ORGANIC CHEMISTRY-II

UNIT 1 NOTES

BENZENE AND ITS DERIVATIVES

- EVIDENCES IN DERIVATION OF BENZENE
- ORBITAL PICTURE, RESONANCE
- HUCKLE'S RULE
- REACTIONS OF BENZENE
- EFFECT OF SUBSTITUENTS OF REACTIVITY AND ORIENTATION OF BENZENE
- STRUCTURE AND USES OF
  - DDT
  - SACHHARIN
  - BHC
  - CHLORAMINE

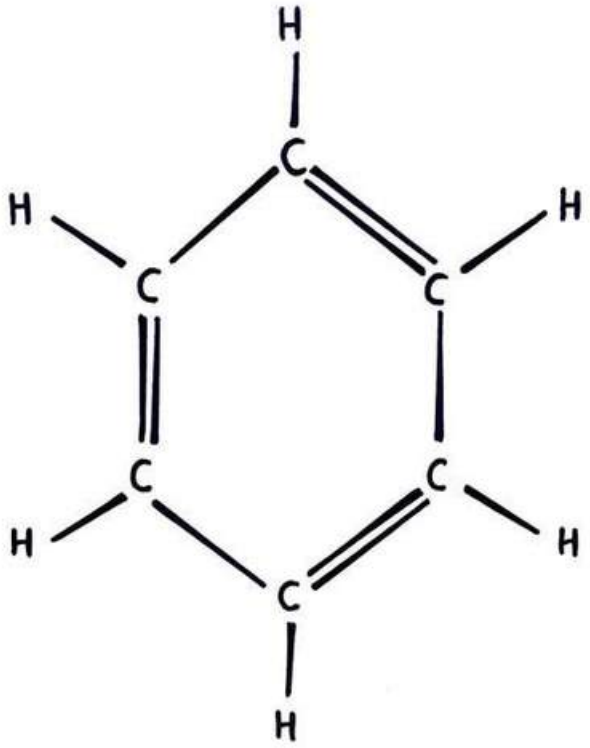
IMPERFECT PHARMACY

BENZENE

- Benzene is an organic, colourless chemical compound.
- It is a highly flammable liquid with a sweet smell & high melting point.
- The chemical formula of benzene is C_6H_6, so it contains 6 carbon & 6 hydrogens, also known as Hydrocarbon.
- It has a boiling point of 80°C & is lighter than water.
- Natural sources of benzene includes volcanoes & forest fires.
- It is also a natural part of crude oils.
- Benzene and all those compounds which resembles benzene in their chemical behaviour are known as **Aromatic Compounds**.
- Benzene is a highly toxic carcinogenic chemical.

STRUCTURE OF BENZENE

- The molecular formula of benzene (C_6H_6) shows a high degree of unsaturation.
- **Sir August kekule** was the first scientist who introduced the chemical structure of benzene as a 6 membered ring structure.
- He also proposed the presence of 3 alternate double bonds in benzene ring
- According to Sir kekule the 3 alternate double bonds in benzene also changes their position rapidly to satisfy tetravalency of carbon.



or

KEKULE STRUCTURE OF BENZENE

- Although kekule structure of benzene satisfies the structural features of benzene and also explain the equivalent nature of hydrogen but yet this structure fails to explain the unusual behaviour of benzene.
- Since this structure of benzene is a great discovery & significant approch by Sir kekule, hence it is still in use.
- Following are the given characteristics that are not explained by kekule's model.

CHEMICAL REACTION : Benzene undergoes substitution reaction rather than addition reaction like other unsaturated compounds.

C-C Bond Length : According to Sir kekule, two kinds of bond present in benzene, single & double bond

- C-C : Bond length (1.54 Å)
- C=C : Bond Length (1.34 Å)
- But experimentally it is seen that bond length between all carbon atoms is 1.39 Å.

STABILITY : kekule's structure couldnot explain the stability of benzene towards oxidizing agents. (All unsaturated compounds undergoes oxidation but benzene does not)

EVIDENCES IN THE STRUCTURE OF BENZENE

There are many analytical, synthetic & other evidences are given in the derivation of structure of benzene as follows :-

Analytical Evidence

- From its elemental composition and molecular weight determination it is found that benzene contains 6-C & 6-H atoms
- Benzene has molecular formula C_6H_6 compared to Hexane C_6H_{14} that confirms benzene as a highly unsaturated compound compare to hexane (C_6H_6).
- So it was concluded that benzene contains =/≡ bonds in its structure.

Synthetic Evidence

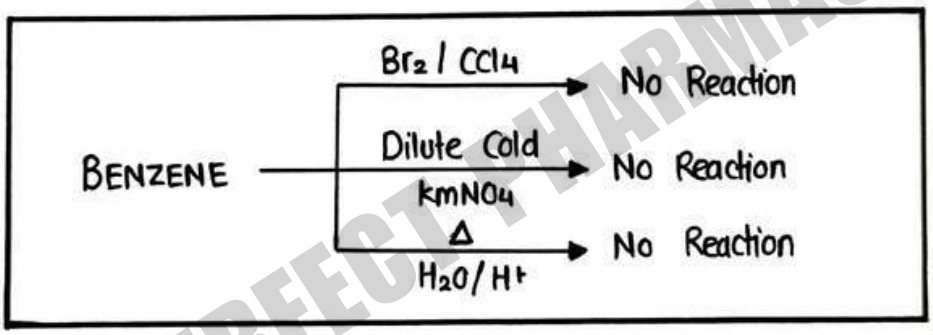
- Since, it was confirmed that benzene has unsaturation, so it could be constructed either as straight chain or in a ring.
- The possible straight chain structure for benzene could have been :

① $CH_2 = CH - C \equiv C - CH = CH_2$

② $CH_3 - C \equiv C - C \equiv C - CH_3$

③ $CH \equiv C - CH_2 - CH_2 - C \equiv CH$

- But all the above structures were ruled out because benzene doesn't give the usual reactions of Alkenes, Alkynes.
- So it was concluded that benzene is a highly unsaturated closed ring structure.

