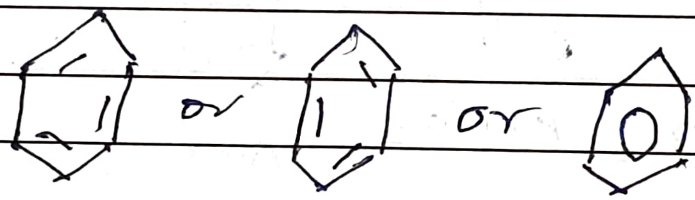
1

BENZENE

Benzene is an aromatic compound having molecular formulae C_6H_6. It contains six carbon atoms, 6-hydrogen atoms and three conjugated double bonds. Aromatic compounds having one or more benzene rings in their molecules are called benzenoid compounds or benzenoids

for example benzene, toluene, xylene, chlorobenzene phenol

Basic structure of benzene is

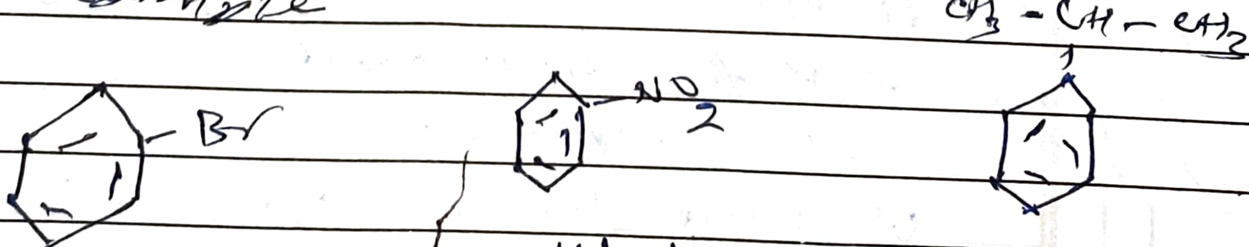


Nomenclature of benzene derivatives.

① For Monosubstituted benzene derivatives

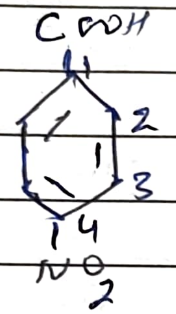
(a) Name of monosubstituted benzene derivatives is obtained by placing prefix (name of substituent) to the word benzene

for example

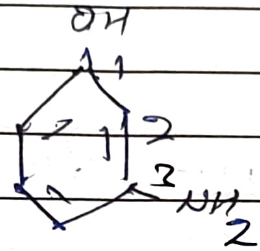


Bromobenzene | Nitrobenzene | Isopropyl benzene

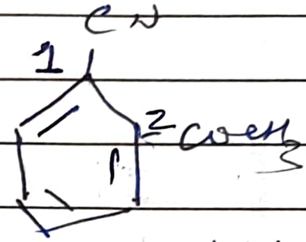
(b) Derivatives having different groups are named as derivatives of the compound with the main functional group at position 1.



4-nitrobenzoic acid

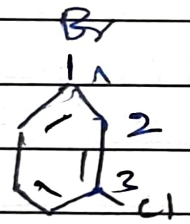


3-amino phenol

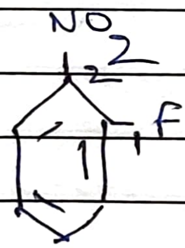


2-acetyl benzonitrile

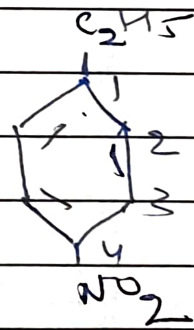
(c) If both the functional group present are substituent functional groups, then they are arranged in alphabetical order



1-Bromo, 3-chlorobenzene



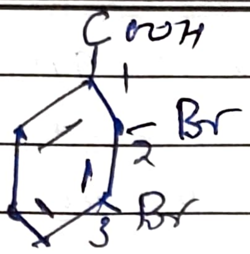
1-fluoro 2-nitrobenzene



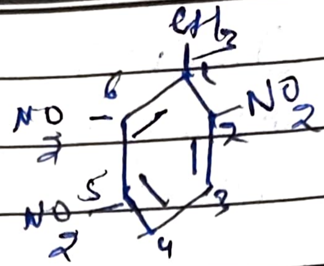
1- ethyl - 4 nitro benzene

(3) For poly substituted benzene derivatives

(a) If any substituent gives special name to the ring then numbering of the ring begins at that substituent and the compound is named as its derivatives

