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Valence Isomers of Benzene

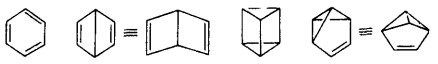
I.G.Bolesov

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I. INTRODUCTION

Throughout the existence of the theory of the structure of organic compounds, probably no one structure attracted so much attention as that of benzene. As experimental data accumulated, the requirements which had to be met by the formula of benzene were defined. It must reflect (1) the high symmetry of the molecule (sixfold axis), (2) its planar structure, (3) the equivalence of all the hydrogen atoms, and (4) the unsaturated nature of the benzene molecule. One of the first benzene formulae (I) was proposed by Kekulé in 1865. This method of representation came to be generally accepted, although it does not take into account all the experimental data. An enormous variety of structures have been proposed as alternatives to the Kekulé formula (for a detailed discussion of this problem, see Menshutkin[1]). Among these the structures proposed by Dewar (II), Ladenburg (III) (prismane), and Hückel (IV) (benzvalene) should be mentioned.



(I) (II) (III) (IV)

For a long time it was believed that these structures not only cannot describe the properties of benzene but are in fact incapable of existence as non-planar valence isomers of benzene. Recently interest was aroused again in the "non-Kekulé" structures (II)–(IV). This is because in many cases, especially in photochemical reactions, it is difficult to account for the behaviour of aromatic compounds without postulating the intermediate formation of structures of the type (II)–(IV). Furthermore, the advances which have been already achieved in the chemistry of valence isomers of benzene have been attracting an increasing number of investigators.

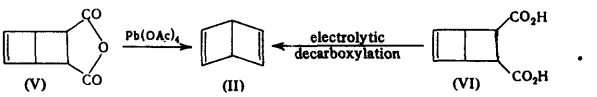
This review presents the main results of studies in the chemistry of this new and unusual field.

The reviews published hitherto on the chemistry of valence isomers of benzene deal with the literature up to the middle of 1965 [2,3] and those on the chemistry of Dewar hexamethylbenzene deal with the literature up to the middle of 1967.[4]

II. METHODS OF PREPARATION OF VALENCE ISOMERS OF BENZENE

1. From Bicyclo[2,2,0]hex-5-ene-2,3-dicarboxylic acid or Its Anhydride

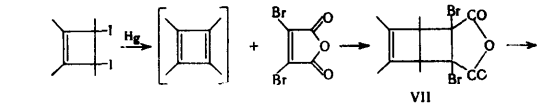
The first valence isomer of benzene, Dewar benzene (II), was obtained in 1963 by oxidising the anhydride (V) with lead tetra-acetate[5]. The yield of compound (II) was about 20%. Later a method of synthesis of compound (II) more convenient for preparative purposes was found—electrolytic decarboxylation of the acid (VI):[6]



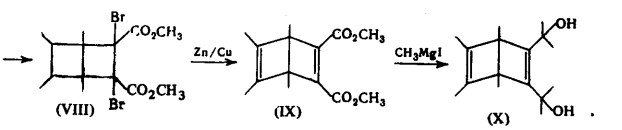
(V) (II) (VI)

2. From Cyclobutadiene Generated *in situ*

In order to obtain derivatives of Dewar benzene with different functional groups, it is necessary to carry out the condensation of tetramethylcyclobutadiene, obtained from 3,4-di-iodo-1,2,3,4-tetramethylcyclobut-1-ene, with dibromomaleic anhydride. The resulting anhydride (VII) is then further converted into the diester (VIII) and the latter is debrominated to form the "ester of Dewar phthalic acid" (IX):[7,8]



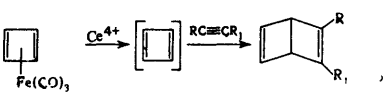
VII



(VIII) (IX) (X)

Compound (IX) readily reacts with methylmagnesium iodide, forming a derivative of Dewar benzene (X).[9,10]

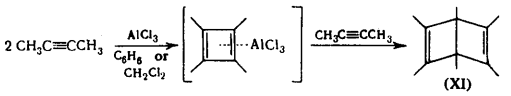
Cyclobutadienyliron tricarbonyl proved to be a convenient source of cyclobutadiene, adding readily to various acetylenes[11,12]:



where R = H and $R_1 = CO_2CH_3$, R = $R_1 = CO_2CH_3$, or R = H and $R_1 = C_6H_5$.