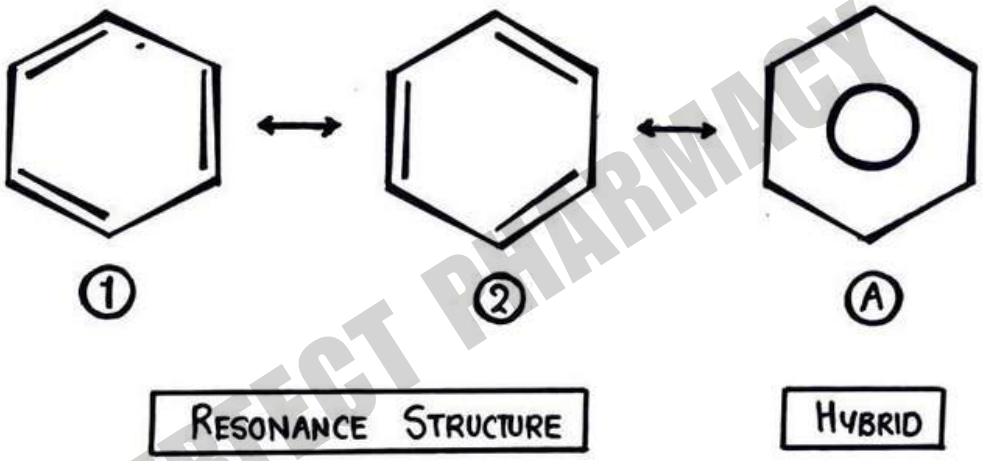


Other Evidences

- Benzene reacts with bromine in the presence of $AlCl_3$ (catalyst) to form Bromobenzene.
- Now only one (mono) bromobenzene is obtained that shows all 6 hydrogen atom in benzene were identical.
- This becomes possible only, if benzene has a cyclic structure of six C atom & each carbon atom is attached with one H atom.

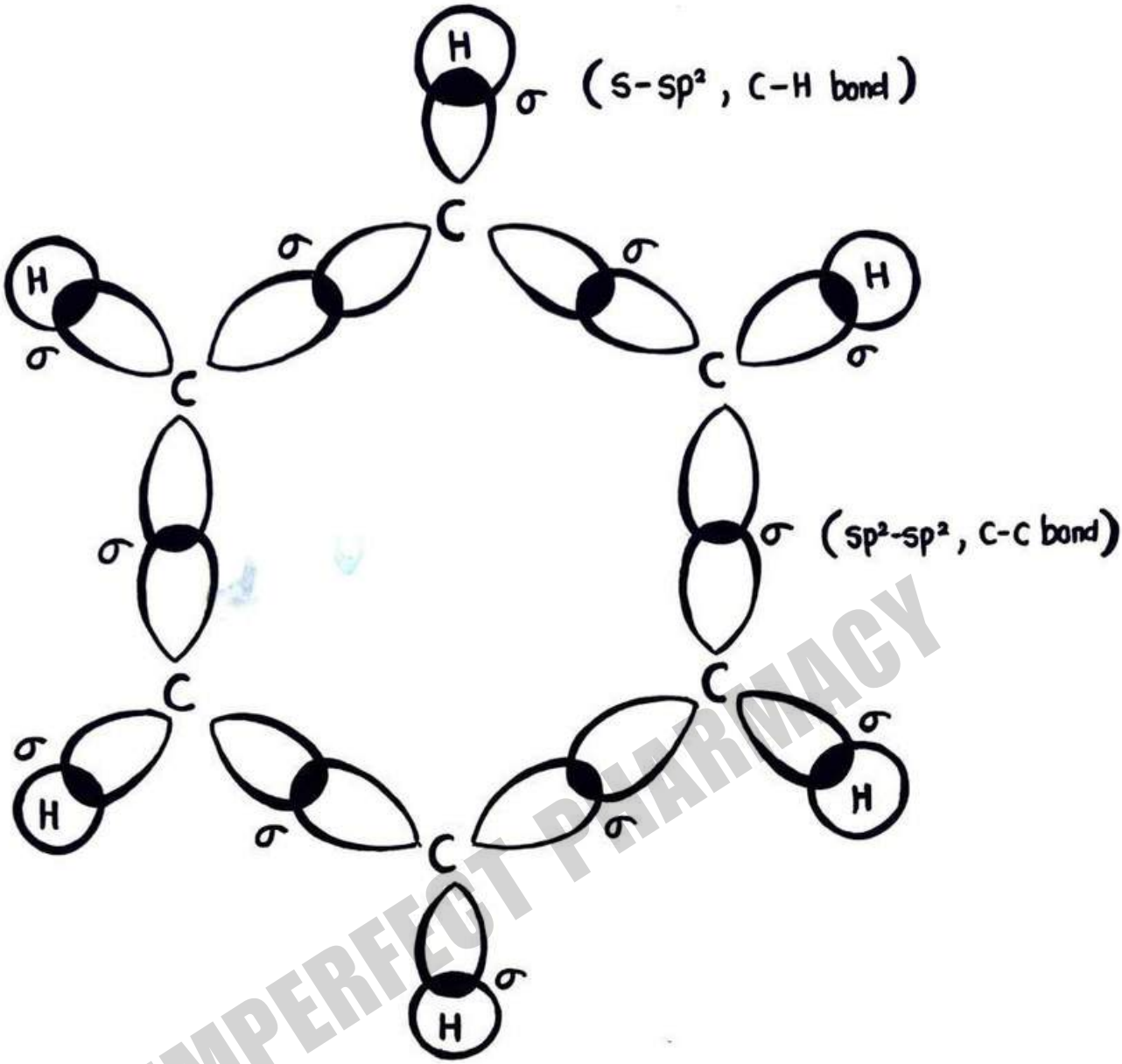
RESONANCE STRUCTURE OF BENZENE

- To explain all the limitations of kekule's structure, it has been proposed that benzene is a resonance hybrid of two kekule structure. (I & II)
- Resonance Hybrid (A) is a very stable structure & this is why benzene undergoes substitution reaction very easily rather than addition reaction.
- Resonance Structure of Benzene explain all the facts like unusual stability & equality of C-C bond length.



MOLECULAR ORBITAL STRUCTURE OF BENZENE

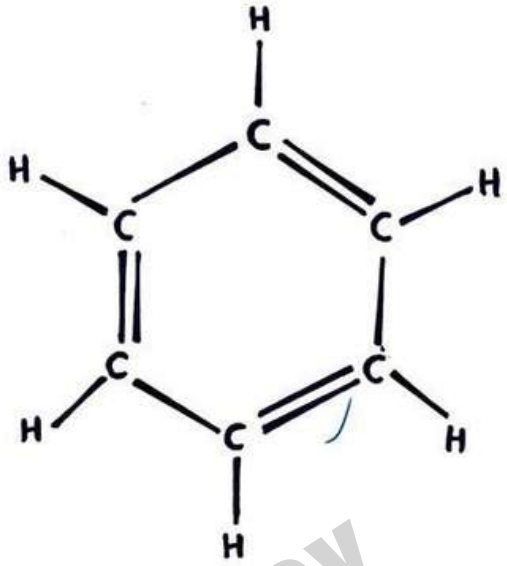
- Molecular orbital theory states that all carbon atoms of benzene are sp^2 hybridized.
- Each carbon atom forms two C-C sigma bonds & one C-H sigma bond
- Carbon atoms are still left with unhybridized P-orbitals that overlaps to form π bonds.



