

Class - B.Sc. Part II (Subsidary)

Subject - Chemistry

Paper - Jr. C, Subsidary

Topic - Structure of Benzene (continue)

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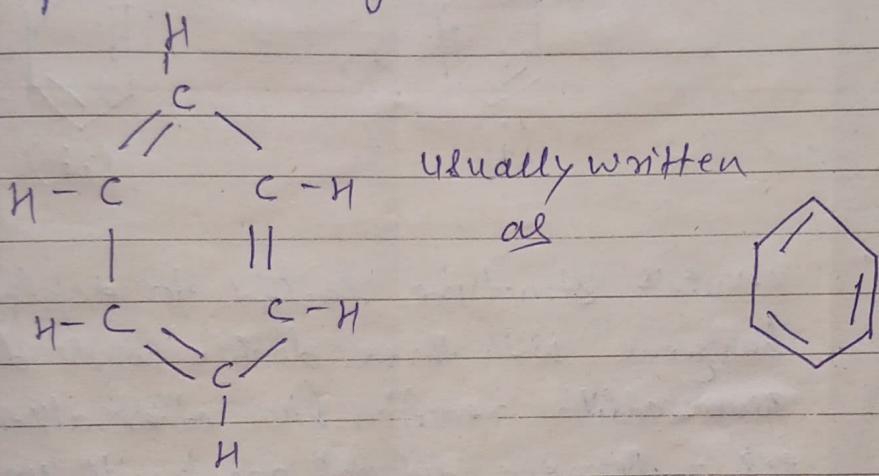
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Continue → Structure of Benzene

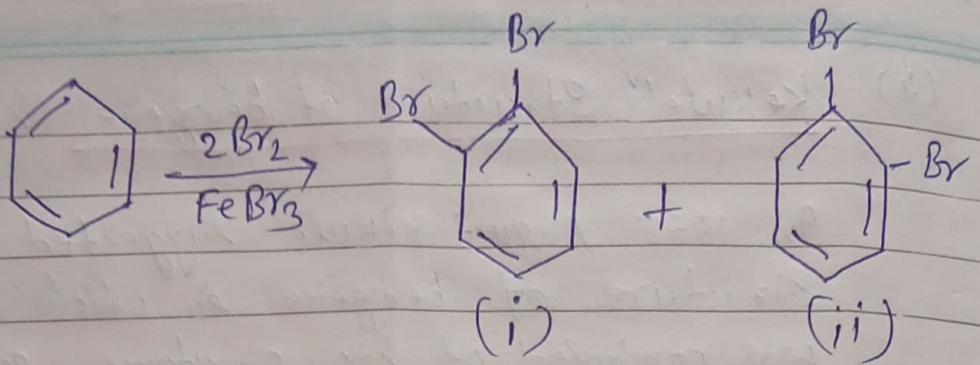
(4) Kekulé¹⁸ Structure of benzene ! —

In 1865 August Kekulé suggested a ring structure of benzene in which the ring was composed of six C-atoms, each of which carries one atom of hydrogen, to satisfy the fourth valency of the carbon atom. He suggested three alternate double bonds. Benzene according to this proposal, was simple 1,3,5-cyclohexatriene.

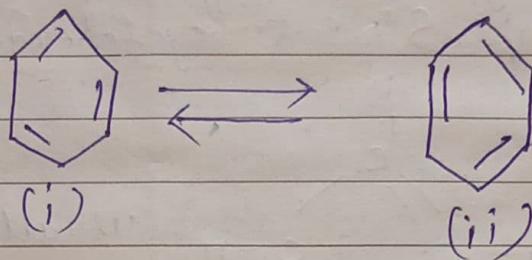


There were two objections! —

- If the Kekulé's structure was correct, there should exist two ortho isomers of dibromo-benzene. In one isomer, the two bromine atoms should be on carbon that are connected by a double bond, as shown in the following structure (i). In the other isomer the bromines should be on carbons connected by a single bond as shown in structure (ii). In fact only one ortho-dibromobenzene could be prepared.



To overcome this objection, Kekulé further suggested that benzene was a mixture of two forms (i) and (ii) in rapid equilibrium.

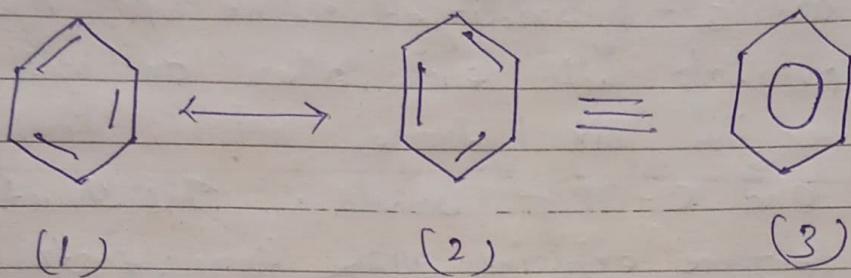


- b. Kekulé structure failed to explain why benzene with three double bonds did not give addition reaction like other alkenes.
e.g. - Benzene did not react with HBr or Br₂ in CCl₄.

(5) Resonance description of Benzene :-

The phenomenon in which two or more structures can be written for a substance which involve identical positions of atoms is called resonance. The actual structure of the molecule is said to be resonance hybrid of various possible alternative structures, referred to as the resonance structures or contributing forms. A double headed

arrow (\longleftrightarrow) between the resonance structures is used to represent the resonance hybrid. Thus in case of benzene, Kekulé's structure (i) and (ii) represent the resonance structures. Actual structure of the molecule may be represented as hybrid of these two resonance structures or by the single structural formula (3) as below -



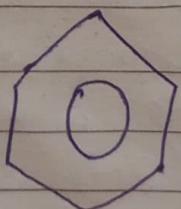
According to Kekulé each structure (i) & (ii) was real but changed rapidly from one form to another. But according to above resonance theory, both Kekulé stru. are imaginary. The real structure of benzene is hybrid, not a mixture of the two Kekulé forms. Spectroscopic measurements show that benzene is planar and that all of its C-C bonds are of equal length 1.40 \AA . This value lies in between the C-C single bond length (1.54 \AA) and the C-C double bond length (1.34 \AA).

Resonance hybrid is more stable than any of its contributing structures. For benzene, the stability due to resonance is so great that π -bonds of the molecule

will normally resist breaking. This explains lack of reactivity of benzene towards addition.

(6) Molecular orbital Structure of Benzene

The structure of benzene is best described in terms of the modern molecular orbital theory. All six carbon atoms in benzene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with $1s$ orbitals of the six hydrogen atoms forming $c-c$ and $c-H$ bonds. This structure of benzene explains all the known facts i.e., planarity of the molecule, bond angles equal $c-c$ bond length and stabilization of molecule. Due to delocalization of π -electrons, benzene molecule acts as a source of electrons and is easily attacked by electrophiles. However, to preserve the delocalization and the corresponding stability, the benzene molecule tends to undergo substitution rather than addition with electrophilic reagents. To show the delocalization of 6π -electrons benzene is represented by a continuous circle or a dotted line circle as given below!



or