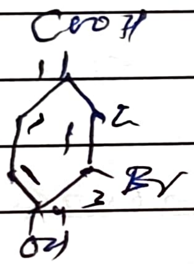


2.3 dibromo benzoic acid

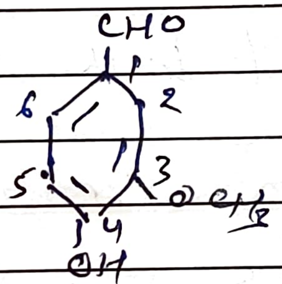


2,5,6-trinitro toluene

(b) If three different functional groups are present, name is done as the derivative of the compound with the principal functional group at position 1.

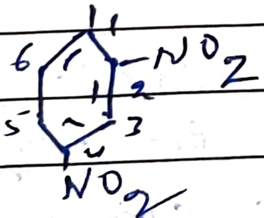


3-bromo-4-hydroxy benzoic acid



4-hydroxy-3 methoxy benzaldehyde

(c) Various groups are arranged in alphabetical order with the group named first in the alphabetical order getting the lowest locant.

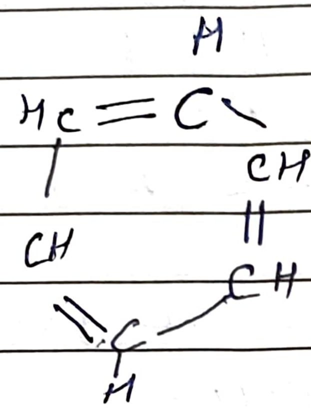


1-chloro, 2.4 dinitro benzene

Roll No......................

STRUCTURE OF BENZENE

Kekule's structure of benzene



The structure of benzene was given by Friedrich August Kekule in 1865.

- acording to him the six carbon atoms of benzene are joined together by alternate single & duble bonds & forms a hexagonal ring. Each carbon is further connected to a hydrogen atom.

But there are three main ~~objective~~ objections to Kekule's structure.

① This structure could not explain the stability of benzene towards oxidizing agents and can not explain this substitution reactions after having three duble bonds.

② According to this structure only one mono substituted and two substituted products exists but in actual only one mono substituted product is known.

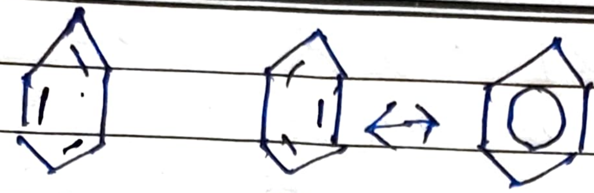
The positions of single and duble bonds are not fixed but they oscillate back and forth which is not explain by Kekule's structure, ③ Kekulae's formulae for benzene contains two kinds of bonds i.e single and duble bonds but X-ray diffractuation shows that benzene is a regular hexagon with an angle of 120° and all the C—C bond length are equal.

So Kekule's structure failed to explain the unusual stability and equality of C-C bond length in benzene.

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 two Kekule's structure (I & II). These two structures are canonical forms of benzene. In actual, the benzene is a resonance hybrid of these two structure (A) It means that any two adjacent carbon atoms of the benzene molecule are neither joined by a pure single bond nor by a pure duble bond. As it the C—C bond lengths are equall i.e 1.39 A and lie in between C=C bond length of 1.34 A° and C-C bond length of 1.54 A.

Roll No........................ Scholar No.........................



I II A

Resonance hybrid is always more stable than its cannonical structures.

Moleculer orbital (MO) structure of benzene

Moleculer orbital theory states that all the carbon atoms of benzene are assumed to be sp2 hybridized. Each 'C' atom forms C-C sigma bond ~~and~~ with the adjacent 'C' atoms and one C-H sigma bond with hydrogen atom. So, overall there are six C-C sigma bonds and six C-H sigma bonds; which lie in one plane and the angle between any two adjacent sigma bond is 120°.

