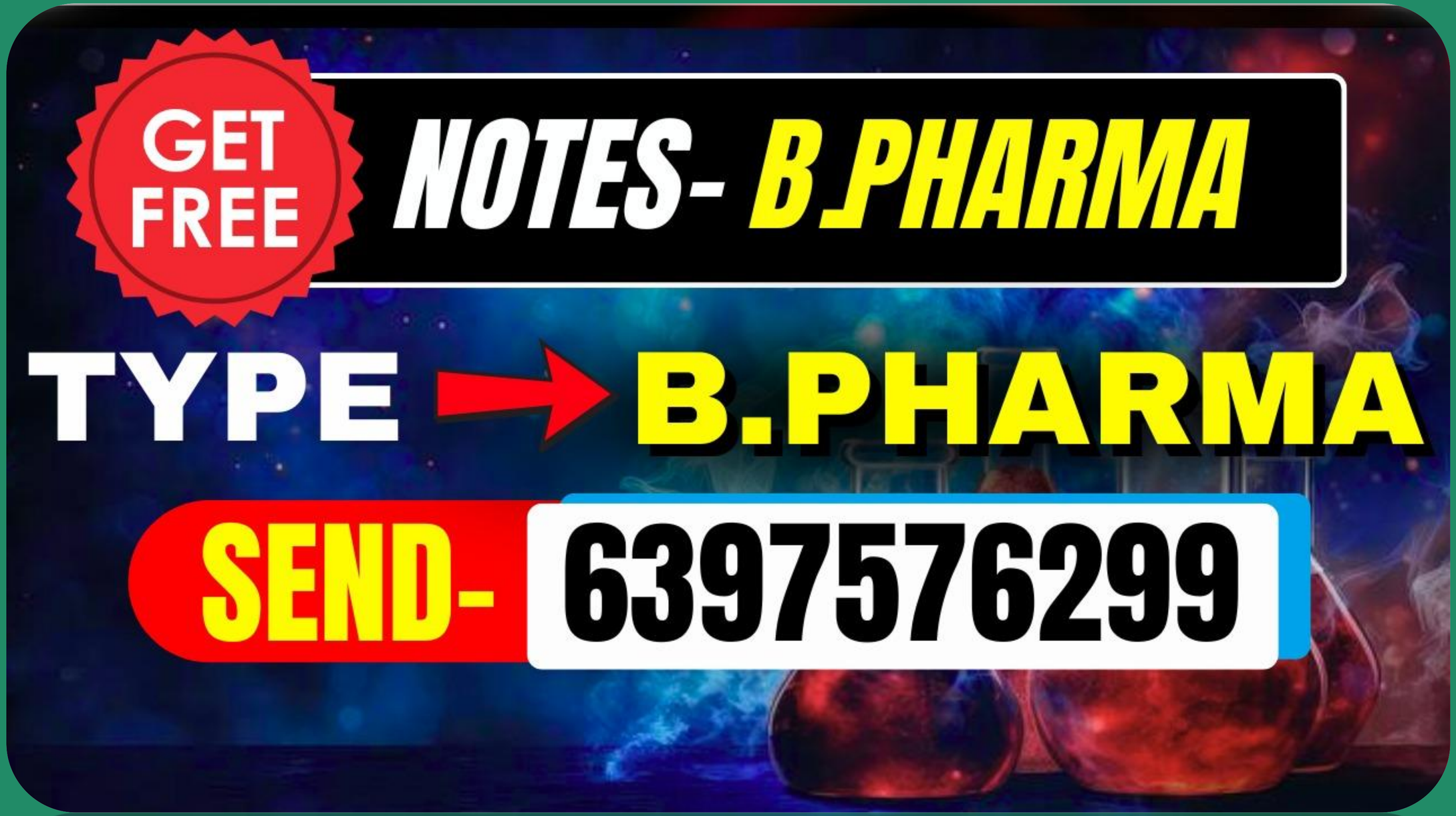
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PHARMACEUTICAL ORGANIC CHEMISTRY II