Molecular Orbital Picture Of Benzene

CHEMICAL STRUCTURE OF BENZENE

- All the sigma bonds in benzene lies in the same plane.
- All bond angle = 120°
- All C-C bond length = 1.40 Å
- All C-H bond length = 1.09 Å
- Chemical Formula = C_6H_6.
- Molecular Weight = 78 g/mol.



AROMATIC CHARACTER (HUCKLE'S RULE)

- Benzene & compounds that resembles benzene in their chemical behaviour are known as Aromatic Compounds.
- They undergoes substitution reaction rather than addition reaction.
- Aromaticity is basically decided by Huckle's Rule.

HUCKLE'S RULE

In 1931, a German scientist Huckle gave certain rules for defining aromaticity of organic compounds as follows:

- Compound should be Cyclic
- There should be a conjugation (delocalised electrons)
- Compound should be Planer
- Total number of π electrons should be $(4n+2)$, where $n = 0, 1, 2....$

CHEMICAL REACTIONS OF BENZENE

- Most commonly benzene undergoes electrophilic substitution reaction (Electrophilic Aromatic Substitution Reaction).
- In these reactions hydrogen atom of the aromatic ring is replaced by an electrophile.

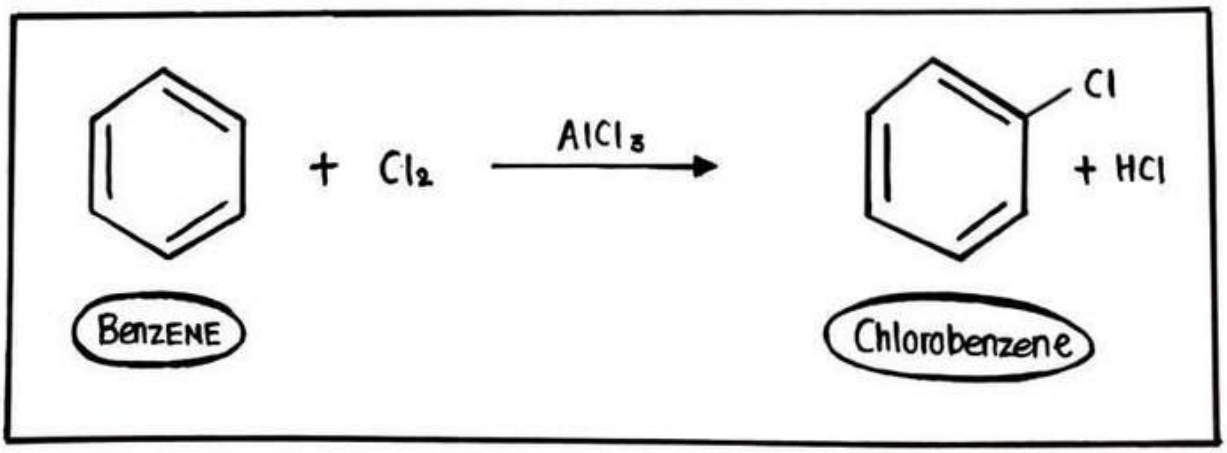
Types Of Electrophilic Aromatic Substitution Reaction

Benzene mainly undergoes 5 types of Electrophilic Aromatic Substitution Reaction.

① Halogenation
② Nitration
③ Sulfonation
④ Friedel Craft's Alkylation
⑤ Friedel Craft's Acylation

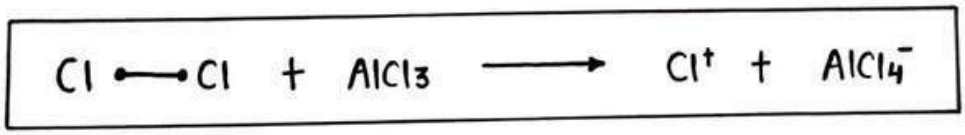
① HALOGENATION OF BENZENE

In Halogenation, benzene reacts with Halogens (Br_2, Cl_2, I_2) in the presence of Lewis acid catalyst ($AlCl_3$) to give Bromobenzene or Chlorobenzene or Iodobenzene.

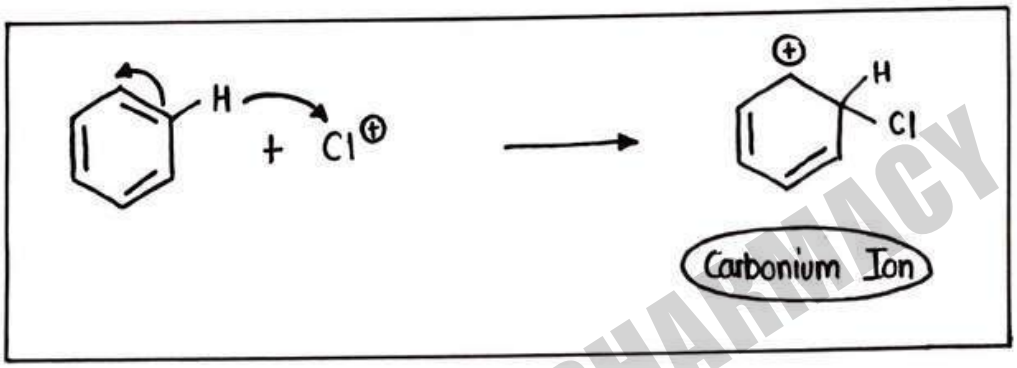


MECHANISM OF HALOGENATION (CHLORINATION)

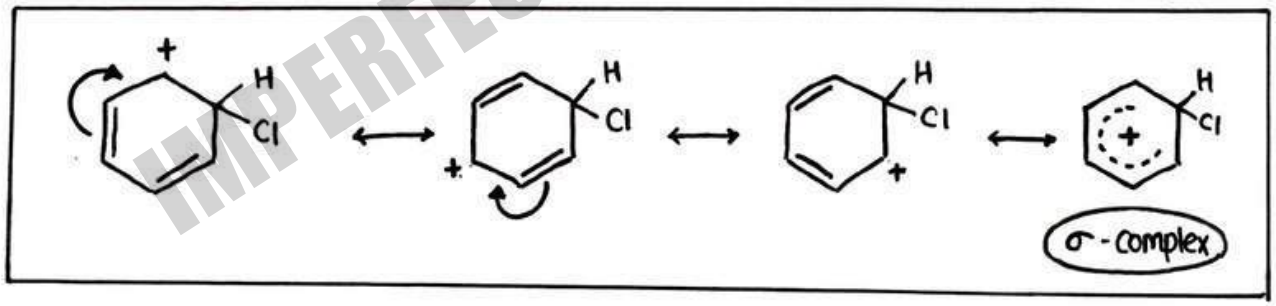
STEP - I : Formation of Electrophile (Chloronium Ion)