Each carbon atom has an unhybridized p-orbital so, six unhybridized p-orbitals have one electron each which are parallel and perpendicular to the plane of sigma bonded carbon skeleton. So, p-orbitals on adjacent carbon atoms can overlap to form three pi bonds

Each 2p orbital overlaps well with adjacent 2p orbital on either side to form two doughnut shape pi electron clouds, one of which lies above and other below the plane of carbon and hydrogen atoms.

When six 2p orbitals having electrons combines, six molecular orbitals result, out of which three are bonding while the remaing three are antibonding. Bonding orbitals are of lowest energy. So, all the six pi electrons occupy three bonding molecular orbitals and are delocalized over the entire conjugated system.

- this delocalization makes the molecule more stable.

Aromacity of benzene
Huckel Rule

In 1931, a German physicist, Huckel gave certain rules for defining the aromaticity of organic compounds.

In order to be aromatic, a compound must fulfill the following criteria.

1. The molecule or ion must be Flat or Planar
2. It should have cyclic delocalised electron clouds above and below the plane of molecule.
3. The total number of π-electrons in the molecules should be $(4n+2)$ where $n = 0, 1, 2, \ldots$ etc.

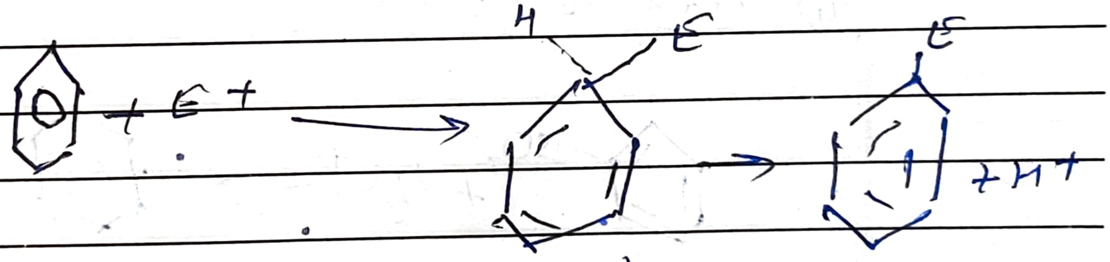
(4) The π-electron clouds should encompass all the carbon atoms of the cyclic system.
- This rule is also ~~know~~ known as $(4n+2)\pi$ rule. A ~~to~~ molecule which does not possess or satisfy one or more of the above conditions are said to be non-aromatics.

Reactions of benzene

Aromatic Electrophilic substitution Reaction

Two diffrent way

(1) Concerted reaction
- single step
- formation of intermediate transition state