3. Trimerisation of Acetylene Derivatives

Preparatively the most simple synthesis of derivatives of Dewar benzene is that of hexamethylbicyclo[2,2,0]hexa-2,5-diene (XI), which consists in the trimerisation of but-2-yne under the action of aluminium chloride[4,13]:

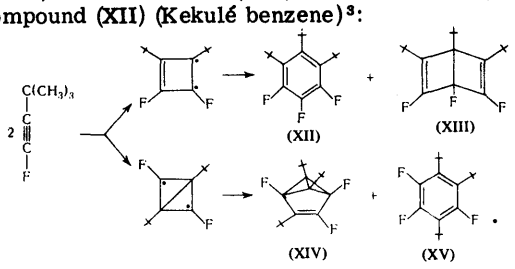


(XI)

Apart from aluminium chloride, aluminium bromide and $RAlCl_2$ (R = C_2H_5, C_3H_7, s-C_4H_9, or n-C_6H_{13}) can be used

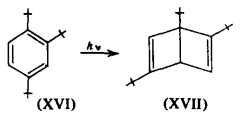
as catalysts. Other Lewis acids ($FeCl_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$, BF_3) and dialkylaluminium chlorides do not catalyst this reaction.

t-Butylfluoroacetylene forms very readily a mixture of trimers from which derivatives of bicyclo[2,2,0]hexa-2,5-diene (XIII) and benzvalene (XIV) were isolated together with compound (XII) (Kekulé benzene)[3]:

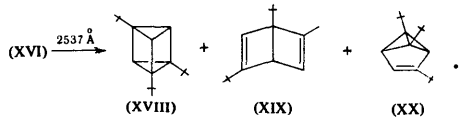


4. Photochemical Reactions of Benzene and Its Derivatives

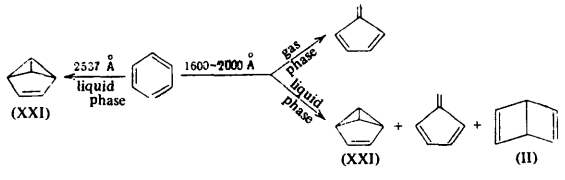
a. Valence isomerisation reactions. In 1962 it was shown that, on irradiation with ultraviolet light, 1,2,3,4-tri-t-butylbenzene (XVI) forms 1,2,5-tri-t-butylbicyclo[2,2,0]hexa-2,5-diene (XVII), a stable substance which can be purified by preparative chromatography on silica gel[14]:



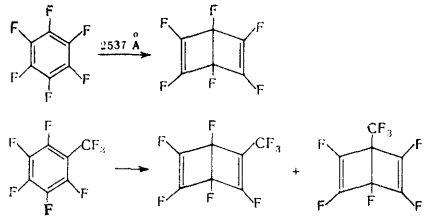
A detailed study of the photoisomerisation of polyalkylbenzenes showed that the observed migrations of alkyl groups are intramolecular processes accompanied by the rearrangement of the aromatic ring into prismane, benzvalene, and bicyclo[2,2,0]hexadiene derivatives, with subsequent rearomatisation[15-18]. Later it was established that, on irradiation with ultraviolet light at a wavelength of 2537 Å, corresponding to the second absorption maximum in the benzene spectrum, 1,2,4- and 1,3,5-tri-t-butylbenzene form a mixture of compounds (XVIII)–(XX), in which the principal component is prismane (XVIII)[18]:



Finally in 1967 it proved possible to synthesize the second (after Dewar benzene) valence isomer of benzene—benzovalene (XXI), characterised by PMR spectra and converted by methanolysis into familiar bicyclohexenyl ethers[19]. This reaction occurred on liquid-phase irradiation of benzene with ultraviolet light at a wavelength of 2537 Å. It is interesting to note that the irradiation of benzene in the gas phase at a wavelength of 1600–2000 Å results mainly in the formation of fulvene[20,21], while liquid-phase photolysis yields benzvalene, fulvene, and Dewar benzene in proportions of 5 : 2 : 1.[22]