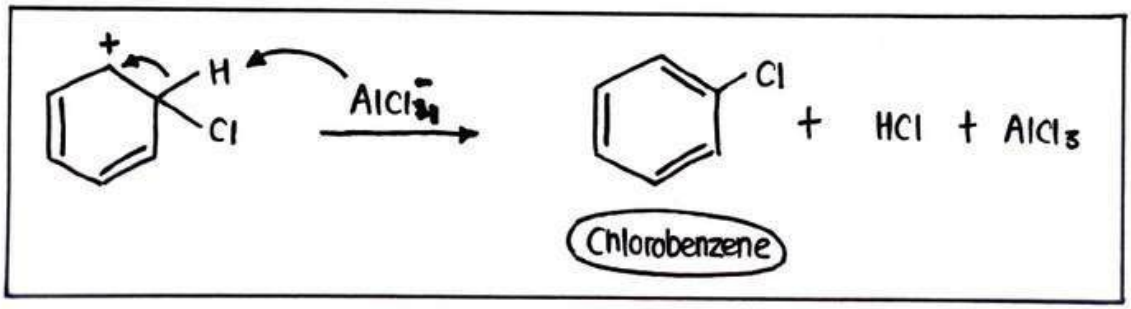
STEP - II Attack of Electrophile on Benzene to form Carbonium Ion



Now the above carbonium ion is resonance stabilized & forms σ complex.

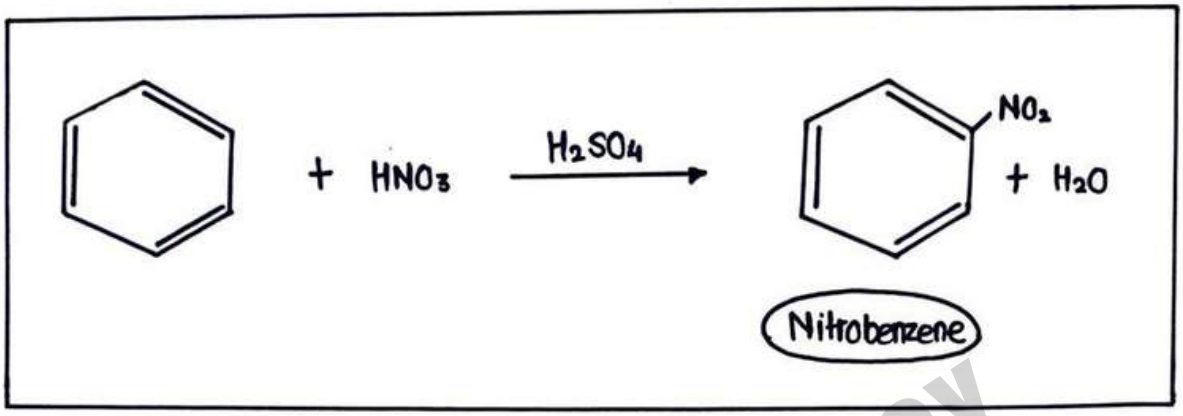


STEP - III : Loss of proton & formation of product (Chlorobenzene)



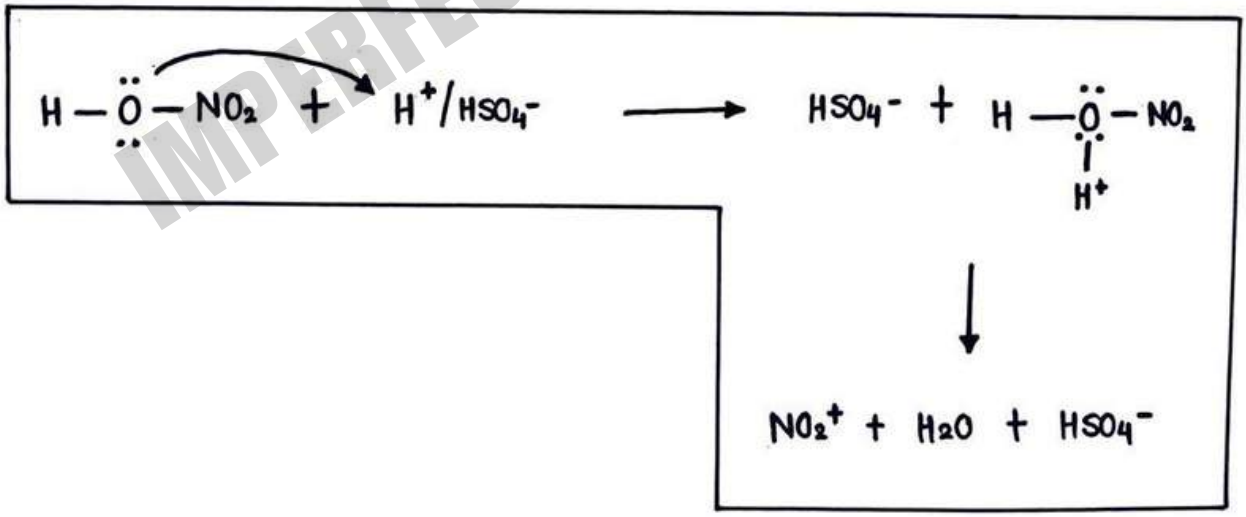
② NITRATION

In Nitration , Benzene reacts with concentrated HNO_3 in the presence of concentrated H_2SO_4 to form Nitrobenzene.