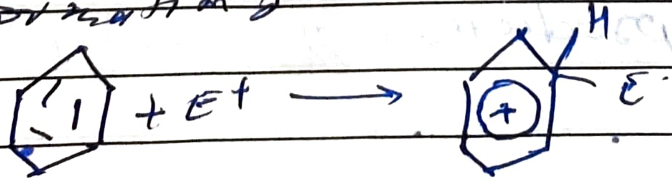
Transition state

Substitution product

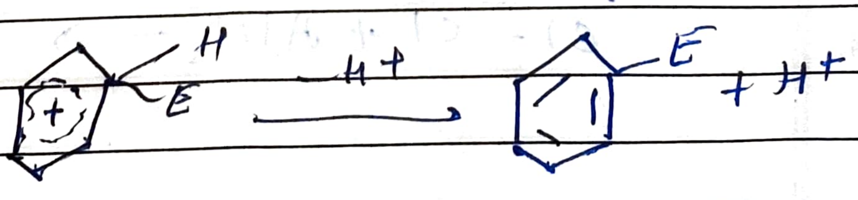
(2) Two step process

formation of carbocation Intermediate

Step I



Step II

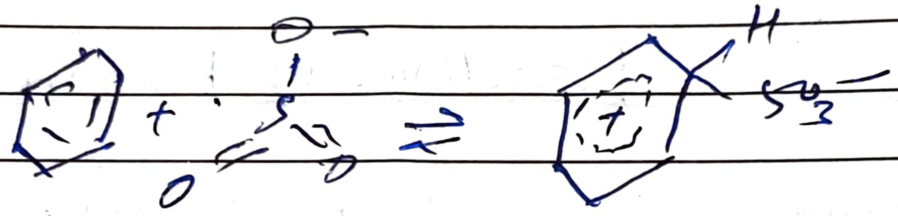


(A) Sulphonation

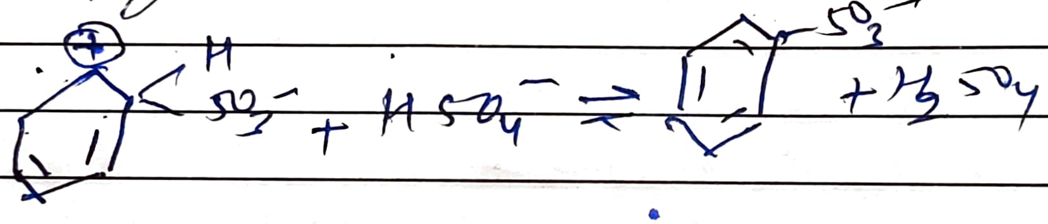
(1) Generation of an electrophile

$$H_2SO_4 + H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$$

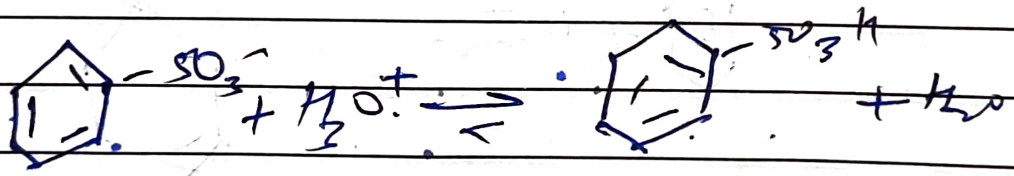
(2) Formation of carbocation intermediate



(3) Loss of proton



(4) Addition of proton



Benzenesulphonic acid

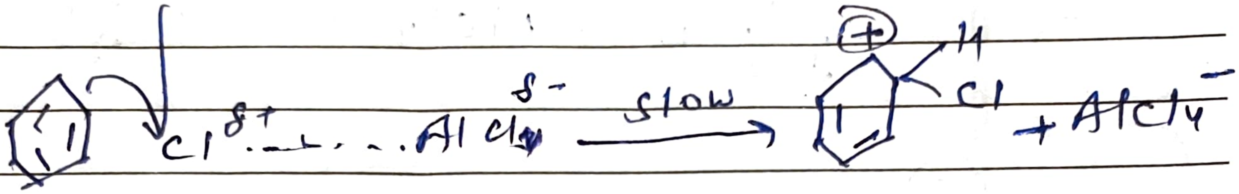
(B) Halogenation

(a) production of electrophile

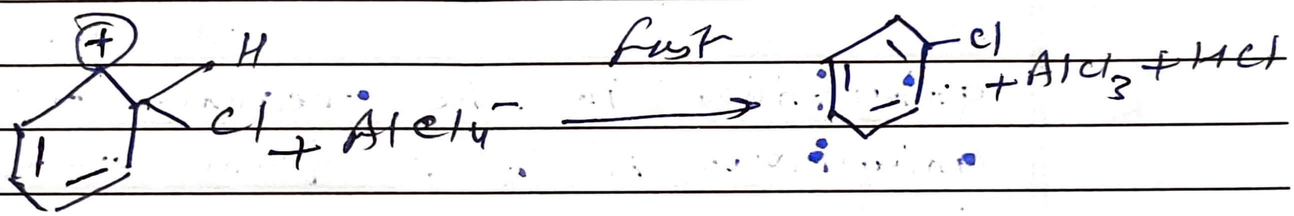
$$Cl-Cl + AlCl_3 \longrightarrow Cl^{\delta+} \text{-----} AlCl_3^{\delta-}$$