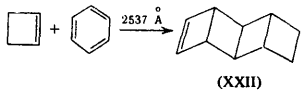


Gas-phase photolysis of hexafluorobenzene or octafluorotoluene results in the formation of the corresponding derivatives of Dewar's benzene,

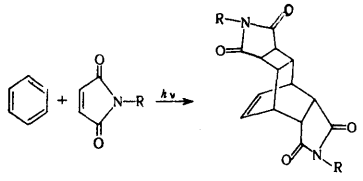


while in liquid-phase photolysis (in cyclohexane, methylcyclohexane, cyclo-octane, and ether) a complex mixture of products is formed[23-25].

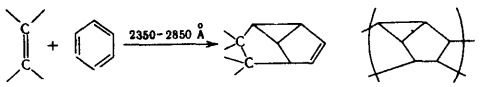
b. Reactions with olefins and dienes. When a 20% solution of cyclobutene in benzene was irradiated, the product isolated was a 1 : 1 adduct to which the structure (XXII) was ascribed[26]:



The imide of maleic acid and its *N*-alkyl, arylalkyl, and *N*-(*o*-tolyl) derivatives form 2 : 1 adducts with benzene, whose structure has been confirmed by synthesis[27]:

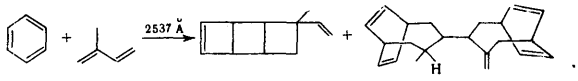


Various olefins (alkenes and cycloalkenes), unconjugated dienes, and ethyl vinyl ether form adducts with benzene as a result of 1,3-cycloaddition[28,29]:

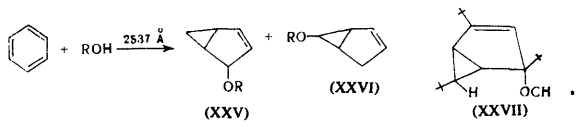


Such addition is accelerated in the presence of β-propiolactone; acetone and benzophenone do not affect the reaction rate[29]. Up to 85% of the adduct (XXIII) is obtained from cyclo-octene. Compounds of type (XXIII), like all other mono-olefins, also add to benzene, which can result in the formation of polymers to which the structure (XXIV) was ascribed (*n* reaches 24).[30]

Isoprene interacts with benzene, toluene, and tetra- and hexafluorobenzene by 1,2- and 1,4-cyclo-addition:[31]



c. Reactions with alcohols and acids. In the presence of methanol, trifluoroethanol, and acetic and phosphoric acids, benzene and 1,3,5-tri-t-butylbenzene form derivatives of bicyclo[3,1,0]hex-2-ene (XXV) and (XXVI):[32-34]



It is interesting to note that compound (XXVII) proves to be the sole product of the reaction of 1,3,5-tri-t-butylbenzene with methanol[34].

The mechanism of the above photoreactions of benzene has not been elucidated, but it has been suggested that these reactions proceed via singlet ($^1B_{2u}$) and triplet ($^3B_{1u}$) states of benzene[35] or via a reactive intermediate (with a Möbius type structure), which differ from the familiar excited states of benzene[36].

III. PROPERTIES OF VALENCE ISOMERS OF BENZENE

The reactivity of valence isomers of benzene has been investigated very little. The only exception in this respect are derivatives of Dewar benzene (especially hexamethylbicyclo[2,2,0]hexa-2,5-diene).

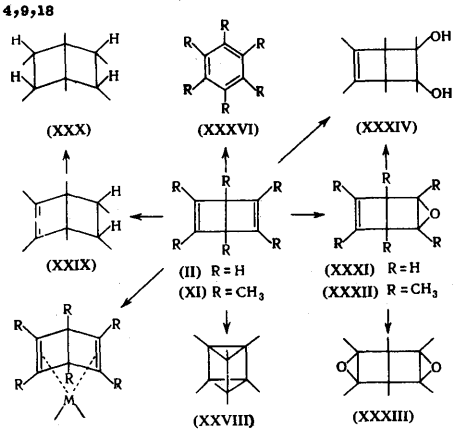
The stability of almost all the valence isomers of benzene examined above is quite sufficient under normal conditions for their isolation and purification.

