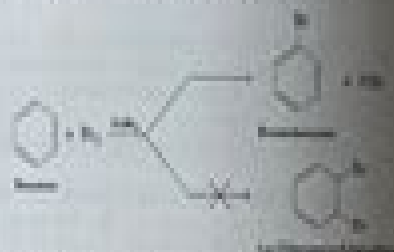


Benzene, the parent aromatic compound, presented a puzzle to chemists at the nineteenth century. The molecular formula C_6H_6 , with its high carbon-to-hydrogen ratio, is indicative of a highly unsaturated structure. Its benzene reacts with electrophiles considerably more slowly than do the unsaturated alkenes or polyenes. Furthermore, the addition reactions typical of unsaturated alkenes (Chap. 5) are not common with benzene and its derivatives. Substitution reactions are characteristic of aromatic compounds.



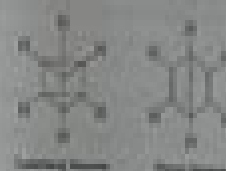
Most of the reactions of aromatic compounds are classified as electrophilic, but we will also see examples of nucleophilic processes. The consequences of aromaticity (Sec. 7-4C), as reflected by physical properties and chemical reactivity, will be the constant thread throughout this chapter.

17-1 Characteristics of Cyclic Polyenes

A. The Structure of Benzene

In Chap. 7 (Sec. 7-1A) we introduced the Kekulé structure for benzene. Although Kekulé structures are now universally used to represent aromatic and related aromatic compounds, the apparent movement toward and away from Kekulé's unsaturated structural representations and the line structure led to many other suggested structures for benzene. Two of the more interesting are the fully saturated Ladenburg benzene (prismane) and the Dewar benzene (the 1,3a,5,6a-tetrahydronaphthalene) proposed—compounds having the

structure of Ladenburg and Dewar benzene were synthesized. They are clearly not benzene.

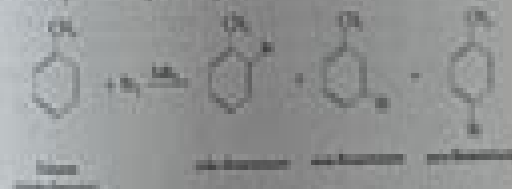


One concern with the Kekulé representation was that two 1,3-cis-disubstituted isomers should exist, depending upon where the double bonds are located.



Ladenburg proposed the prismane structure in answer to this concern. In 1872 Kekulé responded that only one yellow isomer had ever been observed because all of the ring positions in benzene are equivalent. He proposed that a type of oscillation of bonds takes place around the ring to give the equivalence. Today we recognize that the Kekulé structures represent a resonance hybrid (Sec. 7-1B).

Kekulé also recognized that his structural formula imply that substitution reactions of benzene should give rise to two additional disubstituted products. These were designated as the meta (1,3-disubstituted) and para (1,4-disubstituted) isomers. The existence of these isomers was indeed confirmed experimentally, although their identification was often rather difficult.



PROBLEM 17-1

Kramer developed a method for the identification of the ortho, meta, and para disubstituted benzene isomers based on their further substitution. One of the isomers gives only one trisubstituted benzene; one gives two trisubstituted benzenes; and one gives three trisubstituted benzenes. Show which of the disubstituted isomers fits each of these categories.

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