

# FUNDAMENTALS OF ORGANIC CHEMISTRY

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*A.N. NESMEYANOV, N.A. NESMEYANOV*

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FUNDAMENTALS OF ORGANIC CHEMISTRY

*Volume III*

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А. Н. Несмеянов, Н. А. Несмеянов

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ОРГАНИЧЕСКОЙ  
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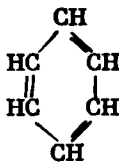
# **AROMATIC COMPOUNDS**



# Benzene and its derivatives

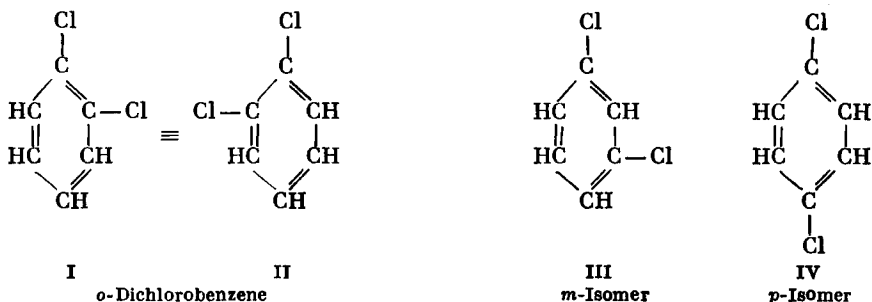
## 7.1. Benzene and Its Structure

We have already said (see Volume I, Chapter 1) about the purely chance origin of the term **aromatic compounds** which was given at the beginning of the XIXth century to benzene, its derivatives and compounds based on hydrocarbons with condensed benzene rings (naphthalene, anthracene, etc.). The first compounds of this series known to chemists (benzaldehyde, benzoic acid, toluene, and others) were either pleasant-smelling compounds or compounds derived from fragrant balsams (toluene from Balsam of Tolu) or from other fragrant exotic products (benzoic acid from gum benzoin, a naturally occurring resin). The parent hydrocarbon of the aromatic series, **benzene**, was discovered in 1825 by Faraday in an illuminating gas from which it crystallized on cooling. The structure of benzene was largely established by Kekulé in 1865, five years after the enunciation of the theory of chemical structure by Butlerov. In spite of this, the constitution of benzene and its derivatives remained to be a puzzle, on which chemists fixed their attention during all the subsequent history of chemical science and which has been resolved only relatively recently. The facts which were known to Kekulé and which served as the basis for the Kekulé formula of benzene were as follows. Benzene

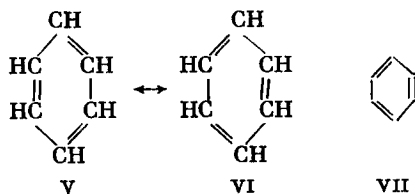


and its homologues may be represented by the formula  $C_nH_{2n-6}$ , which, because of the obvious monocyclic structure for benzene, must signify the presence in it of three double bonds (or one triple and one double bond).

In benzene, all the carbon atoms are equivalent, just as all the hydrogen atoms are, which is consistent only with the assumption of a cyclic structure. Thus, the replacement of any hydrogen atom of benzene gives rise to the same monosubstituted product. On the other hand, there always exist three isomeric disubstituted derivatives of benzene, namely, *ortho*- (abbreviated to *o*-), *meta*- (*m*-), and *para*- (*p*-) isomers. The Kekulé formula given above satisfies all these facts, except for the number of *ortho*-disubstituted benzenes, which was recognized by Kekulé.



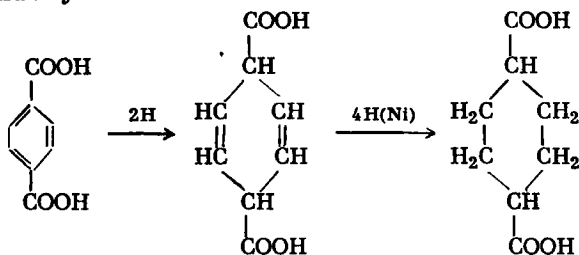
Indeed, if one is guided by the knowledge of the chemistry of the aliphatic series, formulas I and II must correspond to two different structurally isomeric compounds. In actual fact, no such two *ortho*-isomers exist and *ortho*-disubstituted benzenes always exist in the form of only a single compound, just as the *meta*- and *para*-isomers. Kekulé had to introduce a special hypothesis of the rapid "oscillation" of the double bonds in benzene in order to maintain his formula, which is expressed by the double-headed arrow placed between formulas V and VI. For the sake of brevity, one formula is usually written, implying however that the double bonds of the ring are not fixed in certain definite positions. Ordinarily, in writing the formulas of benzene and other aromatic compounds the symbols for carbon and hydrogen atoms are omitted in a hexagon (formula VII):



The subsequent development of chemistry provided numerous confirmations of the Kekulé structure.