1. Bicyclo[2,2,0]hexa-2,5-dienes

The PMR spectra of compounds (II) and (XI) show signals due to two types of protons: with $\tau = 3.45$ and 6.16 in the first case[5] and $\tau = 8.45$ and 8.95 in the second[4], the area ratios of the signals being 2 : 1. The first member of the series of Dewar benzenes—bicyclo[2,2,0]hexa-2,5-diene (II)—isomerises to benzene fairly readily even at 20°C (the period required for 50% conversion is about two days) and very rapidly at 90°C, but remains unchanged for a long time at 0°C in pyridine solution[5]. In contrast to bicyclo[2,2,0]hexa-2,5-dienes (II), the hexamethyl derivative (XI) rapidly isomerises to hexamethylbenzene only at about 150°C: the period of its 50% conversion to hexamethylbenzene is 105 h at 120°C, 5.5 h at 140°C, and 2.1 h at 150°C. The hexamethyl derivative of Dewar benzene has the following constants: b.p. 60°C (at 20 mmHg), m.p. 7.5°C, $n_D^{20} = 1.4479$, and $d_4^{20} = 0.8125$.[4]

Other bicyclo[2,2,0]hexadienes also isomerised to benzene derivatives on heating (in some cases only at 200°C)[4,9-12,14,24,37], under the action of Lewis acids[4], and in the presence of rhodium complexes of olefins[37]. Hexafluorobicyclo[2,2,0]hexa-2,5-diene is stable in the crystalline state but can explode in the liquid phase[24].

Under the action of ultraviolet light, bicyclo[2,2,0]-hexa-2,5-dienes are converted into prismane derivatives (XXVIII):[4,9,18]

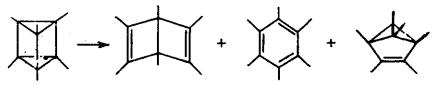


Hexamethylbicyclo[2,2,0]hexa-2,5-diene combines with hydrogen in the presence of catalysts and is reduced with carbodi-imide, forming dihydro-derivatives (XXIX) and tetrahydro-derivatives (XXX)[4,38]. Per-acids oxidise one or both olefinic groups of bicyclo[2,2,0]hexa-2,5-dienes (II) and (XI)[4,6]. Compound (XI) very readily oxidises in air to the diol (XXXIV), which is also obtained in the acid hydrolysis of the epoxide (XXXII)[4]. Treatment of bicyclo-[2,2,0]hexa-2,5-diene (II) with osmium tetroxide yields bicyclo[2,2,0]hexane-2,3,5,6-tetraol[6]. Dewar benzene and its hexamethyl derivatives form complexes with transition metals of type (XXXV)[6,37,39-41]. Other properties which deserve mention are the capacity of bicyclo[2,2,0]-hexa-2,5-dienes to combine with bromine with retention of the bicyclic structure[6,24], to undergo ozonolysis at one or two C=C bonds[4,9], and to exchange fluorine for an alkoxy-residue[24].

2. Prismanes

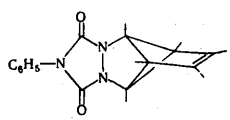
Hexamethylprismane (XXVIII), purified by repeated sublimation, melts at 89–90.5°C; its ultraviolet spectrum shows only terminal absorption characteristic of saturated hydrocarbons and the PMR spectrum has only a sharp singlet with $\delta = 0.97 \times 10^{-6}$.