Electrophile

Step 2. Formation of σ complex or carbocation intermidiate

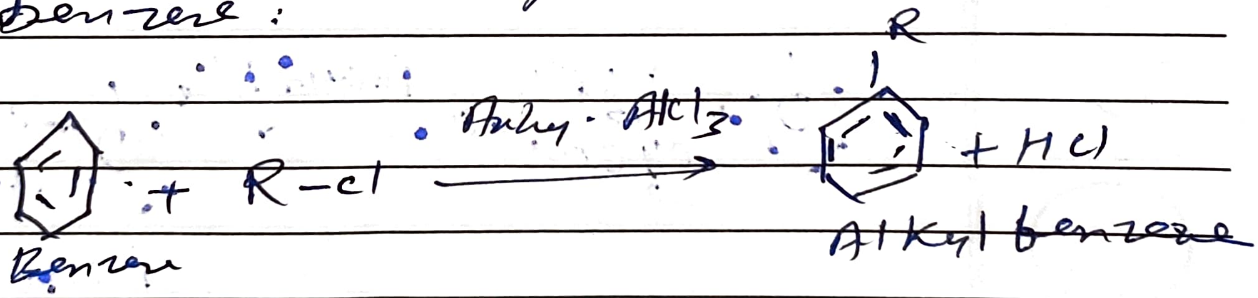


Step 3 loss of a proton from the carbocation intermidiate



④ Fridal craft Alkylation

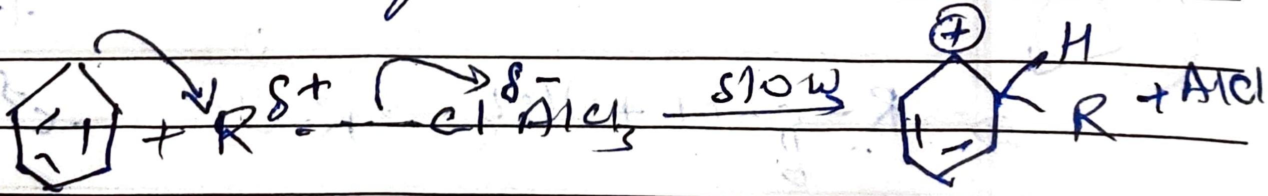
used for prepration of alkyle substituted benzene :



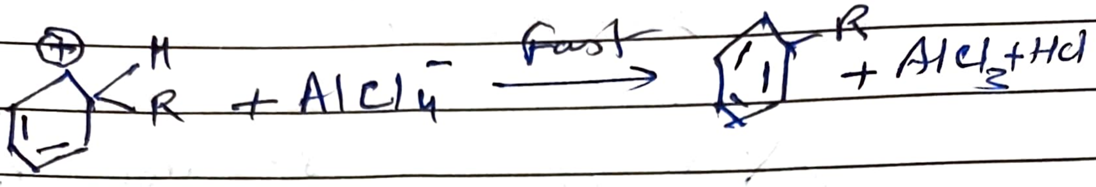
Step 1 Generation of electrophile

$$R-Cl + AlCl_3 \longrightarrow R^{\delta+} --- \overset{\delta-}{Cl}AlCl_3$$

Step 2 Formation of an Intermediate

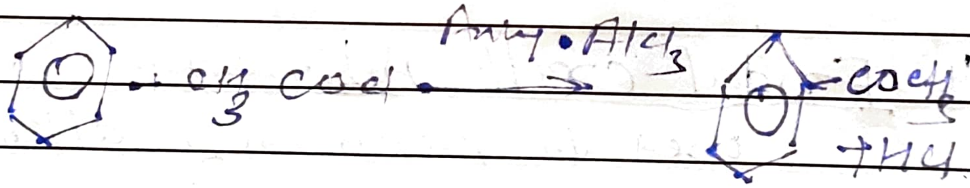


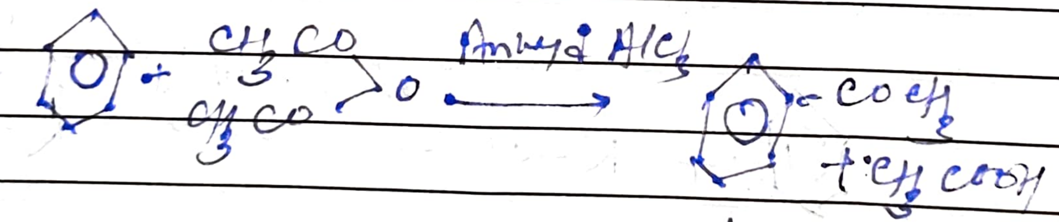
Step 3 Loss of a proton



(e) Friedel-crafts Acylation

- Method useful for Prepration of aromatic Ketones.
- Benzene and other arenes reacts with acid chlorides or acid anhydrides in the presence of anhydrous $AlCl_3$ to form aromatic ketones