BENZENE & IT'S DERIVATIVES

SUBSTITUENTS
EFFECTS OF SUBSTITUENTS ON REACTIVITY

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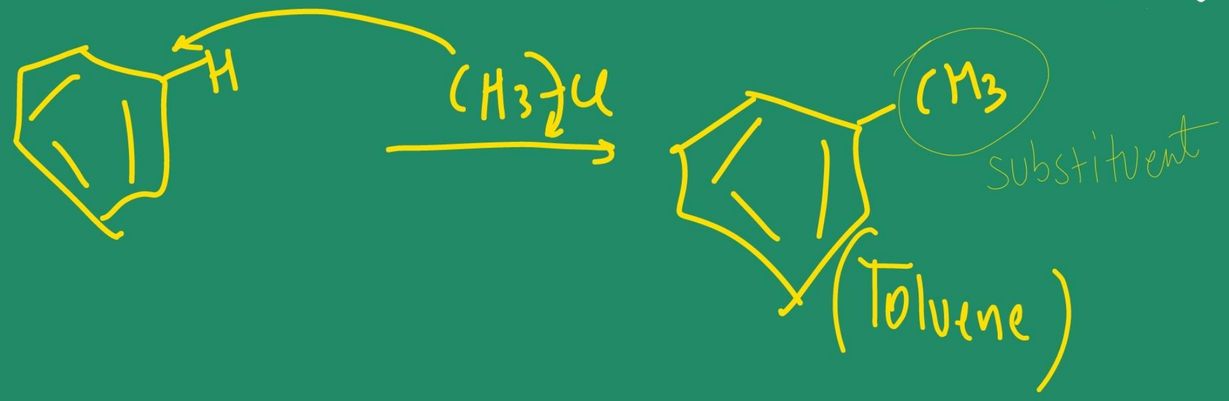
TOPIC: Effect of substituents on reactivity & orientation of Benzene

Effect of substituents

Substituents: Substituents are the atoms / groups that replace any atom in benzene.

This Phenomena is called as substitution.



Since, the Benzene ring is highly reactive due to delocalization of π-bonds.

When substituent attaches with benzene ring, its reactivity changes.
depends on the nature of substituent

In General, we have 2 type of groups;

1→ Ring Activating group

2→ Ring De-activating group.

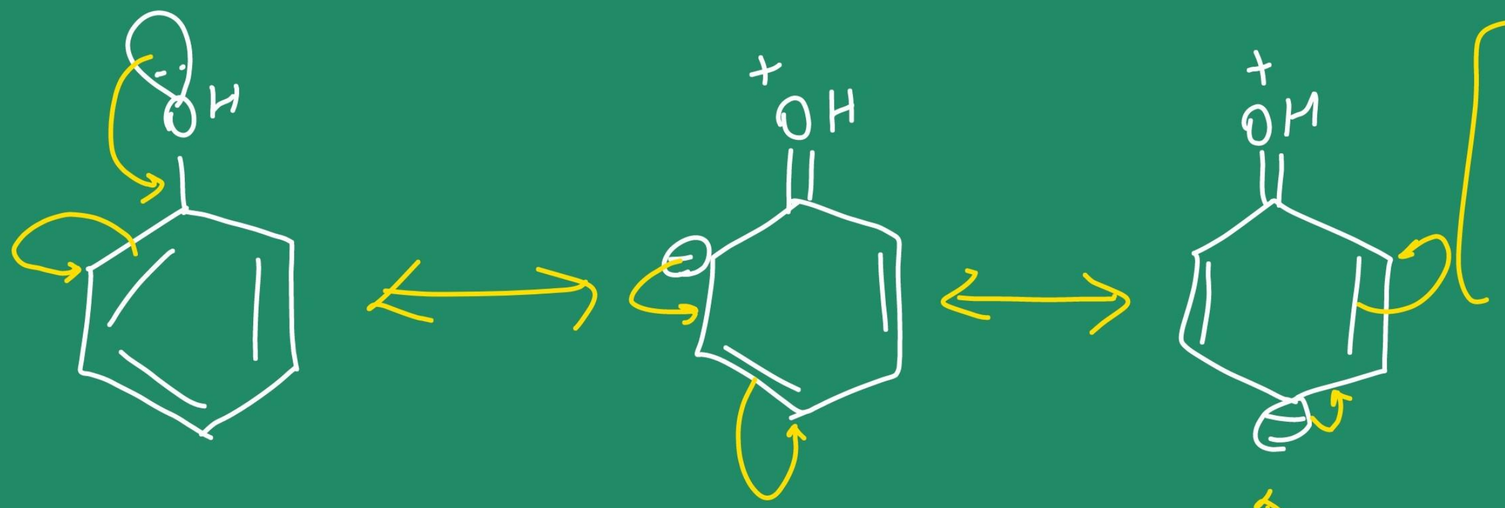
Ring Activating Groups:

These groups, activate the benzene ring by donating electrons.