Like bicyclo[2,2,0]hexa-2,5-dienes, prismanes are unstable at elevated temperatures. Under these conditions, they isomerise into derivatives of Kekulé and Dewar benzene[4,6,18,42]. At 129°C hexamethylprismane is converted to the extent of one third over a period of 30 min into a mixture of compounds (XI) and (XXXVI) in proportions of 2.4 : 1:



Lindlar's catalyst isomerises compound (XXVIII) into compounds (XI) and (XXXVI) and hexamethylbenzvalene (XXXVII). Boron trifluoride-ether causes instant isomerisation of compound (XXVIII) into a mixture of compounds (XI) and (XXXVI)[43]. It has been found that the ratio of compounds (XI) and (XXXVI) varies in the isomerisation of compound (XXVIII) by (a) heat treatment, (b) in the presence of $HF-BF_3$, and (c) in the presence of the rhodium complex of the hexamethyl derivative of Dewar benzene[42]. It has been found that the ratio (XI): (XXXVI) changes markedly under these conditions—from 1 : 30 in case (a) to 1 : 0.05 in case (c).

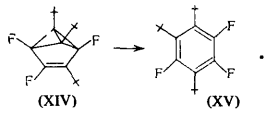
At 20°C hexamethylprismane readily forms adducts with 4-phenyltriazoline-3,5-dione and tetracyanoethylene, the structure (XXXVIII) being adopted for the first adduct[43]:



3. Benzvalenes

Benzvalene (IV), obtained by the liquid-phase photolysis of benzene (at 2537 Å), has a PMR spectrum with three resonance signals of equal intensities: an asymmetric triplet with $\tau = 4.05$, a symmetrical triplet with $\tau = 6.47$, and a quintet with $\tau = 8.16$. When acted upon by a methanol solution of hydrochloric acid, benzvalene (IV) is converted into known bicyclohexenyl ethers[19]. On heating,

1,3,6-tri-t-butyl-tricyclo[3,1,0,$0^{2,6}$]hex-3-ene (XX) isomerises exclusively to 1,2,4-tri-t-butylbenzene[18]. Similarly in the isomerisation of compound (XIV) the sole product is (XV):[3]



(XIV) (XV)

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During the preparation of the review for the press, the following new data on the chemistry of valence isomers of benzene were published.

Electrophilic addition of hydrogen halides (HCl and HBr) and methanol to Dewar hexamethylbenzene (XI), readily available from but-2-yne[4,13], leads to 1,2,3,4,5-pentamethyl-5-(α-X-ethyl)cyclopenta-1,3-dienes (X = Cl, Br, or CH_3O), isolated in yields of 45–85%.[44] To account for this course of reaction, a mechanism has been proposed postulating attack by a proton on the double bond with simultaneous or subsequent migration of the central bond, and stabilisation of the homoallyl cation by the nucleophilic agent X^-. The addition of chlorosulphonyl isocyanate to compound (XI) takes place similarly, the intermediate dipolar ion being stabilised intramolecularly with formation of an azasemifulvalene system[45].

When a methylene group is introduced into compound (XI) by treatment with diazomethane in the presence of cuprous bromide, a mixture of substances is formed[46]. The yield of products and the extent of conversion into cyclopropane derivatives strongly depends on the (XI) to CH_2N_2 ratio.

New data have been obtained on the reaction between compound (XI) and $RhCl_3.3H_2O$. The dark red crystalline compound formed has been assigned the structure of the dimer of pentamethylcyclopentadienylrhodium(III) chloride (XXXIX)[47] and not hexamethylbenzenerhodium(III) chloride, as stated earlier[41]. On being acted upon by triphenylphosphine, pyridine, or *p*-toluidine, compound (XXXIX) is converted into the monomeric adducts $[C_5(CH_3)_5]RhCl_2L$ (XL) (where L = triphenylphosphine, pyridine, or *p*-toluidine), while the reaction with cycloocta-1,5-diene in the presence of sodium carbonate yields (π-cyclo-octa-1,5-diene)(π-pentamethylcyclopentadienyl)-rhodium(I) (XLI). Elemental analysis, measurements of the molecular weight, and PMR spectra of compound (XXXIX) and the products (XL) and (XLI) obtained from it confirm the suggested structures. The mass spectrum of compound (XLI) contains intense peaks due to the molecular ion (m/e = 346) and the ion $[RhC_5(CH_3)_5]^+$ (m/e = 238).