Acetophenone

Mechanism

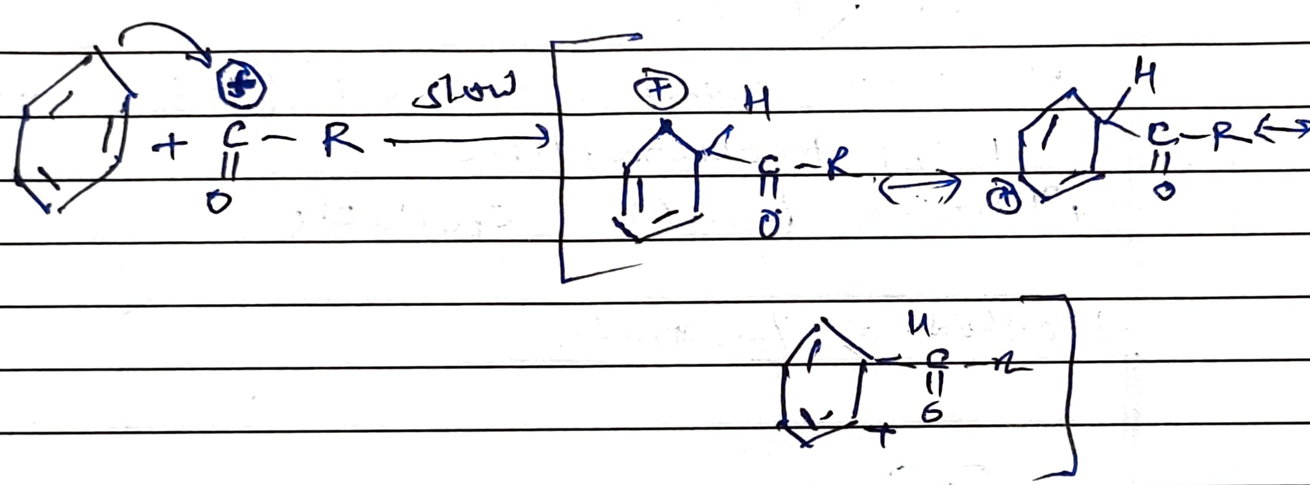
① Generation of an electrophile

$$R-\underset{\overset{\|}{O}}{C}-Cl + AlCl_3 \longrightarrow \left[R-\overset{+}{C}=\ddot{O}: \longleftrightarrow R-C\equiv\overset{+}{O}:\right] + AlCl_4^-$$

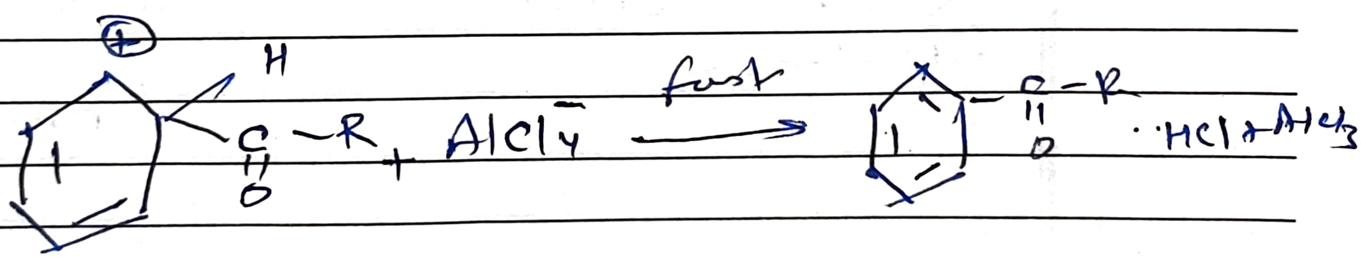
$$R-\underset{\overset{\|}{O}}{C}-Cl + AlCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}{}^{\delta+}\cdots Cl^{\delta-}\cdots AlCl_3$$

$$R-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}^{\delta+} \cdots Cl^{\delta-} \cdots AlCl_3$$