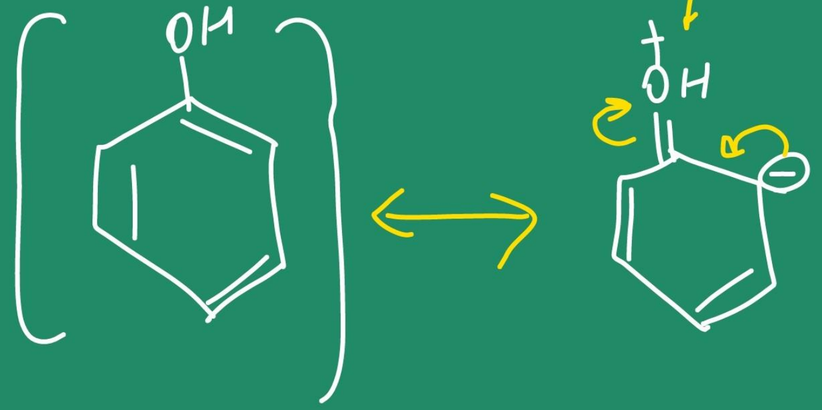
Ring activating groups are also k/a Electron donating groups (E·D·G's) which donate e^- to the ring & activates the ring.

Ring activating (EDG's) increases the e^- density of benzene ring.

eg:- Alkyl groups ($-CH_3$, $-C_2H_5$ etc.), $-\ddot{N}H_2$, Phenyl ($-C_6H_5$) etc.



Charge delocalize → Bond
Bond delocalize → charge

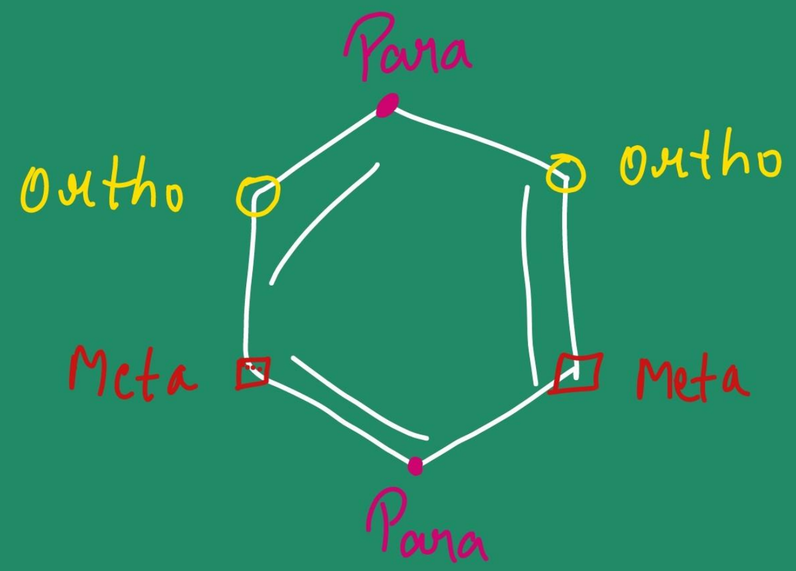


Favours o/p orientation

→ —OH is an E^- donating group.

→ e⁻ density of Benzene ring Increases.

→ This is Ortho / Para directing. E^+ / Nu^- are attacked at o/p Positions.


Para
ortho
ortho
Meta
Meta
Para

Ring Deactivating groups :—

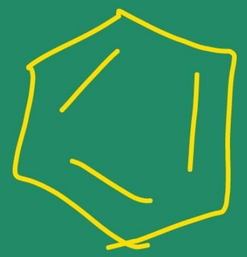
These groups deactivate the benzene ring by withdrawing e⁻ density.