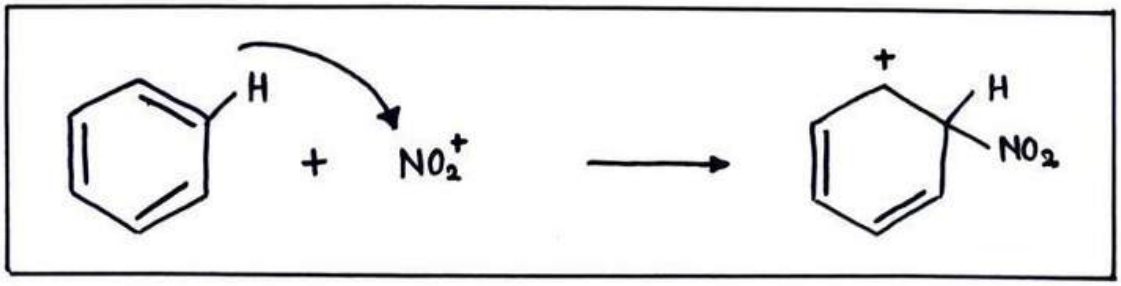


MECHANISM

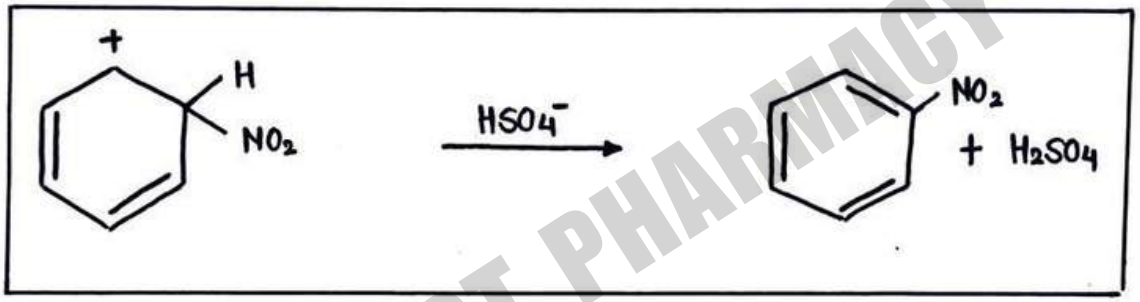
STEP - I : Formation of Electrophile (Nitronium Ion)



STEP - II : Attack of Electrophile to form carbocation intermediate

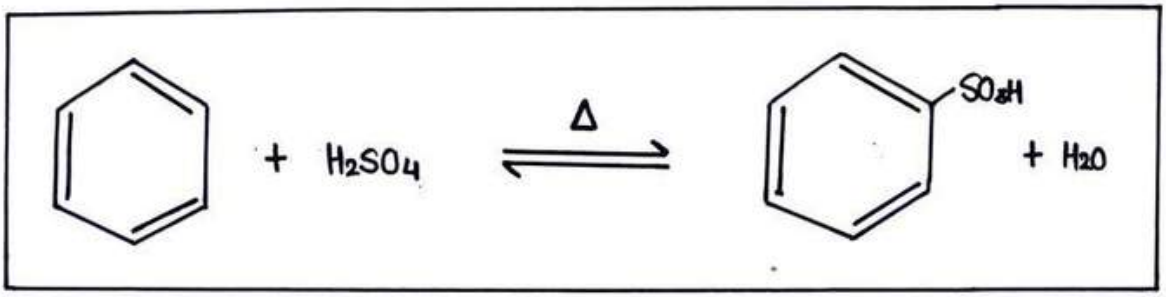


STEP - III : Loss of Proton leads to the formation of Nitrobenzene



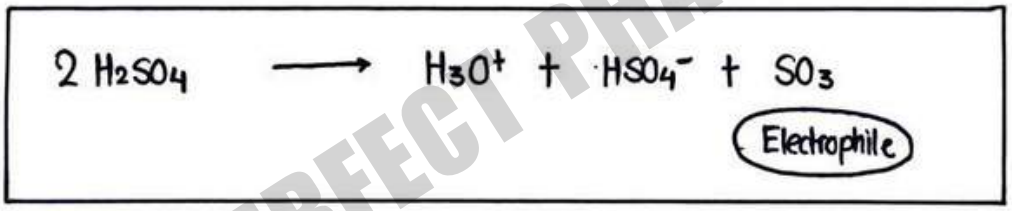
③ SULFONATION

In Sulfonation , Benzene reacts with concentrated or fuming sulphuric acid to form Benzene Sulphonic Acid

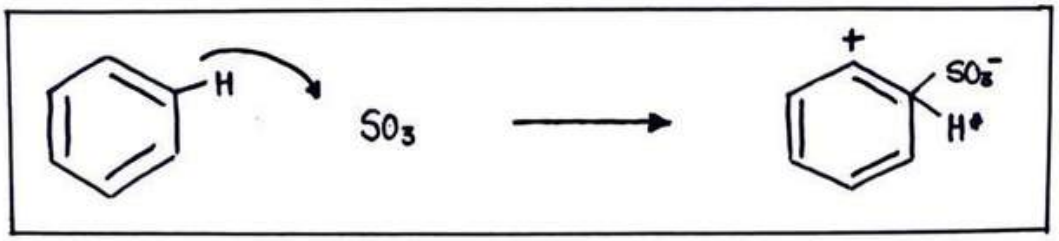


Mechanism

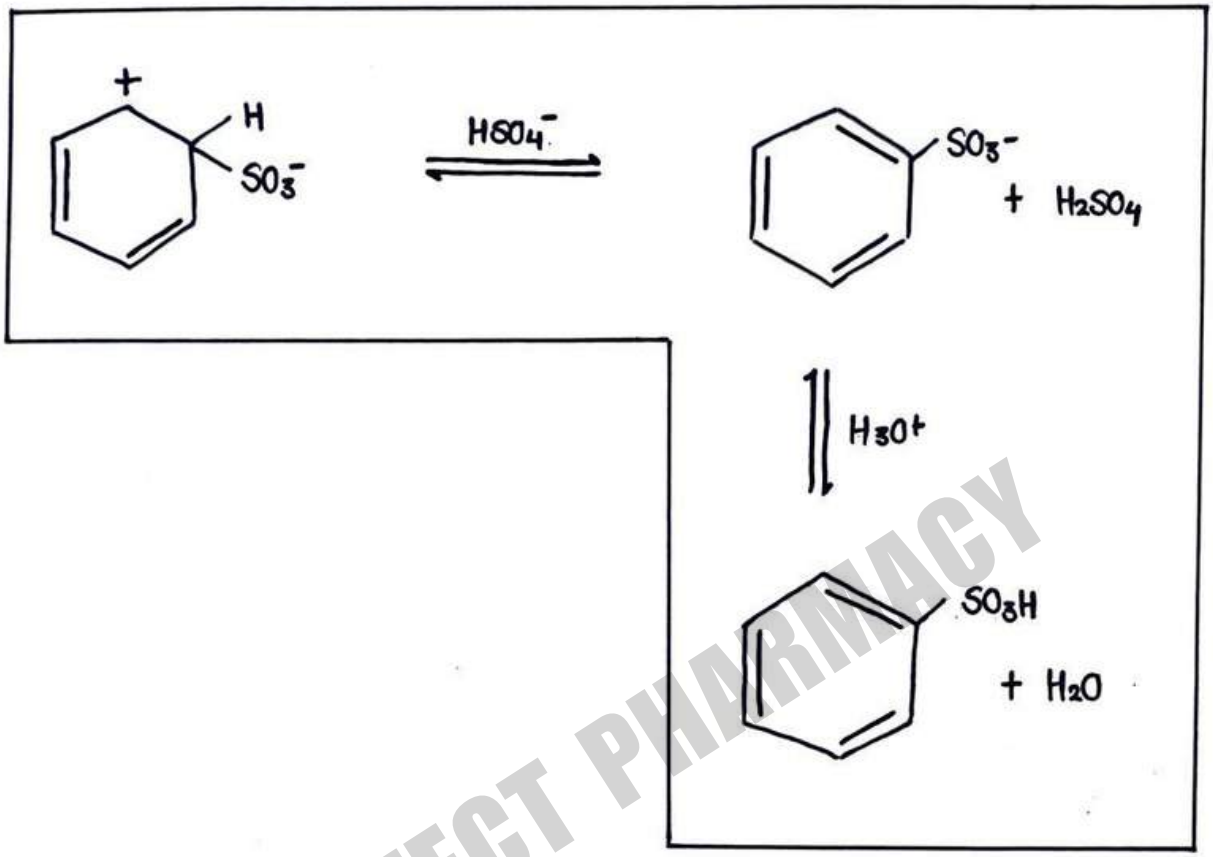
STEP-I : Formation of Electrophile (Sulpher Trioxide / SO_3)