② Formation of a carbocation intermediate



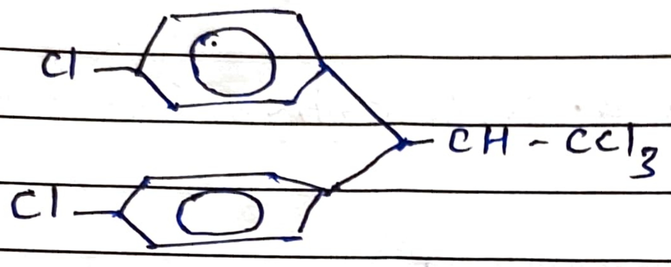
③ Loss of a proton



Roll No............................

1] DDT [Dichloro diphenyl Trichloro ethane)

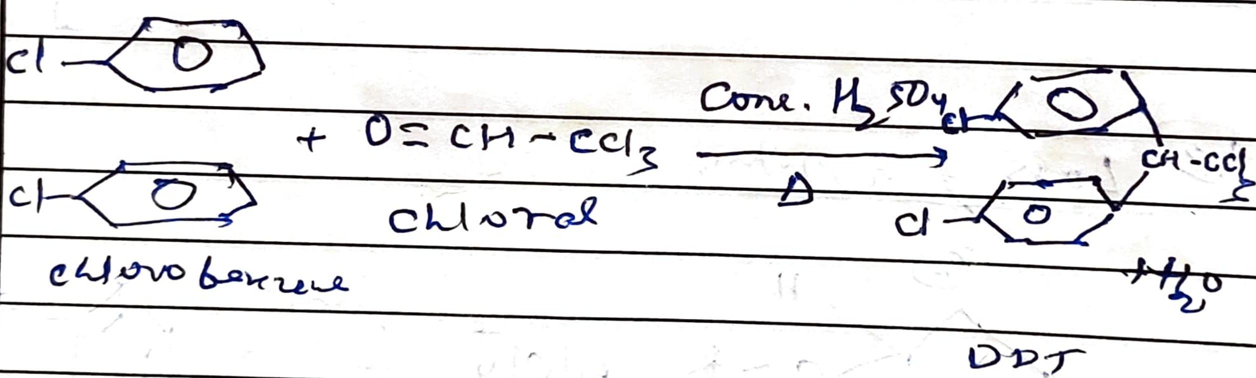
St:-



Its actual name is 2, 2 bis (4-chlorophenyl)-1,1,1 trichloroethane.

- Molecular formula $C_{14}H_9Cl_5$

Method of Preparation



Uses of DDT

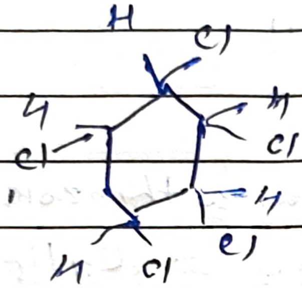
DDT is a powerful insecticide. It is generally used to kill mosquitoes and other insects

- effective against Anopheles mosquitoes which spread malaria.
- It is cheap insecticide

Roll No.......................

(3) BHC [Benzene hexachloride]

IUPAC 1,2,3,4,5,6 - hexachloro cyclohexane.

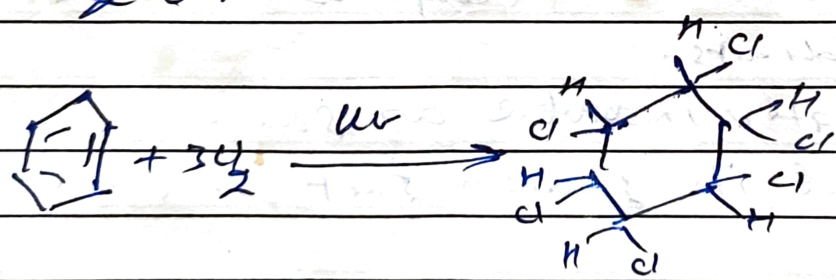


Molecular formula is $C_6H_6Cl_6$

Properties
- white, crystalline, solid
- water insoluble
- soluble in organic solvent, $CHCl_3$,
- ~~very~~ less soluble in esters & hydrocarbons
- very less soluble in short chain alcohols,