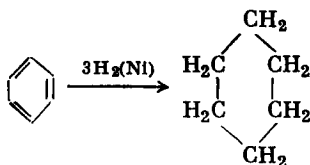
Baeyer established that terephthalic acid (*p*-benzenedicarboxylic acid) could be reduced with nascent hydrogen to cyclohexadienedicarboxylic acid, and that the latter could be hydrogenated to cyclo-

hexanedicarboxylic acid:

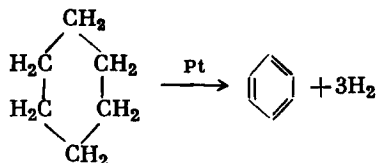


Thus, in this way the benzene and cyclohexane series were for the first time related to each other and the presence of a six-membered ring in benzene was conclusively proved.

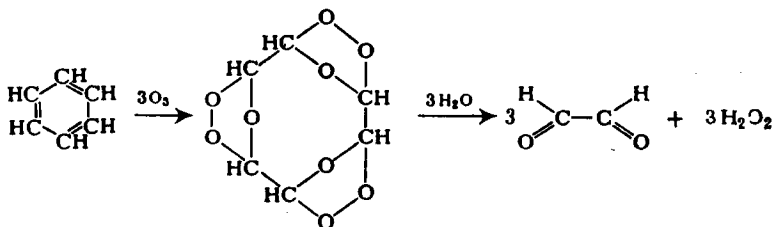
About 1900, Sabatier showed, by using his method of hydrogenation of unsaturated compounds with molecular hydrogen over nickel, that the same interrelationships exist between benzene itself and cyclohexane:



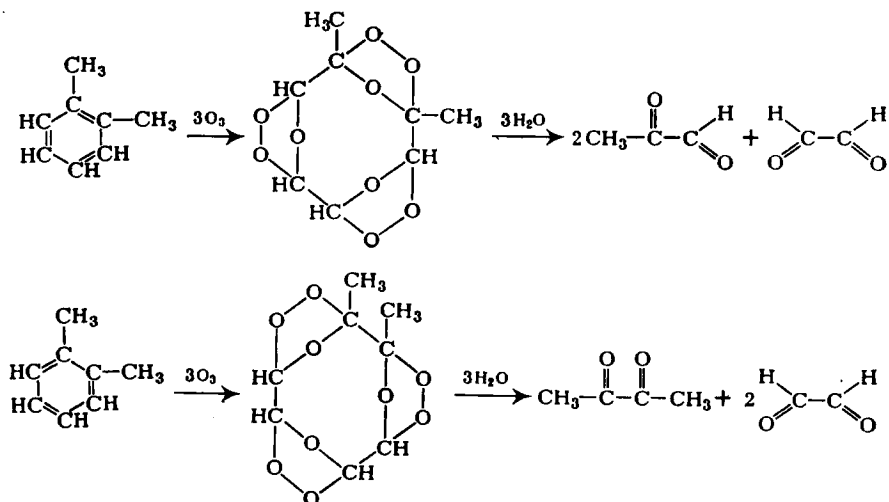
In 1912, Zelinsky accomplished the reverse reaction—the **aromatization** of cyclohexane to benzene over a platinum or palladium catalyst:



In 1904, Harries effected the ozonolysis of benzene, the course of the reaction being similar to that of the ozonolysis of olefins. This proves that all the carbon atoms of benzene are olefinic in valence state; the benzene ozonide on hydrolysis is converted to glyoxal and hydrogen peroxide:

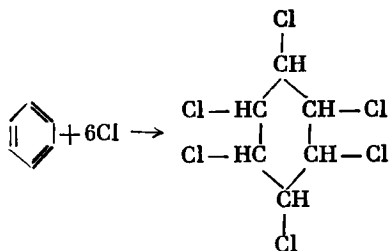


The ozonolysis of *o*-xylene (*o*-dimethylbenzene) leads to glyoxal, methylglyoxal and diacetyl in the molecular ratio 3 : 2 : 1 (Wibaut, 1941):



which clearly proves the complete equivalence of all the carbon-carbon bonds in the ring of *o*-xylene with respect to ozonolysis and hence the oscillation of the double bonds.