STEP-II : Attack of Electrophile on Benzene to form Carbocation

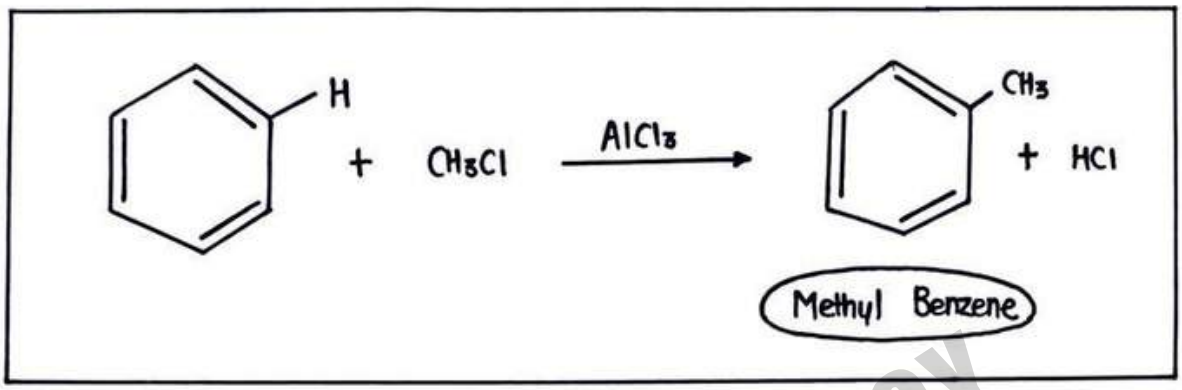


STEP-III : Loss of Proton leads to formation of Benzene Sulphonic Acid.



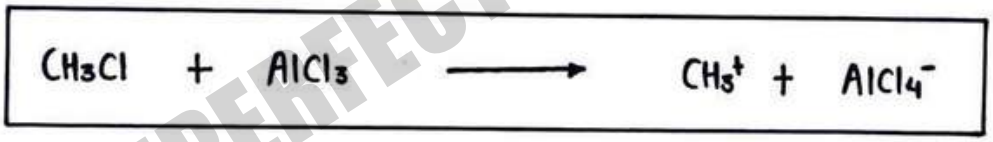
④ FRIEDEL CRAFTS ALKYLATION

In Friedel - Crafts Alkylation (named after a French chemist, Charles Friedel & an american chemist James Crafts) Benzene reacts with Alkyl Group to form Alkyl Benzene.

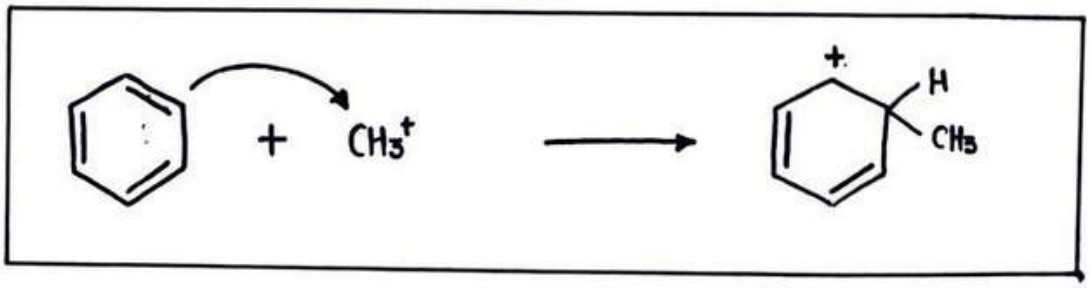


MECHANISM

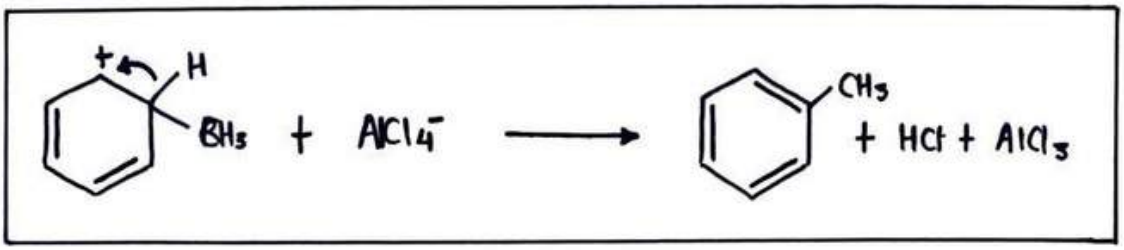
STEP-I : Formation of Electrophile



STEP-II : Attack of Electrophile to form Carbocation Intermediate

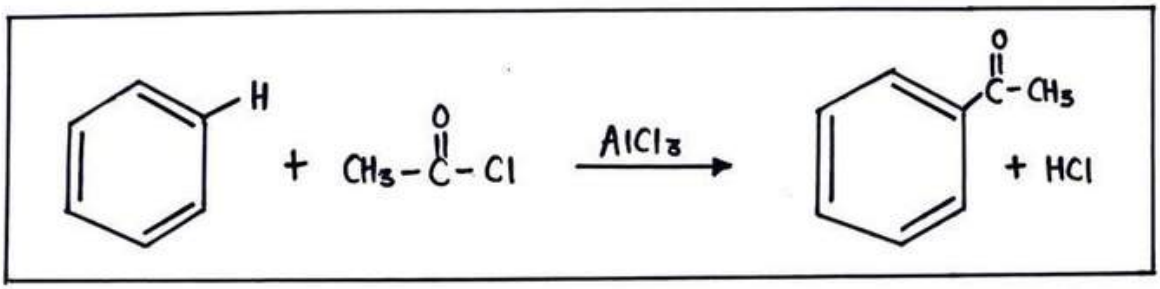


STEP-III : Loss of Proton leads to the formation of Methyl Benzene (Product).