These groups are also known as Electron withdrawing groups (EWG's)

EWG's decreases the e⁻ density from benzene ring & makes it deactivate

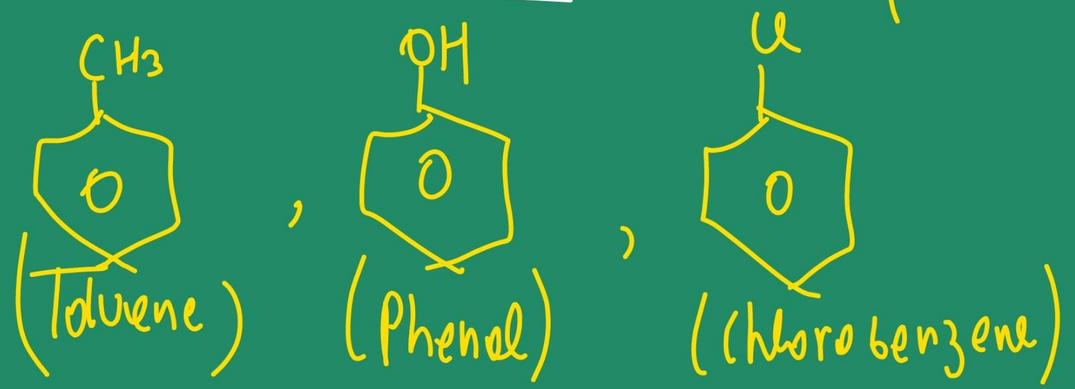
eg :- NO_2, $-CHO$, $-COOH$, $-X$ (F, Cl, Br, I) etc.

Benzene & their Derivatives



Mono derivatives Benzene

(Mono substitution of Benzene)



Orientation Effect

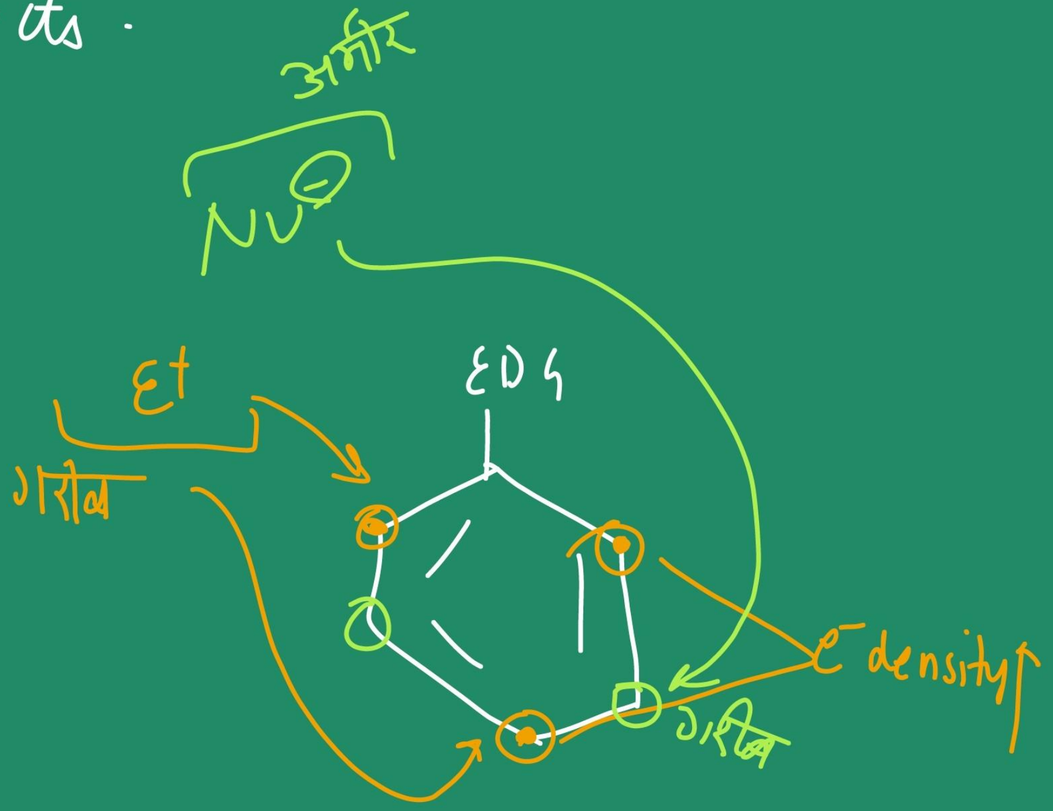
There are two types of Orientation Effects.