Benzene has been found to be capable of adding, in the presence of light, six chlorine atoms and of being converted, as a result, into a mixture of the geometric isomers of hexachlorocyclohexane (benzene hexachloride), including the *gamma*-isomer which is a very powerful insecticide known as gammexane or lindane:

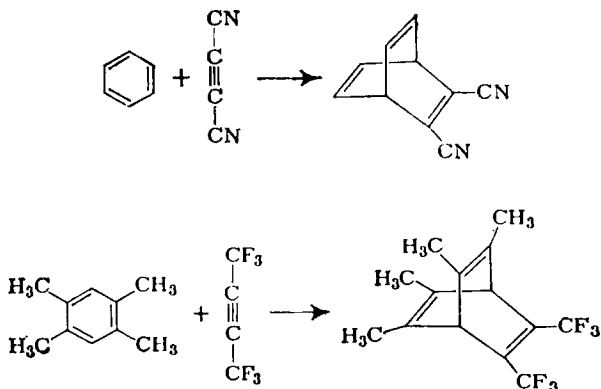


Molecular chlorine dissolves in benzene without entering into reaction with it.

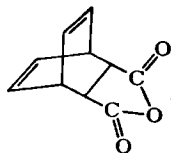
It has recently been established that benzene, and even better its homologues, can also react as dienes, by way of adding very active dienophiles under vigorous reaction conditions. This addition reaction is strongly favoured by aluminium chloride which improves the

yield and reduces the temperature down to room temperature (instead of 150–480°C).

The following are examples of such syntheses, leading to derivatives of bicyclo [2.2] octatriene (Ciganek, 1967; Krespan *et al.*, 1968):



When the reaction mixture is irradiated, maleic anhydride too adds to benzene in the same way as it adds to a diene, to give the following compound

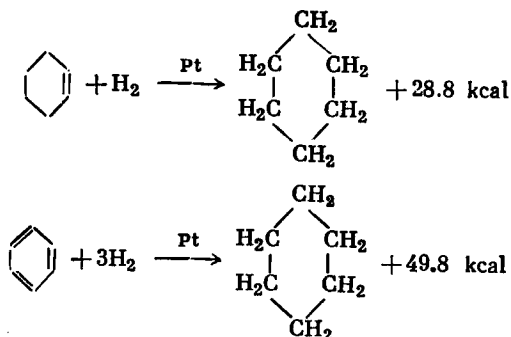


The structure of benzene suggested by Kekulé is confirmed by numerous syntheses of benzene, its homologues and derivatives from compounds of the aliphatic series, which will be given on page 21.

In spite of the seemingly excellent agreement between the Kekulé formula and the experimental facts, many outstanding chemists turned again and again to the re-examination of the structure of benzene and proposed other formulas (Claus, Ladenburg, Baeyer), which are now of only historical interest. Such objections to the formulation of benzene by Kekulé were based on the fact that benzene (and all aromatic compounds) is incomparably more inert in addition reactions than olefins. Only a few addition reactions ( $3\text{H}_2/\text{Ni}$ ;  $\text{O}_3$ ;  $6\text{Cl}$ ) take place, and many of the reagents that add to olefins lead to the replacement of hydrogens in the aromatic series. Especially characteristic is the stability of benzene towards oxidizing agents ( $\text{KMnO}_4$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$ ).

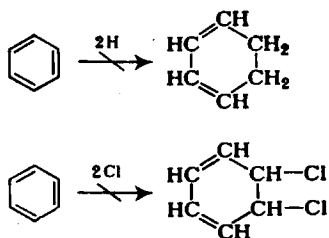


The greater chemical inertness of benzene, as compared with olefins (cycloolefins which are closest to benzene) becomes clear from the following energy comparison:



If each of the double bonds of benzene were energetically equivalent to the double bond of cyclohexene, the hydrogenation of benzene to cyclohexane should liberate  $28.8 \times 3 = 86.4$  kcal/mole, i.e., 36.6 kcal/mole greater than the observed heat of hydrogenation. Benzene is energetically poorer by this amount (and, hence, more stable) than could be expected from a cycloolefin with the fixed Kekulé structure—cyclohexatriene.

Any disturbance of the benzenoid character of an aromatic compound, say, by way of addition of at least a pair of atoms due to the removal of two electrons from the sextet, would lead to an additional loss of the "resonance energy" (36.6 kcal/mole), which is exactly one of the causes why such reactions are rare.



From the molecular-orbital diagrams given earlier (see the MO method in Volume I, page 307 *et seq.*) it is seen that in the case of butadiene one may speak, with certain reservations, of the double bonds between carbon atoms 1 and 2 or 3 and 4, though the  $\pi$ -bonds in butadiene are not localized to such an extent as they are localized in ethylene. This is evidenced by the bond order between carbon atoms 2 and 3, which is significantly different from 2 (ca. 1.45), the