⑤ FRIEDEL - CRAFTS ACYLATION

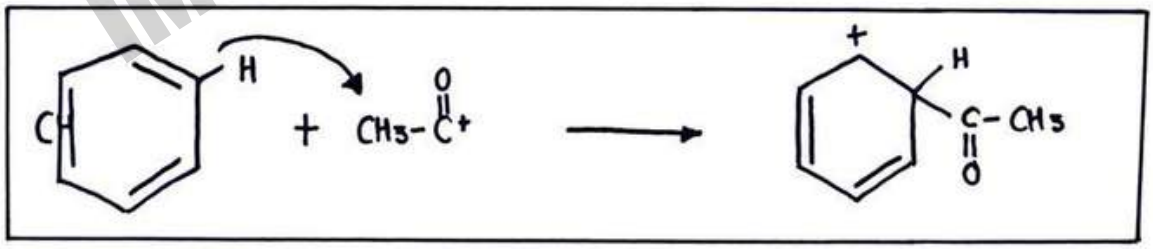
In Friedel crafts Acylation benzene reacts with Acyl Group to form Aromatic ketones (Acetophenone) in the presence of $AlCl_3$.



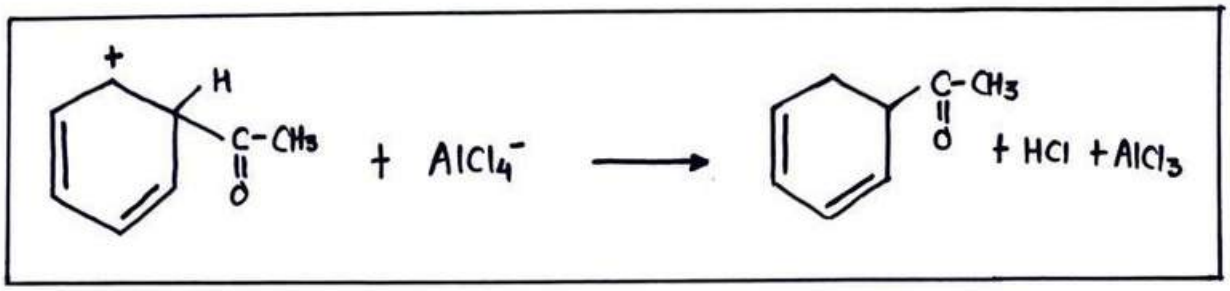
MECHANISM

STEP - I : Formation of Electrophile (Acylium Ion)

STEP - II : Attack of Electrophile to form Carbocation Intermediate

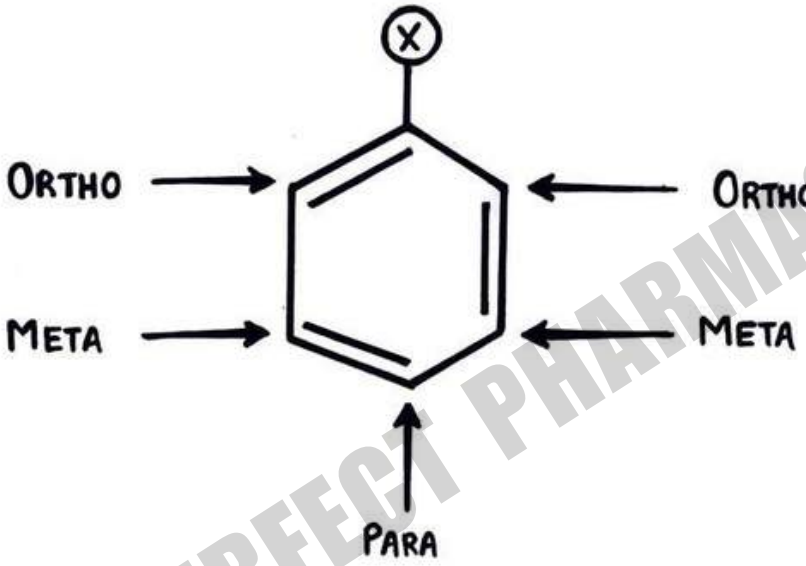


STEP -III : Loss of Proton leads to the formation of Acetophenone (Product)



EFFECT OF SUBSTITUENTS

- Benzene ring contains 6 Hydrogens and all 6 hydrogen of benzene are identical in nature.
- Now when 1 Hydrogen of benzene is substituted by a group then it becomes monosubstituted Benzene.
- Now this Monosubstituted benzene contains 3 positions :



- Now, here in the above structure X can be any substituent.
- Also the nature of X (substituent) decides the reactivity of benzene towards other electrophiles & also their positions.

TYPES OF SUBSTITUENTS / GROUPS

There are mainly two types of Groups :

① Ring Activating Groups
② Ring Deactivating Groups

① Ring Activating Groups

- Groups that increases the elec reactivity of benzene towards Electrophilic Substitution Reaction are known as Ring Activating Groups
- These groups increases the e- density on benzene ring.
- They are also known as Ortho- Para Directing Groups
- These Groups can be further classified into 3 types :

① Strongly Activating : $-\ddot{N}H_2$, $-NR_2$, $-OH$ etc

② Moderately Activating : $-NH-\overset{\delta}{C}-CH_3$, $-OR$ etc

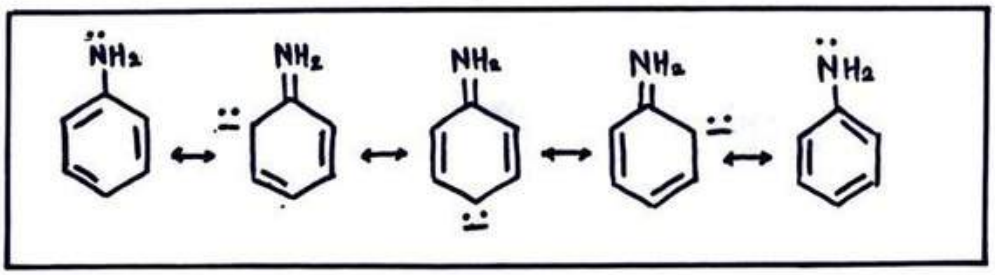
③ Weakly Activating : $-CH_3$, $-C_6H_5$ etc.