① O/P. Orientation :

If EDG is there, any Et will attack on O/P Positions.

But NU⁻ would rather attack at m-Position.

NU⁻ → Meta directing.



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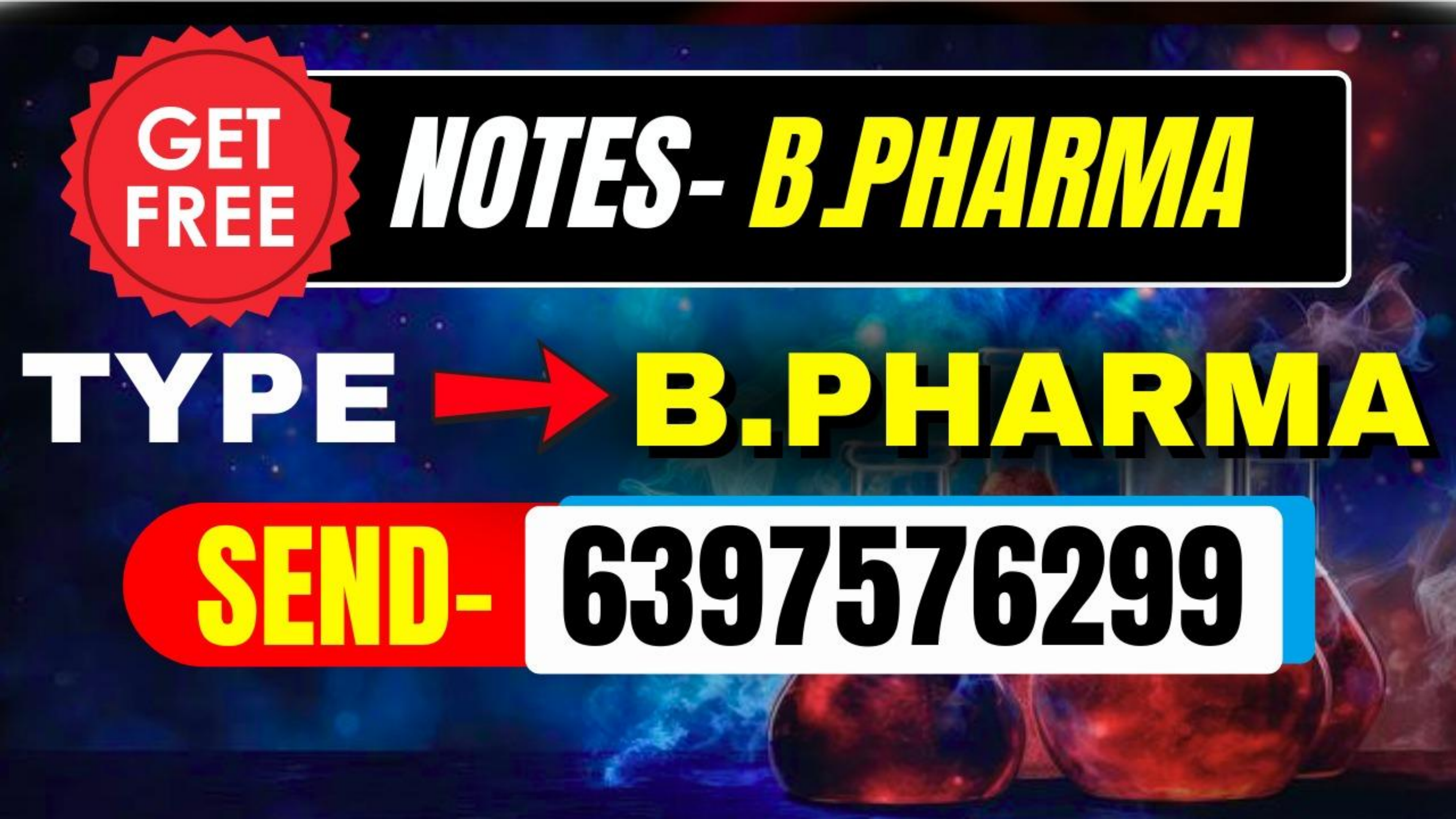
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