Three types of reactions of hexafluorobenzene (XLII) with transition metal complexes have been described[48]: (1) like alkoxide ions[24], the anions $[Fe(CO)_2\pi\text{-}C_5H_5]^-$, $[Re(CO)_5]^-$, and $[Mn(CO)_5]^-$ substitute the vinyl fluorine atom; (2) manganese carbonyls with the general formula $RMn(CO)_5$ (R = H, CH_3, or C_6H_5) add to one multiple bond of compound (XLII); (3) tetrakis(triphenylphosphine)platinum forms a stable crystalline compound $Pt(C_6F_6)[P(C_6H_5)_3]_2$ (XLIII), the NMR spectrum of which contains three groups of signals of equal intensity (48.0×10^{-6}, 88.0×10^{-6}, and 99.8×10^{-6}), which have been ascribed to vinyl, Pt–C–F, and bridge fluorine nuclei. The infrared spectrum of compound (XLIII) contains a 1752 cm^{-1} band, but there is no absorption characteristic of a coordinated double bond. In view of this finding, it has been concluded that the molecule of compound (XLIII) contains a threemembered ring with C–Pt σ-bonds.

It has been shown that, in the vapour-phase photolysis (at 2537–2370 Å) of benzene, benzvalene (IV) is formed at very low concentrations[49]. The amount of compound (IV) increases when the photolysis is carried out in the presence of gases, whose efficiency varies in the following sequence: nitrogen < neopentane < *cis*-but-2-ene.

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Methods of Preparation and Properties of Compounds with Unsaturated Groups at the Phosphorus Atom

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The review deals with problems connected with the synthesis, chemical properties, and applications of organophosphorus compounds with unsaturated groups at the heteroatom. A systematic account is given of the methods of preparation of these substances and the characteristic features and limits of applicability of the synthetic methods, in accordance with the wide variety of structures of the products considered, are noted. The section dealing with the properties of the compounds describes the addition reactions of nucleophilic agents, reactions with substances with a tendency towards homolysis, certain rearrangements, condensations, and other processes. The practical value of compounds with unsaturated groups at the phosphorus atom is noted. The bibliography comprises 344 references.

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I. INTRODUCTION

The chemistry of organophosphorus compounds has developed considerably in recent years. A large number of substances of practical value have been synthesised and compounds with unsaturated groups at the phosphorus atom are of definite interest in view of the wide variety of their chemical properties. Non-combustible and self-extinguishing polymers, effective preparations with a wide variety of physiological activity, etc. have already been obtained on their basis.

At the present time there are no publications dealing with the main features of such investigations and the present review is an attempt to fill this gap. It deals with two topics, the methods of preparation of alkenylphosphorus compounds and their reactivity, the literature data published up to the middle of 1966 being discussed.

II. PREPARATION OF COMPOUNDS WITH UNSATURATED GROUPS AT THE PHOSPHORUS ATOM

Compounds of this type were synthesised about 50 years ago in the study of the reaction of phosphorus pentachloride with olefins, but the principal methods of their preparation have been developed only in the last 20 years.

1. Interaction of Halogeno-derivatives of Phosphorus with Metal Alkyls

This method of synthesis was quite recently developed and is used mainly for the preparation of phosphorus(III) compounds. In 1959 Kaesz and Stone [1] carried out the vinylation of phosphorus trichloride with divinylmercury [1]:

$$(CH_2{=}CH)_2Hg + PCl_3 \rightarrow CH_2{=}CHPCl_2 + CH_2{=}CHHgCl.$$

The yield of vinyldichlorophosphine was 50%; the compound proved to be very sensitive to air and moisture. Sterlin et al. [2] carried out a similar reaction with perfluorovinyl derivatives:

$$CF_2{=}CFMgX + PCl_3 \rightarrow (CF_2{=}CF)_3P.$$

Related methods have been proposed in Foster's [3,4] and Feder's [5] patents. In 1960 Leavitt and coworkers synthesised cyclic phosphorus compounds from dilithium derivatives and phenyldichlorophosphine [6,7]. Next one may refer to the work of Rabinowitz [8], Maier [9], and Zeiss [10] on further improvement of the method and the investigation of the properties of these compounds.

Kabachnik and Chang Jung-Yü [11,12] and Razumov [13] extended these reactions to dialkyl- and dialkoxy-chlorophosphines.