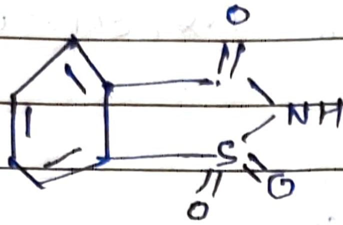
Preparation

by chlorination of benzene in presence of u.v



Uses => . pesticide in agriculture.
- to treat food crops and to forestry product
- As a seed treatment
- soil treatment
- to treat livestock & pets
- Pharmaceutical treatment for lice & scabies and used in the form of shampoo &

③ Saccharin



IUPAC 2-H, 2-Benzothiazole-1,1,3 trione

Molecular formula = $C_7H_5NO_3S$.

- Saccharin is an artificial sweetner about 300-400 time as sweet as sucrose or table sugar

Higher conc. it has bitter or metallic after taste.

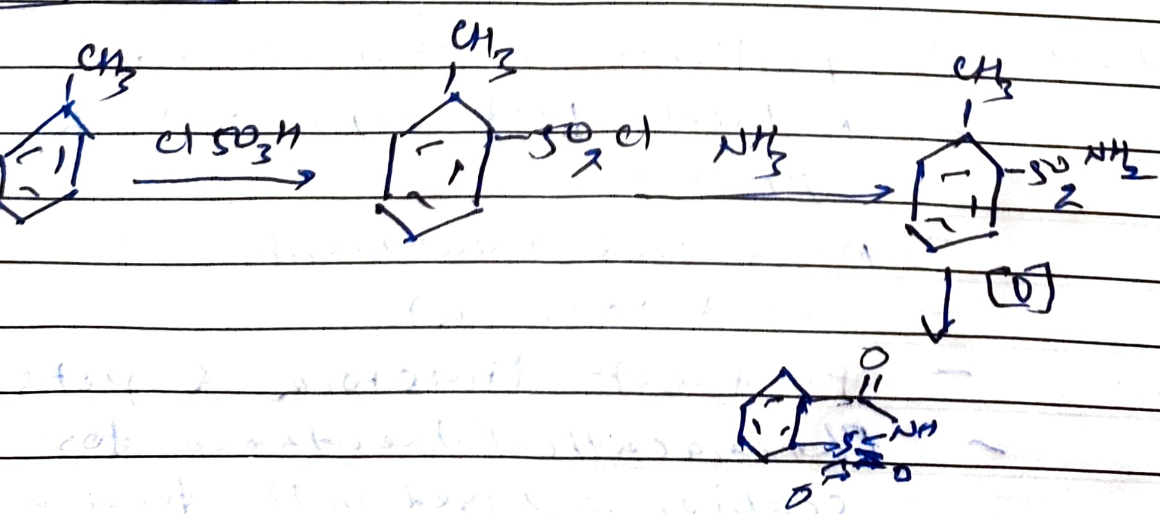
Properties - Heat stable

- inert in nature so it does not react chemically with other food ingredients.

- water insoluble as such

→ but its sodium salt is water soluble.

Prepration



Uses

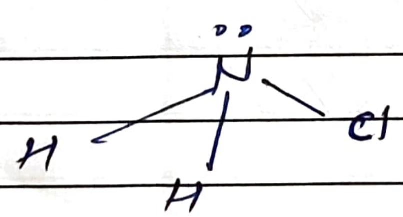
- Used to sweeten the product such as drinks medicines, toothpastes etc.
- It is used in blended form with cyclamate or aspartame in diet carbonated soft drinks.
- It has no nutritional value it is safe to consume for persons with diabeties.
- It can help to reduce consumption of sugar.

CHLORAMINE

M.F = NH_2Cl

- derivative of ammonia.
- family of organic compounds with formulae R_2NCl & $RNCl_2$

Its st. is



Propeties :-

- unstable
- colourless liquid
- MP. 66°C
- soluble in water & ether
- less soluble in chloroform & CCl_4

Preparation

by reaction of ammonia with sodium hypochlorite.

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH,$$

Uses

- Disinfectant for water as it less reactive than chlorine and more stable against light than hypochloride
- Swimming pool dissinfectant.
- Improve odour & flavour of water