Effect On Reactivity

- Since Ring Activating Groups have the tendency to donate e-, hence they increases e- density on benzene ring.
- Now due to this increased e-, benzene ring becomes more reactive towards electrophilic substitution reaction.

Effect On Orientation

- Ring Activating Groups guide the second substituents towards Ortho & Para Positions.
- Given below is the mechanism of Ortho & Para directions.



② RING DEACTIVATING GROUPS

- Groups that decreases the reactivity of benzene towards Electrophilic Substitution Reaction are known as Ring Deactivating Groups.
- These groups decreases the e- density on benzene ring.
- They are also known as **Meta directing Groups**.
- They can be further divided into 3 types :

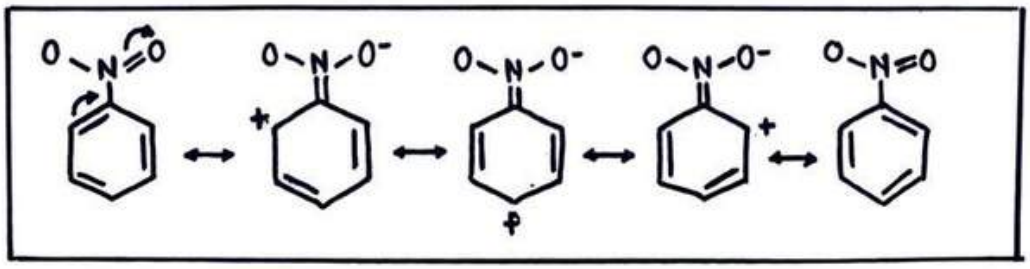
① Strongly DeActivating : $-NO_2$, $-C\equiv N$, SO_3H etc.
② Moderately DeActivating : COOH , $COCH_3$ etc.
③ Weakly DeActivating : Halogens (Br, Cl , F)

Effect On Reactivity

- Since Ring Deactivating Groups have the tendency to accept / withdraw electrons , hence they decreases e- density on benzene ring .
- Now due to this , benzene ring becomes less reactive towards electrophilic substitution reaction.

Effect On Orientation

- Ring Deactivating Groups guide the second substituents towards Meta Position.
- Here is the mechanism of Meta direction.

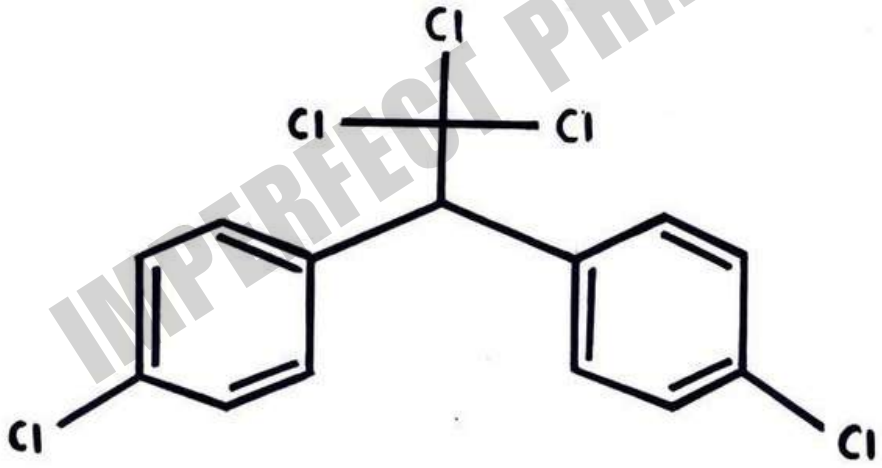


BENZENE DERIVATIVES

- When Hydrogen atoms of benzene are replaced by new groups then, the new structures are known as **Benzene Derivatives.**
- Here, we have to study about structure and uses of following 4 benzene derivatives.

① DDT
② Saccharin
③ BHC
④ Chloromine - T

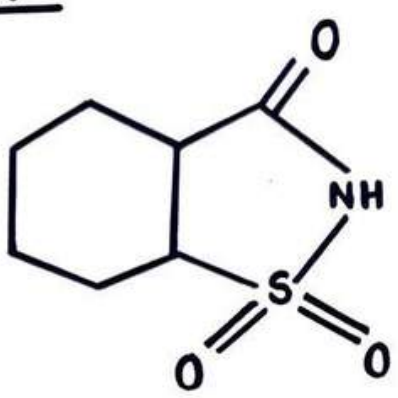
DDT (DICHBORO DIPHENYL TRICHLORO ETHANE)



USES

- It is a highly toxic contact poison for wide variety of insects and works by disorganizing their nervous system.
- It is applied as dusting powder or its aqueous solution is sprayed on the target site

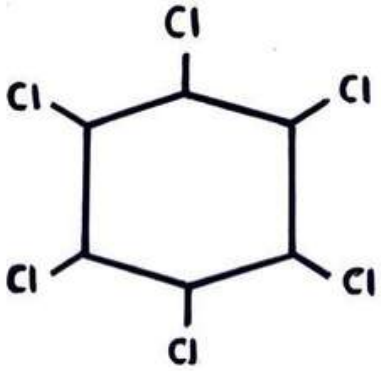
SACCHARIN



USES

- Saccharin is used as an artificial sweetening agent.
- Saccharin provides products with increased stability, improved taste & lower production cost.
- It is also added in various vitamin supplements & medicines.
- Its soluble salt is known as Saccharin Sodium.

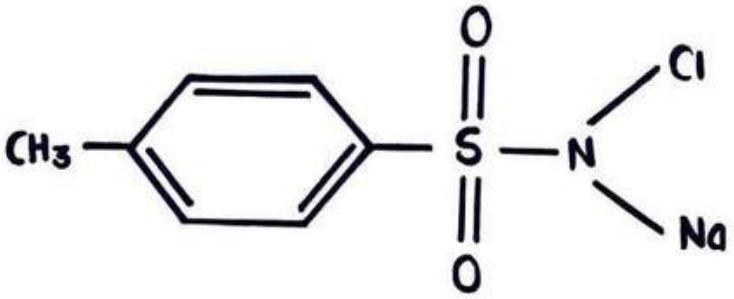
BHC (BENZENE HEXACHRORIDE)



USES

- It is used as insecticides in crops farming.
- It is also used in various pharmaceuticals.

CHLORAMINE - T



USES

- It is mainly used as disinfectant
- It is also used in treatment of burns & wounds.
- It is used as an Oral Mouthwash.

THANK YOU

FOR CHOOSING IMPERFECT PHARMACY AS YOUR STUDY PARTNER

IMPERFECT PHARMACY

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